

12th International Conference on Zinc & Zinc Alloy Coated Steel Sheet - GALVATECH 2020

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Book of Abstracts

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SIMULATION OF DISSOLUTION AND DIFFUSION BEHAVIOR OF ZINC POT AFTER ADDING ZINC INGOT

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In the continuous hot dip galvanizing process, the aluminium content and its fluctuation in the zinc pot have a very important impact on the product quality. In this study, the computational fluid dynamics method was used to study the dissolution and diffusion behavior of zinc pot after adding zinc ingot. The simulation results show that the natural convection effect changes the flow pattern of the zinc bath around the zinc ingot side, and the cold zinc liquid flows to the bottom of the zinc pot, and a large eddy is formed behind the zinc pot; Aluminum melting from low-level aluminum zinc ingot (Zn-0.2%Al) is mainly added into the zinc pot bottom, and the aluminum solubility distribution in the V-area can be adjusted by addition of high-level aluminum zinc ingot (F ingot: Zn-10%Al). This work provides a basis for reducing the fluctuation of aluminum concentration in the zinc pot and optimizing the ingot filling process.

HDG Coating Weight Control by Innovative Technological Concepts / 1

POT ROLL GEOMETRY AND CROSSBOW CORRECTION

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The paper addresses the problem of crossbow correction with a 3 pot roll system. In order to estimate the curvature radius of the strip wrapping the rolls, an elastic assumption is taken. It comes that a single position of the stabilizer or Sink roll cannot correct all the products, especially the thicker ones

Coating Alloy Corrosion Studies / 3

INFLUENCE OF MINOR ADDITION OF Si AND Ti ON THE CORROSION PERFORMANCE OF ZM COATED STEEL

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Zinc and zinc-based alloys are the most important coating materials for corrosion protection of steel. The coatings are deposited by either electroplating or hot-dip galvanizing. Many research and development activities are still ongoing regarding the application of Zn and Zn-alloy coatings. In the last two decades, it turned out that zinc-magnesium (Zn-Mg) and zinc-magnesium-aluminum (ZM) show improved corrosion stability when compared to traditional zinc coatings. However, there is a strong interest to investigate alloying elements in addition to magnesium and aluminum and to evaluate their potential to enhance the corrosion protection provided by zinc, Zn-Mg, Zn-Al and Zn-Al-Mg coatings. In this work Zn-3Al-2Mg, Zn-3Al-2Mg-0.4Ti and Zn-3Al-2Mg-0.5Si coated steel have been produced using a Rhesca galvanizing simulator. Line produced hot dip galvanized steel made of zinc and ZM were also included in the study. The corrosion behavior of the samples has been analyzed in the laboratory using the Scanning Kelvin probe. From the

results it is shown that the addition of Si is beneficial to the corrosion stability of the coating. The samples were also exposed to 2 years exposure at a marine site in Brest (France). The corrosive attack initiates in the eutectics and propagates down to the steel substrate during exposure in marine atmosphere. Corrosion products or the interface substrate/corrosion products containing some silicon formed on Zn-3Al-2Mg-0.5Si were more stable than on Zn-3Al-2Mg. Less carbonates were formed on Zn-3Al-2Mg-0.5Si that could be related to a decrease in the cathodic activity and consequently to a better corrosion behavior

Fundamentals on Absorption of Hydrogen & Fundamentals on Atmospheric Corrosion and Corrosion Modelling / 4

RECENT ADVANCE IN CORROSION MONITORING OF ATMOSPHERIC CORROSION OF GALVANISED STEEL AND ZINC ALLOYED COATED STEEL

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A compact and autonomous corrosion sensor using the principle of electrical resistance variations of its metallic sensitive tracks has been used for different applications under atmospheric corrosion conditions. The measurements of the corrosion rate can be performed in-situ both under laboratory and field exposures. From the results, it is possible to better understand the atmospheric corrosion of zinc and hot dip galvanised steel under various exposure conditions. The technique should also allow the design of reliable and realistic corrosion tests for different industrial applications. From the results it is also shown that the sensor can be a good tool for insitu evaluation of red rust occurrence of zinc coated steel.

Pot Optimization by Numerical Simulation and Material Development / 5

SNOUT TEMPERATURE PREDICTIVE MODEL AND Zn POT THERMAL BALANCE

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Accurate and stable snout temperature can improve the stability of Zn pot temperature and bath chemistry, avoid dross related defects, reduce Zn dust formation, and achieve consistent galvannealing performance. In order to make sure the reliability/accuracy of the snout pyrometer (multiwavelength) for various steel grades (e.g. DP600, DP780 and DP980 etc.) and to monitor the deterioration of the pyrometer due to Zn dust buildup or other causes, predictive models were developed for #5CGL, ArcelorMittal Dofasco. Two approaches (a regression method based on rapid cool wedge-pyrometer readings, and a Zn bath thermal balance method based on Zn pot thermocouples readings) were developed and compared. During stable periods, with the regression method, the prediction bias (vs. snout pyrometer) is $-0.1 \sim +0.8$ 0C, the prediction accuracy (1σ) is $\leq \pm 2.1$ 0C. With the thermal balance method, the prediction bias is $-0.5 \sim +0.4$ 0C, the prediction accuracy is $\leq \pm 2.9$ 0C. The deviation between two models is $\leq \pm 2.4$ 0C. The snout pyrometer generally provides a reliable measurement, including for DP grades. However, large error can occur occasionally ($\sim 2\%$ of coils), with measurements lower than predictions by $10 \sim 40$ 0C, which correspond to sudden changes in surface emissivity (related mostly to sudden line speed slowdown and/or product transition). The models can be applied to monitor the performance of the snout pyrometer, Zn bath thermocouples and Zn pot heating inductors.

Modeling Bearings Wear Rate and Enhanced Pot Roll Coatings & HDG Coating Weight Control by Numerical Simulation and Modeling / 6

PRODUCTION OF HEAVY COATING AT LOW SPEED

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After some review of typical surface defects observed in CGL running at low speed and sometimes heavy coating, the solution of the Navier Stokes equation in that process window is analyzed and discussed. The liquid velocity profile is computed from NO wiping situation to classical wiping. The question of back flow in relation with line speed and coating weight is addressed. From the analysis, the max coating weight that can be reached industrially on wide and smooth strip is proposed in relation with the line speed. The question of special behavior of the liquid back flow at the edge is also discussed with the impact on the surface quality of the final coating. Finally, the liquid flow down after wiping is analyzed. The surface velocity as well as the flow are strongly depending on the coating thickness. A technological solution is proposed to minimize the impact of down flow on the finished product

On-line Measurements - Cleanliness, Austenite Fraction and Coating Defects / 7

NEW APPROACH FOR ONLINE AUSTENITE FRACTION MEASUREMENT FORMED DURING CONTINUOUS ANNEALING PROCESS. PART I: MEASURE ON HIGH STRENGTH MICROALLOYED STEEL GRADES

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This paper presents the results of the development of an innovative methodology for the online measurement of austenite fraction formed during intercritical annealing in HDG lines. The approach is based on the definition of the analytical equation (Feral equation) relating the austenite fraction formed at soaking temperature with the epitaxial ferrite growth occurring during the reverse austenite-to-ferrite transformation on cooling. Following this approach the annealing cycle in HDG or CAL could be described by three parameters: soaking temperature, soaking time and austenite fraction. This allows to achieve products with exceptional uniform tensile properties and at the same way guarantee the best annealing process efficiency. Laboratory tensile tests and metallographic investigations confirmed a good agreement with the online structure-properties characteristics calculated with the developed mathematical model.

Solidification and Formation of Hot Dip Galvanized Coatings / 8

SPANGLE NUCLEATION AND REFINEMENT THEORY IN 55%Al-Zn COATED STEEL

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In this paper we present spangle nucleation and refinement theory in 55%Al-Zn coated steel. We propose that the precipitation of [U+F074]5c intermetallic phase, (Fe₅Si₂Al₂₀+Zn) in the coating overlay is the dominant mechanism for spangle refinement. Under normal process conditions, when the strip emerges from the bath, the Fe in solution in the coating overlay diffuses to the alloy layer and contributes to a third of the alloy layer thickness. At higher cooling rates, as the liquid becomes supersaturated with Fe because of the decrease in the solubility of Fe with a decrease in temperature, IMCs will precipitate in the coating overlay. The precipitation of [U+F074]5c in

the coating overlay is promoted by process parameters such as cooling rate which inhibits the diffusion Fe to the alloy layer which results in the precipitation of fine dispersions of IMCs in the overlay. The [U+F074]5c intermetallic phase provides a potent heterogeneous nucleation site for nucleation and growth of [U+F061]-Al. Using an analytical solution of the diffusion equation for transient conditions, a model is developed to estimate the level of Fe supersaturation in the coating overlay as a function of cooling rate. The effect of cooling rate on spangle refinement is discussed in terms of the Fe supersaturation predicted from the model. The concentrations of Fe supersaturation predicted by the model are in good agreement with measured concentrations of Fe in the overlay of commercial products with varying spangle sizes. The role of fine dispersions of suspended IMCs present in the bath and the effects of strip surface conditions (that result in a discontinuous alloy layer) on spangle refinement are also discussed. Calculations of spangle size based on model predictions indicate that precipitation of IMCs from 10 to 20% of the available Fe would be sufficient to result in spangle refinement. The model predictions were consistent with the results of Fe analysis in the coating overlay of a product with minimized spangle: the product with spangle size of 354[U+F06D]m show Fe content of 0.11wt% compared with 0.02wt% for a product with a spangle size of 2 mm.

Pot Optimization by Numerical Simulation and Material Development / 9

Zn VAPOUR INDUCED CORROSION OF 253 MA STAINLESS STEEL END PLATE AND FLANGE IN RETRACTABLE SNOOTS

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The end plates and flanges used in retractable snouts are fabricated from 253MA, to overcome failure modes associated with long service periods at temperature above 500oC. Alloy 253MA is creep resistant micro-alloyed stainless steel developed for applications requiring high temperature oxidation resistance. In 253MA the alloying elements Si, Ce, and N promote the formation of a very adherent, impervious and fine-grained chromium oxide scale that is protective in high temperature service environments. Ce in 253MA reduces oxide growth rate by promoting the formation of a thin SiO₂ film at the interface between the chromium oxide scale and the 253MA substrate. SEM/EDS analyses of a corroded flange fabricated from 253MA confirms that the protective chromium oxide scale can react with condensed zinc resulting in the rapid deterioration of the end plate. This occurs in the regions of the retractable snout that are not adequately heated to prevent the condensation of zinc vapour. The corrosion of the protective chromium oxide scale leads further to diffusion of Fe, Ni and the microalloying elements Si, and Ce from the substrate into the condensed Zn leading to rapid degradation of the steel. In this paper we propose a mechanism for condensed zinc induced degradation of 253MA. We also propose a mechanism for the formation of periodic and layered structure of Fe-Zn based intermediate phases. The proposed mechanism further considers the long-range diffusion of Fe, Si, Ce, Cr and Ni atoms from the substrate steel and the diffusion of Zn from the surrounding matrix which leads to the formation of alternating and repeating patterns of the intermediate phases observed in the microstructure of the corroded flange.

LME of Resistance Spot Welded Coated Steels: Moving Toward Solutions / 11

THE INFLUENCE OF PRE-PLATING TECHNOLOGY ON THE LME PHENOMENON OF ADVANCED HIGH STRENGTH STEEL

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The galvanized steel plate is developed to protect the car from air-pollution. However, when connecting using spot-welding, since the melting temperature of zinc coating is about 440-460°C, the melted Zn or Zn intermetallic compounds would get penetrated into the grain boundaries, leading to the liquid metal embrittlement (LME). The pre-plating technology has been used to improve the LME resistance property of the galvanized steel. The gleeble tests has been employed to evaluate the crack propagation path. The results of electron probe micro-analyzer (EPMA) show that Zn penetrates along grain boundaries. The pre-plating technology has been found could reduce the quantity of LME micro-cracks. And high strength steel is more likely to form LME micro-cracks.

Poster Session / 12

EFFECT OF THE ATMOSPHERE DEW POINT OF CONTINUOUS ANNEALING FURNACES ON THE QUALITY OF GA COATING ON BAKE HARDENING STEEL

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The steel surface condition after continuous annealing is extremely important to the quality of galvanized coating (GA). The presence of oxides can affect the reactions at the coating/substrate interface and decrease the zinc wettability on the steel surface. To avoid oxidation, a protective atmosphere is used during the annealing. Despite this, it is possible the selective oxidation occurs and dew point is one of the leading factors in order to obtain a favorable surface to galvanizing. This study evaluated the effect of dew point on the quality of GA coatings applied to bake hardening steel. Continuous annealing under dew points from -60°C to 0°C, as well as galvanizing, was performed in a Hot Dip Process Simulator (HDPS). It was found that the dew point has a decisive influence on the amount, distribution and type of formed oxides, and the condition of -30°C provided the coatings with better quality.

Challenges Galvanizing 2nd and 3rd Generation AHSS / 13

CHALLENGINGS IN GALVANNEALING AHSS AT AN INDUSTRIAL HOT DIP GALVANIZING LINE

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Arcelor Mittal Cleveland Hot Dip Galvanizing line produces 260,000 metric tons of Galvanized AHSS products (GA) annually for automotive customers. New AHSS grades and thickness gauges are under constant development for automotive applications to meet the future automotive fuel efficiency standards. The use of alloy elements such as Manganese, Silicon and Aluminum in Dual Phase and TRIP chemistries can lead to challenges to many aspects of the continuous galvanizing process, including galvannealing or alloying. Under galvannealing, or under alloy, of AHSS is one of the major quality concerns. Based on several case studies at the industrial coating line, the present work reviewed various mechanisms that have caused under alloy on both Dual Phase and TRIP steel. Coated steel samples with under alloyed appearances were examined by SEM/EDS, XRD and GDS. Metallography results showed that non-uniform zinc coating and silicon segregation at the edge were two major contributing factors for edge under alloy on TRIP and Dual Phase steel. It was found that unpickled hot band scales and micro flaps were responsible for the underalloyed streaks and patches in Dual Phase steel. It is suggested that selective internal oxidation in the radiant tube furnace can help galvannealing of AHSS, to a

limited extent. DFF pre-oxidation can also enhance galvannealing of AHSS but it can lead to other processing issues such as low surface roughness and high dew point in radiant tube furnace. Both internal oxidation and DFF pre-oxidation practices could produce abnormal heavy coating buildup on strip in zinc pot during line stop which could lead to safety and quality issues. It is believed that when tensile strength for dual phase is over 1180 MPa, ferrite volume fraction plays a critical role in the galvannealing process. The high resistivity and low magnetic permeability of the steel could potentially lead to traditional galvannealing furnace tripping off causing steel not alloyed. The investigations concluded that the homogeneity of alloy elements, incoming steel substrate cleanliness, pot equipment reliability, steel microstructure and galvanneal inductor design are all important aspects to ensure full galvannealing of AHSS.

PHS-ZnFe: New Steel & Coating Developments / 15

DEVELOPMENT OF NEW GRADES OF Zn-COATED PRESS-HARDENABLE STEEL COMPATIBLE WITH THE CONTINUOUS GALVANIZING LINE

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Direct hot press forming (DHPF) of Zn-coated steels presents significant challenges associated with avoiding liquid metal embrittlement (LME) while maintaining robust cathodic protection. As identified by previous studies, a minimum amount of the Γ -Fe₃Zn₁₀ phase (15 vol%) is necessary to provide robust cathodic protection for Zn-coated press hardening steels (PHS). The Γ -Fe₃Zn₁₀ phase is liquid at typical forming temperatures, and the combination of a liquid metal phase present on the surface of the steel and an applied strain creates conditions known to cause LME. Therefore, the dual objectives of avoiding LME and providing robust cathodic protection are ostensibly incompatible under typical hot stamping conditions.

To this end, two prototype PHS steels which have increased manganese contents relative to 22MnB5 were created to enable stamping below the peritectic temperature of 783°C, thus potentially eliminating the liquid phase essential for LME. Experiments have shown that generating fully martensitic microstructures is possible while avoiding the presence of Zn-rich liquids during deformation and providing a sufficient fraction of the [U+F047] Fe₃Zn₁₀ phase to provide robust cathodic protection. The microstructural development, mechanical testing results, coating analysis and fractography of these novel direct press-hardening steels will be discussed as a function of the imposed processing routes.

Fundamentals on Selective Oxidation of AHSS / 16

EFFECT OF PRIOR Ni PLATING ON SELECTIVE OXIDATION BEHAVIOR AND GALVANISABILITY OF HIGH STRENGTH STEEL

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Much more kinds of hot-dip galvanized advanced high strength steel (AHSS) were widely applied on the car body due to requirement on safety and economy. However, the galvanisability of AHSS was dramatically deteriorated on account of the selective oxidation of alloying elements, such as Si, Mn, Cr, on the external surface after being annealed. To figure out this problem, some new technology were developed, including prior plating technology. In this study, a prior Ni plating with 50 to 300 um thickness was electrodeposited on a C-Mn-Si high strength steel followed. Then samples were annealed and galvanized through a Hot Dip Process Simulator. To studied the

selective oxidation behavior of the high strength steel with the prior Ni plating, scanning electron microscopy, glow discharge optical emission spectroscopy, X-ray photoelectron spectroscopy and transmission electron microscopy were applied. Moreover, the morphology of the coating was analyzed by scanning electron microscopy and the composition was analyzed by energy disperse spectroscopy. It could be found that the prior Ni plating with no less than 100 nm thickness could remarkably suppress enrichment of Si to the external surface. Compared with Si, Mn could easily be found on the external surface of the prior Ni plating no matter how thick the prior Ni plating is. With decreasing the thickness of the prior Ni plating, more alloying elements could diffuse to the external surface during annealing. Moreover, A large amount of Si and Mn appear at the boundary of the prior Ni plating. Under the Ni plating, some mixed oxides with Si and Mn could be found. After being galvanized, it could be found that hardly any defect could be found on the Ni plating zone and much naked matrix could be found on the no Ni plating zone. As analyzed by SEM and EDS, a continuous Al enrichment layer could be found between the Zn coating and the Ni plating while the Al enrichment layer for the sample without prior Ni plating is cracked, which indicated improvement coating adhesion and galvanisability by the prior Ni plating.

Challenges Galvanizing 2nd and 3rd Generation AHSS / 17

EFFECT OF CGL-COMPATIBLE HEAT TREATMENTS ON THE SELECTIVE OXIDATION OF A 0.15C-6Mn-2Al-1Si THIRD-GENERATION ADVANCED HIGH STRENGTH STEEL

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The present paper will summarize the selective oxidation and reactive wetting results obtained for a prototype medium-Mn 0.15C-6Mn-2Al-1Si 3G AHSS after CGL-compatible thermal processing. It was previously determined that 3G AHSS mechanical property targets of 24,000 UTS x total elongation < 40,000 MPa% could be achieved using CGL-compatible heat treatments by annealing from a 80% martensite + 20% ferrite starting microstructure. This work summarizes the subsequent interrogation conducted to determine the composition, morphology, and spatial distribution of the selective surface and subsurface oxide species formed during the martensitic pre-treatment and subsequent intercritical annealing cycles. Samples were annealed in a N2-5% H2 process atmosphere with a controlled dew point of either -30°C or -10°C. Auger elemental maps indicated that, for selected samples intercritically annealed for 120s, significant area fractions of the surfaces remained rich in Fe and were, therefore, available for the interfacial reaction required for reactive wetting of the substrate by the conventional GI bath. Auger maps also revealed that Si-rich oxide films were dispersed among Mn-rich surface oxide nodules. X-ray photoelectron spectroscopy results showed surface enrichment of Mn and Si and subsurface enrichment of Al. Reactive wetting test results will be discussed as a function of annealing temperature and process atmosphere.

Fundamentals on Surface Oxidation and Metallic Reactions / 18

EFFECT OF PROCESS ATMOSPHERE DEW POINT AND MINOR Sn ADDITION ON THE SELECTIVE OXIDATION DURING INTERCRITICAL ANNEALING OF A MEDIUM-Mn THIRD GENERATION ADVANCED HIGH STRENGTH STEEL

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Medium-Mn TRIP steels are promising candidates amongst the third generation advanced high strength steels (3G-AHSSs) for meeting automotive weight reduction demands without compromising passenger safety. However, the thermal processing of these steels should be compatible with the continuous galvanizing line (CGL) as it provides cost-effective, robust corrosion protection for autobody parts. Recently, it has been shown that CGL-compatible thermal processing of two prototype medium-Mn TRIP steels of approximate composition 0.2C-6Mn-1.5Si-0.5Al-0.5Cr-xSn (wt.%) can produce 3G-AHSS target mechanical properties (i.e. $UTS \times TE \geq 24,000$ MPa%). In the present study, these prototype medium-Mn steels were subjected to a range of CGL-compatible two-stage annealing heat treatments with two process atmosphere dew points (-30°C and -10°C). The external and internal selective oxides formed during the annealing treatment were analyzed across a variety of length scales. This contribution will evaluate the selective oxide chemistry and morphology as a function of process atmosphere oxygen partial pressure, intercritical annealing parameters and minor surface active element (Sn) addition within the context of developing CGL-compatible process parameters which will produce thin and dispersed external oxides and promote reactive wetting during the continuous hot-dip galvanizing process.

PHS-ZnFe: Liquid and Vapour Metal Induced Embrittlement / 19

ON THE ORIGIN OF MICRO-CRACKING IN ZINC COATED PRESS HARDENED STEELS

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Zn-coated press hardened steels are in high demand in the automotive industry because their high strength enhances passenger safety while supplying robust cathodic corrosion protection. However, micro-crack formation after thermomechanical processing is an issue that limits full deployment. Thereby, the objective of this research was to determine the mechanism for micro-cracking in Zn-coated PHS by focusing on the relationship between the origin of micro-cracks and the diffusion-driven coating microstructural evolution as a function of annealing time. Galvanized 22MnB5 steel sheets were annealed at 900°C for a variety of annealing times ranging from 30 – 780s and were then planar die-quenched with an average cooling rate of 100°Cs⁻¹, resulting in a fully martensitic substrate microstructure. In order to precisely determine the degree of Zn penetration into the bulk substrate, two sets of samples were examined. The first set of samples were annealed for 30s (the shortest time) and 780s (the longest time) and die-quenched while the second set comprised tensile specimens from the 30s and 780s annealing times which were subsequently pulled to failure. The substrate prior austenite grain boundaries (PAGBs) and grain boundaries (GBs) of the Zn-ferrite (α -Fe(Zn)) coating were studied before and after tensile testing to determine if zinc diffusion in these regions contributed to micro-crack formation and propagation. Scanning transmission electron microscopy coupled with electron energy loss spectroscopy (STEM-EELS) indicated significant zinc enrichment in the PAGBs, GBs and at the micro-crack tip in the PAGB region for both the 30s and 780s planar die DHPF samples. Based upon the mentioned results, a new micro-cracking mechanism was proposed which clarified the importance of solid-state grain boundary diffusion and zinc enrichment in micro-crack formation and propagation in Zn-coated press hardened steels.

Fundamentals on Surface Oxidation and Wettability / 20

MITIGATION OF THE ADVERSE EFFECTS OF INCREASING Si CONTENT IN A CMnSi ADVANCED HIGH STRENGTH STEEL VIA CONTROLLING ANNEALING ATMOSPHERE pO₂ AND MINOR Sn ADDITION DURING CONTINUOUS GALVANIZING

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Effects of Si content on the selective oxidation and reactive wetting of two grades of Fe-0.1C-2Mn-xSi (wt.%) (x=1.3 and 1.7 wt.%) advanced high strength steel arising from continuous galvanizing heat treatments were investigated in this research. Experimental steels were intercritically annealed for 120 s in a N₂-5 vol.% H₂ gas atmosphere at dew points of -50 °C, -30 [U+F0B0]C and +5 [U+F0B0]C and continuously galvanized in a 0.2 wt.% dissolved Al bath. A well-developed [U+F068] Fe₂Al₅ZnX interfacial layer, representative of improved reactive wetting, was observed on both grades after being annealed under the highest pO₂ process atmosphere of +5 °C dew point. This was due to the transition from external to internal oxidation resulting in morphological alterations of the surface oxides from thick film-like MnO, MnSiO₃, Mn₂SiO₄ and SiO₂ oxides at -50 °C and -30 [U+F0B0]C dew points to MnSiO₃, Mn₂SiO₄ and MnO particles and thin films at +5 °C dew point. Although increasing the alloy Si content to 1.7 wt.% deteriorated the reactive wetting during continuous galvanizing due to the formation of thicker SiO₂ and MnSiO₃, Mn₂SiO₄ surface oxides, the addition of 0.05 wt.% Sn to this steel effectively changed the morphology of the surface oxides to widely distributed particles and thinner inter-particle films via reducing the kinetics of the external oxidation and altering the surface interfacial tensions. Reaping the benefits of increasing the annealing atmosphere pO₂ and Sn addition, considerable improvements to coating quality were achieved on the Sn-added-1.7 wt.% Si steel annealed under the +5 °C dew point.

Coating Alloy Corrosion Studies / 21

THE EFFECT OF MICROSTRUCTURE ON THE CORROSION STABILITY OF ZINC ALUMINIUM MAGNESIUM ALLOYED COATED STEEL IN ATMOSPHERIC CONDITIONS

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Zinc coatings alloyed with low amount of aluminium and magnesium (Zn-Al-Mg) have been proved to provide better corrosion performance than conventional hot dip galvanized (HDG) steel in various atmospheres, which offers large applications in many industrial sectors such as in the automotive industry. Zn-Al-Mg coatings are characterized by a rather complex microstructure including a dendritic phase of zinc with small amount of aluminium, a binary eutectic MgZn₂-Zn and a ternary eutectic phase MgZn₂-Zn-Al. It is believed that the microstructure induced by the alloying might play a key role in the formation of the protective layers. Indeed, coarse microstructures shall be favorable to the formation of areas with extreme pH at anodic and cathodic sites, while a finer microstructure may indeed avoid such situations by averaging the surface pH, resulting in the creation of layers of improved protective quality. Yet, the relationship between microstructure and corrosion stability of Zn-Al-Mg coating is not fully demonstrated. In this study, model hot-dip Zn-Al-Mg coatings with various microstructures were produced in a galvanizing simulator by changing the cooling rate. The obtained coating variants were investigated in outdoor marine atmosphere and a number of laboratory tests with well controlled conditions. Upon testing conditions, weight loss measurements and cross section observations revealed a tendency for fine microstructures enriched in eutectic phases to be the most corrosion resistant. This was connected to a lower size of cathodic areas at the surface (zinc dendrites), the preferential dissolution of Mg-rich phase (eutectic) and the formation of a stable layer double hydroxide on the surface as detected by FTIR spectroscopy.

Coating Alloy and Modification effects on Corrosion Behaviour / 22

THE EFFECT OF PHOSPHORIC ACID ADDED TO CHEMICAL CONVERSION COATING LAYER ON CORROSION

PROTECTION IN SCRIBED AREAS OF ZINC-COATED STEELS

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Zinc-coated steels are utilized for home appliances, construction materials and automobiles. On zinc-coating layer, chemical conversion coating is formed. Chromate-free chemical conversion coatings generally contain phosphate compounds to prevent zinc corrosion mainly in the flat areas. On the other hand, when zinc-coating layer is damaged during the manufacturing process, the underlying steel can be exposed to the atmosphere and subjected to corrosion factors such as water, oxygen and salt. In this work, with the purpose of establishing guidelines for improvement of anticorrosion property, we investigated the effect of phosphoric acid on the corrosion protection in areas of exposed steel substrate. We showed that, in the salt spray test, phosphoric acid added to a chemical conversion coating enhances corrosion resistance even in scribed area that expose the steel substrate, preventing zinc corrosion from the scribed areas. We think compounds consisting of Zn²⁺ and PO₄³⁻ covered the steel substrate and acted as a barrier against the corrosion factors. In addition, the amount of PO₄³⁻ eluted from the chemical conversion coating during the test correlated with the corrosion rate. We therefore demonstrated that, to effectively inhibit the zinc corrosion in scribed areas, PO₄³⁻ is necessary to be continuously eluted from the chemical conversion coating.

HDG Coating Weight Control by Nozzle Design & Settings / 24

EFFECT OF INITIAL VELOCITY DISTRIBUTIONS IN THE TRANSITION REGION IMPINGEMENT OF SLOT-JET

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The gas wiping is generally used for coating weight control of continuous galvanizing lines (CGL). The gas wiping is the method to scrape off the surplus plating liquid after immersing a steel sheet in the molten plating bath by a gas jet by a slim slot nozzle of one pair of steel sheet front and back. Extensive coating weight control is possible by coordinating gas jet pressure depending on line speed, and it is superior economically. However, several surface defects to be caused by the wiping gas jet such as "bath wrinkle" or "checkmark" being so-called turbulence may occur other than the quality defect that is easy to happen in the steel sheet edge such as edge splashing and the edge overcoat. Parameters to influence impinging jet properties of the two-dimensional jet such as the wiping gas jet include a nozzle shape, distance between gas nozzle and steel sheet, and gas jet velocity. The turbulence properties of the two-dimensional free jet are studied for a long time, it is known that the flow field is divided into "near field" where the jet velocity does not decrease near the nozzle injection port (potential core) exists, "transition region" where mixing with the surrounding fluid proceeds, and "far field" sufficiently downstream from the nozzle. In practice gas wiping is often performed in the transition region, but no studies have been conducted to investigate the effect of the nozzle internal shape in this region. In this report, jets with different initial jet flow velocity distributions were created depending on the internal shape of the nozzle, and the impinging jet behavior in the transition region was evaluated by the flow visualization. In the visualization experiment, two types of nozzles were used: a nozzle provided with a parallel part 25 times the nozzle gap in the flow path of the nozzle injection port, and a nozzle that is curvilinearly contracted toward the nozzle injection port. Water mist as

tracer particles was introduced into the nozzle, the area from the nozzle injection port to the collision plate was illuminated with a laser sheet, and the flow field was photographed with a high-speed camera. The jets ejected from the two types of nozzles differed significantly in the vortex formation at the edges of the jet before the impingement, and there were also differences in the vibration state and frequency of the impinging jet and the state of jet separation on the wall. This suggests that the internal shape of the wiping nozzle greatly affects the plating surface quality.

Furnace III - Rapid Cooling, Furnace Roll Coatings / 25

INVESTIGATION OF "BUILD-UP" GROWTH BEHAVIOUR ON HEARTH ROLLS OF CONTINUOUS GALVANIZING LINE

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Hearth rolls in continuous annealing furnace of CGL sometimes cause the trouble that some small protrusions grow up on the surface. Such troubles are called as "build-up" or "pick-up" and it can be a cause of surface defects of steel strips such as scratches, dents and so on. A lot of tentative theory is told about "build-up" as below: (1) Producing High-alloyed steel strips accelerates the growth speed. (2) Temperature and atmosphere affect the build-up behaviour. (3) The composition of "build-up" is limited, most of all of them are consisted of MnO when the furnace atmosphere is reductive. But the details of the build-up mechanisms are not clear because it happens in high-temperature furnace. In commercial CGLs, build-ups seem to grow up very slowly during production campaign for over a month. During the campaign, the furnace temperature and atmosphere varies with time, and the composition of the steel strip is also varied. Sometimes build-ups disappear by time and cannot be collected and analysed at the maintenance term. In this study, the simplified mechanisms of hearth roll build-up are proposed, and several types of basic experiments were tried to simulate the situation of strip and hearth roll in the furnace. Selective oxidation tests by heating in reductive atmosphere were tried to clarify the oxide film formed on the strip surface. Selective oxidation is enhanced when the Mn, Si content of the strip gets higher. But the stable oxide phase is different with Mn and Si composition ratio. Reactivity of such oxides and roll surface (thermal splayed layer) was measured to clarify the build-up nucleation behaviour in the earlier stage. And the sintering behaviour of selective oxides were also investigated to clarify grow-up behaviour in the latter stage. It is suggested that the build-up behaviour can be explained and simulated by combining these basic experimental results.

Fundamentals on Selective Oxidation of AHSS / 26

EFFECT OF INTERNAL OXIDATION GENERATED DURING HOT-ROLLING COILING ON SUBSEQUENT PICKLING AND COLD ROLLING

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Varieties of advanced high-strength steel (AHSS) and ultra-high strength steel (UHSS) have been developed due to their great potential to improve the passenger safety and reduce the weight of body in white in the automotive industry. However, the production of AHSS and UHSS is still a great challenge for the steel makers. The selective oxidation of the alloy elements in the continuous annealing process and its effect on the galvanizability have been widely studied. While in the practise of UHSS production, it is found that selective oxidation of alloy elements also

occurs in the hot rolling process, but their effects on the subsequent surface quality of the pickled and cold rolled steel are still not clear. Therefore, the characterization of the scale and the internal oxidation of different hot rolled steel samples was performed and pickling and cold rolling experiments were conducted on selected hot rolled steel sheets in current work. It is found that both the formation of the scale and the internal oxidation of Si and Mn depend on the coiling temperature and the position of the strip coil. With a relative high coiling temperature, a large amount of internal oxidation was observed on the samples cut from the middle of a coil. The depth of the internal oxidation zone reached more than 10 μm and a thin iron layer above the scale was observed in some cases. It is considered that the formation of the iron layer is caused by the reduction reaction between Si, Mn and iron oxide during the slow cooling process after the steel strip is coiled. The scale pickling is delayed significantly by the formation of iron layer above the scale, resulting in under-pickling defect frequently. In addition, the internal oxidation zone is hard to be pickled entirely except the grain boundaries where internal Si and Mn oxidation enrich. The surface of the cold rolled steel sheet is ruined due to the remained oxidation zone in the subsurface of pickled steel. It is strongly suggested to precisely control the internal oxidation during the hot rolling coiling to improve the surface quality of high strength steel.

Fundamentals on Surface Oxidation and Wettability / 27

REACTIVE WETTING OF MEDIUM-Mn ADVANCED HIGH-STRENGTH STEELS BY A Zn-Al-Mg BATH

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Two medium-Mn advanced high strength steels, a reference 0.1C-6Mn-2Si alloy and a 0.05 wt pct Sn added grade, were hot-dip galvanized in a conventional Zn-0.2Al and a Zn-2Al-2Mg bath in order to compare the reactive wetting behavior of these model third generation alloys. Despite being known for providing superior corrosion protection and higher performance, the steels immersed in the Zn-Al-Mg bath exhibited inferior coating appearance and adherence compared to those that were galvanized in the Zn-0.2Al bath, where a variety of coating defects such as bare spots and micro-cracks in the MgZn₂ phase were detected. TEM+EELS analysis of the Fe-Zn interfaces determined that partial formation of an inhibition layer had occurred during immersion in all cases; however, it was also found that the higher Al content of the ternary bath did not necessarily translate into a higher overall reactivity vs the conventional galvanizing bath. Aside from the macro-scale defects and bare areas in the Zn-2Al-2Mg coatings, which are primarily rooted in bath management and dross formation problems, the presence of sub-micron dross particles along with brittle MgZn₂ intermetallics at the Fe-Zn interface had also contributed to the poor coating adhesion and flaking of these ternary coatings upon bending.

Fundamentals on Absorption of Hydrogen & Fundamentals on Atmospheric Corrosion and Corrosion Modelling / 28

ATMOSPHERIC CORROSION BEHAVIOURS OF AUTOMOTIVE STEEL SHEETS EXPOSED IN EAST AND SOUTH-EAST ASIA REGIONS

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Global expansion of automotive market leads to demand for optimization of materials selection corresponding to the corrosion severity in environments. Although great efforts have been devoted

to study the corrosion behaviour of steel products in East and Southeast Asia, reports concerning corrosion occurring in the automotive body in those regions are still quite limited to the date. Atmospheric corrosion and corrosion occurring in automotive bodies in these regions are considered to be relatively mild compared to those in de-icing salt deposited area like North America or North Europe because of lower salinity. However, it is pointed out recently that corrosion-rate estimating formula advocated by ISO may underestimate the corrosion rate in the Asian regions, and actual corrosion data of automotive materials correlated with environmental factors have been largely demanded. In this paper, results of short-term (2 years) atmospheric exposure tests of several automotive body materials such as cold rolled steel sheets (CRS) and zinc coated steel sheets demonstrated at exposure sites located in Japan and Indonesia will be presented. In addition to bare (unpainted) panels, test pieces which simulate automotive body are studied, and their corrosion behaviours are analysed by using physical analytical techniques like X-ray diffraction (XRD), Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX). Relationship between corrosion behaviours of iron, zinc or zinc alloys and environmental factors will also be discussed.

Poster Session / 29

SURFACE CHARACTERISTICS OF GALVANIZING COATING IN ROLLING PATTERN

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When magnesium is added to the hot-dip galvanized steel sheet, corrosion resistance is greatly improved, but causes black spots. Rolled steel sheet has the effect of concealing black spot. And Rolling the pattern during the hot dip plating line can minimize the damage of many plating layers and can process various patterns.

PHS-ZnFe: New Steel & Coating Developments / 30

THE MECHANICAL PROPERTIES AND CRYSTAL STRUCTURE OF Fe-Zn SOLID-SOLUTION IN HOT-STAMPED GA COATING

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The hot-stamping (HS) process has been widely used to produce automobile components, because of the great demand for higher strength steel sheets. Moreover, coated steel sheets, including galvanized steel sheets (GA), are being applied as HS material [1,2]. The structural change of GA coating during the HS heating process has been researched [2,3]. However, the mechanical properties of this Fe-Zn solid solution has not yet been clearly understood. In this study, the hardness and the compressive deformation property of Fe-Zn solid-solution were investigated. Hot stamped GA samples were prepared by heating them in an air furnace at 900°C for 4 minutes and then cooling them rapidly by pressing with flat mold tools. The hardness was measured by the micro-Vickers hardness test. The compressive deformation property was evaluated in the micropillar compression test. These micropillar specimens of Fe-Zn solid-solution single crystal were prepared with FIB. The crystal structure was measured by using XRD. The hardness of Fe-Zn solid-solution was about 300 Hv. This is about six tenths of that substrate after hot-stamping

(martensite), and about one-and-a-half times as hard as the substrate before hot-stamping (ferrite). In the compression test, the yield stress of Fe-Zn solid-solution single crystal was about 800 MPa, about half of that of the substrate (martensite). Furthermore, Fe-Zn solid-solution could be deformed by 9 percent. In these results, it was revealed that a Fe-Zn solid-solution is softer than the substrate of martensite, and that Fe-Zn solid-solution has a certain amount of plastic deformation capacity of compression. By analyzing the lattice spacing with XRD pattern, it was revealed that Zn atoms are located randomly in the Fe-Zn solid-solution lattice. Therefore it is presumed the mechanical properties of Fe-Zn solid solution are derived from those of ferrite.

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Poster Session / 32

Development and application of new electromagnetic drive technology for top dross in the zinc pot on continuous hot dip galvanizing line

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Abstracts The mechanism for the formation of top dross in the zinc pot on a hot-dip galvanizing line was studied. The detrimental effect of the top dross on the coating quality was discussed. The need for the continuous removal of top dross accumulated on the bath surface was emphasized. A novel technology was developed by utilizing a travelling electromagnetic field to guide the motion of the top dross to designated areas for the easy removal by an existing robotic arm. The technology has passed a plant trial on a galvanizing line at Baosteel. Test results demonstrated the feasibility and the potential advantages of the travelling electromagnetic field technology.

Automotive Applications - ZnAlMg Coatings / 33

INVESTIGATION OF HOT-DIP ZnMgAl COATINGS FOR AUTOMOTIVE APPLICATIONS

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In recent years, steel industries have been various studies to apply ZnMgAl coatings to automobiles. Initially, the solidification experiment of ZnMgAl coating on steel was investigated by using *in-situ* real time x-ray scattering, we confirmed that the solidification proceeds in the order of Zn, Zn/MgZn₂ binary eutectic and Zn/MgZn₂/Al ternary eutectic phases. Also, we evaluated the properties such as wettability, surface roughness, fluidity and corrosion resistance according to Mg and Al with varying contents. The difference in corrosion products between the general hot-dip galvanizing (GI) and ZnMgAl coating was confirmed in detail. In the case of ZnMgAl coating, the dense corrosion products were formed on surface, thus the corrosion resistance was superior than GI material. In addition, the ZnMgAl coated steel sheet was excellent in formability due to its low coefficient of friction. Phosphate treatment, weldability and adhesion properties were similar to those of general hot-dip galvanized steel sheets to apply for automotive.

Poster Session / 34

EFFECT OF ALLOYING ELEMENTS ON SURFACE CHARACTERISTICS AND ELECTROCHEMICAL CORROSION BEHAVIORS OF AlSi BASED COATING FOR THE STEEL SHEET

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The effect of Mg and Zn addition on microstructure and corrosion resistance of AlSi based coating for the steel sheet was investigated using a range of analytical methods, scanning electron microscopy (SEM), X-ray diffraction spectroscopy, glow discharge spectroscopy (GDS), and x-ray photoelectron spectroscopy (XPS). This study revealed that the combined addition of Mg and Zn lead to the formation of intermetallic compound such as MgZn₂ and Mg₂Si. The preferential dissolution of the intermetallic phase at an early stage of corrosion process can facilitate the formation of the corrosion product with protective nature, which suppressed both anodic and cathodic current densities on the coating surface, and improved the corrosion resistance.

Steel-Coating Interfacial Layer and Coating Phase Developments / 35

QUANTITATIVE EVALUATION OF NANOSCALE MECHANICAL PROPERTIES OF Zn-Al AND Zn-Al-Mg COATINGS ON STEEL SHEET BY NANOINDENTATION

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While mechanical properties of zinc coatings are well-known and have been studied in detail during the last decades [1,2], the fundamental behaviour of coatings of zinc- or aluminium-based alloys is much less understood. Understanding the contribution of the different micro-phases in their complex solidification structure requires new approaches.

Nanoindentation coupled with data post-processing has been proven to be a powerful technique to draw two-dimensional mechanical mappings and to obtain the mean elastic modulus and hardness of constituent microscale phases in heterogenous materials [3,4]. The microstructure of low-alloy zinc-based coatings consists mainly of phases having hexagonal close-packed (HCP) crystal structure, like η -Zn in the form of dendrites or eutectic phases (Zn/Al or Zn/Al/MgZn₂) and MgZn₂ in the form of eutectic phases (Zn/MgZn₂ or Zn/Al/MgZn₂). The Al-rich phase in the Zn/Al and Zn/Al/MgZn₂ eutectic phases, is a solid solution of Al and Zn having a face-centered cubic (FCC) structure. The elastic behaviour of HCP single crystals is usually highly anisotropic, meaning that the stiffness of the material strongly depends on the direction of loading. In addition, the hardness of Zn crystal has been reported to be also highly anisotropic [5].

In this study, the microstructure of Zn-5Al and Zn-3.7Al-3.0Mg coatings was investigated using scanning electron microscope (SEM) coupled with an electron probe microanalyzer (EPMA). Mechanical property maps were built using a grid nanoindentation technique [3,4] and were quantitatively correlated to the microstructure map. Electron backscatter diffraction (EBSD) was used to determine the crystallographic orientation (Euler angles) of each indented phase in order to determine the angle between the direction of indentation and the hexagonal orientation [0001] of the phase (η -Zn or MgZn₂). By combining all these techniques, the effect of the anisotropy of η -Zn and MgZn₂ crystals on the mechanical properties of Zn-Al and Zn-Al-Mg coatings was quantified.

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LME of Resistance Spot Welded Coated Steels: Assessments / 38

EVALUATION OF INITIATION AND PROPAGATION OF LME CRACKS ON Zn COATED 3G-AHSS USING INTERRUPTED RESISTANCE SPOT-WELDING ALONG WITH AND WITHOUT EXTERNAL TENSILE STRESS

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In zinc coated 3rd Generation advanced high strength steels (3G-AHSS), liquid metal embrittlement (LME) occurs due to liquid zinc or zinc alloy penetration along the grain, grain boundaries and pre-existing cracks of the steel sub-surface area in the presence of critical amount of external tensile stress during resistance spot welding. Due to penetration of liquid metal, cohesion between grains of steel decreases and causes embrittlement. Most of the zinc coated 3G-AHSS are used in the automotive industry where multiple layers of coated steel sheets are joined together using resistance spot welding (RSW) technique. High temperature exposure, presence of tensile stress during welding and liquid metal are the three key parameters responsible for LME during spot welding of zinc coated AHSS. The LME crack initiation and propagation depend on the states and condition of the above three factors. Present study deals with the determination of onset of LME crack formation and the propagation during interrupted spot welding of Zn coated 3G-AHSS. All the spot welding has been carried out at constant electrode force along with constant welding current, only the welding cycle (time) has been varied. In addition, to evaluate the effect of external stress along with the stress required for RSW on LME crack formation and propagation, interrupted RSW has been carried out in the presence of external tensile stress. Results show that LME crack formation and propagation are very much dependent on the welding cycle which eventually controls the total heat input and stress condition. It has been also observed that with Zn coated 3G-AHSS the welding cycle (time) as well as stress affects the structural change at the steel/coating interfacial area.

Challenges Galvanizing 2nd and 3rd Generation AHSS / 39

EFFECT OF STEEL SUB-SURFACE STRUCTURE ON MECHANICAL PROPERTIES OF GALVANIZED 3rd GENERATION ADVANCED HIGH STRENGTH STEELS

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In order to meet the demands for improved safety, fuel economy and comfort from the automotive industry, various 3rd Generation (3G) advanced high strength steels (AHSS) with the product of TS (Tensile Strength) and TEL (Total Elongation) higher than 10GPa% have been developed. To guarantee their use as auto body parts, corrosion resistance has been assured by zinc coating on the steel surface by continuous galvanizing process. New chemistries to produce 3G-AHSS involve the addition of several alloying elements into the steel, amongst them Si, Mn, Al and Cr are selectively oxidized externally on the steel surface during annealing in the continuous galvanizing lines when industrial dry dew point is maintained. This external selective oxidation of alloying elements renders the steel surface unsuitable for subsequent galvanizing. To produce a steel surface suitable for galvanizing, the selective oxidation behavior of an alloying element can be changed from external to internal (below the steel surface) in the presence of a high partial pressure of oxygen by maintaining a high dew point annealing atmosphere. These internal oxides mostly form along the grain boundaries as well as inside the grains of the steel sub-surface area. It is also well known that carbon plays a key role in determining the tensile properties of 3G-AHSS. The presence of a high partial pressure of oxygen associated with the high dew point atmosphere reacts with steel alloying element Carbon and forms a decarburized layer at the steel sub-surface area. Thus, the annealing atmosphere necessary to produce the galvanized coated 3G-AHSS modifies the steel sub-surface area. The decarburized layer along with network of internal oxides has a considerable effect in determining the tensile strength as well as the elongation of 3G-AHSS. The present study deals with the systematic evaluation of the effect of an annealing condition suitable for a good galvanized coating on the tensile properties of 3G-AHSS. It has been observed that the sub-surface structure not only deteriorates the tensile strength but also affects the elongation of the steel. This effect has been more prominently observed with the increase of the alloying elements added to the steel. This study also evaluates through interrupted tensile test, the effect of network of internal oxides along with decarburized layer present in the steel sub-surface on the crack initiation and propagation.

Solidification and Formation of Hot Dip Galvanized Coatings / 41

INFLUENCE OF SURFACE ROUGHNESS OF FULL HARD STEEL ON SPANGLE OF GALVANIZED STEEL AND ACTUAL APPLICATION RESULTS

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This study was carried out to improve the surface quality of galvanized steel, which are widely used in exposed automotive panels. To control zinc grain called as spangle that occurs during solidification of galvanized steel, In view of the metallurgical aspects, we considered a new method increasing the surface area of full hard steel associated with nucleation of molten zinc in the solidification during galvanizing by applying an improved surface treatment in work roll of tandem cold mill(TCM). As a result, among various parameters of surface roughness, we found that RPc(Peak count, cm-1) is associated with surface area more than Ra, moreover, through experiments by hot-dip galvanizing simulator, spangle of galvanized steel based on full hard steel having high surface area was found to be significantly tiny. By using these experimental results, we changed the processing method on final stand work roll of tandem cold mill(TCM) in the site and finally we were able to greatly reduce the spangle size of galvanized steel for exposed automotive panels compared to existing size without any additional facility investment.

Poster Session / 42

EFFECT OF Al CONTENT ON THE CORROSION BEHAVIOR IN Mg-Zn-Al ALLOY COATED STEEL SHEET

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A steel is used in all industries because it has many advantages such as high strength, easy workability and high-quality paintability. Nevertheless, steel can not be used for a long time due to the occurrence of rust caused by various factors. In order to improve the corrosion resistance of steel, the development of a high corrosion resistance steel with Mg and Al is being studied. Also, we should replace the galvanized steel owing to rising prices and depletion of zinc resources, deterioration of the corrosive environment, competitiveness of market and so on. However, it is difficult to add more than 3wt.% Mg because of oxidation problem of bath at the production process, therefore, research is being conducted to increase the Al content. In this study, the effect of corrosion resistance on a different Al content was compared through a microstructure analysis of the coating layer, accelerated corrosion resistance test, potentiodynamic polarization test. As a result, it has been observed that the corrosion current is reduced as the Al content is increased.

Fundamentals on Surface Oxidation and Wettability / 43

AHSS SURFACE OXIDE PHASE FORMATION DURING ANNEALING AND PREDICTING THEIR TYPE USING GIBBS ENERGY MINIMIZATION (GEM) THERMODYNAMIC PRINCIPLE

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In order to improve fuel efficiency and to reduce carbon emissions, automakers are using advanced high strength steels (AHSS) to lightweight vehicles without compromising passenger safety. In manufacturing, the steel sheet is annealed in a continuous galvanizing line (CGL) to achieve the desired mechanical properties. During annealing, alloying elements such as Si, Mn, Cr, Al, etc. in the steel can form oxides, which pose coatability challenges. Knowing the morphology and the type of these oxides can help pinpoint the defect source and improve AHSS coatability. The present work was conducted to determine the oxide phases formed as a result of annealing temperature and annealing furnace atmosphere. The annealed steel surface was evaluated using various surface analytical techniques. The oxide type and coverage were predicted by combining GDOES chemical depth profile with thermodynamic calculations using the Gibbs Energy Minimization (GEM) principle.

Coating Alloy Corrosion Studies / 44

CORROSION EVALUATION OF THIN Zn-Al ALLOY COATINGS IN A SEVERE MARINE ENVIRONMENT

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Due to the increasing demand for material and cost reduction, there has been a global trend to reduce the coating thickness of continuously galvanized sheet and coil products. As the lifetime of a metallic coating depends mainly on its coating weight, reducing the coating thickness could compromise the durability and performance of the coating. Comparatively, Zn-Al alloy coatings, such as GF (Zn-5%Al) and GL (Zn-55%Al-1.5%Si), which are usually two to four times more corrosion resistant than a galvanized (GI) coating, are more likely to provide equivalent corrosion

protection to steel with a lighter coating weight. However, there is a lack of published studies on the corrosion performance of thin Zn-Al alloy coatings in corrosive environments.

In the present study, samples of GF and GL, both of which had a coating weight of 30-40 g/m²/side, were exposed at Belmont Beach, Australia, in August 2015. This is a severe marine site falling into the atmosphere corrosivity category of C5 (ISO 9223). For comparison, exposed samples also included GI and GA (galvannealed) coatings with normal coating weight (70 g/m²/side). During the exposure test, a number of samples were retrieved from the site at periods ranging from 311 to 1373 days, and then examined using stereoscope, X-ray Diffractometer (XRD) and Scanning Electron Microscope (SEM). In addition to evaluating the cut-edge protection, the corrosion behavior of each coating was studied based on the corrosion product formation and the corrosion of coating microstructure. The polarization and electrochemical impedance of the collected samples were analyzed to evaluate the remaining protection of the corroded coatings.

Poster Session / 45

EFFECT OF STRIP ENTRY TEMPERATURE ON THE Zn-Al-Mg PHASE FORMATION IN HOT-DIP COATED HOT STAMPING STEELS

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The hot stamping steels are widely applied to improve the safety of automotive and reduce the weight of car body, due to the advantage to perform parts with ultra-high strength and better formability at high temperatures and exhibit no springback on the final part. The Al-Si and Zn-based coatings are developed to prevent scaling and decarburization during hot stamping processes, especially improve the corrosion property of the final hot stamping parts. In the present research, a new kind of Zn-Al-Mg coating for hot stamping steel was developed. And the effect of strip entry temperature on the Zn-Al-Mg intermetallic phase formation in hot-dip coated hot stamping steels with the bath chemistry of Zn-7.2Al-1.6Mg (wt.%) was investigated. The microstructure of the metal coating was characterized by Scanning Electron Microscope (SEM). It was decided that the microstructure components of the metal coating are crucially influenced by the strip entry temperature from 460 [U+2103] to 490 [U+2103]. After hot stamping process, the coating microstructure transforms into Fe-Zn-Al phase layer. The content of Al in the coating layer is increased gradually from inside to outside, whereas that of Zn is decreased. Mg is enriched at the surface of coating. Small cracks are formed in the layer locally, but compare to the Al-Si coating, the Zn-Al-Mg coating demonstrated excellent high temperature resistance.

Non-Automotive Applications: ZnAlMg Coatings / 48

MECHANICAL PROPERTIES AND CRACKING BEHAVIOR OF HOT-DIP GALVANIZED ZnAlMg COATINGS

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ZnAlMg coatings produced by hot-dip galvanization process have shown superior corrosion resistant, anti-galling and wear performances. Nevertheless, currently these coatings exhibit lower cracking resistance and ductility compared to conventional galvanized zinc (GI) coatings on steel sheets during forming processes. In this study, mechanical properties and cracking behavior of ZnAlMg galvanized steels have been investigated thoroughly. Microstructure, mechanical properties and key causes of cracking initiation and propagation have been scrutinized by utilizing scanning electron microscopy (SEM), orientation imaging microscopy, nanoindentation and in-situ

SEM tensile/bending tests. Ultimately, effective plastic deformation-based factors are obtained to understand and explain the cracking behavior and consequently link the microstructural features to cracking tendency of these coatings. The findings of this study are employed in designing new microstructure controlled ZnAlMg coatings with superb cracking resistance.

Furnace II - Current Topics from Preoxidation to Galvannealing / 49

ArcelorMittal GENT PRODUCES 3rd GEN. AHSS INCL. Q&P ON THE UNIQUE ANNEALING FURNACE FROM ANDRITZ

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ArcelorMittal Gent is one of the first steel suppliers to have invested in a fully versatile furnace with the objective to produce a high amount of third generation Advanced High Strength Steels, such as Q&P steels. ArcelorMittal chose the ANDRITZ Group to supply the necessary equipment, in particular the ANDRITZ Selas furnace, to insure that the specific thermal and process cycles needed for these steel grades can be realized. The furnace performances allowed to produce new grades such as Q&P steels after 12 weeks of operation, respecting specific heating paths and extreme cooling patterns, necessary for these high-end products, without jeopardizing coating quality.

HDG Coating Formation & Dross Management / 50

A MODELING FRAMEWORK FOR TOP SKIMMING FORMATION IN GALVANIZING BATH

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In continuous galvanizing line operations, the thickness and the uniformity of the zinc coating are governed by the gas jet wiping process; a complex multi-phase, multi-scale phenomenon. Though efficient, the process leads to the undesired top skimming formation. To better understand the intricate interactions among the moving strip, the unsteady turbulent jet, the falling excess liquid zinc and the local skimming generation, an efficient and accurate numerical model would be highly valuable. This work describes a modeling framework for top skimming formation, focusing on the coupling between the gas jet wiping process and the phenomenological model for local skimming formation.

HDG Coating Weight Control by Nozzle Design & Settings / 51

WIPING PRESSURE DYNAMICS AND THEIR EFFECTS ON GALVANIZING COATING SMOOTHNESS

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The variation of thin metallic coating thickness produced in continuous galvanizing lines (CGLs) is attributed partly to the fluctuations in both the spatial profile and gradient of the impingement wall pressure. A fluctuating pressure profile can significantly alter both the magnitude of the maximum pressure gradient doing the majority of the wiping work and its location. A wiping jet with more stable pressure profiles is expected to produce smoother coating than fluctuating ones. However, the dynamics or time variation characteristics of impingement wiping jet wall pressure has not been addressed adequately in the literature. This study experimentally investigated the dynamics of impingement wall pressure of a planar air jet. Both time-averaged and time-varying wall pressure were measured and analyzed. The effects of the ratio of jet-surface distance, H , to jet nozzle width, d , and Reynolds number, Re , based on d and mean jet velocity, U_0 , have been elucidated. The measured time-averaged wall pressure profiles agree well with the published data (Tu and Wood, 1996) and LES Computational Fluid Dynamics (CFD) simulations results. It was found that the time-averaged pressure profiles are primarily influenced by H/d ratio. However, both H/d and Re affect the standard deviation of the time-varying wall pressure. The ratio of the largest standard deviation relative to time-averaged stagnation pressure increases linearly with H/d , whereas with the same H/d , this ratio decreases as Re increases. Additionally, the spectra of the time-varying pressure are distinguished between two scenarios of i) $H/d < 6$: the spectrum is dominated by high frequencies characterized by the jet or the frequencies from the fluctuation of supply pressure, whichever effect is dominant, and ii) $H/d \geq 6$: the spectrum is independent of the jet characteristics and the supply pressure fluctuation and have a wide range of low frequencies. This phenomenon can be explained by the mixing of jet shear layers beyond the jet core for high H/d (≥ 6) cases. The key application of the present study outcomes together with the analytical model of coating (Johnstone et al., 2017, 2019) is a prediction of H/d and Re ranges where coating ripples are expected to occur.

Non-Automotive Applications: ZnAlMg Coatings / 53

DEVELOPMENT OF ADVANCED PRE-PAINTED Zn-11%Al-3Mg-0.2%Si COATED STEEL SHEETS

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Advanced pre-painted steel sheets were developed by applying Zn-11%Al-3%Mg-0.2%Si coated steel sheets, which are greatly superior to mainstream galvanized steel sheets in corrosion resistance. The basic concept of the development was to create more environment-conscious products and the vital goals to realize the concept was following two. Firstly, they were aimed at much more durable even in a harsh environment such as heavy salt damage district. Secondly, they were aimed at much thinner in painted film keeping equivalent performances to conventional pre-painted Zn-0.2%Al coated steel sheets (pre-painted GI). In this paper, the development of the advanced pre-painted Zn-11%Al-3%Mg-0.2%Si coated steel sheets (pre-painted Zn-Al-Mg) for outdoor-appliances was mainly discussed. Some of the predominant challenges to practical use were shown and the fundamental properties of newly developed products which resolved those were also provided.

Non-Automotive Applications: ZnAlMg Coatings / 55

DEVELOPMENT OF ONE LAYER PRE-PAINTED STEEL SHEET

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The pre-painted steel sheet is widely used as the panel of audio visual systems and office automation equipments (flat-panel TV, DVD, and so on). [U+3000]The pre-painted steel sheet generally has

the primer-paint and the top-paint on a chemical conversion galvanized steel sheet. These paints are solvent-based and applied in the coil coating line. The total paint thickness of conventional pre-painted steel is 15 μm or more, and exhibit the excellent appearance, formability, and many performances of the steel sheet. However, due to intensifying competition and lower prices for home appliances, development of low cost and high productivity pre-painted steel sheet has been desired. [U+3000]To meet these demands, we had developed new pre-painted steel sheet coated with one layer solvent type painting that can be manufactured at EGL inline painting. To develop this pre-painted steel, we pursued to make the film thinner than before for the cost reduction. Furthermore, to apply it in the galvanizing line, we also needed to achieve a shorter baking time for the productivity. However, in order to achieve these goals, we have to improve the appearance of paint film, corrosion resistance and solvent resistance and so on. In this paper, we introduce the development contents and performance of the developed pre-painted steel sheet.

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DEVELOPMENT OF NEW Al COATED STEEL WITHOUT LME CRACKS AND EXCELLENT CORROSION

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Recently, the demand for high strength hot-dip galvanized steel sheet is continuously increasing due to light weight and safety of automobiles. However, in the case of hot-dip galvanized steel sheet, it is found to have a problem that LME(Liquid Metal Embrittlement) cracks occur during welding process, therefore it is limited to supply to the automakers. The hot dip galvanized steel sheet having a low melting point of the coating layer has a problem in that the coating layer melts and penetrates along the grain boundaries during welding process. Aluminum coated steel sheets used in HPF do not produce LME due to the formation of Al-Fe intermetallic compounds having a high melting point at the interface of the coating layer and the substrate, but have no sacrificial corrosion resistance such as Zn. To solve these problems, POSCO has developed new product that are free of LME cracks and have excellent sacrificial corrosion resistance. The new product was developed by adding Zn and Mg to ensure corrosion resistance on Al-base coating which does not generate LME cracks. Although Zn and Mg tends to suppress the formation of Al-Fe intermetallic compounds with high melting point, 1162 [U+2103], it promoted the formation of Al-Fe intermetallic compounds during the welding process and suppresses penetration of the molten metal. It also improved the anti-galling properties because of hard coating layer and showed no micro cracks in the bending test. ecause of hard coating layer and showed no micro cracks in the bending test.

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NEW ZnAlMg ALLOY COATINGS WITH ULTRA HIGH CORROSION RESISTANCE

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ZnAlMg-based alloy hot-dip galvanized steel sheet, as known, has high corrosion resistance. Also, several types of composition systems are commercially produced and applied to various fields. However, these steel sheets characteristically contain up to 3% magnesium. The improvement of corrosion resistance is the attractive point of the product and the goal to pursue forever. In recent years, there is a demand for higher corrosion resistance in harsh corrosive environments. Therefore, the effects of corrosion resistance on the variation of Mg and Al contents were investigated, and

main properties and performances were evaluated. New alloy coated steel with ultra high corrosion resistance was developed.

Solidification and Formation of Hot Dip Galvanized Coatings / 59

RAPID DESIGN OF NEW Zn-Mg-Al-Sn COATINGS WITH LOW MELTING POINT FOR AUTOMOTIVE SHEET APPLICATIONS VIA MACHINE LEARNING

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New generation advanced high strength steels (AHSS) are utilized in automobiles to reduce weight while enhancing fuel efficiency and crash performance. Zn-based coatings are commonly applied on sheet steels to achieve sacrificial corrosion protection. Galvanizing of AHSS is challenging due to the relatively high application temperature of these coatings (460 °C for hot-dip galvanizing). High application temperatures may affect the microstructure and resulting mechanical properties of the substrate AHSS. New coatings with significantly lower melting points and acceptable corrosion resistance would enable new substrate processing alternatives. From a design perspective, this presents an exciting optimization challenge with respect to identifying chemistries in multi-component space that simultaneously satisfy multiple performance criteria. Traditional materials development, starting from research to commercialization, typically takes 10-20 years. This work presents a new approach through a combination of computational and data-driven efforts for accelerating the development of the novel coating alloys. In this study, machine-learning (ML) algorithms trained on i) existing corrosion data and ii) computed liquid/solid phase stabilities are used to optimize the synthesis of novel coating alloys. The ML models are used to predict corrosion current, corrosion potential, and melting temperature of the coatings in high-dimensional Zn-Mg-Al-Sn alloy space. The ML models are also applied to find feature correlations and to predict new coating alloy compositions with enhanced corrosion resistance for specified conditions of the corrosion environment.

Origins of Hydrogen Embrittlement / 60

EFFECT OF ANNEALING ATMOSPHERE ON HYDROGEN EMBRITTLEMENT OF ADVANCE HIGH STRENGTH STEEL

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Recently, the tendency to improve the fuel efficiency by reducing the weight of the car body and using advanced high strength steel(AHSS) has affected the automotive industry. In order to secure the strength of the AHSS above 1Gpa, various elements such as Mn, Si, and Al are added. Additionally, annealing process is performed at high temperature to form an austenite phase and at high hydrogen concentration atmosphere to cool rapidly. In this process, hydrogen penetrates into the austenite grain boundary, which could cause hydrogen embrittlement. Most of the problems of hydrogen embrittlement have been reported that hydrogen generated during corrosion process penetrates into steel and thus leads to embrittlement, but the effects of hydrogen penetration during heat treatment should be studied. In this study, the effect of atmosphere during annealing process on hydrogen embrittlement of 1470MPa martensitic steel was studied. To determine the hydrogen embrittlement behavior after the heat treatment, the elastic deformation

was maintained below the yield strength, and the time up to the fracture was evaluated. The content of the diffusible hydrogen was also evaluated using TDS. The hydrogen embrittlement behavior showed a tendency to vary according to the concentration of hydrogen introduced during annealing process of 1470MPa martensitic steel. In addition, bare(CR) and galvanized(GI) materials were advantageous in terms of hydrogen embrittlement, and galvanized(GI) materials showed inferior properties. Hydrogen absorbed in the bare steel(CR) immediately exits after heat treatment, and in the case of galvanized steel(GI), hydrogen is released during the galvanizing process. However, in the case of galvanized steel(GI), hydrogen absorbed into the steel is blocked in the coating layer and thus leads to hydrogen embrittlement behavior. Additionally, diffusible hydrogen analysis showed that the hydrogen content of galvanized steel was relatively higher than that of other steels.

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EFFECT OF BORON ON THE ADHESION FORCE BETWEEN SUBSTRATE AND Zn-LAYER IN GALVANIZED STEEL

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In the automotive industry, the development of advanced high strength steel(AHSS) sheets is continuously required to respond to the environmental issues such as carbon reduction and securing a passenger safety. Various alloying elements such as Si, Mn, Al and so on, are added to improve the strength of the steel sheets, such steel sheets are galvanized to improve the corrosion resistance. It is well known that B can economically improve the hardenability of steel but addition of B is limited due to reduction of the adhesion force between substrate and Zn layer in galvanized steel(GI). In this study, we studied the effect of B on the adhesion force in two types of GI sheets and we tried to improve adhesion force of the steel sheets by controlling the heat treatment condition. Samples of this study were manufactured under various heat treatment conditions like heat temperature and dew point using galvanizing simulator, the adhesion force of them was qualitatively evaluated through V-bending test and ball impact test. X-ray photoelectron spectroscopy(XPS) and glow discharge optical emission spectroscopy(GDOES) were used to analyze the surface state of samples, and the interface structure of substrate and Zn layer were observed by scanning electron microscopy(SEM). The study result shows that surface segregation of B was found as the heat treatment temperature increased and the dew point decreased. The adhesion force was also reduced as surface segregation of B increased on the surface of substrate steel. And the delamination of Zn layer occurred. Concentrated B on the surface formed BN and/or B₂O₃ that weakened the wettability of Zn and substrate. The reduction of wettability resulted from the decrease of volume fraction and non-uniform formation of the inhibition layer(Fe₂Al₅). With increasing the dew point, B was trapped in the base material by internal oxidation phenomenon, so the B segregation and delamination of Zn layer were not observed.

Electro galvanizing - Process and Product Developments / 62

EFFECT OF THIOGLYCOLIC ACID ON THE MORPHOLOGY OF Zn ELECTRODEPOSITED ON STEEL SHEETS

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Electrogalvanized steel sheets are widely used for electrical appliances and OA equipment because of their suitable appearance. It is well known that the lightness, the gloss, the press formability and the corrosion resistance of electrogalvanized steel sheets change depending on the crystal morphology of deposited Zn. Because control of the Zn morphology is important to improve these properties, many studies have been done on the effects of electrolysis conditions. Among the electrolysis conditions, the addition of organic compounds to the bath is known to change the morphology of deposited Zn drastically, however there are still many unexplained parts about the mechanism of changing the morphology of Zn. In this study, as for organic compounds adding to the bath, thiol compounds (R-SH) were used in consideration of adsorption ability to metal surface. Zn was electrodeposited on a steel sheets from the sulfate bath containing thioglycolic acid. Zn electrodeposition was conducted under galvanostatic conditions. The particle size and crystal orientation index of deposited Zn were determined by the result of X-ray diffraction intensity. The particle size of deposited Zn decreased and the crystal orientation index of (0002) Zn increased by the addition of thioglycolic acid. As the result of investigating the electrochemical behavior using the bath containing thioglycolic acid, adding thioglycolic acid reached to decrease of overvoltage for Zn deposition, acceleration of hydrogen reduction reaction and acceleration of Fe dissolution reaction. It is assumed that the increase of orientation index of (0002) Zn by adding thioglycolic is the effect of decrease of overvoltage for Zn deposition.

Coating Alloy and Modification effects on Corrosion Behaviour / 63

CORROSION RESISTANCE OF Mg-ADDED GALVANNEALED STEEL SHEETS WITH NANO-COMPOSITE COATING

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As competition among global automakers intensifies, demand for materials that are more strict in price and performance is increasing. While steel and plastic materials compete for automotive fuel tanks, plastic materials have advantages in terms of light weighting of automobiles, but have high prices. Accordingly, in this paper, four types of Zn-X plated steel sheets, electroplating (X=none, Sn) and galvanized (X=Fe, Fe-Mg), were manufactured and the applicability as a fuel tank material was evaluated. Nano-composite coating solution with good conductivity was treated on the surface of plated steels by using roll coater and then cured through induction furnace to improve corrosion resistance. Quality characteristics such as corrosion resistance, fuel resistance to diverse gasoline and diesel fuels, and seam weldability, were evaluated for the above plated steels, and their properties were compared and analysed with the conventional Zn-Ni electroplating steels. Among the above plated steels, Zn-Fe-Mg galvanized steels coated with nano-composite coating exhibits superior properties compared to other steels. Detailed experimental results suggest that evenly distributed Mg elements on the coating layer play a key role in the enhanced quality performances.

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NEW INDUSTRIAL ACRYLIC RESIN COIL-COATING BOTH ON MECHANICALLY PATTERNED GI AND STS SHEETS

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In the past, both galvanized (GI) and galvanized (GA) steel sheets with white color coating produced by continuous coating line (CCL) has been widely used for home appliance such as

refrigerator, washing machine and air conditioner. On the other hand, in premium home appliance market, either mechanically polished or physical vapor deposited (PVD) stainless steel sheets was used due to their aesthetical appearance, although rather higher price is known as one of the limitation for alternation of white color coating. In the present study, to answer more economical aspect, an acrylic resin coating with black and yellow colors having different dispersions such as nano carbon and organic pigment for industrial CCL has been successfully developed on hair lined EG, GI and STS steel sheets. The key factor for an effective dispersant of nano carbon and organic pigment is represented by its ability of homogeneous dispersing and stable properties. Mechanical properties, hardness, chemical and detergent resistance were also measured. Up to date, more than forty thousand tons were commercially produced for home appliance and construction.

Automotive Applications - ZnAlMg Coatings / 65

COMPOSITIONAL AND STRUCTURAL OPTIMIZATION OF THE Zn-Mg ALLOY COATING FOR INDUSTRIAL APPLICATIONS

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The protective pure Zn coatings serve as a barrier and a galvanic protection to steel applied in the automotive industries. However, Zn has some economical issues such as too high demand exceeding the supply and wide fluctuation of price. Additionally, the weaknesses of the Zn coatings have been reported steadily such as insufficient corrosion resistance under severe corrosive aqueous solutions. Efforts to develop high performance coatings with decreasing coating thickness and increasing corrosion resistance have been made extensively, and recently various Zn-based alloy coatings as adding other elements such as Cr, Ni, Al, and Mg have attracted much attention for the enhanced corrosion resistance. In this work, various Zn-Mg coatings were synthesized using magnetron sputtering system by controlling different processing variables such as working temperature, input powers, etc.. The Mg contents were varied in the range from 3wt.% to 15wt.%, and the microstructures changed from columnar to featureless amorphous structure as Mg content increased in the coatings. The Zn-Mg coatings with high Mg content exhibited higher corrosion resistance than those with low Mg content due to the formation of the Zn-Mg intermetallic phases in the coatings. The Zn-Mg coatings with high Mg content, however, showed very poor adhesion strength due to their brittleness. Therefore, the double layered Zn-Mg coatings with different Mg contents and layer thicknesses were designed to improve the adhesion properties, and the adhesion of this coating was enhanced extensively compared to that of the single layered Zn-Mg coating with a high Mg content. Based on these results, the possibility of applying the PVD Zn-Mg alloy coatings to the protective coating for an automotive industries were demonstrated.

Bath dross analysis and coating characterization / 66

STRUCTURAL AND MECHANICAL CHARACTERIZATIONS OF TOP DROSS IN A MOLTEN ZINC BATH

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In a molten zinc bath in a continuous galvanizing line, top dross particles crystallize as Fe-Al-Zn intermetallic compounds. These particles easily adhere to the steel sheets causing surface defects. Therefore, controlling the top dross particles is a key issue. The present study focused on the

structural and mechanical characterizations of top dross particles using an electron probe micro analyzer, X-ray diffraction, electron back scattering diffraction, and Vickers hardness measurement. The following results were obtained: (1) The crystal structure of top dross particles Fe₂Al₅Zn_x having Fe: 37~38 wt%, Al: 44~45 wt% and Zn: 18~19 wt% belongs to the orthorhombic system with a lattice constant of a=7.61 Å, b=6.48 Å and c=4.23 Å. The a axis of Fe₂Al₅Zn_x becomes shorter, while the b and c axes become longer compared to those of binary Fe₂Al₅. (2) Top dross crystallizes with clear facet planes. (3) The hardness and the elastic modulus of the top dross particles are the lowest in the [001] direction like Fe₂Al₅, and are lower than those of Fe₂Al₅. (4) The fracture toughness of top dross particles is approximately 1.1 MPa·m^{1/2}, which is slightly lower than that of Fe₂Al₅. The structure of top dross particle containing Zn will be discussed in detail.

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EFFECT OF Mg CONTENT OF COATING ON CORROSION BEHAVIOR OF ALUMINIZED STAINLESS STEELS

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Hot-dip aluminized stainless steels are widely used for automotive exhaust parts by excellent heat and corrosion resistance than ferritic stainless steels. But corrosion behavior of aluminized steels for automotive exhaust gases is considered to be different than conventional corrosive environment. Refer to evaluate the difference of corrosion behavior, two types of corrosion test, such as conventional seawater spray test and exhaust gaseous test, were carried out for aluminized stainless steels prepared by hot-dip process at immersion temperature of 953 K and studied the effect of Mg content up to 5 wt.% of coating. The results show that exhaust gaseous test has more severe condition for corrosion than seawater spray test and corrosion resistance increases as function of Mg content of coating in case of seawater spray test but decreases for exhaust gaseous test. This phenomenon can be explained that caused by difference of reactivity between Mg and ions included seawater and gases, also caused by change of corrosion rate at different pH levels.

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A STUDY ON THE QUALITY OF UNIFORM ALLOYING IN GA WIDTH DIRECTION

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Recently GA automotive steel plates require more high-grade products, and thus the defects that occur during press are reported. A lot of complaints are happening. Among them, defects in powder ring are representative, and it can lead to customer's claim through powder ring that occurs during press. GA steel sheets will undergo alloying heat treatment after passing through Pot- Airknife. Before going through the alloying heat treatment process, they will be removed from the Edge. Because the temperature drop is larger than the center part, the overall alloying temperature is raised to prevent non-alloying of the Edge part.

As a result, unnecessary heat is injected into the center part compared to the edge part, and the quality of the alloying will be adversely affected. In this study, we studied the method of creating uniform alloying quality across the entire width and installed the Edge Burner Type facility. The effects of alloying quality improvement were verified according to application, and for strengthening operation and facility management aspects.

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AN OPTIMIZATION OF SPANGLE MINIMIZER FOR Al-Si COATED STEEL SPANGLE CONTROLLEE, Jong Beom¹¹ *HYUNDAI STEEL***Corresponding Author(s):** smartuk@hyundai-steel.com

Al-Si coated steel is required to have a beautiful surface according to the application, and spangle size is one of the important factors to satisfy this. To control the Spangle size, Various studies have been conducted. In this study, Conditions of Spangle Minimizer which is using the Al powder spraying method after Al-Si pot were investigated, which is one of the methods to control the spangle size. Through this study, it is possible to get the optimum condition of the spangle minimizer under different line speed conditions.

HDG Coating Weight Control by Innovative Technological Concepts / 70

ONLINE PHASE FRACTION MEASUREMENT IN A CONTINUOUS ANNEALING FURNACE WITH X-CAP® TECHNOLOGY**Author(s):** KRAUTHÄUSER, Horst¹**Co-author(s):** Mr. TERLAU, Tobias¹ ; Dr. BRÜHL, Fritz² ; Mr. SASSE, Caesar² ; Dr. IONESCU, Cornelia³ ; Dr. FRENK, van den Berg³ ; Dr. FINTELMAN, Danique³ ; Dr. MELZER, Stefan³ ; Mr. MONTAGNA, Ernesto⁴ ; LHOEST, Alexandre⁵ ; Mr. DI-GIOVANNI, Amedeo⁵ ; Dr. SOMMERS, Ulrich²¹ *IMS Messsysteme GmbH*² *SMS group GmbH*³ *Tata Steel Europe*⁴ *SEGAL, Belgium*⁵ *Drever International***Corresponding Author(s):** h.krauthaeuser@ims-gmbh.de

X-ray diffraction is a technique, which is widely used in material analysis. It is typically utilized in the laboratory to reveal information about the microstructure of materials. IMS developed in cooperation with SMS group and Drever International a new measuring system, which applies the x-ray diffraction technology to the harsh environment of a production line. The new system provides a continuous online measurement of the fraction of the austenite content during heat treatment in an annealing furnace. The result is used as main control variable for the X-CAP® (X-Ray Controlled Annealing Process). This presentation will describe the measures, which are necessary to manage the challenges of online measurement like temperatures and measuring geometry. We will discuss the performance of the system and the compensation of environmental influences. Furthermore, we would like to sum up the experiences which we achieved during the first year of operation in a CGL of Tata Steel SEGAL in Belgium.

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STUDY ON CORROSION RESISTANCE AND ADHESION OF PAINT COATED Zn-Al-Mg GALVANIZED STEEL**Author(s):** OH, Se-Young¹**Co-author(s):** Mr. LEE, Jae-Won¹ ; Ms. PARK, Bora¹¹ *POMIA (Pohang Institute of Metal Industry Advancement)***Corresponding Author(s):** liliy530@pomia.or.kr

Iron is corroded by various factors such as moisture, salt and air exposure, causing problems in the building's exterior and structure. To solve this problem, studies have been continued about

rust-resistant iron. Most of the galvanized steel used for outdoor applications are coated again painting on the galvanizing layer. More than that, Magnesium-added Zn-Al-Mg coated steel sheet is excellent for corrosion resistance of cut surfaces. In this study, adhesion was analysis using Scanning Kelvin Probe(SKP) and corrosion resistance of coated steel sheet was evaluated by Salt spray test and Electrochemical Impedance Spectroscopy(EIS) analysis.

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IN-SITU OBSERVATION OF THE CRYSTALLIZATION AND GROWTH BEHAVIOR OF Fe-Zn INTERMETALLIC COMPOUND ("BOTTOM DROSS") IN THE MOLTEN ZINC USING X-RAY TRANSMISSION IMAGING METHOD

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“Dross” is solid intermetallic compound generated in molten zinc baths of CGL, and it can be the cause of surface defects of hot dip galvanized steel sheets. Their behavior in the molten zinc such as thermochemical stability is well investigated before, but its crystallization or growth behavior is not understood yet because their reaction occurs in high-temperature and opaque molten zinc. In this study we tried in-situ observation of crystallization and growth behavior of Fe-Zn intermetallic compounds (“bottom dross”). X-ray transmission imaging has been tried using SPring-8 BL20XU. From the X-ray upstream, X-ray shutter and slit, sample stage with heater in a vacuum chamber, and high resolution X-ray image detector, are equipped. The selected X-ray energy is 25keV and the pixel resolution of the detector is 0.5um, time resolution is 2 fps. Zn-0.10wt%Al-0.10wt%Fe alloy (sample A) and Zn-0.10wt%Al-0.15wt%Fe alloy (sample B) were selected in order to observe crystallization and growth behavior of Fe-Zn intermetallic compounds. The Zn alloy ingot was cut and polished into the 100um thickness thin specimen. The specimen was set on the sample stages and melt homogeneously in the low pressure environment by heating up to 600°C. Then specimen was cooled by various rates. The X-ray transmission imaging has been recorded during the cooling process. Fe-Zn intermetallic compounds has higher mass density and X-ray absorption coefficient than molten zinc, they can be observed as darker contrast crystals in the zinc matrix. Their growth behavior by time can be observed. In sample A, their nucleation frequency is not changed by changing cooling rate, but their nucleation frequency is accelerated and its crystal size gets smaller by faster cooling rate in sample B. This technique can be a strong method to understand the behavior of dross particles in the molten zinc baths. We are going to discuss about the relation between the published thermochemical stability data and observed crystallization or growth behavior. Acknowledgment: These experimental results were obtained from the use of Spring-8 industrial application No.2018A1551, 2018B1587 and 2019A1627.

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CORROSION RESISTANCE OF VARIOUS METALLIC COATING ON HOT PRESS FORMING (HPF) STEEL

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Hot press forming (HPF) steel has been widely used to produce high strength and complex shaped car parts because it provides high mechanical properties and formability. Process of

press hardening is carried out at high temperature over A3 line, which cause the oxidation of the steel surface. Since oxide removal is required for welding and painting, many different coatings have been introduced to suppress oxide formation. The aluminum coating is widely used and commercially successful. However, its low cathodic protection causes cosmetic and perforation corrosion of HPF steel. The Zn and AlZn based coatings are developed to enhance the resistance of corrosion. Galvanized steel is effective for suppressing corrosion, but the occurrence of microcrack is unavoidable. To maintain resistance of corrosion and microcrack, Al-Zn-Si coating on HPF steel has been developed in laboratory and validated through pilot plant. This paper demonstrates the excellent anticorrosive effect of the newly developed coating layer. After heat treatment of press hardening, Ecorr of the Al-Zn-Si coating was similar to the Ecorr of Zn-HPF. The coating layer containing zinc was shown to be beneficial in cathodic protection. This new coating shows that reduced corrosion of steel compared to AlSi HPF and improved spot weldability without additional shot-blasting. In addition, liquid metal embrittlement and microcracks caused by the zinc containing layer were not observed

Industrial Status of Galvanizing Production Technology / 75

HOT-DIP GALVANIZING LINES - CHALLENGES AND SOLUTIONS FOR THE INDUSTRIAL PRODUCTION OF COATED 3rd GEN AUTOMOTIVE STEELS

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Advanced high-strength steel grades (AHSS-grades) of the third generation offer significant ecological and economic potential in the automotive industry for reducing automotive weight, improving fuel efficiency, and thus decreasing emissions. Their properties are based on special chemical compositions and microstructures. The annealing and galvanizing process of these grades challenges the plant technology.

This paper presents solutions for the industrial production of coated AHSS-grades and shows new production aspects with advanced furnace and coating technology. It will introduce the intelligent furnace concept with X-CAP® technology for a precise closed-loop controlled heat treatment process based on material properties. Furthermore, it presents equipment technologies for the galvanizing process and surface quality. Finally, the most recent and innovative references for hot-dip galvanizing lines will be introduced.

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FORMATION OF INTERMETALLICS IN Fe-BASED MATERIALS DURING LONG-TERM DIPPING IN AISi MELT

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The durability of metals in molten aluminium is of high importance for technical processes. Parts, for example rollers for fire-aluminizing, are exposed to high material abrasion through a combination of wear and metal-physical corrosion by reaction with the liquid aluminium. In this paper, long-term dipping tests were done with different materials in an Al-based metal bath. The used materials were austenitic manganese steel, chromium chilled iron, austenitic high-temperature steel, ferritic carbide chilled iron and grey cast iron, in which the phosphorus and silicon content varied. The samples were dipped for 96h and 300h in a 650°C hot Al-Si bath.

Furthermore, samples were dipped into the Al-Si melt for a short time then aged for 1h at 920°C before long-term immersion. After aging and generating an intermetallic phase, a long-term immersion test was carried out again for 96h in the 650°C hot Al-Si melt. The analysis and characterization of the resulting interfacial reactions was performed by stereomicroscope, light microscope, scanning electron microscope, EDX, XRD and hardness measurements. The results show that steels with a low carbide content, such as the austenitic manganese steel that was used, have a lower durability in liquid aluminium. The reduction of the diameter is up to 30% compared to ferritic carbide chilled cast iron or grey cast iron, where the reduction of the diameter is about 5%. Optical light and scanning electron microscopy reveal that two different intermetallic phases formed. A lighter intermetallic phase at the base material and a darker intermetallic phase at the boundary to an Al-Si layer. The lighter layer in the scanning electron microscope has a percentage of 60 at.-% Al and 25 at.-% Fe, while the darker layer has a percentage of around 70 at.-% Al and 10 at.-% Fe. It can also be seen that chromium carbides do not dissolve and are surrounded by the brighter intermetallic phase. The hardness measurements show that the brighter phase with 60 at.-% Al varies between 800-900 HV0.05. The darker phase with 70 at.-% shows a higher hardness of approximately 1000-1100 HV0.05.

On-Line Measurements and Galvanizing Bath Control Development & Bath Al Chemistry Effects on Coating Quality and Bath Management / 77

CFD MODELING AND VIRTUAL EVALUATION OF THE USE OF PUMPS IN A CGL BATH

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A system to alter the behavior of dross in a CGL bath utilizing pumps in the zinc bath was evaluated utilizing CFD Modeling. The mesh of a conventional bath was modified with virtual pump intakes and discharge ports with minimal modification to the existing mesh. The propensity for dross formation was inferred by temperature variations between the firing of the pot inductors. This approach resulted in shorter computational times and allowed for different pump variations to be cost effectively evaluated. The jet of material from a pump discharge was more effective at altering flows as compared to a pump intake. The change in bath flows was most significant with a central pump pushing zinc into the area above the sink roll and two pumps pulling from each side of the strip/sink roll nip. Although the circular currents above the pot roll could be altered with the use of pumps, smaller circular currents were induced along with an increased size of a low temperature region near the stabilizer roll. The use of CFD modeling allowed the effect of pumps in the galvanizing bath to be explored, with no impact on production.

Fundamentals on Absorption of Hydrogen & Fundamentals on Atmospheric Corrosion and Corrosion Modelling / 78

RELATIONSHIP BETWEEN HYDROGEN ABSORPTION AND CORROSION BEHAVIOR OF ELECTROGALVANIZED STEEL SHEETS IN DRY-WET CORROSION ENVIRONMENT

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Zinc coated high strength steel sheets are applied to the automotive part due to the superior corrosion resistance and the lightweight of car body. The hydrogen absorption into the high strength steel sheet has been known to be promoted by zinc coating during corrosion, however,

its behavior has not been clarified. In this study, the effect of corrosion status of zinc coating on the hydrogen absorption behavior was investigated. Dry-wet corrosion test was conducted after applying NaCl solution to the zinc coated steel sheets. The permeating hydrogen during the corrosion test was measured by electrochemical technique. It was found that the hydrogen permeation was not observed at early stage of corrosion while significant hydrogen permeation was observed at middle stage of corrosion. Then, the hydrogen permeation decreased gradually at later stage of corrosion. In order to clarify the mechanism of this behavior, surface morphologies of corroded specimens were analyzed by Electron Probe Micro Analyzer. It was found that the hydrogen permeation was observed when the steel substrate was partially appeared, indicating that galvanic corrosion is related to the hydrogen permeation.

Fundamentals on Absorption of Hydrogen & Fundamentals on Atmospheric Corrosion and Corrosion Modelling / 79

ANALYSIS OF COSMETIC CORROSION BEHAVIOR BY IN-SITU OBSERVATION IN WET AND DRY CONDITIONS

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Zinc coated steel sheets are used in order to protect corrosion of automobile bodies. It is well known that the type of automotive corrosion can be divided into perforation corrosion and cosmetic corrosion. Although the mechanism of the perforation corrosion has been studied well, the mechanism of the cosmetic corrosion has not been clarified yet. In this study, an in-situ observation technique was developed and an analysis of cosmetic corrosion was performed. Cold rolled steel sheets without galvanizing were used as test samples. After painting with ED, the surface of the samples was scratched with a cutter. The corrosion resistance was evaluated under the test condition which is in accordance with SAE J2334 (1 cycle: Salt dip, 15 min => Dry process, 17 h, 45 min => Wet process, 6 h) . The cosmetic corrosion behavior of the samples in initial 2 cycles was observed in-situ by the developed in-situ system. The samples were taken out at regular time intervals and analyzed. As results, it was found that the progress of under-film corrosion consisted of 3 steps. The 1st step is in the initial stage in the dry process of the 1st cycle. In this step, red rust gradually changed to black rust composed of magnetite at the scribed part, implying that the rust changed from iron hydroxide to magnetite by a cathodic reaction. The 2nd step is in the latter stage in the dry process, and in this step, under-film corrosion progressed from the scribed part. Cl was enriched at the scribed part when under-film corrosion started, and then it moved to the tip of under-film corrosion. The progress of under-film corrosion in the 2nd step is based on the Funke mechanism. The 3rd step is in the wet process, and in this step, the tip of the under-film corrosion grew so as to swell. It is assumed that water penetrated at the Cl-enriched part of the tip of the under-film corrosion by osmotic pressure. In 2nd cycle, the 2nd step and 3rd step in 1st cycle was repeated. The under-film corrosion progressed at almost the same rate as 1st cycle, and the under-film corrosion of the 2nd step was dominant as to the total corrosion rate. This in-situ observation technique can be also applicable to zinc coated steel sheets and will lead to a new coating design.

Solidification and Formation of Hot Dip Galvanized Coatings / 80

PERITECTIC STRUCTURE EVOLUTION IN HOT-DIP Zn-Al ALLOY COATINGS

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Hot-dip Zn-Al alloy coated steel sheets such as 55%Al-Zn-1.6%Si and Zn-5%Al coatings are widely used in the construction industry because of their higher corrosion resistance than

zinc coatings. It is well known that the corrosion resistance of hot dip Zn-Al alloy coatings depends on the microstructure formed through solidification process¹). Thus, controlling the solidification microstructure is important to control the corrosion resistance. When we consider the microstructural evolution process, suitable phase diagram is necessary. While, there are two kinds of Zn-Al binary phase diagrams^{2, 3}). One includes peritectic reaction but another doesn't. In most of the former studies, the phase diagrams without the peritectic reaction were used to consider the microstructure of Zn-Al alloy coatings. Meanwhile, according to the Zn-Al binary phase diagram with peritectic reaction, the peritectic structure should form when the Al content is higher than 13%. Therefore, the present study investigated the microstructure in hot-dip Zn-(11, 22)%Al coatings in order to clarify which Zn-Al binary phase diagram is more suitable for understanding the solidification microstructure evolution of hot-dip Zn-Al alloy coatings. Zn-(11, 22)%Al coatings on mild steel substrates were prepared by using a hot dip simulator machine. The temperatures of the molten Zn-(11, 22)%Al bathes were set at 480, 500 [U+2103], respectively. The dipping time was 3 seconds and the average cooling rate was controlled at 10 [U+2103]/s from the bath temperature to 150 [U+2103] by using Nitrogen gas flow. The morphology and compositions of microstructure in coating samples were examined by means of X ray diffraction (XRD), scanning electron microscopy (SEM). As a result of microstructural investigations, the peritectic structure formed inside of dendrites in the Zn-22%Al coating, but not in the Zn-11%Al coating. This indicates that the peritectic reaction occurred in the course of solidification process in the Zn-22%Al coating. Therefore, the Zn-Al binary phase diagram including peritectic reaction is considered to be suitable for understanding the solidification microstructure evolution of hot-dip Zn-Al alloy coating steel sheets.

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Coating Microstructure Analysis and Steel/Coating Surface Reactivity / 81

DENDRITIC MORPHOLOGIES OF HOT-DIP GALVANIZED Zn-0.2 WT.% Al COATINGS: EXISTENCE OF THIRD PREFERRED GROWTH DIRECTIONS

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Hot-dip galvanized Zn-rich coatings on steel sheets often exhibit dendritic morphologies formed by the primary Zn phase during solidification. The corrosion resistance and surface quality of the galvanized coatings depend not only on the coating chemistry and grain size, but also on the dendritic morphologies of individual coating grains. Therefore, it is of fundamental importance to understand how the dendritic morphology depends on the crystallographic orientations of coating grains. In this study, the dendritic morphologies of hot-dip galvanized Zn-0.2 wt.% Al coatings on steel sheets were systematically examined as functions of the inclination angle and axis of the Zn basal plane with respect to the sheet surface by using electron backscattered diffraction. When the inclination axis of the basal plane was <1-210>, the dendrite changed its morphology by following the sequence of six-fold → eight-fold → elongated X → elongated X+C patterns with increasing inclination angle from 0 degree to 90 degrees. When the inclination axis was <10-10>, the sequence of morphological patterns was six-fold → eight-fold → two-fold → four-fold. These morphological changes of dendrites could not be explained based on the two previously known families of preferred growth directions, <10-10> and <0001>, but they suggested the existence of a third family of weakly preferred growth directions, which were close the normal directions of the {1-211} planes. Based on the morphological observations of Zn dendrites, we proposed an anisotropy function of the growth kinetics as a function of the polar angle and the azimuthal angle. In the presentation, we will demonstrate using three-dimensional phase-field simulations that most of the morphological characteristics, such as the sequences of the morphological changes depending on the inclination axis and the existence of the two-fold, eight-fold and elongated

X patterns, can be reproduced only when the third preferred growth directions are taken into account.

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NONLINEAR MODEL PREDICTIVE TEMPERATURE CONTROL OF A COMBINED DIRECT- AND INDIRECT-FIRED STRIP ANNEALING FURNACE

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In a hot-dip galvanizing line for the production of zinc-coated steel strips, the heat treatment of the strip is an important process step. In order to achieve the desired material and surface properties, the strip has to be heated according to a predefined temperature trajectory. From the viewpoint of control, this is a challenging task, in particular in transient furnace operation, e.g. when a welded joint traverses the furnace or when the strip velocity changes. Because the product diversity, the demands on the product quality, and the desire to minimize the energy consumption are steadily increasing, there is a need for an advanced process control concept that accounts for all these challenges. In this paper, a nonlinear model predictive controller for the strip temperature in a combined direct- and indirect-fired annealing furnace is described. The controller was implemented at a hot-dip galvanizing line of voestalpine Stahl GmbH, Linz, Austria and measurement results from three years operational experience are presented.

The basis for the model predictive controller is a first-principles dynamical model of the furnace, which is characterized by moderate complexity and which captures the essential dynamical behavior of the real furnace. The model incorporates sub-models describing the flue gas, the wall, the radiant tubes, the rolls, the strip, and the relevant heat transfer mechanisms. Using this furnace model and the estimated current system state, the model predictive controller selects optimal trajectories for the fuel supply so that the strip temperature reaches its desired target temperature. In the control algorithm, a tailored constrained nonlinear optimization problem is numerically solved by the Levenberg-Marquardt method. The gradient and the approximated Hessian matrix of the objective function are analytically computed using an adjoint-based approach. This computationally highly efficient algorithm ensures that the controller can be executed in real time.

Measurements from the implementation at the industrial plant of voestalpine demonstrate the excellent performance of the developed control concept. It ensures compliance with all temperature constraints and achieves accurate strip temperature control in both steady-state and non-steady-state furnace operation. A long-term analysis shows the significant improvement of control performance in terms of accuracy and homogeneity of the strip temperature compared to the previous implemented PI temperature controllers. Encouraged by excellent feedback from three years operational experience, the developed control concept is currently transferred to the other hot-dip galvanizing lines of voestalpine.

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INFLUENCE OF DROSS BUILD-UP INDUCED ROUGHNESS ON FLOW STRUCTURES AND HEAT-TRANSFER OF SINK ROLLS IN HOT-DIP GALVANIZING LINES

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This paper presents a CFD simulation study of the influence of roughness on the flow near stationary and rotating bath equipment. During production, the roughness of bath rolls is significantly increased by dross build-up. The latter is one major reason for undesired maintenance cycles. Understanding the interaction between roughness and zinc flow facilitates the interpretation of dross build-up growth mechanisms. The turbulent zinc alloy flow in the global zinc bath is computed with a k-w SST turbulence model. The flow, temperature and thermodynamics are mapped on a highly resolved sub-model, surrounding the rotating sink roll, with a sufficiently fine grid ($y^+ < 1$). The effect of roughness is modelled on this sub-model with the high roughness approach. The turbulence and roughness models are validated with measurement data from literature. It was found that flow velocity decreases significantly away from the rotating roll, with a decay of ~30% of the rotation velocity at a distance of 1mm. This steep velocity gradient is decreased by higher roughness. Rough peaks cause additional drag and increase the turbulent intensity. Thus, at higher roughness, the heat and mass-transfer towards the surface, where the growth of dross build-up occurs, is increased.

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EFFECT OF ANNEALING HEAT TREATMENT ON THE ADHESION STRENGTH OF THE EMH-DEPOSITED Zn-Mg/Zn COATING ON TRIP STEEL

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The advanced high-strength steels (AHSS) such as a dual-phase (DP) steel, twinning-induced plasticity (TWIP) steel, and transformation-induced plasticity (TRIP) steel have been used extensively in automotive industries to reduce the weight and to improve the safety of automobiles. To ensure the corrosion resistance of AHSS, the advanced coating materials and coating process to replace the conventional galvanizing process are necessary. The Zn-Mg coating is a strong candidate for the corrosion protective coating of AHSS, and physical vapor deposition (PVD) process is a promising process for the deposition of the Zn alloy coating. Previously reported was the enhanced corrosion resistance of Zn-Mg coatings with increasing Mg content in the coatings due to their dense amorphous microstructure. The Zn-Mg coating with high Mg content, however showed insufficient adhesion properties due to a very brittle nature of the coating compared to the pure Zn coating. In this study, the Zn-Mg/Zn double-layered coatings were synthesized on TRIP steel substrate using electro-magnetic heating (EMH) evaporation process, and the annealing treatment at 200°C in vacuum were conducted with various annealing times to improve the adhesion strength of the Zn-Mg/Zn coating. The gradient Zn-Mg coating was resulted from the annealing treatment and it was also observed that various intermetallic compounds such as Mg₂Zn₁₁, MgZn₂, FeZn₇, Fe₃Zn₁₀ etc., formed at the interface between the Zn interlayer and the steel substrate during annealing by diffusion of Zn and Mg. The gradient Zn-Mg coatings resulted from the annealing treatment showed much improved adhesion strength of the coatings in the lap shear test over those of the commercial galvanized steel. Detailed experimental results will be presented.

Furnace II - Current Topics from Preoxidation to Galvannealing / 85

Numerical Simulation on Electromagnetic Driving Dross for Continuous Hot Dip Galvanizing Line

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The floated zinc dross is easily accumulated around zinc pot walls (backward wall is furnace nose) during continuous hot dip galvanizing. The main cause is that the accumulated zinc dross is lack of tangential flowing along zinc pot walls. Aiming at the distribution characteristics of the floated zinc dross on the top of zinc bath in hot-dip galvanizing pot, a new method called by Electromagnetic Driving dross for Continuous Galvanizing Line (CGL-EMD) was proposed, by which the top of zinc bath in a zinc pot will be driven flowing by exerting traveling wave electromagnetic field at a certain height above the zinc bath, and then the dross will be certainly dragged flowing and re-distributed on the top of zinc bath. Through sequential coupling simulation of electromagnetic field and flow field, several flow fields of the zinc bath under different EMD layouts were simulated. The results show that EMD, namely the exerted traveling wave magnetic field force can effectively promote the tangential flow of the surface zinc liquid in a galvanizing bath, and the maximum tangential velocity can be up to 0.8m/s. According to the measured data of the flow velocity of the zinc liquid under air knife injection and gas blowing, It can be seen that the zinc dross can be driven flowing while the EMD tangential flow rate is above 0.15 m/s. In fact, the tangential flow rate of the zinc liquid by EMD is much larger than the flow rate of the zinc liquid under the air knife gas blowing, which fully confirms that the proposed EMD method is feasible and effective. In addition, the simulation results also show that the tangential flow velocity of the zinc bath in the zinc pot is less affected by the EMD time of the applied magnetic field force, however, increases with the increase of the applied magnetic field force, and the EMD depth of the applied magnetic field force is only within 100-200 mm range below the zinc bath. Further then, by defining the time factor, the dross removal efficiency of different EMD layouts is discussed. Finally, the development and industrial practice of EMD system in Baosteel are briefly introduced, and the future is prospected.

Furnace I - Temperature Control Challenges / 86

APPLICATION OF A PHYSICS-BASED EMPIRICAL MODEL FOR ESTIMATION OF RADIANT TUBE TEMPERATURES IN A GALVANIZING LINE

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Measurements at high-temperature facilities such as galvanizing lines are often possible only to a limited extent. Moreover, many of the processes involved are too complex to apply existing numerical methods such as CFD to provide the desired information. Therefore, an empirical method was developed to estimate process data which is not measured. The method was demonstrated by determining the surface temperature of radiant tubes. During operation these tubes are exposed to high thermal loads, which can result in failure. For this reason, close monitoring of their state is necessary to improve operation and increase the lifetime of the tubes. Using detailed measurements from a single tube and thermodynamical principles, the most significant influences on the tube's surface temperature were identified. Subsequently, these transport equations were approximated by introducing stochastic parameters. Lastly, the parameters were adjusted by applying a direct search algorithm. Validation of the results was performed by using an extensive control set. It has been shown that the model can produce realistic results, even when exceeding the range of data that was used when training the model. Furthermore, guided by thermodynamic principles, the model can retain a more efficient and comprehensible structure when compared to competing machine learning methods e.g. neural

networks. Ultimately, the modular concept of the presented method allows for it to be transferred to other facilities or processes for which only limited information is available.

Automotive Applications - Zn and ZnFe Coatings / 87

THE ROLE OF STEEL SHEET AND ITS IMPACT ON AN OUTSTANDING QUALITY PAINT USED FOR AUTOMOTIVE OUTER SKIN

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In order to meet the increasing demand for a flawless and attractively painted car, surface topography of sheet metal is becoming more and more into focus of optimization. Besides inhomogeneous painting, disturbing surface texture with long wavelength proportions can make the appearance of a coating disturbed and inferior. In order to measure and display these inhomogeneity's, new characteristic values such as the Wsa1-5 value or the Wa0.8 value were introduced with the aim of characterizing surfaces and evaluating them to predict the resulting effect on the final painting. The measured values consider the proportion of long wavelength structures in the topography and provide information about the wave height. However, not only the surface, but also the material plays an important role in meeting the highest painting requirements. In addition, forming conditions during component production can create and reinforce visible textures. This effect is associated with an increase in waviness and is a result of material inhomogeneity, which can be found along the sheet metal cross-section and inside the sheet metal plane. Thereby a direct dependence between the waviness values and material isotropy is deduced. This results in a direct dependence between the waviness values and material isotropy. The article explains the identified relationships between texture characteristic and material isotropy in a typical steel for the automotive industry.

Poster Session / 88

NUMERICAL SIMULATION OF PHYSICAL FIELD IN A CONTINUOUS HOT-DIP GALVANIZING BATH

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In this paper, the computational fluid dynamics method was used to study the influence of the addition of zinc aluminum ingot in a zinc pot. The simulation results show that the natural convection effect changes the flow pattern of the zinc bath around the zinc ingot side, and the cold zinc liquid flows to the bottom of the zinc pot, and a large eddy is formed behind the zinc pot; The whole temperature fluctuation of zinc pot is small, the lowest temperature is at the ingots addition position, while the temperature is higher at the inlet and outlet of the inductor; Aluminum melting from low-level aluminum zinc ingot (Zn-0.2%Al) is mainly added into the zinc pot bottom, and the aluminum solubility distribution in the V-area can be adjusted by addition of high-level aluminum zinc ingot (F ingot: Zn-10%Al). This work provides a basis for reducing the fluctuation of aluminum concentration in the zinc pot and optimizing the ingot filling process.

Automotive Applications - Zn and ZnFe Coatings / 90

THE EFFECT OF BONDING STATE BETWEEN THE GALVANIZED STEEL SHEETS AND THE ADHESIVE ON DETERIORATION BEHAVIOR OF ADHESIVE JOINT

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In the automotive industry, the needs of adhesive bonding are increasing. It is well known that the deterioration over time of adhesive joined parts is one of the problems. Therefore, we investigated the deterioration behavior of adhesive joined parts using various steel sheets. As a result, deterioration over time was caused by the becoming weaker in interfacial adhesion strength between the metal surface and the adhesive, and degree of the deterioration depended on the type of metal coating. Furthermore, the deterioration behavior was affected by the difference of bonding state depending on the type of metal coating and adhesives. In this paper, we estimated the bonding state by examining the adhesion work on each surface of steel and some kinds of galvanized steel sheets, and discussed the aging mechanism of adhesive bonding.

HDG Coating Weight Control by Innovative Technological Concepts / 91

THE BEHAVIOR OF LIQUID ZINC FLOW IN FULL SPLASHING

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Gas wiping is one of the most important processes which determine the product quality in continuous galvanizing line. Here, there are many problems known as, stability of coating weight, edge splashing and full splashing. We focused on the full splashing phenomenon which the runback flow of zinc detaches the substrate and pours on the gas nozzle. Generally, this phenomenon is known to occur when the shear stress of the gas becomes too high compared to the surface tension of the liquid film. In this paper, further experiments were made by using molten zinc bath and rotating cylinder. And the effect of gas wiping condition on the behavior of the runback flow and full splashing was clarified.

Fundamentals on Selective Oxidation of AHSS / 92

SELECTIVE OXIDATION IN A BAKE HARDENING STEEL FOR DFF - RTF ANNEALING CYCLES

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The selective oxidation of Boron in bake hardening steel sheet is investigated in a hot dip process simulator for a typical DFF RTF cycle with two levels of pre-oxidation. The time in the RTF (85, 125 and 220 seconds), the RTF dew point (-40, -25 and -10 oC) and the hydrogen content (1, 3 and 5 %) of the RTF atmosphere are varied. The samples were analysed with FEG-SEM, EDX and GDOES. A few cases were analysed with Auger to get more information about the condition of the outer surface. Both the annealed substrate as the inhibition layer formed in a MagiZinc bath containing 1.6 % Aluminium and 1.6 % Magnesium was analysed. The amount of Boron enrichment at the surface increases when the dewpoint is decreased from -10 to -40 oC which is an indication of more external oxidation of Boron. Pre oxidation leads to a lower Boron enrichment at the surface. The effect of pre oxidation is biggest for the cases with lower dewpoints (-40 and -25 oC) and it is limited for a dewpoint of -10 oC which is in accordance with results from literature. The longer times in the RTF and soak showed saturation of Boron at the surface

for a dewpoint of -40 oC, this did not happen for the higher dewpoints. The inhibition layer showed small holes where we could still detect oxides on the substrate. In some cases evidence of an inhibition layer was still found that can indicate reduction of oxides by the MagiZinc bath.

Modeling Bearings Wear Rate and Enhanced Pot Roll Coatings & HDG Coating Weight Control by Numerical Simulation and Modeling / 93

A SIMPLE MODEL TO ESTIMATE AND TRACK THE WEAR RATE OF POT BEARINGS

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The lifetime of pot bearings is one of the major sources of maintenance shutdowns on a continuous galvanizing line. However the lifetime between different lines can be very different whereas the general process windows may look the same. A simple model is proposed to quantify the expected wear rate, considering the bearing geometry and process parameters. A viable model would help operators understand if a decrease of the bearing life is linked to variations in the process window. The model has been used to explain the differences in bearing wear on several CGL using the same bearing materials. Validation showed that the observed trend is in relation with the model prediction. Next step will consist in comparing various lines and maybe set some coefficients to include the differences in bearing materials used (e.g. superalloys and ceramic). This model approach attempts to put a little more science into bearing lifetime prediction.

HDG Coating Weight Control by Innovative Technological Concepts / 94

EASY ANALYSIS OF AIR KNIFE PERFORMANCE BY STATIONARY FLOW CALCULATIONS

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Increasing revenues in Hot Dip Galvanising can be achieved by increasing the line productivity. Therefore, the industry trend is to increase line speed. However, in elevating line speed of a hot dip galvanising line the drag out of molten zinc on the strip increases. As a consequence, more molten metal has to be wiped from the strip. To accomplish this air knives are of increasing importance. In the process of selecting the optimum air knives for a galvanising line, performance data supplied from the manufacturers are being used. However, more tangible ways to select air knives would be favourable. A method for selection could be based on the air knife flow; based upon the flow characteristics various air knives can be compared. The air knife performance mainly depends upon gradient of the stagnation pressure. Unfortunately, it is very difficult to calculate this gradient at the interaction point with the liquid metal however, the stagnation pressure at exit nozzle conditions is easily calculated from compressible fluid flow together with thermodynamics. A comparison of the stagnation pressures reveals the relative air knife performance. This paper describes a flow model for the nozzle characteristics and this model has been validated by laboratory measurements. Thermodynamics have been used to establish an indication of the air knife stagnation pressure and it is demonstrated that these calculations can be used for air knife evaluation.

Origins of Hydrogen Embrittlement / 95

INFLUENCE OF Zn-BASED COATING ALLOYS ON HYDROGEN DIFFUSION AND CORROSION RESISTANCE IN A DP STEEL

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In advanced high strength automotive steels, small amounts of diffusible hydrogen can lead to a deterioration of mechanical performances, especially a loss of ductility, in the simultaneous presence of internal stresses and of a sensitive microstructure. In the hot-dip galvanizing process, hydrogen is mainly absorbed during high temperature operations in hydrogen-containing atmospheres before hot-dipping, when the solubility of hydrogen in steel is the highest. After hot-dipping, the metallic zinc overlay coating can act as a hydrogen barrier, and also the Fe-Zn intermetallic layer inhibits hydrogen diffusion out of the metal. As a result, an excess of diffusible hydrogen remains in the steel substrate and can subsequently leads to a possible embrittlement.

In this work, the effects of the coating nature on the hydrogen diffusion and embrittlement of a 980MPa dual phase steel (DP980) are investigated. The attention is focused on three Zn-based coating alloys: galvanized (Zn-0.23%Al), galvanized (Fe-Zn based on Zn-0.12%Al) and Zn1.2Al1.2Mg. Indeed, if the behaviour of classical galvanized zinc coating with respect to hydrogen is well known, it is however not the case for its alternatives.

The hydrogen permeability of the coatings is first assessed through degassing experiments at room temperature on samples prepared with a hot dip galvanizing process simulator. The influence of cracks developed in the coating of the galvanized samples is investigated, as these are not present in GI and Zn1.2Al1.2Mg coatings. Secondly, hydrogen uptake of these coated samples due to their corrosion in cyclic SAE J2334 corrosion testing is analysed. Finally, mechanical performances of corroded samples are evaluated. In all cases, the diffusive hydrogen content is measured through a thermal desorption analysis, with a critical assessment of the methodology.

Poster Session / 97

HOW MODEL PREDICTIVE CONTROL ENHANCES STRIP TEMPERATURE REGULATION

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In continuous galvanizing lines (CGL), strip annealing temperature is, though not the only one, the most significant physical parameter in the annealing process and therefore is used as the main indicator for product qualification. Annealing furnaces today are mostly regulated by Proportional Integral Derivative (PID) controllers or with the help of static based models. Those methods, though applicable, are providing non optimal control during transitions due to their limited ability in forecasting the furnace behaviour. To address this issue Fives has built comprehensive dynamic models of annealing furnaces and used them in Model Predictive Control (MPC). This paper shows how MPC helps reacting in advance of a process change and provides better strip quality as well as enhanced plant productivity. For two different annealing furnaces, Radiant Tube Furnace (RTF) and Direct Fired Furnace (DFF), the main components of the furnace models are first given. Then the MPC and examples of its application within Virtuo® Level 2 system are detailed.

Industrial Status of Galvanizing Production Technology / 98

CELES ECOTRANSFLUX™, A DISRUPTIVE TECHNOLOGY FOR HEATING GEN3 AHSS

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Steel manufacturers are continuously developing higher performance steel grades by optimizing the chemistry at the steelwork and by changing the process parameters, in particular the heat cycles to be applied in the annealing furnaces. In hot dip galvanizing lines, the production of the latest Gen3 AHSS require higher annealing temperatures which are difficult to be achieved by using gas fired radiant tubes. The new thermal cycles also require a quenching followed by an induction rapid heating where the strip may still have a big fraction of austenite which results in poor magnetic properties for a heating by a conventional inductor. This also raises concerns in the case of the galvannealing induction heating process for the same reasons. To fulfil the requirements of the new annealing cycles, i.e. heating the strip at high temperature (above Curie point) or rapid heating the strip with poor magnetic properties, the transverse flux induction is the unique industrial solution.

Fives has been developing the CELES EcoTransFlux™ technology since more than 20 years, first for rapid heating of stainless steel in strip processing lines. Today, this advanced technology is becoming a key equipment for processing the latest Gen3 AHSS and also for developing higher performance electrical steel products.

This paper presents the main features and performances of Celes transverse flux induction technology as well as different industrial applications and references.

PHS-ZnFe: Liquid and Vapour Metal Induced Embrittlement / 99

DEVELOPMENT OF A Zn-Al-Mn-Sb ALLOY COATING FOR PRESS HARDENABLE STEELS

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As galvanized or galvannealed coatings (GI or GA) are often challenged by excessive zinc evaporation and liquid metal embrittlement (LME), aluminized coatings have become dominant for press hardenable steels (PHS). However, compared to aluminized coatings, galvanized coatings are more cost effective. Galvanized coatings not only provide cathodic protection to the steel substrate; they are also superior in weldability and paintability. In view of these advantages, there is a need to develop a practical industrial PHS application of galvanized coatings, through effective measures, to overcome the relevant issues resulting from the press hardening process.

In the present study, a galvanizing bath was modified with the addition of a small amount of Mn and/or Sb. Samples of a boron steel were galvanized/galvannealed in the bath using a hot-dip galvanizing simulator. The coated samples were press hardened following an austenitization treatment at various temperatures for different dwell times. The samples were then examined to compare them with the press-hardened samples of a conventionally-galvanized PHS in terms of LME cracking and cathodic protection. The addition of these alloying elements to zinc was found to facilitate the Fe-Zn diffusion and reduce zinc evaporation during the press hardening, thereby minimizing the LME cracking and improving the cathodic protection of resultant coatings.

Automotive Applications - Zn and ZnFe Coatings / 100

STUDY OF ANTI-GALLING PROPERTY OF ORGANIC LUBRICANT FILM COATED HIGH-STRENGTH GALVANNEALED STEEL SHEET

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In recent years, high-strength galvanized steel sheet is widely used for automotive for the sake of lighten its weight and enhance the collision safety performance. While high-strength galvanized steel sheet has outstanding mechanical properties, it has less formability. On the stamping process, high-strength steel sheet requires high punching force and difficult to have good dimensional accuracy. Moreover, it tends to have die galling problem which reduce productivity. To improve such defects, coating of steel sheet, die surface, lubricants, or processing methods are developed. In this study, we investigate the anti-galling property of organic lubricant film coating on stamping process compared with base steel. As a base steel, 980 MPa grade high-strength galvanized steel sheet was used for experiment. Organic lubricant film which consisted of acrylic resin designed to be removed at alkaline degreasing process was coated by roll-coater. Organic coating layer was 1 g/m². Continuous stamping of shrink flanging by 110-tonnage press was adopted to evaluate die galling at several processing speed. Organic lubricant film coated galvanized steel sheet (organic-coated GA) had lower friction coefficient than not coated galvanized steel sheet (non-coated GA). Then stamping test was conducted, at 50 spm, die galling occurred after 1100 shots with non-coated GA. On the other hand, in the case of organic-coated GA, die galling didn't occur until 1700 shots. Similar results were obtained stamping at 20 and 65 spm. Thus organic-coated GA shows good anti-galling property. In addition, during continuous stamping, while die temperature increased at the same rate until die galling occurred on those steel sheets, organic-coated GA showed smaller die temperature rise after die galling occurred. It's suggested that organic lubricant film layer kept better slipping ability even after die galling occurred. These results show organic lubricant film coating could improve formability of high-strength galvanized steel sheet and extend die lifetime by its anti-galling property.

Fundamentals on Absorption of Hydrogen & Fundamentals on Atmospheric Corrosion and Corrosion Modelling / 101

APPLICATION OF DATA SCIENCE TO ATMOSPHERIC CORROSION PREDICTION

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For prediction of corrosivity of steel products used in atmospheric environments, exposure tests in the actual environment have been widely conducted. Long-term corrosion loss has been predicted by extrapolating the change of corrosion loss with time in exposure tests. However, the data of exposure test in regions where we would like to know corrosion rate doesn't always exist. In this case, exposure test has to be newly started, and it consumes much time to obtain long-term data. For this reason, some atmospheric corrosion prediction formula which is composed of relation between corrosion loss and environmental factors, like temperature and amount of airborne sea salt, have been suggested. One example is dose-response function defined in ISO9223. However, it is difficult to predict long-term corrosion loss with high accuracy by using the formula, since there is limitation on building one formula from complex relation between corrosion loss and environmental factors. In contrast to that, data science is considered to be useful for analyzing complex data. In this study, data science was applied to atmospheric corrosion of carbon steel. The most suitable prediction model of data science was selected on the basis of experimental data analysis, and new prediction method for atmospheric corrosion was suggested. To increase accuracy, we established a prediction model which can treat the following three characteristics of exposure test data. (1) Multicollinearity: there is correlation between environmental factors. (2) Nonlinearity: there is nonlinear relation between corrosion loss and environmental factors. (3) Small data sets: normally, large data sets are needed to increase prediction accuracy, however, we have small data sets since exposure test takes a long time and many works are involved. In our model, we chose temperature, relative humidity, amount of airborne salt and SO₂ as input variables to predict the corrosion loss. To solve multicollinearity, our model uses latent variables as explanatory variables instead of input variables. The latent variables are created by transforming the input variables orthogonally and can explain the variance direction in the response variable. In addition, by using the locally weighted regression, "nonlinearity" was treated. It predicts by a linear regression model fitted strongly to the training data that are closer to the data we are trying to predict. Thus, high prediction accuracy is secured even if small data sets. This method

gave us an accurate prediction of corrosion loss in comparison with dose-response function in ISO9223.

Furnace II - Current Topics from Preoxidation to Galvannealing / 102

MULTILAYER ANGULAR ROLL MODEL FOR ONLINE CONTINUOUS CONTROL OF GALVANIZING LINES DRIVEN BY FURNACE MATHEMATICAL MODEL

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Today, steel producers find in their portfolio many kind of steels, including the new high strength steels, each with their specific heat cycle. Adding to this the final customer specifications, and on the top of it the requirements of various sizes, the coil schedule faced day-by-day on production level stretches into an extensive mix. A modern galvanizing line must be a flexible tool able to cope with continuous changeover of the process conditions.

Controlling a continuous galvanizing furnace requires to master the physical behaviour of its components. On vertical annealing furnaces, the processed strip is deflected by rolls at each pass and between the process sections. During operation, repetitive contacts between the transported strip and the furnace rolls take place. The unceasing changes in the annealing process linked to the variability of the production schedule, leads to recurrent thermal exchange between the strip and the rolls.

The heat transfer by contact between the strip and the rolls is very effective and take place in short time. However, the rolls have a big thermal inertia with long time constant, hence the need for a roll model. In the roll models used in mathematical applications for furnace control we find for example radial models, which consider the roll size in the heat transfer. These models showed themselves to be too simple in relation to the physical behaviour. Today, an angular and multilayer roll model considering the heat exchange along the contact between the strip and the rolls, as well as the heat transfer through the roll thickness is implemented in Drever's Mathematical Model for continuous control of galvanizing furnaces and lines.

The implementation of an angular and multilayer roll model provides another dimension to higher level functionalities of process control. When used along the furnace transition management, advanced control with process forecast is achieved. Industrial results will be presented.

Coating Alloy and Modification effects on Corrosion Behaviour / 103

EFFECT OF MAGNESIUM ON THE MICROSTRUCTURE AND CORROSION RESISTANCE OF 55% Al-Zn COATING

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Hot dip galvanized 55%Aluminum-Zinc coating was successful industrialized. In order to improve the performance of 55%Aluminum-Zinc coating [U+FFOC] the expected structure and the better property could be obtained by adding 1~3%Magnesium into 55%Aluminum-Zinc coating. In this paper, magnesium on the structure and corrosion Resistance of 55%Aluminum-Zinc Coating

was researched by different analysis between 55%Aluminum-Zinc coating and 55%Aluminum-Zinc-2%magnesium coating. The surface observation, the coating structure, polarization curve and surface corrosion of two different kinds of samples were analysed by EDS, electric chemistry workstation and salt spray test. The results showed that the numbers of coating surface spangles by adding 2%magnesium are not changed obviously; The structure of 55%Aluminum-Zinc-2%magnesium coating appears the eutectic Mg Zn 2 phase besides rich aluminum phase and rich zinc phase; The corrosion capacity of 55%Aluminum-Zinc-2%magnesium coating becomes more powerful than before.

Electrogalvanizing - Process and Product Developments / 104

INFLUENCE OF ELECTROLYTE COMPOSITION AND TEMPERATURE ON ENERGY DEMAND AND ZINC STRUCTURE DURING ELECTRO-GALVANIZING

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Electro-galvanizing of steel strip represents an important industrial process of corrosion protection and surface finishing. Electro-galvanized steel sheets are used e.g. in the automotive industry, for household appliances, and in the electronics industry. The zinc coatings show a very homogenous microstructure, a good spot weldability, as well as excellent surface appearance and painting adhesion properties.

However, the demand for electric energy in the electro-galvanizing process is high. High current densities of up to 200 A/dm² are needed to enable fast and economical production. Because of the high current densities, a sufficient electrolyte flow is needed to avoid current densities close to the limiting current density and thus preventing formation of dendrites or powdery zinc deposits. This can be achieved by different cell designs with forced electrolyte flow.

In order to be able to optimize the energy demand, a basic understanding of the underlying principles is needed. The energy demand for the zinc deposition is mainly composed of the cell voltage and the cathodic current efficiency. The influence of electrolyte composition and temperature on current efficiency and energy demand has been investigated in literature for low current densities of up to 5 A/dm². However, there are only a few studies on the behavior of current efficiency with higher current densities.

In this contribution, the influence of the electrolyte composition and temperature on cathodic current efficiency and cell voltage for relevant current densities are investigated. For this purpose, laboratory tests are carried out in a flow cell. The results are translated into an overall model that allows to predict the total energy consumption. Furthermore, the resulting zinc coatings are analyzed in terms of zinc adhesion, morphology, and zinc crystallography.

Fundamentals on Surface Oxidation and Metallic Reactions / 106

UNIQUE SIMULTANEOUS RAPID COOLING AND ZINC COATING TECHNOLOGY - NO BAINITE BEFORE ZINC POT

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A new type of martensitic steel by utilizing the concept of Quenching and Partitioning (Q&P) has recently been established known also as "Low-End cycle". A too high partitioning treatment temperature at 465°C will not provide the best metallurgical results of the Q&P-treatment which are possible to be achieved without the hot-dip coating at the last step of the metallurgical

heat treatment chain. Recently a North American car maker has modified its Dual Phase steel specifications by replacing partly hard martensite with bainite preferably free of coarse carbides. The target is to balance formability by mainly improving hole expansion properties. Since 1984 it has been known from Japan that the best forming properties of the advanced high strength steels will be achieved with Tri-phase steels (ferrite- bainite-martensite). They have also proposed that the heat treatment cycle of Roll Quench/CAL having the direct cooling over 30°C/.sec from about 860 C to the end-point at 260°C and austempering at 260°C about 180 sec will provide superior mechanical properties for GIGA-steels with a very high hole expansion ratio, twice higher than Q&P980-GI presented at GDIS 2019. The purpose of this paper is to present a brief review of the work done to develop the new technology for simultaneous rapid cooling and hot-dip zinc coating to produce high formable GIGA-GI-steels with the similar heat treatment cycle to RQ/CAL and even with a higher cooling capability. This new technology will produce GI- coated AHSS/UHSS from lean/low-alloyed steel chemistries extremely cost-effectively and with improved coatability. The key design target has been that there is no bainite in steel strip before the zinc pot because the strip flatness problems during zinc off wiping has been found to be caused by transformation of bainite from austenite before zinc coating. Additionally the step time of strip at 450°C is less than five seconds i.e. bainite even with the low alloyed steels is formed after the zinc pot as Lower Bainite instead of Upper Bainite with coarse carbides. This paper will also briefly describe the production of GI-coated cold-formable UHSS-products with tensile strength over 1500 MPa from spot weldable steel chemistries (Si/C \leq 7 and Mn-eq $<$ 2.9%).

Fundamentals on Surface Oxidation and Metallic Reactions / 107

GALVANIZING OF TRIP-Si STEELS

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The development of galvanised high strength steels requires a better understanding of the gas – metal reactions during continuous annealing and their influence on steel – zinc reactivity during hot dip galvanising. Indeed, external selective oxidation, mainly formed during soaking, will hamper the formation of the inhibition layer, which is a key step for zinc wetting and further adequate coating adhesion. Therefore, the influence of the atmosphere of the different parts of the furnace on steel surface chemistry and by the way on zinc wetting and coating adhesion has been investigated by in situ surface analyses, wetting measurements and adhesion tests. This study is focussed on the behaviour of a TRIP-Si steel, which has been submitted to a Q&P annealing cycle and galvanized in GI and Zn-1.1%Al-1.1%Mg baths. The influences of an oxidation during heating and a higher dew point during soaking have been more particularly investigated. It can be concluded that if water vapour injection already enhances the coating quality, an additional improvement can be obtained with an oxidation step during heating, even if the process window is relatively narrow.

Fundamentals on Selective Oxidation of AHSS / 108

SELECTIVE OXIDATION OF Fe-Mn (1WT.%) BINARY ALLOY DURING CONTINUOUS ANNEALING

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The study presented here focuses on the selective oxidation of Fe-Mn (1wt.%) binary alloy. The samples were annealed by means of a laboratory furnace with a temperature profile relevant to

the galvanizing line practice. The sample was first heated to 800°C at a rate of approximately 6°Cs⁻¹. It was kept at that temperature for 60 s before being cooled to room temperature. The gas atmosphere consists in a mixture of N₂ - 5 vol.%H₂ with a dew point of -40°C. To obtain information on the nucleation and growth of oxide particles, we interrupted annealing at 700°C during the heating phase. Some specimens were held at 800°C during 0, 60, 120 and 300 seconds. The rapid cooling of the samples that occurs when the annealing furnace is stopped is considered to act like a dip for selective oxidation reactions.

During annealing the native iron oxides are reduced and the manganese diffuses to the surface where it is preferentially oxidized and forms MnO oxide particles. These selective oxide particles were characterized using several complementary analysis techniques. The surface of the samples was observed in a Field Emission Gun Scanning Electron Microscope (FEG-SEM) to obtain high resolution images and analyzed by Electron Back-Scattered Diffraction (EBSD). Image analysis was used to measure the geometric parameters that characterize oxide particles in two dimensions. Thin cross-section were extracted from the oxidized samples using a Focused Ion Beam Microscope (FIB) and characterized in a Transmission Electron Microscope (TEM).

We studied the oxide particles present on three ferrite grain orientations: Fe(100), Fe(110) and Fe(111) as a function of annealing time. It has been demonstrated that, on our model material, MnO particles are monocrystalline. Their shape, size, nucleation and growth depend on the ferrite grain orientation where they are formed. Elementary mechanisms of the oxidation reaction are proposed and discussed to explain this behavior.

Modeling Bearings Wear Rate and Enhanced Pot Roll Coatings & HDG Coating Weight Control by Numerical Simulation and Modeling / 110

OFFLINE SIMULATION OF GALVANISING BATH JOURNAL BEARINGS AS A COST EFFECTIVE SOLUTION TO IMPROVE LINE PERFORMANCE AND MITIGATE RISK

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Modern automotive grade continuous galvanising lines (CGL) are presented with a significant risk when considering online trials of new galvanising bath submerged journal bearings. Such trials of submerged bearings can pose significant financial loss should untested bearing components fail, resulting in unplanned maintenance stops. This limits opportunity for hardware improvements on modern CGLs where the cost of unplanned maintenance is high and as a result conventional materials and geometric designs of bearings remain unchanged for several years with limited optimisation effort.

To optimise new galvanising bath journal bearings an online trial is essential to ensure confidence in the technology. However, to mitigate the risk of testing new journal bearings materials and designs, a bespoke bearing test rig has been developed. This paper describes the development of an off-line bearing test rig and also explores the financial comparison between the development of the machine and unplanned online maintenance.

The experimental rig allows test samples to be rotated in a 200 kg bath of molten zinc or zinc alloy at a maximum rate of 300 RPM. This converts to a maximum simulated line speed of 200 m/min. A self-aligning test bearing housing ensures that the rotating journal specimen maintains a constant angle of abrasion with the bushing component. Displacement sensors which share a common linear velocity to the journal will provide real time measurement of wear rate and are capable of recording displacements as small as 10 µm. Acoustic emission is measured and bearing friction can be calculated through comparison of the torque meter and signal outputs from the motor. Initial tests have shown that this novel rig permits the safe and accurate testing of new bearing materials and designs. It can test small scale bars or full bearing assemblies, affording flexibility and more adventurous testing. Automation of the testing rig is permissible through an

incorporated process control system which permits the rig to run continuously and safely for five weeks, simulating a galvanising campaign.

Mathematical modelling and measurement of the galvanising bath hardware in service conditions provide key information for designing and constructing the offline testing rig. The design process of the new bearing testing rig is then explored, with an emphasis on simulation of accurate line. The financial incentive of offline testing are outlined which draw comparisons between the development cost of the bearing rig compared to the predicted cost of a bearing failure and line stop.

Poster Session / 111

SIMULATION AND OPTIMISATION OF A WIPING KNIFE ON THE LAB SCALE

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In the present study Computational Fluid Dynamics (CFD) were used to design a new air-knife for the hot-dip galvanizing simulator of Salzgitter Mannesmann Forschung in order to improve the flow field inside the knife and at the nozzle exit. The overall objectives were to improve the surface quality of coated samples and enhance coating control capabilities compared to the existing air-knife by optimising the gas flow inside the knives. The existing configuration yields coating thicknesses from 7 μm on, although coating homogeneity could be optimised. The flow field inside the nozzle was modelled by transient RANS simulation. An ideal air-knife should create a uniform gas flow with low turbulence at the nozzle exit. However, this is difficult to achieve, being affected by various factors. It could be shown that the existing air-knife bears some significant fluidic disadvantages at the gas inlet and distribution inside the nozzle, causing an inhomogeneous, unsteady flow. A new air-knife design with optimised inlet and an innovative shape for rectified fluid deflection and distribution was designed. The additional application of a turbulence manipulator and an improved feeding geometry of the exit channel finally lead to a much more uniform gas flow. The turbulence of the flow is reduced significantly by the new design, compared to the existing nozzle.

Coating Microstructure Analysis and Steel/Coating Surface Reactivity / 112

ON GRAIN BOUNDARY TOPOGRAPHY AND SURFACE REACTIVITY DURING HOT-DIP GALVANISING

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Under certain conditions of oxygen shortage and high temperatures as could occur after coiling a hot-rolled strip, alloying elements with high oxygen affinity can diffuse and oxidise preferably along the grain boundaries. This selective internal oxidation can be increased by additional heat induced from phase transformations in the coiled state and depends on steel composition. This diffusion to the grain boundaries and subsequent oxidation causes a depletion of solute alloying elements in a surface near area.

When oxides are present along grain boundaries, pickling can alter the surface topography by selective dissolution of these oxides on the μm -scale (μ -topography). This altered topography

and the depletion of alloying elements influence diffusion properties during intercritical annealing prior hot dip galvanizing, leading to changed surface segregation of alloying elements. This effect was exemplified by pickling and subsequently cold rolling a hot rolled high strength steel strip with and without internally oxidized grain boundaries, using an adapted process. Samples with and without altered μ -topography were galvanized in a hot-dip simulator with varying annealing parameters. The annealed and galvanized samples were characterized in terms of surface enrichment of alloying elements by GDOES, inhibition layer density by potentiostatic dissolution and SEM measurements, as well as crash relevant automotive zinc adhesion tests. Surfaces with altered μ -topography show higher reactivity through lower surface segregation of alloying elements and can build more dense inhibition layers during hot-dip galvanising under identical annealing conditions. This effect could be helpful to enhance galvanisability of future difficult steel grades.

Industrial Status of Galvanizing Production Technology / 113

THROUGH-PROCESS OPTIMIZATION (TPO) - A MODERN APPROACH TO RAPID PRODUCT DEVELOPMENT

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Product development is an essential factor for steel producers striving to maintain the position of steel in the competitive market for structural materials. Launching new products on the market and improving their properties is a strategy that allows manufacturers to remain competitive and to cope with changing customer requirements. Metallurgical models, automation systems and through-process quality control systems are all essential to product development. Modern simulation tools are able to simulate individual processes of the entire steel production route. Here, both physical and computer simulators are used. Recently, there has been a rapid growth in the significance of the digitalization of metallurgical and production processes. In particular, the systematic collection of data from all production stages and the subsequent application of data analysis, including a self-learning approach and prediction models, also makes it possible to implement rapid product development. Through-Process Optimization (TPO) is a toolbox consisting of IT solutions and know-how packages designed to help steel producers optimize product development in order to achieve guaranteed results in the shortest possible time. This paper describes the product development process, including computer simulation, labor scale simulations, data collection and data analysis using TPO.

Origins of Hydrogen Embrittlement / 114

CHARACTERIZATION OF RESIDUAL STRESSES AT SHEARED, MILLED AND LASER CUT EDGES IN MARTENSITIC STEELS

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High strength steels are increasingly used, particularly by the automotive industry where reduction of vehicle weight and emission of greenhouse gases have high priority. With increasing strength, the material becomes more sensitive to hydrogen embrittlement. Hydrogen can enter the steel during the production process, for instance when electro galvanizing. The combination of a sensitive material, high stresses, and hydrogen in the material constitutes a risk for fractures. Slitting and punching operations in a manufacturing process will introduce additional stresses at the cut edges. The stress levels depend on cutting method, cutting parameters and tool conditions. Poor edge quality increases the risk for fractures initiated at the edges. Increased knowledge about how cutting methods and cutting conditions affect residual stresses are therefore important. In this work, we have used synchrotron radiation at beamline P21.2 of PETRA III at DESY Hamburg, to study residual stresses at cut edges. Cold rolled martensitic steel was cut using three types of cutting operations; shearing, shearing followed by milling, and laser cutting. Long range, macro stresses were determined using measured shifts in Bragg diffraction peaks and short range, micro stresses using the widths of diffraction peaks. Micro Vickers hardness measurements were used to map the hardness close to the cut edges. Constant load tests combined with in-situ hydrogen charging were performed to compare the sensitivity of different edge conditions to hydrogen embrittlement.

The evaluation of residual stresses shows that synchrotron radiation is a powerful tool to map stresses at cut edges with good lateral resolution. Shearing is the cutting operation that affects the material the most and causes the largest amount of stress underneath the cut surface. The affected zone extends to a depth of approximately 1 mm. Milling after shearing removes this zone and creates a shallower stress zone formed by the milling operation. Laser cut edges have a thermally induced stress profile. Fresh martensite forms at the laser cut surface and a heat affected zone forms underneath. The micro hardness measurements show that the hardness is higher near the surface of the edge than in the bulk. The laser cut edge shows a lower hardness in the heat affected zone than in the bulk.

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NEWEST GENERATION OF METRIS ADVANCED FURNACE CONTROL FULFILLS HIGHEST QUALITY DEMANDS

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To ensure a constant high productivity and quality for the newest AHSS, Andritz developed a new generation of its Metris Advanced Furnace Control. It consists of a modular design with a newly developed cooling model and a brand new multi model predictive control. The precise physical model for all heating and cooling sections act as virtual sensors, which gives a good insight of the temperature distribution within the furnace and acts as a huge source for Big Data. The multi model predictive control ensures collaboration between all models to enable a constant high quality and productivity. The system was successfully installed at a well know steel producer. The results show a significant increase in quality and productivity.

Poster Session / 116

SCHEDULING SOLUTIONS SUPPORT SUSTAINABLE PRODUCT QUALITY OF GALVANIZED COILS BY PROVIDING PRODUCTION SCHEDULES IN REPEATABLE QUALITY

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The production of galvanized coils requires stable operating conditions for achieving sustainable product quality. In order to reach stable operation conditions for high quality products it is essential to prepare the production process according certain constraints. Those constraints include building schedules with a coffin shape ensuring that width and thickness changes are within certain limits, next to taking into account mechanical properties and surface requirements. The coffin shapes need to include smooth transitions in the production schedule to ensure that the transition of the furnace temperature between coils can be facilitated and that the service life for submerged equipment in the galvanizing bath can be extended. Furthermore, it needs to be taken care that the production orders are sorted in such a way that surface critical orders are scheduled first and high strength products in a second step. By clustering the product mix in batches and campaigns high line stability can be ensured. This scheduling strategy enables that roll wear is in-line with desired surface tolerance limits. For set-up purpose it is also essential to include into the schedule at specific positions production orders with low surface quality, e.g. prepare the right thermal cycle conditions and to clean polluted rolls and remove zinc dross and dust from zinc pot. Additionally, work roll type, roughness and type of post-treatment have to be considered for production scheduling at processing lines as well.

The compilation of those schedules is a complex endeavor and pivotal for achieving sustainable production results. Software solutions can be used to build the schedules automatically according to stated constraints, allowing that schedules are being built with repeatable quality. However, the crucial element is to configure the scheduling software close to the optimal constraints as not only technical requirements need to be taken into consideration but also commercial constraints such as promised delivery times.

This paper shows that it is a critical success factor to translate the available process know-how into rules when the scheduling system is being installed and fine-tuned. It needs to be taken care that the expert implementing the rules into the software solutions understands the requirement of the production to leverage the potential of the scheduling software to its full extent.

Furnace III - Rapid Cooling, Furnace Roll Coatings / 117

NON STICKING FURNACE ROLLS FOR STEEL PRODUCTS TO IMPROVE SERVICE LIFE AND PRODUCT QUALITY IN CONTINUOUS ANNEALING AND GALVANIZING LINES: PRELIMINARY STUDY ON CHEMICAL INTERACTIONS AND PICKUP MECHANISM

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Thermal spray cermet coatings are successfully applied on furnace rolls in continuous annealing and galvanizing lines. However, when processing HSS with high manganese and/or high silicon

content, oxide pickups can be formed on the rolls working in the different furnace zones. The aim of this study was to acquire knowledge on the pickup mechanisms and the chemical interactions occurring between different cermet coatings and steel grades as a function of factors such as dew point, furnace temperature, surface roughness, etc. Aged Cr₃C₂-NiCr and Al₂O₃-Co based matrix coatings were made to interact with pre-oxidized steels characterized by different levels of Mn and of Si by high temperature (800°C < T < 900°C) static reactivity tests and low temperature (400°C < T < 600°C) dynamic tests, which allow the friction of a roll on a steel strip at controlled temperature and furnace atmosphere. The interaction surfaces were then characterized by XRD, GDOES, AES, SEM-EDS. The high temperature interaction tests results indicate that when aged cermet coatings have at their surface Cr₂O₃ and/or Al₂O₃, then MnAl₂O₄ and Mn_{1.5}Cr_{1.5}O₄ spinels will form with all the steels that have a sufficiently high Mn content. However, if coatings are aged at a DP of -30°C/-40°C, a nitride surface layer is produced that seems to affect the interactions with MnO. Dynamic tests at low temperatures results indicate that coating roughness strongly influences pickups, and has to be limited as much as possible. In laboratory tests and industrial lines, iron pickup is principally observed. Some silicon oxide pickup has also been reported on industrial rolls during electrical steel processing. The pickup studies at high temperatures have also indicated MnO pickup, which is in good agreement with analyses made on industrial rolls in the soaking area. Again the coating roughness has a significant effect on pickup, but the presence of Al and Cr oxides on the roll surface also increases reactivity with the formation of spinels after the reaction with the selective oxidation covering the strip. Therefore, the suppression of the metallic Al/Cr incorporated in the NiCr and Co/Ni matrix of the cermet coatings should suppress this reactivity and could limit the pick-up.

Furnace I - Temperature Control Challenges / 118

INCREASING LIFETIME OF METALLIC RADIANT TUBES IN VERTICAL GALVANIZING LINES

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The main focus of the proposed paper is on the design and efficient operation of metallic recirculating radiant tubes installed with recuperative or regenerative burners in vertical strip galvanizing lines. Premature tube failures may result in loss of production capacity arising from reduced heat input or, worse, unplanned plant shutdowns. As a galvanizing line furnace equipped with around 200 radiant tubes is not an uncommon case, the factors influencing tube life need to be thoroughly examined. From the perspective of the suppliers and end users of both the radiant tubes and the galvanizing line furnaces, the following aspects influencing tube life form the central themes of the paper:

- burner control and tube structural design,
- tube installation and process conditions in the furnace, and
- tube and burner maintenance.

Creep and the corresponding thermal stresses play a dominant role as a limiting factor in the lifetime of these radiant tubes. This is not only due to their exposure to high temperatures (> 900 °C) during operation, but also because of the resulting inhomogeneous surface temperature distributions and also, their own dead-weight. Recent investigations conducted in the Department for Industrial Furnaces and Heat Engineering in the field of radiant tube technology show that it is possible to determine an optimal burner position and tube geometry in order to maximise the recirculation of gases inside the tube and thereby, minimize the thermal stresses in the tube arising from temperature gradients on it. In addition, these tubes sustain alternating temperatures during the furnace operation, e. g. during burner on/off-firing or process-related changes such as change of the strip's speed or cross-section. The effects of these temperature changes are much

more detrimental than previously thought. Furthermore, the influence of the tube's surroundings, i.e. neighbouring tubes or strip, is seen to exacerbate the material weakening phenomena and lead to a further shortening of its service life.

The results are from multiple public-funded research projects as well as collaborations with different burner manufacturers and furnace operators. Numerical simulations have been validated against experimental measurements from in-house test benches. Particular emphasis is on best-practices for furnace operation and on the tubes' structural design (including its end support) for the improvement of its service life. Concluding remarks also include an outlook on future research topics.

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WELDER DESIGN FOR 3RD GENERATION STEEL PROCESSING

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Third-generation advanced high-strength steels (AHSS) are a major opportunity for steel industry as they push the limits of both tensile strength and elongation to an outstanding level. This evolution is benefiting to everyone and brings major advantages: increased safety level, lower weight, more complex geometry and reduced energy consumption. Of course to be able to produce this new product range, the furnace is the key equipment that must be perfectly designed but is it the only one? Of course not. The new steel chemistries and mechanical properties require a new or major upgrades on the design of the Cold Rolling Mill plant lines and their processing equipment. Obviously the welder is significantly impacted, which reshuffles the cards from the functionality and process control standpoints. Primetals Technologies has fully evaluated and analyzed the incidence of this new products on the machine capability, lifetime and reliability. Following this analysis a new range of machine has been manufactured so has to answer to this new requirements: The Solid state LW21M and associated centering and notcher equipments.

On-line Measurements - Cleanliness, Austenite Fraction and Coating Defects / 120

SIAS® 4.0 - THE NEXT GENERATION OF AUTOMATIC SURFACE INSPECTION SYSTEM USING CONVOLUTIONAL NEURON NETWORK FOR DETECTION AND CLASSIFICATION OF SURFACE DEFECTS

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The surface quality of a finished product on a galvanizing line is a very important criteria, especially for automotive and home appliance exposed products. To control it, automatic surface inspection systems (ASIS) have been developed since many years and are installed on all galvanizing lines dealing with high product quality. A highly performant ASIS from Primetals Technologies has been developed for many years and is especially protected under the worldwide known Trademark SIAS®. In the last ten years, ASIS performance improvements are mostly due to the integration of new developments in lighting and camera technologies. Deep-learning and artificial intelligence are fast developing technologies. Convolutional neural networks have proved to be the most efficient tool to address many image processing problems like image retrieval and classification. It remains still very challenging to use these technologies industrially for real-time applications

on large video streams. A new online real time defect detection/classification system using full convolutional network has been developed and the prototype of this system is installed in Liège on the EUROGAL galvanizing line (ArcelorMittal Belgium). The added value is expected to be threefold: [U+F0B7] Improved defect detection/classification performances (for textured product in particular). [U+F0B7] Provide an easier tuning on multi-camera systems integrating several lighting conditions. [U+F0B7] Decrease the sensitivity to the tuning parameters and provide a more generic detection configuration, easier to transfer from one product or one line to another. This paper presents the principle, the first results of the prototype which is installed at EUROGAL. We will present also the vision of the future of surface inspection system, dealing with training the neural network on multiple sites, and the SIAS Fleet Management System.

Poster Session / 122

FAST AND NON-DESTRUCTIVE METHOD FOR PHASE QUANTIFICATION IN ZINC ALLOYED COATED STEEL SHEET

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A fast and non-destructive method based on X-ray diffraction for phase quantification in zinc alloyed coatings is presented. Post-annealed hot-dip galvanized steel sheets may contain various Fe/Zn alloys (Γ -Fe₃Zn₁₀, Γ 1-Fe₁₁Zn₄₀, δ -Fe₁₃Zn₁₂₆, ζ -FeZn₁₃) arranged in a layered conformation and with a predictable stacking order. Each phase within the coating has a different crystalline structure implying a heterogeneous mechanical behaviour: the phase quantification is therefore crucial for controlling further product behaviour, i.e. formability under press.

The determination of the individual layer thicknesses remains a challenging, time consuming and typically destructive task. Compared other methods, X-ray diffraction provides a unique fingerprint for each alloy constituting the coating. The so-called Rietveld method typically applies to an infinitely thick (compared to x-ray penetration depth) and homogenous mixture of phases. In the software TOPAS, the industry standard for quantitative phase analysis, the Rietveld method can be adjusted to a conformation of stacked phases by applying additional corrections related to (i) limited layer thicknesses and (ii) x-ray absorption through successive layers. A calibration of the beam flux allows for consideration of layer thicknesses as refinable parameters, acting then as unique scaling factors for each phase. Consequently, TOPAS delivers fast (few seconds of refinement), meaningful and absolute quantification results. Further coating parameters like coating weight, chemical alloying or phase ratios can be derived from the refined layer thicknesses.

A dedicated industrial diffractometer, D8 ENDEAVOR, equipped with an optimized diffraction geometry (DBO) provides high quality data in short measurement times (few minutes). No sample preparation, fast data acquisition, a large sample magazine with 66 positions and a fully automated evaluation contribute to an ideal solution in QC environment with high sample throughput.

HDG Coating Formation & Dross Management / 123

CFD-DPM MODELLING AND ANALYSIS OF DROSS PARTICLE DYNAMICS IN HOT-DIP GALVANIZING BATHS

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The surface quality of galvanized steel sheets is considerably influenced by intermetallic dross particles, which inevitably form during operation. η -phase Fe₂Al₅ top dross and δ -phase FeZn₇ bottom dross particles have been reported to be entrapped into the coating causing functional and optical defects. Moreover, particles are frequently mentioned to adhere to the stationary and the moving bath equipment. Particularly, dross particles which are adhered to sink and stabilizer rolls can cause imprints on the surface of the steel strip. Furthermore, the cleaning of the rolls is related to down times of the mill. An efficient management of dross particle dynamics is thus a key criterion for running galvanizing mills. CFD-DPM models give a comprehensive insight into the dynamics of dross particles and their tendency to come in contact with relevant surfaces. Buoyancy and settling effects of dross particles, which lead to the accumulation of top and bottom dross in regions of the galvanizing bath are predicted with the model. A special focus is put on a sub-model investigation of the surrounding of the sink roll. Factors of influence on the dross dynamics and accumulation such as particle type, particle size, wall roughness and line speed are elucidated with the DPM model. In addition, a new approach in modelling dross based on scalar transport equations is presented, which enables the inclusion of the thermodynamics and the reaction kinetics of dross formation.

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EFFICIENT AND EFFECTIVE OPERATION OF A HOT DIP GALVANIZING SUPPLIED BY DANIELI

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Efficient and effective operation of a hot dip galvanizing line depends from several technological aspects: mechanical, thermal, chemical, automation and control. The synergy and the harmonization among all aspects is the key to get the best performance in terms of productivity and quality. Danieli is recently achieving outstanding results in their new lines, thanks to a specific focus on the integration among all technological equipment installed in a hot dip galvanizing line, with a special regard to furnace, automation and air knife.

Based on this experience and driven by the latest requirements coming from the market, it is possible to produce thin and wide strips, arriving to an high ratio width/thickness with quite interesting results in terms of final products. This achievement is the result of an extremely accurate control of strip speed, tension and furnace zones temperatures, involving mechanical, thermal and automation aspects.

Danieli is providing the fully integrated automation, from the level 1 up to the level 3 system, allowing a complete control of the production. Particular attention is put on the introduction of intelligent process models, data analysis and the introduction of virtual sensor to retrofit the process models of the galvanizing line and the reheating furnace. A strong integration with all the automation levels allows to manage the process in an innovative way driven by the collected data. The latest design of Danieli zinc pot air knives is achieving excellent results in terms of maximum speed versus low zinc coating weight, targeting high productivity and enhanced quality.

Furnace I - Temperature Control Challenges / 125

EFFECT OF ANNEALING ATMOSPHERE AND STEEL ALLOY COMPONENTS ON SURFACE TOPOGRAPHY AND RADIATIVE PROPERTIES OF ADVANCED HIGH STRENGTH STEEL STRIP DURING CONTINUOUS GALVANIZING

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Substandard advanced high strength steel (AHSS) mechanical properties produced through continuous galvanizing can often be traced back to temperature excursions during intercritical annealing, caused by errors in the pyrometrically-inferred temperatures used to control the furnaces. These errors originate from the changing surface state of the steel strip, in terms of roughness and oxide formation, which causes wavelength-dependent variations in spectral emissivity that are unaccounted for in the pyrometry measurement model. In recent years, there has been a research effort to investigate the correlation between surface state and spectral emissivity of AHSS during inter-critical annealing. It was found there exists significant spectral emissivity variations during annealing. In addition, it has been shown that the variation of spectral emissivity also depends on the annealing atmosphere, since this causes different types and morphologies of oxides to form. Consequently, the effect of annealing atmosphere on surface state and spectral emissivity of AHSS with different alloy compositions, and the actual correlation between surface state and spectral emissivity during inter-critical annealing need to be studied in detail to produce AHSS strip that conforms to accepted standards.

This paper elucidates the effect of annealing atmosphere and material alloy components on both the surface state and radiative properties of DP980 coupons. AHSS samples having different alloy compositions (i.e. Mn/Si ratios) are heated in a continuous galvanizing simulator within an atmosphere consisting of 95% N₂ and 5% H₂. The measurements were performed at two dew points, 10°C and -30°C, using heating schedules similar to that of industrial annealing line. The surface state of the coupons, including oxide type and surface topography, are characterized using scanning electron microscope, X-ray diffractometer, 2-D surface profilometry and atomic force microscopy, while the radiative properties (e.g. spectral emissivity) are measured using an FTIR spectrometer. Wagner's diffusion model is applied to delineate the level of internal or external oxide formation given the annealing atmosphere and alloy components. This study highlights how annealing atmosphere and alloy components affect oxide formation and surface topography, and the connection with the radiative properties of AHSS steel strip during galvanizing.

Poster Session / 126

CONTINUOUS ANNEALING TEMPERATURE INFLUENCE ON THE MICROSTRUCTURE AND MECHANICAL PROPERTIES OF GALVANIZED DUAL PHASE STEEL (DP980)

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Dual phase steels are strongly dependent on the microstructure obtained during production to meet the needs in its application and the required mechanical properties. Besides the parameters associated with chemical composition, hot rolling and cold rolling, the process of continuous intercritical annealing directly affects the microstructure and consequently the mechanical properties. In this study, the influence of intercritical soaking temperature and quenching start temperature on microstructure and mechanical properties of a cold-rolled galvanized DP steel 980 MPa class, from simulation of the complete annealing cycle on a thermomechanical simulator Gleeble were evaluated. Analysis via scanning electron microscopy (SEM) revealed increased volume fraction of second phase with increasing soaking temperature associated with the formation of larger volume fraction of austenite during intercritical annealing, resulting in the increased yield strength and tensile strength. From the soaking temperature of 750°C the tensile strength was greater than 980 MPa, reaching values higher than 1100 MPa at 840°C. The microstructure and mechanical properties did not change with the variation of quenching start temperature.

On-Line Measurements and Galvanizing Bath Control Development & Bath Al Chemistry Effects on Coating Quality and Bath Management / 127**AN INTEGRATED METHODOLOGY FOR THE ROOT CAUSE ANALYSIS OF MECHANICAL AND METALLURGICAL DEFECTS OF HOT-DIP GALVANIZED COATINGS****Author(s):** DAL'MAZ SILVA, Walter¹**Co-author(s):** Mr. SAINT-RAYMOND, Hubert ¹ ; Mrs. DULCY, Claudie ¹¹ *ArcelorMittal***Corresponding Author(s):** walter.dalmazsilva@arcelormittal.com

This paper has the aim at presenting a methodology of defect root cause analysis for hot-dip galvanized coatings. It has been developed to provide a global overview of all aspects related to the Materials Science pyramid – the processing route, the material properties, the structure and in-use performance – all linked by the material's characterization. Its final aim is to provide not a single parameter leading to failure or poor performance, but to identify the space of parameters and their combinations leading to the undesired outcomes for a given coating system. In order to perform such an integrated analysis a minimal set of process parameters must be identified, generally through brainstorming.

Management of data acquisition and communication between production site, characterization team, quality surveillance, and engineering must be carefully carried out with full traceability of data to allow the assembly of the Materials Science pyramid database. Process parameters shall be acquired for a statistically significant population (comprising accepted and rejected coils) and each coil's coating microstructure must be analyzed to provide the base of the dataset. A quality control parameter related to the coating being studied is required to finish the triangle of process-property-structure.

The method is composed by three main steps. First, establishing a set of parameters representing the structure-related features of the coating material, what is followed by data clean-up for ensuring stability of conditions for each coil. Finally, the application of clustering techniques, proves more reliable and efficient than classical statistical analysis, for interpreting the parametric effects over the quality issue being analyzed rather than studying the tendencies promoted by individual parameters.

Coating Microstructure Analysis and Steel/Coating Surface Reactivity / 128**MICROSTRUCTURE AND TEXTURE ANALYSIS OF A NEAR-EUTECTIC Zn-Al COATING DEPOSITED ON STEEL BY HOT-DIP GALVANIZING****Author(s):** CHAIEB, Housseem Eddine¹**Co-author(s):** Dr. NOZAHIC, Franck ² ; Prof. MAUREL, Vincent ³ ; Prof. FOREST, Samuel ³ ; Prof. KÖSTER, Alain ³ ; Prof. AMMAR, Kais ³ ; Mr. MATAIGNE, Jean-Michel ⁴ ; Mr. DE STRYCKER, Joost ⁵¹ *Mines ParisTech*² *ArcelorMittal Global R&D Ghent*³ *Centre des Matériaux / MINES ParisTech*⁴ *ArcelorMittal Global R&D Maizières*⁵ *ArcelorMittal Global R&D Gent***Corresponding Author(s):** houssem-eddine.chaieb@mines-paristech.fr

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Zinc based coatings deposited on steel by hot-dip galvanizing are well known to present a strong basal orientation. This has been highlighted in several previous works [1, 2]. This orientation tendency is less pronounced in Zn-5Al coating and orientation heterogeneities are witnessed. Understanding the origin of such heterogeneities and linking them to the solidification process requires the development of new guidelines.

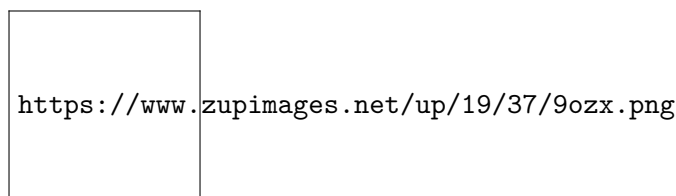


Figure 1:

Figure 1. SEM image of Zn-5Al coating

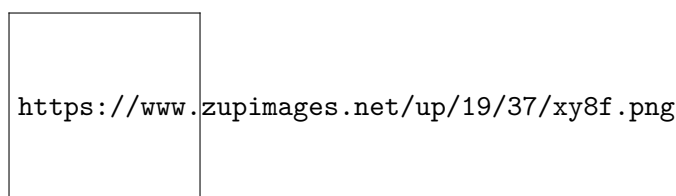


Figure 2:

Figure 2. EBSD of Zn-5Al coating

An epitaxial relationship between certain zinc dendrites and binary eutectic appears to be present. In this study, we aim at describing the microstructure and the texture of the near-eutectic Zn-5Al hot-dip galvanized coating. Several experimental techniques (SEM, EBSD, Optical Microscopy) and preparation methods are applied in order to investigate the consequences of the solidification process of this grade of coatings and to link it to the observed crystallographic orientations.

The microstructure analysis was done both on the surface and the cross-section of the sample. A link between the microstructure and orientations' heterogeneity is to be established. The observed complex morphologies of different phases yield a multiscale aspect of the coating microstructure that will be discussed.

[1] R. Parisot, S. Forest, A. Pineau, F. Grillon, X. Demonet, J.-M. Maigne, Deformation and damage mechanisms of zinc coatings on hot-dip galvanized steel sheets: Part I. Deformation modes, *Metall. Mater. Trans. A.* 35 (2004) 797–811. doi:10.1007/s11661-004-0007-x.

[2] R. Parisot, S. Forest, A. Pineau, F. Grillon, X. Demonet, J.-M. Maigne, Deformation and damage mechanisms of zinc coatings on hot-dip galvanized steel sheets: Part II. Damage modes, *Metall. Mater. Trans. A.* 35 (2004) 813–823. doi:10.1007/s11661-004-0008-9.

Furnace I - Temperature Control Challenges / 129

NOVEL APPROACH TO REDUNDANT STRIP TEMPERATURE MEASUREMENT ON CONTINUOUS COATING LINE FURNACES

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The conventional configuration for strip temperature measurements on continuous horizontal annealing furnaces is a single pyrometer pointing down a water-cooled sight tube positioned normal to the strip surface. When on-line testing of different make and model pyrometers is desired, the control pyrometer has to be removed, which often restricts the timing and duration of the test. The desire to use these existing pyrometer ports drove the design and fabrication of a housing adapted for two pyrometers, i.e., a dual-pyrometer mounting fixture.

A key feature of each fixture is a unique optical mirror that directs the line of sight of both pyrometers down onto the strip. Both pyrometers view and measure emitted infrared energy from the same spot on the heated strip. Two highly polished surfaces of the optical mirror have a hard and stable, pure gold-plated coating, making them highly reflective.

Validation tests confirmed the use of these gold surfaces does not alter the temperature readings. In addition to redundant temperature measurements, concurrent testing of pyrometers (single, multi- and dual wavelength, different manufacturers) is now possible, permitting direct comparisons without interruption to the primary control pyrometer.

Fundamentals on Selective Oxidation of AHSS / 130

KINETICS OF WÜSTITE FORMATION IN SHORT TIME ON PURE IRON IN THE GAS MIXTURE OF CO₂+CO OR H₂O+H₂

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One of the challenges on the development of new steel products is the possibility to predict or control surface behaviour through-process. The lack of prediction, together with the difficulty on simulating the behaviour of the surface in pilot processing, lead to the evaluation of the product after costly industrial trials. Therefore, knowledge on the kinetics of oxide formation on steels is of significant importance for the steel industry. Hot rolling is one of the steps in steel making during which oxidation plays an important role. This oxidation can enormously affect the further stages (e.g. coiling). The formation of a Wüstite scale occurs, when a hot iron sheet is in an atmosphere with oxygen partial pressure (pO₂) above that for Wüstite formation, e.g. above 1.2×10^{-15} atm at 1273 K. This kind of oxidation has been studied extensively in a mixture of oxidants as CO₂ and H₂O as well as reductants CO and H₂ for long times. The aim of this study is to investigate the kinetics of Wüstite layer formation on pure iron in short times (less than one minute). To predict surface oxidation for short times, a model is developed for the kinetics of Wüstite formation on pure iron in CO₂ + CO and H₂O + H₂ gas mixtures as a function of temperature and gas composition. The thermodynamic and kinetic data needed for the calculations, are obtained using the FactSage and Thermo-Calc database packages. The model is compared with a set of experiments carried out using Thermal Gravimetric Analysis (TGA) and also with recently reported experimental results from literature. It is shown that the initial oxidation of pure iron in such oxidizing atmosphere follows a linear kinetics that is controlled by the surface reactions at the gas-scale interface. A set of chemisorption reactions of oxidant molecules are suggested as the rate controlling reactions. The experimental findings on the oxidation of iron will be compared with the model calculations.

Bath dross analysis and coating characterization / 131

INVESTIGATION OF ORANGE PEEL DEFECT ON GALVANIZED DP STEEL SHEET

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With the increasing use of galvanized high-strength steel sheets in automobiles, the surface quality requirements of galvanized sheets are also increasing. When hot-dip galvanized C-Si-Mn dual-phase steel (such as DP600~DP1000) is produced, a serious orange peel-like rough surface defect appears on the surface of the steel sheet, which is mainly found in the middle area of the middle section of the coil. The orange peel-like defect samples are investigated and analyzed by Keynes microscope, scanning electron microscope (SEM) and glow discharge spectrometer (GDS). It was found that the zinc grains on the surface of orange peel defect area was abnormally large, about 300 microns, while it was only about 50 microns in normal area. After the zinc coating was etched by hydrochloric acid, the morphology of the inhibition layer was irregular, and there were transverse microcracks perpendicular to the rolling direction on the surface of the substrate and the full hard coil. The Al content at the interface between zinc layer and matrix is lower than that in the normal region. The analysis shows that the microcracks on the surface of the full hard coil are closely related to the type and composition of the scale of the hot rolled steel sheet. The hot-rolling coiling temperature is lowered to 580 °C or less, avoiding the eutectoid transformation of FeO, changing the surface oxide scale and composition, and eliminating orange peel defects. The analysis shows that the microcracks on the surface of the full hard coil are closely related to the type and composition of the scale of the hot rolled steel sheet. When the coiling temperature is lower than 580 °C, the orange peel-like defect is eliminated. Due to the avoidance of the eutectoid transformation of FeO, the type of scale is changed, and the surface enrichment of Si during hot rolling is suppressed.

Poster Session / 132

INVESTIGATION OF LITTLE BRIGHT SPOT DEFECT ON HOT-DIP GALVANIZED STEEL SHEETS

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Little Bright spot defects on galvanized steel sheets were studied by optical microscope, scanning electron microscope(SEM) and Energy Dispersive Spectrometer (EDS) in this study. The research shows that the coating thickness of little bright spot defect is much lower than normal area which caused by the substrate defect justly under little bright spot, and when skin passed, the little bright spot defect area can not touch with skin pass roll which result in the surface of little bright spot is flat while normal area is rough. The different coating morphologies have different effects on the reflection of light and which cause the little bright spot defect lighter than normal area

Steel-Coating Interfacial Layer and Coating Phase Developments / 133

FORMATION SEQUENCE OF Fe-Al INTERMETALLIC PHASES IN HOT-DIP Zn-Al-Mg ALLOY GALVANIZED STEELS

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In the present study, we characterized the Fe–Al intermetallic phases formed in interstitial-free (IF) steel hot-dipped in a Zn–6Al–3Mg (wt%) alloy melt at different temperatures (400, 460 and 500°C) and dipping times (from 2 to 3600 s). Chemical composition analyses indicated Fe dissolution into the Zn alloy melt even after 2 s of dipping. Microstructural characterization revealed the initial formation of a continuous theta-Fe₄Al₁₃ phase layer, followed by the local growth of eta-Fe₂Al₅ phase toward both steel and Zn alloy melt sides during the hot-dipping process. After long-term hot-dipping, further growth of the eta phase was accompanied by significant dissolution of Fe into the Zn alloy melt, resulting in the loss of thickness of the IF steel sheets. Altogether, we rationalized the formation mechanism of Fe–Al intermetallic phases and their associated growth in hot-dip galvanizing process using the Zn–Al–Mg alloy melts in terms of a Zn–Al–Mg–Fe quaternary phase diagram calculated. The thermodynamic calculations

assessed the formation sequence of Fe–Al intermetallic phases in various hot-dip Zn–Al–Mg alloy galvanized steels.

Pot Optimization by Numerical Simulation and Material Development / 134

FLOW PATTERN ANALYSIS INSIDE AN IMMERSING SNOOT WITH A PARAMETRIC SIMULATION MODEL

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Many surface defects of hot-dip galvanized steel strip are associated with the zinc flow inside the immersing snout. This paper presents an automated simulation workflow, which is used to study the flow patterns inside this critical plant component to give a better understanding of the fluid flow.

The comprehensive numerical model of a zinc bath is the basis for this study. A prismatic domain around the immersing snout is extracted for typical process conditions of a galvanizing line. The automated workflow based on commercial software consists of a parametric CAD (computer-aided design) model, which is linked to a CFD (computational fluid dynamics) code with a bi-directional interface. The geometry is divided into simple bodies and meshed with a selective approach to assure high quality of the computational grid. The CFD simulations to analyze the flow patterns of the liquid zinc inside the snout are carried out automatically while critical flow information is monitored to assure good convergence of the steady-state analysis. In a post-processing step, the quantities of interest are calculated for further evaluation. With this interconnected workflow, extensive parametric studies can be conducted and the sensitivity of fundamental fluid flow conditions to geometric modifications of the snout are studied. Exemplary the influence of the snout wall angle and constant strip pass-line on the bath surface velocity distribution is shown.

Bath dross analysis and coating characterization / 135

SEGREGATION MECHANISM OF Al-BASED OXIDES ON Zn-0.2MASS%Al HOT-DIP GALVANIZED STEEL SHEETS

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Hot-dip galvanized steel sheets (HDG) are one of the popular automotive materials because it is easier to satisfy both high corrosion resistance and low manufacturing cost due to the ease of controlling the thickness of the Zn coating layer than other Zn based coating. Generally, less than 1 mass% of Al is added to molten Zn bath in the HDG manufacturing process in order to decrease dross and to prevent Zn from alloying with the substrate steel. Although the amount of added Al is small, it has been reported that this Al segregates on HDG surface as oxides with aging time increasing. Hoshino et al. have investigated the effect of these Al-based oxides on the friction coefficient and reported that the friction coefficient of HDG decreased due to the existence of the Al-based oxides on the surface. However the segregation mechanism of Al-based oxides on HDG surface has not been clarified yet. In order to understand the segregation mechanism of Al-based oxides on the surface of HDG, HDG with and without temper rolling aged in air at 20°C and in liquid-nitrogen were investigated, in this study. Conventional HDG with and without temper rolling, which have Zn coating weight of 55-57 g/m² including 0.19-0.20 mass% of Al, were used as test specimens. The surface and cross-sections of HDG after aging were observed and analyzed with XRF, SEM-EDX and EBSD. As results, it was found that the velocity of the Al-based oxides segregation on the surface of HDG with temper rolling was much larger than that

of HDG without temper rolling owing to the difference of the area where the Al-based oxides can form. It was also found that the Zn crystals in Zn coating layer was refined by the contact with the temper roll due to recrystallization, and some grains remained including strain inside. This could promote the velocity of the Al-based oxides segregation because Al diffusion path to segregate on the surface as oxides such as the grain boundaries and dislocations in the grains were increased. From the cross-sectional observation and analysis, it was suggested that the Al oversaturated in the Zn coating layer due to low solubility of Al in Zn. This could cause the fast diffusion of Al in Zn even at room temperature.

Automotive Applications - ZnAlMg Coatings / 138

ANTI-CORROSION PERFORMANCE OF ZnMg AND ZnMgAl-COATED STEELS FOR AUTOMOTIVE APPLICATIONS

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Zn alloy-coated steels such as ZnMg and ZnMgAl have been recognized as a potential automotive materials replacing traditional Zn-coated steels such as galvanized (GI) and galvanized (GA) steel with enhanced corrosion resistance under harsh corrosive environment. There are two representative Zn alloy coatings, PosMAC®1.5 (ZnMgAl coating) and PosPVD® (ZnMg coating) for automotive application in POSCO steel products. These have been developed to meet the requirements for automotive parts for weldability, surface quality, phosphating and paintability, and corrosion resistance with low alloy contents in Zn-based coating. Because applications of newly developed steel product require careful consideration, POSCO makes efforts to obtain performance data from various corrosive conditions and find solutions for proper applications. In this study, the anti-corrosion performance of PosMAC®1.5 and PosPVD® were investigated from the viewpoint of automotive body structures. Corrosion resistances of flat surface, bimetallic joint and lap-joint surface were compared with conventional Zn-coated steels by cyclic corrosion tests (CCTs) and proving ground (P/G) test. In the results of these tests, the Zn alloy-coated steels exhibited better corrosion resistance compared to that of GI and GA steels despite the lower coating weights and prove its potential as a high corrosion resistant automotive steels. Finally, the corrosion life of the coatings were quantitatively predicted based on the vehicle corrosion (P/G) test results.

Fundamentals on Surface Oxidation and Wettability / 139

WETTABILITY OF Mn AND Si ALLOYED STEEL SURFACES AFTER ANNEALING PRIOR TO GALVANIZING

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The high contents of alloying elements in next generation steels (NGS), tend to segregate to the steel surface upon annealing and can be selectively oxidized prior to hot-dip galvanizing (HDG) zinc deposition. These surface oxides are detrimental to the wettability of NGSs, hindering the formation of a fully sealed inhibition layer during HDG. Consequently, the adhesion of the zinc coating to the steel substrate as well as protection against corrosion is diminished. Therefore, we

present a so-called de-wetting method to study the wettability of NGS after annealing at different conditions.

In this study Fe - 1.8 at.% Mn and Fe - 1.9 at.% Mn - 1.0 at.% Si steel alloys were annealed at 950 °C for 1 hour in a gas mixture of Ar plus 5 vol.% H₂ with dew points in the range of -70, to +10 °C to create different surface oxide compositions and morphologies. The surface of the annealed samples was analysed with scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). A Pb film of about 500 nm in thickness was deposited onto the surface of annealed steels. Then, the thin film broke up into discrete Pb droplets by heating shortly at 400 °C under a protective gas mixture of Ar with 20 vol.% H₂. The contact angle or wettability of Pb on the annealed steels was determined using SEM with the aid of the ImageJ software. The relation between the contact angle on the one hand and the dew point of the annealing ambient and the composition of the oxides at the surface on the other hand will be discussed.

As a benchmark for an optimum contact angle, the wettability of pure iron is studied. In this case the contact angle can also be predicted by calculating interface and surface energies from a thermodynamic model. The experimental findings on the wettability will be compared with the theoretical prediction.

LME of Resistance Spot Welded Coated Steels: Moving Toward Solutions / 141

EFFECT OF METALLIC COATING TYPE ON THE SPOT WELDING LME OF QP STEEL SHEETS

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Two important objectives of the automotive industry are the decrease in car weight and improvement in safety, the third generation AHSS especially QP steel sheets with zinc-coated are developed in recent years. However, liquid metal embrittlement (LME) issue easily occurs in spot welding of QP galvanized steel sheets, It affects the further application of QP steel sheets. In this paper, three different type metallic coating GI, GA and EG of QP980 steel sheets produced by the commercial line are evaluated for the spot welding LME, The order of sensitivity to LME is GI, GA and EG.

Modeling Bearings Wear Rate and Enhanced Pot Roll Coatings & HDG Coating Weight Control by Numerical Simulation and Modeling / 142

COATING WEIGHT CONTROL BY PROCESS ADAPTION

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In coating process of continuous galvanizing line, transverse crossbow is frequently found in the case of thick gage or high strength steel processing. This transverse crossbow arises due to the unbalanced residual stress distribution along the thickness, which is made by the elasto-plastic behavior that the steel sheet experiences during roll to roll transportation under continuous steel strip processing like surface cleaning and annealing. Because this crossbow makes the air knife to strip gap distribution uneven, it is difficult to get the uniform coating weight distribution along the transverse direction. In order to correct the crossbow of steel strip at the zinc coating position, correction roll displacement is used. While the mathematical model that calculates the crossbow curvature with theoretical and experimental background is introduced for the proper crossbow correction roll displacement determination, it is very difficult to guarantee the accuracy of its calculation because of many uncertain parameters that govern the model. In this study, a model adaptation method was developed to enhance the steel strip crossbow estimation accuracy using coating weight data and coating weight estimation model. This estimation method was applied to the classified operation results of many high strength steel and thick gage strip to verify

the model estimation performance. The analysis of this application results shows the improved accuracy of the estimation model. Furthermore, future works for refining the developed model as well as the achievement with it will be discussed in this paper.

PHS-ZnFe: Liquid and Vapour Metal Induced Embrittlement / 143

THE EFFECT OF Si ADDITION ON Zn-ASSISTED LIQUID METAL EMBRITTLEMENT IN 22MnB5 PRESS HARDENING STEEL

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22MnB5 press hardening steel is widely applied for automobile parts due to its reduced spring back effect after forming. In press hardening process, 22MnB5 steels are deformed by the press at high temperature and simultaneously quenched to obtain fully martensitic microstructure after the austenitization process. However, during the press hardening of Zn-coated 22MnB5 steels, the presence of liquid Zn generates microcracks on the steel surface, which is related to Zn-assisted liquid metal embrittlement (LME). The present work has investigated the effect of Si addition on Zn-assisted LME in 22MnB5 steels. 22MnB5 steels with 0.25 wt.% Si and 1 wt.% Si were prepared for comparison. Both of 22MnB5 steels were heated to 900 °C to be austenitized. After the austenitization, the specimens were air-quenched to 700 °C and isothermally deformed to 40 % engineering strain. All the process was conducted by Gleeble 3500. The heating speed and the holding time at 900 °C were controlled to investigate the LME sensitivity depending on the various austenitization conditions. The Zn-assisted LME was severer with faster heating speed and shorter holding time, and the Si-added 22MnB5 steel exhibited higher LME sensitivity. The deformed specimens were cut cross-sectionally to analyse the microstructures of steel/Zn coating interface and the steel matrix. The Fe-Zn alloying reaction at the steel/Zn coating interface was strongly related to the Zn-assisted LME of 22MnB5 steel.

Poster Session / 144

PHASE EQUILIBRIUM AND CRYSTAL STRUCTURES OF SEVERAL HIGHLY ORDERED Fe₂Al₅ PHASES WITH THE FRAMEWORK STRUCTURE OF η -Fe₂Al₅ PHASE

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Hot dip galvanized steel is widely used in the field of automobile since the galvanized coating layer protects mother steel from corrosion. The molten Zn bath commonly contains small fraction of Al to suppress the preferential formation of the brittle Fe-Zn intermetallic compounds that often provoke flaking off the coating layer during stamping or forming of coated steel. It is well known that minor addition of Al to the molten Zn bath results in preferential formation of the Fe₂Al₅ intermetallic compound layer. This coated layer has been considered to be the orthorhombic η phase (space group Cmcm). On the other hand, our group has recently found that the layer phase often crystallizes into highly ordered atomic arrangement most likely termed as the η'' phase even during short-term dipping. Besides, recent researches address there exists several

ordered phases similar to the η'' phase with the framework structure of η phase¹. According to Burkhardt's study¹, the η phase is composed of a full occupied framework structure (4 Fe and 8 Al atoms) and partially occupied chains along the c-axis (6 Al sites). The c-axis chain is considered to allow chemical tenability and various kinds of atomic orderings: the formation of various kinds of ordered phases is considered to be responsible for how Fe and Al atoms order in the c-axis chain sites. However, the crystal structures of some of these ordered phases are still controversial and phase equilibrium among them are not consolidated. In this study, we have examined the phase equilibrium among these phases and refined their crystal structures. Experiments are carried out with scanning electron microscope, energy dispersive spectroscopy, X-ray diffraction, transmission electron microscope, scanning transmission electron microscope. There are some invariant reactions: the η phase is found to dissolve into the η'' and η_m phases around 350 [U+2103] while the η phase has been thought to be stable at low temperature. Some of the ordered phases are found to have highly ordered long-period structures with periodic antiphase boundaries.

Reference: 1 H. Becker et al., *Intermetallics*, **93**, (2018) 251-262. 1 U. Burkhardt et al., *Acta Cryst*, **B50**, (1994) 313-316.

LME of Resistance Spot Welded Coated Steels: Moving Toward Solutions / 145

EFFECT OF Zn-COATING PROCESS ON LIQUID METAL EMBRITTLEMENT OF TRIP STEEL

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The resistance spot welding is widely employed by automotive manufacturers because of its low cost and fast process. However, when the galvanized TRIP steel plates are joined by resistance spot welding, cracks are generated by liquid metal embrittlement (LME) because the substrate gets exposed to liquid zinc. These cracks deteriorate mechanical reliability of welds and limit the application of TRIP steel. The present study investigated the microstructural evolution and LME sensitivity of differently Zn-coated TRIP steels. Three Zn-coated TRIP steel sheets were prepared by applying different coating process: (i) continuous galvanizing, (ii) galvannealing, and (iii) electrogalvanizing. Hot tensile testing and microstructural analysis exhibits that the coating method influences Fe-Zn reaction which controls the contact between steel substrate and liquid Zn alloy at the high temperature. The electrogalvanized TRIP steel exhibits the highest resistance to LME, while the galvanized one shows the lowest resistance.

Pot Optimization by Numerical Simulation and Material Development / 146

EFFECTS OF HEAT TREATMENTS ON THE MORPHOLOGY AND MECHANICAL PROPERTIES OF A CoCrW ALLOY FOR HOT DIP GALVANISING APPLICATIONS

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Cobalt based alloys are widely used in demanding environments due to their strength, wear and corrosive resistance properties at elevated temperatures. They are commonly used in molten zinc applications as bearing components on continuous galvanising lines (CGL). Despite these properties, the CGLs have to be stopped regularly to replace the Co-based bearings assemblies

due to in service degradation resulting in significant production losses. The mechanical properties of the alloys can be attributed to the distribution and morphology of the carbides within the microstructure which can be modified through thermal treatments. This paper investigates the effects that heat treatments have on bearing performance. Initially samples were heated at 1265°C for 6 hours, to promote carbide diffusion into solid solution before being water quenched. Subsequent age hardening at 850°C was carried out for 2, 4- and 8-hour treatments. Results show the initial treatment resulted in a change in microstructure morphology, but the hardness remained similar to the untreated sample. Subsequent age hardening experienced no further changes in microstructure morphology, but alloy bulk hardness increased by a maximum of 35% where the hardness of the untreated alloy increased from 420Hv to 575Hv after a 4-hour ageing treatment. Nanoindentation revealed that both the matrix and eutectic carbides experienced an increase in hardness which contributed to the overall increase in material hardness.

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THE PROPOSAL FOR IMPROVEMENT OF INTERSTITIAL FREE STEEL MECHANICAL PROPERTIES IN CGL PROCESS

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The Zinc Alloy Coated Steel Sheets are mainly used for the plates of Automotive. Especially, the interstitial free steel is used to the outer panel and it is manufactured by press forming in the process of automotive manufacturing. The materials are needed of high formability because the press formed parts have some complicated shape, therefore high elongation of mechanical properties are important. The mechanical properties are mainly ruled in the component and a CGL heat pattern can make fine adjustment. The mechanical properties can only be measured by off line tensile testing. However it is difficult to change the properties after CGL manufacturing if the test results don't meet the criteria. Here we show the prediction model of the mechanical properties based on the records of CGL heat pattern experience. By using this model, you can predict the mechanical properties and can adjust CGL heat pattern optimization at once.

Physical Vapour Deposition of Zn and ZnMg Coatings / 149

PosPVD – A NEW TYPE OF Zn-Mg ALLOY COATING ON METALLIC STRIP BY PHYSICAL VAPOR DEPOSITION PROCESS

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POSCO has installed the full width PVD (Physical Vapor Deposition) pilot plant as a final achievement in the development stage. There are three elementary sections responsible for vacuum-locks (vacuum strip transportation system with rolls and sealing parts), plasma pretreatment, high-deposition rate coating source by induction heating and air-to-vacuum raw material feeding system for continuous process. By PVD technology, POSCO has developed a new type of Zn-Mg alloy coating products with the trade name PosPVD® (POSCO Physical Vapor Deposition). We are able to produce Zn-Mg alloy coating products in various compositions of Mg and multilayer structure according to customer requests. PosPVD® products have many advantages compared with conventional Zn coated products such as electro-galvanized (EG) or hot-dip galvanized (GI) steel. First, Zn-Mg coated products have excellent corrosion resistance. Second, the coating has higher hardness compared with conventional Zn coating, resulted in good galling and press performance. Third, PVD coating products show no or low hydrogen delayed fracture in UHSS grad. Also, due to the top Zn layer of multilayer structure, various post-treatments including phosphate treatment and sealant can be applied as it is. Plus, the metal color and high glossness

of Zn-Mg coating can be used for decorative purposes in home appliances and construction application. PosPVD® received favorable reviews from many customers until now. We believe that the various advantages of PVD products will create new markets in the near future.

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FIVES' EYERON™, ALL-IN-ONE QUALITY MANAGEMENT SOFTWARE

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A large range of digital solutions and equipment exists in order to manage quality requirements of high end products on strip processing lines. But in the end day-to-day users have to juggle between dozens of solutions and finally get lost in trying to link data from different software or finding the right tool adapted to their situation. Solving defect crises requires rather applying the right methodology and using a limited set of tools in order to be efficient. Fives' Eyeron™ advanced quality management software is an all-in-one integrated solution designed by and for metallurgists that gathers all necessary tools in one single place to efficiently solve any defect crisis faced during production. By providing easy and clear visualization of all plant data such as process, surface inspection, order or claim information, as well as powerful data analysis and control features, Eyeron™ allows its users to tackle any quality issue directly from one interface. Eyeron™ gives then the possibility to perform automatically product quality certification and even provides recommendations to reallocate products at any production step from slab down to finished rolled product, considering the quality required by each customer. This paper will presents how Fives' Eyeron™ software can be used by process and quality engineers to resolve defect crisis on hot dip galvanizing line, to assess daily progress in terms of quality yield and evaluate overall achieved quality performance.

PHS-AlSi & PHS-ZnFe: Controlling Surface Properties / 152

THE PROTECTION OF GA COATED HOT STAMPED STEEL THROUGH THE APPLICATION OF MoS₂

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The automotive industry have come under increased pressure to reduce vehicle emissions whilst simultaneously improving safety. Light weighting through downgauging is a common strategy employed by steel makers to address these issues. This has led to increased volumes of Advanced High Strength Steels (AHSS), Ultra High Strength Steels (UHSS) and Press Hardenable Steels (PHS) being used in Automotive Body in White. Press hardenable steels (PHS) are formed at high temperature (~950°C) whilst in the austenitic region before being quenched to room temperature within a press to form the harder martensitic phase. The heat treatment is conducted in atmospheric conditions to allow the rapid transfer in and out of the furnace. Oxygen within the atmosphere causes decarburisation of the substrate's outer layer leading to the undesirable formation of ferrite phase upon quenching. A further problem with the use of PHS is in service corrosion protection. Traditional hot dip galvanised (HDG) coatings evaporate at 907°C meaning they do not survive the heat treatment process for PHS. Therefore a novel strategy is required to provide some level of processing and in-service protection of PHS. This paper investigates the use of a 10 µm Galvanneal (GA) coated PHS, overcoated with 15 - 40 µm Molybdenum Disulphide (MoS₂) with a view to providing protection of the GA during heat treatment. MoS₂ is a thermally stable 2D material commonly used to provide lubrication to sliding components. Scanning electron microscopy and Scanning Vibrating Electrode Technique (SVET) was used

to elucidate the effectiveness of the MoS₂ layer in preventing the loss of zinc rich phases from the surface of the steel. Visual inspection of samples post heat treatment showed the MoS₂ coated sample provided greater protection than uncoated GA. The MoS₂ coated samples showed no evidence of decarburisation of the PHS. SVET experiments on the cut edges of the coated material were performed on post heat treated samples in 3.5% NaCl solution at 21°C. The SVET is able to resolve anodic and cathodic events occurring on the surface in solution. Results showed the MoS₂ overcoated GA coating is still able to provide galvanic protection post heat treatment at 950°C. SEM images reveal the presence of zinc on the substrate of the coated MoS₂ samples. The results demonstrate that the overcoating of GA coated PHS is a promising strategy for providing process and in-service protection.

Furnace III - Rapid Cooling, Furnace Roll Coatings / 153

DEVELOPMENT OF AN ADVANCED ULTRA-FAST COOLING SECTION

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The realisation of economic and ecological aims led to a development of improved structural materials. Third generation Advanced High-Strength-Steels and their application in automotive bodies in white are one example of this trend. Those steels are often processed as thin strips in combined continuous annealing and galvanizing lines and require new heat treatment possibilities to acquire their beneficial mechanical properties with price efficient alloying concepts.

Disregarding higher soaking temperatures those heat treatments have high demands on the cooling strategy. Enhanced cooling rates with ideal uniformities over the length and width of the strip are required as well as a good flatness. Most commonly jet impingement gas cooling is used in these lines. The jets are formed using arrays of round or slot nozzles or combinations of both. In this study we present the development of an advanced cooling section in collaboration of a university research institute and an industrial plant manufacturer.

A fundamental, experimental study was conducted to find an efficient nozzle design for the application. Efficiency in nozzle design means to reach high heat transfer coefficients per needed fluid power. The experimental set-up enables the measurement of local and integral heat transfer coefficient distributions in near industrial sized nozzle fields. Further the flow properties are continuously monitored allowing both, determination of the design efficiency and the influence of typical nozzle array parameters.

Based on the previous investigation a prototype is designed and manufactured. The prototype is then analysed regarding the process limitation strip stability. Strip stability is investigated measuring the strip vibration in a cooling section model. The stability quality is quantified by means of the peak-to-peak value, the minimum and maximum strip displacement within a thirty second interval for a certain flow state.

After the successful start-up of the industrial cooling section the experimental results are compared to in-plant measurements to validate the accuracy of the estimations.

Physical Vapour Deposition of Zn and ZnMg Coatings / 154

MECHANISMS STABILIZING GENERAL VAPOUR-PHASE GALVANIZING

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Physical Vapor Deposition have now entered the panel of technologies for fabricating metallic Zn-rich coatings on steel. We have recently demonstrated that General Vapor-Phase Galvanizing can coat complex-shape steel articles after fabrication with a fully alloyed Fe-Zn coating.

Surface activation is a key step of the process because the coating results from the reaction of zinc vapor with steel in a range of temperature between 350°C and 550°C. We have tested several industrial protocols able to clean the surface and stimulate its reactivity. Our results show the importance to produce surface sites providing a sufficient diffusive flux of iron and where zinc atoms can adsorb for nucleating Fe-Zn aggregates. The influence of roughness on reactivity will also be discussed. The other genuine aspect of our process is to maintain an adsorption-desorption equilibrium of zinc atoms to and from the surface so that complex-shape articles can be coated at once without making shadows, nor producing over-thickness. Then, complex-shape articles can be coated at once without requiring a complex handling device into the evaporation chamber. These conditions depart from the one of standard (deposition-condensation) PVD or reactive-PVD (deposition followed by the diffusive reaction), and produce uncommon specific microstructures. We will discuss the surface mechanisms that drive and stabilize the process.

The phase composition of coatings fabricated by GVPD is similar to the one of GA steel. However, coatings produced by GVPD are usually two to three time thicker than the GA coatings. GVPD coatings are especially efficient for the fabrication of high standard duplex coatings. Fabrication in the low range of fabrication temperature (350°C – 390°C) can treat high strength steels without producing a significant tempering of martensite. Coating in vacuum after the fabrication of parts bypass the problem of producing a coating compatible with hot stamping.

HDG Coating Formation & Dross Management / 155

OPTIMAL CONTENT OF ALUMINUM IN ALUMINUM-ZINC ALLOY IN HOT-DIP COATING ON THE STEEL STRIP

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Currently, the optimum aluminum content in the alloy for Aluminum-zinc coating considered wt.55%. In addition to aluminum and zinc, the alloy contains 1.6 wt.% Silicon, which is introduced to suppress the exothermic reaction of the melt with iron. Cold-rolled steel coils with such a coating, has gained wide popularity and produced in many countries of the world. A coating with 55% aluminum has high corrosion resistance, and its production allows replacing zinc with aluminum and thereby reduces the specific gravity of the coating material, leading to savings of up to 75% zinc. However, the production of aluminum-zinc coating is associated with a large number of difficulties associated with the aggressiveness of the aluminum-zinc alloy with respect to the steel strip and the material of the pot equipment. As a result, a large amount of dross is formed, including the lower dross, which must be removed during each replacement of pot equipment. Compared to hot dip galvanizing, the campaign time for pot equipment is drastically reduced by 2–3 times. The plastic properties of the coating on the strip also deteriorate due to the thick intermetallic coating layer. This paper presents laboratory studies of the aggressiveness of alloys with different aluminum contents (from 5 to 55%) to steel base and materials of pot equipment. Based on the studies of the chemical activity of alloys with different aluminum contents, as well as metallographic and corrosion studies obtained coatings, the optimal composition of aluminum-zinc alloy for coating a steel strip was selected. The coating of the optimal composition has a corrosion resistance comparable to 55% Aluminum-Zinc Coating, also can significantly reduce the cost of the coating material compared to hot dip galvanizing, and its production is free from the inherent drawbacks of 55% Aluminum-Zinc Coating - the formation of lower dross and short life of pot equipment.

Poster Session / 156

THE INFLUENCE OF TECHNOLOGICAL PARAMETERS OF PRODUCTION ON THE FLUTING DURING BENDING OF PRE-PAINTED LOW CARBON STEEL**Author(s):** ADIGAMOV, Ruslan¹**Co-author(s):** Mr. YASHCHUK, Sergey ² ; Mr. GLUKHOV, Pavel ¹ ; Mr. DMITRIY, Rybin ¹¹ *JSC "Severstal management"*² *JSC Severstal Management***Corresponding Author(s):** rradigamov@severstal.com

When using low carbon steel to produce pre-painted steel, there is a risk of a defect called fluting. Fluting is a series of sharp parallel kinks or creases occurring in the arc when sheet steel is formed cylindrically. One of the options for eliminating this defect is the use of interstitial free steel not subject to aging in the process of applying a pre-painted steel, but this leads to an increase in the cost of production. Therefore, the search for a technological solution for the production of pre-painted steel of low carbon steel is an urgent task. The paper presents laboratory and industrial studies of the influence of the chemical composition of steel and the technological parameters of production pre-painted coils on the formation of fluting in the process of low carbon steel bending. The optimal chemical composition of the steel, the parameters of hot rolling, heat treatment and skin pass in the hot dip galvanizing line, taking into account the subsequent continuous coil coating process, which ensure the absence of fluting during subsequent bending, were selected.

HDG Coating Formation & Dross Management / 157**INFLUENCE OF Al CONTENT IN THE ZN BATH ON GALVANIZED COATING FORMATION OF HIGH STRENGTH STEELS****Author(s):** ELEUTERIO, Henrique¹**Co-author(s):** Dr. BARBOSA, Aldo Henrique ¹ ; Mr. COSTA, Elias Barbosa ²¹ *Usiminas*² *Unigal Usiminas***Corresponding Author(s):** henriquelacerda@yahoo.com.br

The control of Al content in the bath of molten Zn in Continuous Galvanizing Lines (CGL) allows to improve the surface quality of coated products, particularly in the case of galvanized (GI) coating, to minimize the precipitation of Fe-Zn intermetallic particles in the bath, named dross particles, and to improve operational efficiency by increasing the process velocity. The control of Al content in the Zn bath is even more important during high-strength steels galvanizing, due to the presence of alloying elements in these steels that compete with Al for the formation of coatings with good surface quality during the immersion of steel sheets in the Zn bath. In this context, the influence of Al content in the Zn bath on the formation and surface quality of GI coating of steels with high Mn addition has been determined, in pilot scale, using a Hot Dip Process Simulator (HDPS). It was possible to assess this influence on the formation of interfacial layer, called inhibition layer, and to optimize the Al content in the Zn bath to produce GI coatings with good surface quality and adhesion to the substrate, providing conditions to achieve greater operational flexibility.

On-Line Measurements and Galvanizing Bath Control Development & Bath Al Chemistry Effects on Coating Quality and Bath Management / 158**IN-LINE BATH CHEMISTRY MONITORING: REVOLUTIONARY RELIABILITY OF THE NEW DIODE-BASED LASER INDUSTRIAL LIBS SENSOR****Author(s):** NADEAU, Alexandre¹

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It is well known that the steel industry is going through an important period of change, driven in part by new paradigms in the car industry and by the popularity of new alloys of competing metals. Coatings have become a strategic part of this puzzle and, now more than ever, bath composition is playing a key role. From the challenges on coatings from press hardened steels to the great potential of magnesium enriched galvanizing recipes, bath composition has become a huge center of discussion. In the past decade, industrial LIBS sensors have demonstrated their capacity to simultaneously monitor all the elements of interest for both established processes like Galvanneal and Galvanize, as well as for more recent coatings like magnesium-aluminum zinc alloys and new generation of Galvalume. In this paper, we present industrial data from the next generation of in-line LIBS sensor. This new generation has moved from lamp-based laser sources to diode-based laser sources. A diode-based laser source provides a more stable measurement and does not require water cooling, therefore removing the burdens related to moisture management and premature optical degradations. Results about for GA, GI and mag-alu processes are presented. Industrial data shows that the new generation LIBS sensor requires significantly less maintenance and less calibrations throughout the year.

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IN-LINE SEAM WELD INSPECTION USING LASER-ULTRASONIC RESULTS FROM AN INDUSTRIAL TRIAL

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With ever increasing targets on productivity, unpredictable down times caused by a weld break can become an important problem. Lately, partly because of drivers like the rise of multiple high strength steel grades and the retirement of highly experienced operators, we have seen CGL lines experience an increase in weld break events. Technologies like pressure sensors, current sensors, cameras and pyrometers are used to help characterize the weld quality. Nonetheless, these instruments cannot be trusted for an automatic rejection or acceptance of the weld. Recently, a new approach was proposed using laser-ultrasonics to characterise the weld in-line with the welding process. It uses ultrasounds through the weld itself, an approach broadly accepted in the world of non-destructive testing. The topic of this paper is about the industrial implementation of a laser-ultrasonic instrument optimized for weld inspection. Results on a long term trial in a North American plant are presented. The impact of steel alloy, weld preparation and surface conditions on the acceptance threshold are discussed.

Challenges Galvanizing 2nd and 3rd Generation AHSS / 160

U. S. STEEL XG3 – 3rd GENERATION STEEL: CUSTOMER-FRIENDLY CHEMISTRY, PROPERTIES, AND MANUFACTURABILITY ENABLED BY UNIQUE PROCESSING

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Hot-dip galvanized (GI) and galvalume (GA)-coated third generation steels have been developed and commercialized at minimum tensile strength levels at both 780 and 980 MPa. These coated steels feature a combination of superior formability which, with targeted steel compositions and unique processing, have been shown to result in more customer-friendly properties and

excellent residual ductility after automotive assembly. The steel microstructure is developed by the application of a novel heat treatment that results in improved uniform and total elongation; strength, n-value, local formability, transverse uniformity, and reduced anisotropy. In addition to providing improved properties, the heat treatment provides other benefits. These include decreased alloy costs, improved production yields, and decreased silicon content. The low silicon hot-dipped steel compositions provide five areas of benefits. First, lower silicon improves coat-ability, which has been demonstrated in advanced laboratory simulations and commercial production; second, it allows galvanneal (GA) alloying at more moderate GA peak metal temperatures (PMT) and thus, less degradation of retained austenite, even with thicker 50 g/m² class GA coatings; third, it reduces silicon-affected welding carbon equivalent, which helps to minimize liquid metal embrittlement (LME); fourth, the avoidance of high silicon helps to minimize the need for hot charging of thick slabs prior to hot rolling; fifth, steels which avoid high silicon typically have improved hot band de-scaling pickling and coated surface quality. Cooperative development efforts with automotive manufacturers have revealed properties that favorably combine to produce cold-stamped components that can potentially replace hot-stamped components of higher strength ratings. Significant yield strength increase after forming, combined with potent bake hardening results in a final yield strength that compares favorably with press hardened steels that can experience softening during automotive paint baking treatment. The result of these synergistic responses to vehicle assembly practices is higher residual ductility, and crash energy absorption with reduced fractures. The development of these steels benefited from advanced simulation equipment including a new direct-fired furnace (DFF) simulator as well as two hot-dip coating and annealing process simulators (an upgraded Surtec Research A-3 and a newly installed A-6). In addition to laboratory optimization of heat treatments and coat-ability, the steelmaking pilot operations and simulation equipment also heavily influenced capital expenditures at the manufacturing operations. Design of experiments optimized the process parameters prior to commercial trials.

PHS-ZnFe: New Steel & Coating Developments / 161

PHASE TRANSFORMATION TEMPERATURES AND Fe ENRICHMENT OF A 22MnB5 Zn-Fe COATED STEEL UNDER HOT STAMPING CONDITIONS

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In the last years, press-hardening steels have contributed to the automotive industry successfully to meet the increasing regulations for reducing fuel consumption and stringent greenhouse gas emissions while improving passenger safety by manufacturing lightweight car body parts. Zn-Fe coating is an alternative to prevent corrosion or even enhance the corrosion resistance in these steels. However, Zn-Fe coating is prone to liquid melting embrittlement (LME) during the hot forming process. To prevent LME, the coating must be fully transformed into a solid solution before the forming operation, avoiding the contact of the Zinc liquid phase with the steel substrate. This work aimed to determine the phase temperature transformations and critical cooling rate to define the process window for a 22MnB5 sheet with a Zn-Fe coating when submitted to a higher heating rate in comparison to the direct conventional hot forming process. The experimental results indicated that a fully martensitic microstructure is obtained with a cooling rate of 30 °C/s. The adopted two-side Zn coating weights of 45 and 80 g/m² heated at 53 °C/s to 900 °C is fully transformed into Fe- α solid solution in 0 and 23 seconds, respectively, which is an industrial gain compared to longer dwell times required in the conventional heating furnace processes.

LME of Resistance Spot Welded Coated Steels: Moving Toward Solutions / 162

QUANTITATIVE ASSESSMENT OF THE INFLUENCE OF STARTING MICROSTRUCTURE ON THE LIQUID METAL EMBRITTLEMENT SUSCEPTIBILITY OF 3rd GENERATION ADVANCED HIGH STRENGTH STEELS

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Third generation advanced high strength steels (AHSS) were developed as automotive structural materials capable of enhancing vehicle fuel efficiency and crashworthiness. The use of zinc (Zn) coated AHSS is limited by Zn-assisted liquid metal embrittlement (LME) that leads to surface cracking during high temperature processing. It has been reported that AHSSs are generally more sensitive to Zn-assisted LME compared to conventional mild and high strength low alloy (HSLA) steels; the factors controlling the LME sensitivity of AHSSs are not precisely established. AHSS grades have tailored multi-phase microstructures and relatively rich alloy compositions; microstructural and alloying variations may influence LME susceptibility. In this work, the influence of starting microstructure variations on Zn-LME sensitivity is studied using a 0.25C-2.7Mn-1.45Si steel alloy, continuous annealed to generate different AHSS microstructures: martensitic, quench and partitioned (Q&P), dual-phase (DP), and transformation-induced plasticity (TRIP)-assisted bainitic ferrite (TBF). High temperature tensile tests were conducted on electrogalvanized (EG) sheets of different starting microstructure variants to compare Zn penetration characteristics, and the critical temperatures and stresses required for inducing LME. The results are interpreted in the context of the specific influence of starting microstructure on LME behavior during resistance spot welding of Zn-coated AHSS sheets.

On-line Measurements - Cleanliness, Austenite Fraction and Coating Defects / 163

PRODUCER EXPERIENCES AND ADVANCEMENTS WITH AN ONLINE, NON-CONTACT SURFACE CLEANLINESS MONITOR

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Over the past two years, four CGLs have installed an online, surface cleanliness monitor system utilizing a non-contact, laser ablation technique to evaluate the contamination layer on the moving sheet. The CGL operators using the system obtain unprecedented detail about the sheet's surface cleanliness along the entire length of each coil.

The system has been improved over the last two years with customer feedback and hard lessons learned about laser quality. The most notable system enhancements are the addition of a different industrial laser technology and an all-new, instrument head design enabling field serviceability of lasers using interchangeable laser modules.

CGLs using the system have immediate feedback of how adjustments to the cleaning section affect surface cleanliness out of the cleaning section, or sometimes, seeing the adjustments have no effect on cleanliness. With an instrument head before the cleaning section, the incoming cold-rolled sheet can be monitored. The system allows cleaning section performance to be bench marked before and after significant changes: for example, changing brushing technology; electrolytic cleaning phase change or power protocols; evaluating new solution types or operating temperatures; etc. For one CGL operator the continuous, online, surface cleanliness data has launched an Industry 4.0 project towards automating cleaning section control using artificial intelligence to evaluate

the surface cleanliness data along with other inputs. The prospects of advancement in process control around cleaning are promising with many anecdotes and data to share.

In summary, this non-commercial paper will explain details about the benefits and challenges found by CGL operators using the surface cleanliness evaluation system by showing detailed data, plots, and explaining anecdotal use-cases from CGL operators who have implemented the system. A very brief, contextual overview about surface cleanliness will be included to make the session as applicable as possible; why cleanliness is important, key historical methods used to measure surface cleanliness – with pros & cons, along with some fundamentals of cleaning section troubleshooting.

Coating Alloy Corrosion Studies / 165

ZnAlMg METALLIC COATINGS IN HARSH ENVIRONMENTS: A COMPARATIVE AND CHALLENGING STUDY

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ZnAlMg (ZM) metallic coatings are already in use since the start of their development in the late 2000's, while the production still benefits from a steady volume increase. It has been proven already that this type of metallic coatings is having an excellent corrosion resistance in diverse harsh environments.

One of the highly used markets for this type of metallic coatings is the solar panel market, where different Zn-based metallic coatings are used as supporting structures for solar parks. These parks are typically installed in environments where the conditions can be quite harsh. Supporting poles need to be buried into the soil, where different soil parameters are influencing the corrosion. Another way of burying profiles in soil is by embedding them in concrete, which can also cause important corrosion, mainly during the initial drying phase after installation. In the exposed part of the structures, several mechanisms of corrosion will take place, depending on the location. Atmospheric corrosion is the main one, but in desert areas (with a high amount of sunny hours, making them a preferred location to install large solar parks) also sand abrasion needs to be taken into account. It will be shown in this work to be an important factor influencing the lifetime of the protecting metallic coatings. In this study, the performance of ZnAlMg was compared to other well-known Zn-based coatings in several of these harsh environments.

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THROUGH-PROCESS QUALITY CONTROL (TPQC) SYSTEM - ANY DATA, ANY TIME

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Through-Process Quality Control is a quality system intended to cover the entire production line, from the liquid phase to the finishing and packaging lines of the final end product. The term "Through-Process" has been coined to specifically emphasize this idea. TPQC is a quality management system for steel production, which helps to continuously monitor and to manage quality across all production processes throughout the entire production chain, from steelmaking to sheet galvanizing. The system collects all process parameters and measured production data, starting in the liquid phase until the final product leaves the packaging line for shipment.

FEATURES • Intelligent storage of high resolution data, encompassing the entire product genealogy and ensuring fast access to all quality-relevant production data of the final strip • Product Explorer: in-depth analysis of process data based on time or length of product • Quality and process assistance: rule-based quality checkpoints, root cause analyses, and suggestions for corrective actions • Automatic rule-based surface grading • Surface defect density map generated by the integration of surface inspection systems • Tailor-made reporting • Statistical Process Control (SPC) & Key Performance Indicators (KPIs) • Data Analysis: TPQC data can be accessed using data-mining tools to deepen the knowledge about quality & process • Primetals Technologies provides training and service packages for the different TPQC features **BENEFITS** • Efficient troubleshooting and fast access to the required information in one system • Quality management & quality certification support • Reduced manual product inspection, rework, and downgrades • Reduced influence of human factor • Digitalization of know-how • Big data analysis and self-learning systems—leverage your own production data • Suggestions of root causes, and for corrective, and compensational actions • Supporting system to achieve conformity with ISO9001/IATF16949 and other automotive standards • To ensure continuous improvement and stable, well understood production processes, new know-how is created This paper describes how to use the TPQC integrated know-how-based IT solution to improve efficiency and quality for processing lines.

Origins of Hydrogen Embrittlement / 167

IN SITU INVESTIGATION OF HYDROGEN ENTRY AND HYDROGEN EMBRITTLEMENT OF ZINC-COATED HIGH STRENGTH STEELS INDUCED BY ATMOSPHERIC CORROSION

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Hydrogen embrittlement of advanced high strength steels (AHSSs) in atmospheric exposure conditions is of utmost importance for automotive industry as the application of AHSSs grows steadily due to desirable mechanical properties. Different aspects of the hydrogen embrittlement phenomenon such as hydrogen entry caused by atmospheric corrosion reactions are currently under intensive research. This study was focused on understanding the effect of atmospheric climatic and exposure conditions on atomic hydrogen formation, entry and diffusion in bare and zinc coated AHSSs. Several complementary techniques allowing for in situ investigation of hydrogen entry and permeation through complex phase and dual phase AHSSs and their mechanical properties have been employed on bare steel and zinc coated specimens with artificial defects. KircTec sensor is a new device for hydrogen permeation measurements based on monitoring of electric resistance changes. One side of a steel specimen was exposed to wet-dry cycling conditions in a corrosion chamber after application of sodium chloride solution in order to induce atmospheric corrosion, while hydrogen content was measured by the KircTec sensor attached to the opposite side. Scanning Kelvin Probe Force Microscopy (SKPFM) measurements with lateral resolution allowing for identification of permeation paths and the effect of microstructure as well as scanning Kelvin probe (SKP) measurements were conducted using a similar setup, recording changes in contact potential difference in controlled atmospheres. The effect of atmospherically induced hydrogen on mechanical properties of AHSSs was assessed by a Slow Strain Rate Test (SSRT) in real time. The paper will present results on the effect of wet-dry cycling, presence of corrosion products, zinc coating as well as on the mechanism of atomic hydrogen entry.

HDG Coating Formation & Dross Management / 168

THE MODIFICATION PROCESS OF THE DROSS BUILD-UP STRUCTURE ON SUBMERGED HARDWARE IN Zn-Al AND Zn-Al-Mg BATHS

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During hot-dip galvanizing dross particles form in the zinc bath and develop over the surface of submerged pot hardware. This accumulation of dross on the hardware is known as dross build-up. Dross build-up is a critical factor in the pot hardware lifetime. The surface quality of the hardware directly influences the quality of products produced on the galvanizing line. More dross build-up could lead to more defects on the coated product, which is undesirable for customers and creates higher scrap rates and lost production tonnage. The mechanisms of dross build-up in a typical GI zinc bath have been extensively researched in recent years.

In addition to typical GI zinc coatings, Tata Steel also produces Zn-Al-Mg coated steels with 1,60 wt% Al and 1,60 wt% Mg called MagiZinc. The pot hardware is used in production for both GI zinc pots and subsequently in MagiZinc coating baths. There is some evidence that the dross build-up layer on the bath hardware created in the typical GI bath changes when the hardware is submerged in the MagiZinc bath.

This thesis project aimed to identify the characteristics of this modifying behaviour in MagiZinc of the dross build-up that is formed on bath hardware when submerged in typical GI zinc bath. In general, it was observed that the intermetallic dross particle/liquid Zn interface changes the structural morphology of the dross build-up creating a more open structure with reduced cohesion of the grain boundaries of the intermetallic dross particles. This reduction in cohesion may lead to particle detachment at the grain boundaries when enriched with Zn. Furthermore, heating and cooling of the pot hardware during pot changes also contributed to breakdown of the dross build-up layer.

Based on the results obtained from experiments in this study it can be concluded that the separation process of the intermetallic dross particles in a MagiZinc bath is a combination of intergranular diffusion of Zn and crack formation as a result of thermal shock.

Furnace II - Current Topics from Preoxidation to Galvannealing / 170

SIMULATION OF FLASH PRE-OXIDATION IN AN ANNEALING SIMULATOR

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Galvanizing lines often apply pre-oxidation and reduction in their annealing cycle to ensure successful galvanizing of Advanced High Strength Steels with good coating appearance and excellent adhesion. Tata Steel uses flash pre-oxidation by means of an oxygen bar, by which an oxygen-rich gas mixture is blown onto the steel strip. The thickness of the Fe-oxide layer formed during the pre-oxidation step is crucial, as both too little and too much pre-oxidation can lead to poor adhesion and/or bare spots or coating defects. To ensure a continuous good coating quality in the Hot Dip Galvanizing line with various steel grades and process conditions, it is crucial to understand which parameters have the largest influence on the growth kinetics. Lab pre-oxidation studies are an important tool in this. In order to simulate the oxidation process by the oxygen bar in the lab, the hot dip process simulator was adjusted to allow an instant change of atmosphere at the sample. Furthermore, the oxidation of the sample was monitored with an in-situ optical measurement system. This study focusses on the effect of temperature, oxygen percentage, and chemistry of steel substrate and formed oxides during fast oxidation.

Coating Alloy and Modification effects on Corrosion Behaviour / 171

CATASTROPHIC BEHAVIOR OF GALVANIZED STEEL EXPLAINED BY FUNDAMENTALS OF CORROSION SCIENCE

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After two experiences with the premature failure of the roof of a secondary steel factory, an approach was developed to identify the reasons for the quick failure, and consequent loss of almost one million dollars each time. Problems concerning with the depolarization of the cell Zn/Fe, the design principles to corrosion prevention, the establishment of nests of sulfates and the cycle of acid regeneration, were enough to explain the accelerated directional phenomena. In this work are presented a description of the problem, the findings, a theoretical discussion, and the proposed intervention.

Physical Vapour Deposition of Zn and ZnMg Coatings / 172

JET VAPOUR DEPOSITION: A TECHNICAL ECONOMIC ALTERNATIVE TO ELECTRO-GALVANIZING FOR Zn COATINGS OF FUTURE STEELS

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Jet Vapour Deposition (JVD) technology is industrialized at ArcelorMittal since mid of 2016. This technology, developed in partnership with CRM Group, constitutes an attractive technical and economic alternative to Electro-Galvanizing (EG) deposition process. JVD is a vacuum deposition process fully compatible with high line speeds, which allows the deposition on all kinds of steels of pure zinc coatings with in-use product properties similar to EG coatings ones. Furthermore, thanks to its flexibility, a wide range of coating thickness that can be different on each side, is accessible according to the request of customers. For automotive market, the current production concerns Advanced / Ultra High Strength Steels (AHSS / UHSS) higher than 1000 MPa used for structural parts in vehicles. This request is motivated by the fact that JVD is an hydrogen free process, with no risk of embrittlement by hydrogen for these steels. This is a major advantage of JVD compared to EG, since EG requires a post-thermal treatment to degas hydrogen trapped in steel during Zn deposition. But JVD may also be suitable for drawing steels used for external / exposed parts of vehicles, which require a very good aspect quality. JVD has a limited impact on the steel topography parameters. Using automotive exposed formats leads to JVD Zn coated steels fulfilling exposed specifications. Lastly, JVD is a green process compared to EG: less energy and water are required to produce a similar coating.

LME of Resistance Spot Welded Coated Steels: Assessments / 173

COMPARATIVE ASSESSMENT OF GI AND GA COATED AHSS LME SENSITIVITY DURING SPOT WELDING

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Liquid Metal Embrittlement (LME) is a complex phenomenon which may occur during spot welding of zinc-coated Advanced High Strength Steels (AHSS) developed for the Automotive market.

Zinc or zinc alloy in liquid state penetrates along the steel grain boundaries and may cause, depending on conditions, grains' decohesion and cracks' initiation and propagation under given mechanical stresses.

LME sensitivity depends on the steel mechanical properties and surface / sub-surface characteristics, the coating composition and microstructure and the spot welding process itself.

In this study, a comparative assessment of conventional Galvanized (GI) and GalvAnnealed (GA) coatings in terms of LME behavior has been done on the same sensitive AHSS material with the same welding process configuration and parameters. The intrinsic effect of the type of coating (GI vs GA) on the LME performance could therefore be properly evaluated.

On-Line Measurements and Galvanizing Bath Control Development & Bath Al Chemistry Effects on Coating Quality and Bath Management / 174

HDG POT PRODUCTIVITY

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During production of galvanized products, the Hot Dip Galvanizing bath is managed with additions of ingots allowing to guaranty the stability of the bath level and composition. Hot Dip Galvanizing pot productivity (in kg/h) is then defined as the amount of materials melted in the pot during a given time. The pot productivity is generally monitored to maintain the HDG bath at a stable level and vary depending on the production conditions (coating weight, line speed and strip width). In case of extreme process conditions (high coating weight, high line speed and wide strip), the pot productivity may become bottleneck, resulting on the necessity to limit the line speed to maintain the stability of the bath level, and thus affecting the HDG line productivity.

In the present paper, the different parameters affecting the pot productivity are highlighted and discussed considering the constraints induced by the ingots loading technology, but also by the ingots melting kinetic itself. Different ways to improve the pot productivity are then proposed and were investigated based on laboratory ingots melting trials, numerical simulations and on-line industrial trials with instrumented ingots.

HDG Coating Weight Control by Nozzle Design & Settings / 175

A NOVEL MULTI-SLOT AIR-KNIFE DESIGN FOR LIGHTER MORE CONSISTENT COATING WEIGHTS IN THE GAS JET WIPING PROCESS

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This study experimentally investigated the ability of a novel multi-slot air-knife design to reduce high-intensity tonal noise and produce thinner coating weights in the continuous galvanizing gas jet wiping process. Coating weight measurements were carried out over a wide range of operating conditions to correlate the effect of the multi-slot jet operating parameters on the final coating thicknesses. These experiments showed that the resulting coating weight agreed with the predictions of the Elsaadawy et al. 1 analytical model and could produce thinner coatings versus the conventional single-slot geometry for the same main jet velocity with relatively low auxiliary jet velocities. Further experiments showed that the novel multi-slot air-knife design reduced the tonal noise and jet oscillations of the aeroacoustics feedback mechanism exhibited by conventional single slot air-knives, where the use of the auxiliary jets resulted in an average reduction in the acoustic tone intensity by 85%. Furthermore, the oscillation of the air-knife due to the large vortices of the aeroacoustics feedback mechanism was reduced by 45%, which resulted in a decrease in the fluctuating pressure at the substrate by 75%. The coating weight experiments also confirmed a correlation between suppressing the aeroacoustic feedback mechanism and lighter coating weights. The findings of this work indicate that the multi-slot design can be a more effective wiping actuator in the continuous hot-dip galvanizing line, producing more consistent and lighter coating weights with less intense tonal noise when compared to the single jet design. This paper will discuss the results of these investigations in detail.

Plenary Talk 5 - China / 177

DEVELOPMENT OF ZINC AND ZINC-ALLOY COATED STEEL SHEET IN CHINA

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With China's economic expansion having moderated to a "new normal" pace and manufacturing industry upgrading, the total amount of zinc and zinc alloy coated steel sheets in China has remained stable, but the demand for high-end zinc and zinc alloy coated steel sheets has gradually increased. This paper gives overviews of development and application of zinc and zinc alloy coated steel sheets in China in recent years, and briefly introduces recent progress in galvanized advanced high strength steels (AHSS), galvanized 3rd generation automobile steels. Developments of Zn-Al-Mg coatings, continuous PVD coatings, functional coatings and environmentally friendly post-treatments are also described. The paper finally discusses the development trend of zinc and zinc-alloy coated steel sheet in China.

Poster Session / 178

NUMERICAL SIMULATION OF BUILD-UP GROWTH COUPLED WITH HYDRODYNAMICS

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The present paper presents a front tracking interface numerical model for the simulation of faceted crystal growth, taken into account the incidence of flow. This model was applied to the build-up growth (Fe₂Al₅ faceted crystals) occurring during the production of Zn coated steel

sheets (Galvanizing industry) on the bath hardware. In the galvanizing industry their occurrence is a problem and therefore it should be limited. Different cases were simulated where the relative flow velocity was varied from 0 m/s to 1 m/s. These cases reproduce the industrial conditions of the growth on the stationary hardware as on the rotating bath hardware. Comparison was made between simulation and experimental observation of crystals shape and size. The growth was found to be coupled with the relative flow velocity and the roughness of the surface roll, being the result of interface kinetics and flow hydrodynamics induced kinetics.

Physical Vapour Deposition of Zn and ZnMg Coatings / 179

FEEDING TECHNOLOGY FOR A CONTINUOUS PVD COATING LINE

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For a practical application of PVD as a competitive coating technology in the steel industry, it is essential to have a continuously running line. A challenging processing step in such a line is the introduction of the steel strip into the vacuum and back out again. However, it is not only the steel strip that is removed from the vacuum but also the coating material, the sole purpose of the whole operation. This means, that it is also required to transport the coating material from atmospheric condition into a low vacuum surrounding. This feeding can be done using solid or liquid material. In this paper both methods will be evaluated with respect to their advantages and dis-advantages. The method that prevails will be determined by the boundary conditions which include the required capacity of the line and the coating weight. It is believed that to be able to compete with zinc base coatings produced on Electro or Hot Dip Galvanizing lines, the liquid feeding method, although presenting a bigger technological challenge, is the preferred option. Different liquid feeding technologies have been examined and the most promising technology, using an electromagnetic concept, was used to build a prototype together with Hazelett Strip Casting Corporation. The outcome of the tests with the prototype will be presented in this paper showing the potential of this technology.

PHS-AISI & PHS-ZnFe: Controlling Surface Properties / 180

NANOSCALE STRUCTURE AND COMPOSITIONAL ANALYSIS OF SURFACE OXIDES ON HOT-DIP GALVANIZED PRESS-HARDENED STEEL

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Insights into the structure of surface oxides on Zn-coated press-hardened steel (PHS) are indispensable for further processing like welding or adhesive bonding. The main oxide on top of

galvanized steel is Al₂O₃ from the primary galvanizing process. This oxide is strongly altered during final austenitization annealing before hot-forming respectively press-hardening, depending on the annealing time. The role of steel alloying elements on the oxide composition is investigated by the means of scanning and transmission electron microscopy with energy dispersive X-ray spectroscopy as well as Auger electron spectroscopy.

Four different steel grades are investigated, whereupon two are standard galvanized and the other two are galvanized. For both coatings, we can show that the main oxides after austenitization heat treatment are native ZnO and the initial Al₂O₃. Moreover, our results indicate that the main alloying component Mn forms (Mn,Zn)Mn₂O₄ spinel, which also contains traces of Fe and is embedded in the upper ZnO layer. Also noticeable was a varying, nanometre thick Cr enrichment at the initial Al₂O₃ layer depending on the availability of Cr in the steel alloy. Additionally, small precipitates of further alloy elements can be found at this (Cr,Al)₂O₃ layer. Further experiments with time-of-flight secondary ion mass spectrometry attached to a Helium Ion Microscope allowed to reliably distinguish between ZnO and Zn(OH)₂, which are both present in the oxide layers. All specimens show high local differences related to skin-passing prior to final heat treatment. This is especially the case for shorter annealing times, where thermodynamic equilibrium is not yet reached.

Thus, we can conclude that the oxide composition does change with the chemical composition of the steel alloy. Therefore, alloying agents do not only affect the mechanical respectively metallurgical properties of the used steel grades, but also influence surface oxides, and can have an impact on processing steps like welding or bonding.

Origins of Hydrogen Embrittlement / 183

INVESTIGATIONS ON CORROSION BEHAVIOR AND HYDROGEN EMBRITTLEMENT SUSCEPTIBILITY OF GALVANIZED DUAL-PHASE STEEL

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One of the most important aspects for a material used in automotive industry is the reliability in service regarding corrosion resistance, safety and functionality. However, hydrogen embrittlement can cause a dramatic deterioration of mechanical properties, especially in case of advanced high strength steels (AHSS). Thus, it is essential to clarify the mechanisms of hydrogen insertion into the material as well as the effect of hydrogen on the mechanical behavior. Corrosion is one source for hydrogen in steel. Therefore, the present work is based on a comprehensive approach using electrochemical and thermal desorption techniques to study the hydrogen insertion into hot-dip galvanized dual-phase steel during corrosion. The effect of hydrogen from corrosion at defects as well as at cut edges is investigated and discussed. Results from hydrogen determination experiments are compared with those from mechanical tests to reveal the impact on the mechanical properties.

One focus of the present work is the influence of the corrosion conditions: pH sensitive hydrogels are used to visualize pH changes at these special areas where galvanic corrosion between steel

and coating contributes to the overall corrosion process. A second focus is put on the influence of thermal and mechanical sample pre-treatment on the hydrogen entry into the material. Therefore, coated samples were pre-strained to uniform elongation and/or annealed, to simulate the heating cycle in the cathodic dip painting process, before immersion into sodium chloride solution to induce corrosion. Surface analysis of the differently pre-treated samples before and after corrosion was performed via scanning electron microscopy (SEM). Via thermal desorption mass spectrometry (TDMS) the amount of diffusible hydrogen after immersion of coated samples in aqueous sodium chloride solution was determined. Constant load test (CLT) and step load test (SLT) revealed the effect of corrosion and inserted hydrogen on the mechanical properties of the steel. Scanning Kelvin probe (SKP) and scanning Kelvin probe force microscopy (SKPFM) enabled in situ detection of inserted hydrogen during corrosion. In this manner, the role of defects in the coating as well as diffusion pathways of hydrogen within the steel microstructure was studied.

On-Line Measurements and Galvanizing Bath Control Development & Bath Al Chemistry Effects on Coating Quality and Bath Management / 184

THE ADVANTAGES OF CORELESS COATING AND PREMELT POTS USED ON CONTINUOUS GALVANIZING LINES FOR ZINC-ALUMINUM COATINGS

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The primary focus is to explore the advantages of coreless coating and premelt pots compared with traditional channel inductor coating pots. To start we will first explore the basic theory behind induction melting in order to provide a better understanding of the fundamental differences between a coreless furnace and a traditional channel inductor.

We will then take a closer look at how these fundamental differences impact induced current densities and distributions as well as electromechanical stirring effects to provide unmatched temperature and bath chemistry uniformity, the two key process advantages of coreless technology. Three specific case studies of bath temperature and chemistry uniformity will be presented including field data from production units.

Both single and two phase electromechanical stirring will be explained with animated stirring models generated using FEA software.

We will then continue on to explain the other operational advantages of coreless coating pot technology and conclude with an in depth comparison of total cost of ownership for coreless versus traditional channel inductor coating pots. Total cost of ownership will be broken down into several sub-categories including initial capital investment, maintenance, downtime (lost production) and finally operational costs including a look at energy consumption.

PHS-AlSi & PHS-ZnFe: Controlling Surface Properties / 185

INFLUENCE OF OXIDE COMPOSITION AND SHOT BLASTING PARAMETERS ON SURFACE RESISTANCE OF GALVANIZED PRESS HARDENED STEELS

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For galvanized press hardening steels, a low and homogeneous surface resistance is important to ensure good welding behavior for body in white assembly. Surface resistance and oxide composition was studied for steel grade 20MnB8 with different coatings (GI vs. GA) and different annealing times. The results were also compared to standard steel grade 22MnB5 coated with GI. Oxide composition was determined by grazing angle XRD measurements, SEM investigation and EDX measurements on cross section polished samples. Surface resistance was measured with an

in-house built instrument at room temperature. Samples were clamped between to spot welding electrodes. 22MnB5 coated with GI shows the highest surface resistance compared to the other studied samples. Especially when annealed for longer furnace dwell times. The 20MnB8 coated with GI has lower resistance compared to 22MnB5. 20MnB8 with a galvanized (GA) coating has the lowest surface resistance with the smallest variation even after annealing for longer times. It will be shown that the low surface resistance of 20MnB8 is attributed to formation of Hetaerolit ($ZnMn_2O_4$). Hetaerolit has a spinell like structure. The lower resistances of GA compared to GI is probably caused by the absence of aluminum resp. of the diffusion inhibiting Fe_2Al_5 – layer and/or slower coating transformation from GI to GA during the PHS process in comparison to the galvannealing process in the HDG-line. This enables manganese diffusion to the surface already in the early stages of annealing during press hardening. In case of 22MnB5+GI which has a inhibiting layer and a lower manganese content, the formation of ZnO is more pronounced. If an annealed sheet of 20MnB8+GA coating is annealed for a second time in an reducing atmosphere with $\lambda < 1$, decomposition of Hetaerolit takes place and the surface resistance increases 10 to 20 times of the initial value. For excellent welding behavior, shot blasting is a measure to ensure welding performance also for long annealing times in the PHS furnace. Three different steel shots were compared in terms of impact energy, surface coverage in respect to resulting surface resistance. Shot blasting energies have been assessed with Almen-strips. Impact of a spinning plate shot blasting system in comparison to a conveyor belt shot blasting line, which is used in the production of press hardened parts, and a blast cabinet was also investigated. It is shown that the more the merrier is not generally effective.

On-line Measurements - Cleanliness, Austenite Fraction and Coating Defects / 186

IN-LINE CHARACTERISATION OF THE AUSTENITE LEVEL TO ENSURE THE MECHANICAL PROPERTIES ALONG THE COIL

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During the manufacturing of the modern high strength steels, it is very important to know the austenite level compared to ferrite at given positions in the line during the steel production. Indeed, ensuring the constancy of the austenite fraction is mandatory for the constancy of the mechanical properties of the final product. There are several positions in the line where it is essential to know the fraction of austenite, namely for example, the exit of zinc bath or several intermediate locations in the furnace in steel galvanising lines. These positions induce many constraints which are very difficult to address. Indeed, this new sensor aims to overcome the limitations of current measurement devices of the austenite level in steels. In particular, the sensor allows the measurement at low or high temperature of the steel strip (850°C). It allows the measurement at a distance of several tens of millimetres of the strip while keeping a sufficient sensitivity. The measurement is not influenced by the vibrations of the strip as well as by abrupt change of the distance sensor – strip. This sensor is also able to work above and below the Curie temperature. The modularity of this sensor allows characterising not only the full width but different zones on the width and, particularly, the sides and borders of the strip which can show different properties due to different behaviour during the heating or cooling phase.

Electro galvanizing - Process and Product Developments / 187

IMPACT OF SURFACE TOPOGRAPHY OF ELECTRO GALVANIZED STEEL SHEET ON PAINT APPEARANCE

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Along with the design of the body in white, the paint is very important for the unique esthetic impression of a car. Accordingly, car manufacturers put great emphasis on the quality and visual appearance of the paint. Many R&D- programs investigated the influence of roughness parameters (roughness, waviness, peak count) on the paint appearance of hot-dip galvanized steel sheet, but only few publications dealt with the influence of roughness parameters of electro galvanized steel sheet on paint appearance. Electro galvanizing offers the unique possibility to adjust the roughness (Ra) and the peak count (R_{Pc}) by varying the plating conditions and/or the electrolyte composition. Thus eight sets of samples with Ra- values ranging from 0.45 – 1.50 μm and peak counts from 40 – 170 cm^{-1} were prepared in a lab electro galvanizing cell. The steel substrate was a cold rolled, annealed and skin-passed bake- hardening steel with a roughness of 1.1 μm and a peak count of 120 cm^{-1} typically used for exposed parts. In close collaboration with three OEM's this set of samples was passing the whole industrial painting process from cleaning to the application of the clear coat. Afterwards the paint appearance of the samples was evaluated at the respective OEM, as well as in our labs by a wave- scan device returning values for waviness (long and short) and distinctness of image (DOI). Neither the measurements at the OEM's nor our own evaluations showed any significant differences in paint appearance related to the surface structure of the electro galvanized steel substrate. Moreover a visual assessment could complete this picture. Additionally the friction behavior and adhesive bondability were checked and did not reveal any differences between the samples. In conclusion we are able to say, that the electro galvanizing process allows a great variety of surface structure without adversely affecting the appearance of a high quality automotive paint.

PHS-ZnFe: New Steel & Coating Developments / 188

NANOSCALE INVESTIGATION OF GRAIN BOUNDARY WETTING AND MICRO CRACKS OF PRESS HARDENED GALVANIZED 20MnB8 STEEL

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Grain boundary weakening caused by grain boundary wetting is a potential precursor for liquid metal embrittlement in a Zn coated press hardening 20MnB8 steel. Galvanized press hardened steel samples, deformed by bending, and not deformed (flat) steel samples were analyzed by means of electron backscatter diffraction (EBSD), Auger electron spectroscopy (AES), energy dispersive X-ray analysis (EDX) and transmission electron microscopy (TEM) on the nanometer scale. Sample cross sections were prepared by Ar ion milling and subsequently analyzed via EBSD. Measurement of all possible phases such as bcc iron, different Zn/Fe phases (Zn-ferrite, gamma, delta) and ZnO was successful. We showed micro cracks which were formed between prior austenite grains and identified structures developed after micro crack formation. Zn as well as oxygen was detected by Auger electron spectroscopy on top of the micro crack surface. Zn/Fe phases were present at the wedge shaped crack tips, smaller than 100 nm in size. Zn distribution indicated that Zn penetrated from the crack tip further into the martensite bulk. For a complete picture, including the material state before micro cracking, we used electrolytic galvanized resp. Zn coated and not deformed samples. The thermal press hardening treatment was equally to hot dip galvanized 20MnB8. Cross sections were prepared by breaking the sample in a fracture stage and characterizing the interface coating steel by Auger spectroscopy. A Zn signal could be detected up to a depth of 25 μm near to the interface steel coating by those Auger measurements. By TEM EDX measurements, Zn could be found at prior austenite grain boundaries near to the interface coating steel. The quantity was one atomic layer or even less. The effect of Zn at prior austenitic grain boundaries on micro crack formation, due to grain boundary weakening, can not be ruled out from a physical characterization point of view.

PHS-ZnFe: Liquid and Vapour Metal Induced Embrittlement / 189

AVOIDING ZINC INDUCED CRACKING IN HOT FORMING

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Galvanized press hardened steel (PHS) is in serial production more than 15 years. Zinc provides excellent cathodic corrosion protection for PHS parts, but can cause Liquid Metal Embrittlement (LME) and micro cracks. One can dispose of this LME risk by using the indirect hot forming process and avoiding tensile stress at high temperatures. To eliminate LME for the direct hot forming process there are two approaches. One approach is to use thin zinc coatings so that the whole coating after the PHS annealing furnace is pure zinc ferrite but the lower zinc content in the coating also reduces the cathodic corrosion protection. Another approach is pre-cooling (< 650°C) to avoid liquid zinc due to transformation to ZnFe-intermetallic phases before starting hot forming. Serial production of several hundred thousand tons has proved that all this countermeasures are successful. In contrary to micro cracks caused by liquid zinc and forming at high temperatures, (depths up to several 100 µm) at forming temperatures below 650 °C and under special conditions small micro cracks (depths up to several 10 µm) may occur. Those micro cracks are also known as 2nd order micro cracks. They sometimes arise in parts with high frames and are often located in the frame near to the flange. Several mechanisms have been discussed about the origin of those 2nd order micro cracks. The weakening of austenitic grain boundaries near to the interface by zinc penetration and LME by residues of liquid zinc or LME by friction induced hot spot temperatures, were the most intensively discussed explanations so far. We could prove by several experiments resp. lab investigations and real part production, that 2nd order micro cracks are due to vapor metal embrittlement (VME). This results from the high zinc vapor pressure of the ZnFe-intermetallic phases. The cracking of the ZnFe-coating during hot forming generates high moveable Zn. If there is not sufficient oxygen to form immediately zinc oxide, there is a chance that Zn atoms reach the steel surface and weaken the austenite grain and/or austenite grain boundary. Special hot forming conditions, for example close local contact between part and tool together with high tensile stress may cause 2nd order micro cracks. Because of the limited amount of zinc atoms created by this mechanism, these micro cracks are limited to several 10 µm in depth. Measures to eliminate also these small micro cracks are proposed.

On-line Measurements - Cleanliness, Austenite Fraction and Coating Defects / 190

CLEANLINESS MEASUREMENT BY INNOVATIVE LIBS METHOD

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Nowadays, automotive steel customers are more and more strict on the coating quality, especially for the exposed parts that should not have any aspect defect. To satisfy this requirement at the exit of galvanising line, one important parameter is the cleanliness of the substrate surface after the cleaning section at the entry of the line in terms of carbon pollution and iron fines. Indeed, if carbon (as component of the mill oil) is still present at the surface when entering the furnace, furnace pollution will occur in the long term by production of soot that will not only stay on the furnace walls but will eventually lead to dirt falling on the rolls and/or on the strip. Besides, the iron fines can also lead to roll pick-up defects inside the furnace, to an increase of dross in the bath by combination with zinc and aluminium and also to a drift of the bath composition. These phenomena will eventually result in aspect defects on the final product.

A direct on-line measurement is so mandatory to fully evaluate and control the surface cleanliness all along the coil and is more and more required by customers as an assurance of final product quality. Using this cleanliness measurement, the cleaning section can be optimised by adjusting

relevant parameters, such as the brushes pressure, the solution composition, the current applied if electrolytic cleaning is used. On the market, no on-line methods are able to separately measure the mentioned pollutants. CRM has developed an innovating method based on LIBS principle which succeeds in an on-line independent measurement of both pollutants. This will be realised by using a groundbreaking approach that will allow reaching the measurement sensitivity required after the cleaning section sensitivity (i.e. 10-15 mg/m² for carbon, 20 mg/m² for iron fines) thanks to atmosphere conditioning around the plasma and use of adequate spectral lines for carbon and iron fines levels measurement. This system can be used at a later stage of development in a control loop for the optimisation of the final cleaning line and of the production speed.

Fundamentals on Surface Oxidation and Metallic Reactions / 191

UNDERSTANDING THE EVOLUTION OF SURFACE OXIDES UPON DUAL PHASE STEELS DURING AN ANNEALING CYCLE

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Dual phase (DP) steels are known for having issues with hot dip galvanizing due to the formation of surface alloy-oxides 1. These oxides appear during the annealing step, preventing a good zinc adhesion to the base metal 1. This work aims to give a fundamental understanding of the nucleation and growth mechanisms of the oxides. DP800 steel samples were oxidised in a flowing argon atmosphere, with approximately 10ppm O₂. Due to the minimal moisture content within the atmosphere, oxidation occurs at a reduced rate enabling a thorough and in-depth, stepwise investigation of the oxide formation as function of increasing temperature. In an infrared (IR) furnace under vacuum, samples were heated sequentially from 450°C to 850°C in increments of 50°C. The samples were held at their respective temperatures for a few minutes to allow the oxidation process to take place. These temperatures were chosen as they imitate the heating step of the annealing cycle during Hot Dip Galvanizing. The surfaces and oxides were then analysed by Scanning Electron Microscopy (SEM) for visualisation; Energy-Dispersive X-ray Spectroscopy (EDS) for elemental analysis; Transmission Electron Microscopy (TEM) for visualisation and elemental analysis and Raman Spectroscopy (RS) for oxide characterisation. In the temperature range 550°C - 600°C well-defined particles started to appear on the surface, which are attributed to the oxides. Islands of oxides form in a manner which is consistent with differing oxidation behaviour of the multiphase/high strength steel phases. As will be shown, as the temperature reached 800°C – 850°C, large thick regions of oxides develop. Silicon was found to be mostly in defined globular regions, which were the oxides themselves, as opposed to aluminium which was speckled across the whole surface. An explanation for this variance in elemental behaviour is discussed and a suggested mechanism for the oxidation of the alloying elements is proposed. This initial research was performed to fully characterise the steel surface as precursor to a coating step, either via hot dip galvanizing (HDG) or physical vapour deposition (PVD) and to understand the specific surface oxidation mechanisms influencing the surface before coating deposition.

Electro galvanizing - Process and Product Developments / 192

PREDICTION OF ANODE LIFE TIME IN ELECTRO GALVANIZING LINES BY BIG DATA ANALYSIS

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In industrial electro galvanizing lines, the performance of the dimensionally stable anodes (Ti + IrOx) is a crucial factor for product quality. Ageing of the anodes causes worsened zinc coating distribution on the steel strip and a significant increase in production costs due to a higher resistivity of the anodes. Up to now, the end of the anode lifetime has been detected by visual inspection every several weeks. The voltage of the rectifiers increases much earlier, indicating the deterioration of anode performance. Therefore monitoring rectifier voltage has the potential for a premature determination of the end of anode lifetime. Anode condition is only one of many parameters affecting the rectifier voltage. In this work we employed machine learning to predict expected baseline rectifier voltages for a variety of steel strips and operating conditions at an industrial electro galvanizing line. In the plating section the strip passes twelve "Gravitel" cells and zinc from the electrolyte is deposited on the surface at high current densities. Data, collected on one exemplary rectifier unit equipped with two anodes, have been studied for a period of two years. The dataset consists of one target variable (rectifier voltage) and nine predictive variables describing electrolyte, current and steel strip characteristics. For predictive modelling, we used selected Random Forest Regression. Training was conducted on intervals after the plating cell was equipped with new anodes. Our results show a Normalized Root Mean Square Error of Prediction (NRMSEP) of 1.4 % for baseline rectifier voltage during good anode condition. When anode condition was estimated as bad (by manual inspection), we observe a large distinctive deviation in regard to the predicted baseline voltage. The gained information about the observed deviation can be used for early detection resp. classification of anode ageing to recognize the onset of damage and reduce total operation cost.

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INFLUENCE OF INTERCRITICAL ANNEALING CYCLES ON THE MICROSTRUCTURE AND MECHANICAL PROPERTIES OF DP980 ADVANCED HIGH-STRENGTH STEEL

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The work studied the effect that processing parameters have on microstructure and mechanical properties of dual-phase steel grade 980. This was achieved by subjecting steel coupons to various annealing cycles featuring different heating rates, cooling rates and intercritical annealing temperatures using a dilatometer. Following heat treatments, the microstructures and mechanical properties of the coupons were compared. Experimental results showed that when partial austenitisation is performed, the cooling rate does not affect phase transformation, microstructure or microhardness if kept within the studied range (-2.1 °C/s to -7.1 °C/s). By contrast, the intercritical austenitisation temperature affects the phase transformations significantly during cooling. Thus, the amount of austenite formed during intercritical annealing influences the phase transformation kinetics during cooling.

Poster Session / 195

STUDY ON THE ENVIRONMENT-FRIENDLY PASSIVE FILM TECHNOLOGY FOR 55%Al-Zn ALLOY COATED STEEL SHEET

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In order to meet the requirements of users for high corrosion resistance and spraying coating, the environment-friendly surface treatment technology for the 55% Al-Zn alloy coated steel sheet was studied, and the technology of passive film with high corrosion resistance and coating ability was formed. The morphology, composition and properties of passive film were tested and studied by infrared spectroscopy, scanning electron microscopy, energy dispersive spectrometer, electrochemical analysis, neutral salt spray corrosion test, spraying coating and other test methods. The environment-friendly passive film was made of water-borne resin as main film-forming material and zirconate as auxiliary film-forming material. The surface of the passive film was compact and uniform, so the film had good sealing property, then the corrosion resistance and water resistance were remarkably improved. The amide functional group and hydroxyl functional group in the film improve the combination of the passive film with ceramics or other coatings through enhancing the polarity, then improve the coating performance. The corrosion current of the environment-friendly passive film for 55% Al-Zn alloy coated steel sheet was reduced, the corrosion area of the 55% Al-Zn alloy coated steel sheet was less than 5% after NSST/200h, and that was less than 20% after NSST/500h, so the passive film had excellent corrosion resistance. After spraying coating, the adhesion of the spray coating reaches grade 0, so passive film had good coating ability. In addition, the passive film also had good fingerprint resistance and water resistance. So the 55% Al-Zn alloy coated steel sheet with environment-friendly passive film could be meet the requirements of users.

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A STUDY ON RESISTANCE SPOT WELDABILITY OF Al-Fe ALLOY COATED 1.5GPa HPF STEEL SHEETS

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Al-Fe alloy-coated steel sheets for hot press forming is manufactured by performing a batch annealing process to the Al-Si coated sheet. It has an advantage of prolonging the mold life by suppressing the reaction between blank and mold. However, Al-Fe alloy-coated steel sheets are inferior in spot weldability to conventional Al-Si coated steel sheets. In addition, welding current ranges decrease with increasing heat treatment temperature and hot press forming process time. The increase of current causes spatter problem during welding due to high contact resistance of thick oxide layers and intermetallic compound such as FeAl₂ / Fe₂Al₅. To improve this problem, in this study, a pre-pulse current pattern is suggested to reduce the contact resistance between interfaces of steel sheets during welding. Applying the pre-pulse current pattern, sufficient nugget growth and good fracture mode were obtained in Al-Fe alloy coated steels. Microstructural analysis on the coating layer was also conducted to identify the constituents of coating layer and their effect on the spot weldability.

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RESISTANCE SPOT WELDING JOINT PROPERTY OF 2GPa HOT STAMPING STEEL WITH AISi COATING

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Abstract: In this paper, Al-Si coated and bare hot stamping steels with the tensile strength of 2GPa were resistance spot welded. The welding current, properties and mechanical performance of the joints were compared. The coating slightly affected the welding current required for the

attaining conventionally acceptable weld fusion zone size of $4 \times \text{square}(t)$, and the welding current range. The energy absorption, fatigue life and failure mode transition of the weld shows no correlation to the surface condition.

PHS-ZnFe: Liquid and Vapour Metal Induced Embrittlement / 199

SCANNING ELECTRON MICROSCOPE INVESTIGATION ON ZINC INDUCED CRACKS OF COATED PRESS HARDENED COMPONENTS

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Zinc coatings offer the advantage of a galvanic corrosion protection instead of a conventional barrier corrosion protection. Thus zinc coatings prevent the corrosion of the steel substrate even in the case of a damaged coating layer. It is therefore of interest to use zinc coatings in the automobile industry particularly for components of the body in white. These components are often produced by the direct press hardening process consisting of a hot forming and a subsequent quenching step in the die. Zinc is known to have an embrittling effect on the sheet's base material at elevated temperatures leading to surface cracks in the steel substrate during forming. To be able to numerically simulate the press hardening process including a reliable damage indicator model it is necessary to understand the crack mechanism of zinc induced cracks in detail. To this end metallographic investigations of galvanized press-hardening steel sheets (20MnB8) using a light optical microscope as well as a scanning electron microscope comprising Electron-Backscattering-Diffraction (EBSD) and Energy Dispersive X-Ray Analysis (EDX) were conducted on selected cracks appearing during press hardening experiments of simple hat shaped components. The crack depth and distribution along the formed component's cross sections were determined by light optical microscopy for establishing a subsequent correlation to the simulated load and temperature conditions. The crack propagation path in the substrate was correlated to the lattice orientation obtained from EBSD measurements. Thereby it was determined if cracks propagated along prior austenite grain boundaries or martensite block boundaries to analyze whether or not zinc penetration in prior austenite grain boundaries is an influencing factor for crack formation. The presence of zinc in the vicinity of the crack was detected by means of EDX scans. The investigations showed that the cracks propagate along prior austenite grain boundaries as well as martensite block boundaries. Hence zinc penetration in prior austenite grain boundaries does not seem to be the only relevant factor to zinc induced crack formation. Knowledge of the crack distribution, the cracks' propagation paths and the zinc distribution in the crack near regions enables to better understand the mechanisms leading to zinc induced crack formation, which is crucial for developing a valid damage criterion taking into account the most important influencing factors.

Fundamentals on Surface Oxidation and Metallic Reactions / 200

ENHANCEMENT OF HOT DIP GALVANIZING ON AS-CAST HIGH-Mn STEEL BY FABRICATION OF FUNCTIONALLY GRADED MULTILAYERS THROUGH LASER CLADDING OF LOW CARBON STEEL

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To improve the surface feature of high-Mn steel, such as wettability with liquid Zn, a functionally graded multilayer was fabricated on the top of as-cast high-Mn steel slab by laser cladding process. For the alloying material, low carbon steel powder (0.07C, 1.83Mn) was deposited. To investigate the optimum condition for wettability, four different samples were prepared: bare high-Mn steel sample (LC-0), once, twice and three times clad samples (LC-1, 2, 3). The thickness of clad layers was 2~4mm and that of slab was 140mm. Due to substrate re-melting effect of laser cladding, compositional gradient along the deposition direction appeared, resulting in different microstructure by layer. The first layer with 9% Mn had a dual-phase microstructure (martensite + interdentritic austenite) followed by bainitic and fully ferrite layers along the deposition direction. All samples were hot and cold rolled, and hot-dip galvanized in molten zinc bath. Defects in Zn coating and oxides, which were formed during the annealing prior to hot dipping, were investigated using SEM Energy Dispersive Spectrometry and X-ray Photoelectron Spectroscopy. As the number of deposited layer increased from LC-0 to LC-3, Mn content of the top surface of the sample decreased and the fraction of ferrite increased. MnO was dominant in LC-0, but as the number of deposited layer increased, the fraction of MnO-SiO₂ oxides and Al₂O₃ increased. It is because Mn/Si and Al decreased as the number of clad layer increased and the diffusivity of Si and Al in ferrite is much higher than that of Mn in austenite. Because the laser cladding process turned coarse grains of the substrate into finer grains, oxides in LC-1, 2, 3 were smaller and finer, and evenly distributed than that of LC-0. When the surface was modified by laser cladding, internal oxidation along grain boundary also decreased, but there was almost no difference between sample LC-1, 2, 3. The reason would be attributed to the melt pool convection flow and the evolved solidification structure during the laser cladding process.

PHS-AlSi & PHS-ZnFe: Controlling Surface Properties / 201

ON THE REDUCTION OF TEMPERATURE GRADIENTS WITHIN AISi-COATED BLANKS WITH NON-CONSTANT SHEET THICKNESS FOR HOT PRESS FORMING APPLICATION

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When heating steel blanks with different sheet thicknesses within prior to a hot press forming process, local heating rates may differ significantly. Therefore, the process window for heating the blanks is narrow, especially when aluminium-silicon (AlSi) coated material is used. The thicker part of the blank determines the minimum furnace dwell time for alloying of the coating to achieve sufficient paint adherence. The thinner part limits the maximum dwell time to ensure spot weldability. Additionally, when the heat treatment exceeds the process window, the amount of absorbed hydrogen from the furnace atmosphere may become detrimental.

This study explores a modified AlSi coating concept for blanks with varying sheet thickness to minimise the temperature gradient within a blank and the hydrogen pickup during heating prior to press hardening. The approach used here is to form an iron rich layer on the AlSi coating surface by an adapted conversion treatment process. This results in elevated surface heat absorption and increased heating rates.

Samples were produced by partly reducing the thickness of 22MnB5+AS150 blanks in a laboratory cold rolling process. The coating modification was applied before or after the cold rolling step. Additionally, a welded blank was produced in which only the thicker part was modified by a conversion treatment. The as produced samples were heated in a laboratory furnace, recording the heating rates of the thinner and thicker areas of each sample. Additionally, the amount of hydrogen pickup was analysed by thermal desorption analysis (TDA) from a separate set of samples.

It has been found that the temperature gradient within a blank can be reduced significantly for all modified samples compared to the reference material without any surface modification. This is due to a greatly increased heating rate of the thicker part of the sample. Therefore, the minimum furnace dwell time can be reduced, enlarging the process window.

LME of Resistance Spot Welded Coated Steels: Assessments / 202**NUMERICAL MODEL FOR PREDICTING LIQUID METAL CRACKING DURING RESISTANCE SPOT WELDING OF ADVANCED HIGH STRENGTH STEELS****Author(s):** PRABITZ, Konstantin Manuel¹**Co-author(s):** Dr. ECKER, Werner ¹ ; Prof. ANTRETTNER, Thomas ² ; Dr. BEAL, Coline ³ ; Mr. SCHUBERT, Holger ⁴ ; Mr. HILPERT, Benjamin ⁴ ; Mr. GRUBER, Martin ⁵ ; Mr. SIERLINGER, Robert ⁵¹ *Materials Center Leoben Forschung GmbH*² *Institute of Mechanics, Montanuniversitaet Leoben*³ *Institute of Materials Science, Joining and Forming, Graz University of Technology*⁴ *Daimler AG*⁵ *voestalpine Stahl GmbH***Corresponding Author(s):** konstantin.prabitz@mcl.at

Corrosion protected galvanized advanced high strength steels with high ductility (AHSS HD) like the investigated dual phase steel (DP1200HD) tend to show an elevated risk of liquid metal cracking (LMC) during resistance spot welding (RSW). LMC is an intergranular cracking mechanism driven by temperature, tensile stresses, plastic deformation and the presence of liquid zinc. Crack initiation and growth is caused by liquid metal embrittlement (LME) where the material experiences a drastic loss of ductility of up to 95 percent depending on the loading conditions. The aim of this work is to experimentally investigate LME and to develop a model to predict the local LMC during RSW. The prediction of LMC is addressed with laboratory scale hot tensile tests with uncovered and galvanized steel sheets at a Gleeble 3800 thermomechanical simulator and extensive laboratory scale resistance spot-welding tests. All gained material and process data are subsequently used for creating a physically based and validated LMC indicator, which is dependent on temperature, plastic strain and strain rate. Newly developed and validated finite element models of the welding process accounting for all relevant multi-physical phenomena provide deep insight in the RSW process and help to understand the influence of different conditions leading to LMC. The LMC indicator enhances the capabilities of these models and provides predictions for the onset of LMC. Taking advantage of the LMC indicator allows modifying the welding process such that a significant reduction of LMC during RSW can be achieved.

Furnace III - Rapid Cooling, Furnace Roll Coatings / 203**HEAT TRANSFER BY ARRAY OF ROUND NOZZLES AT HIGH REYNOLDS NUMBER: IMPACT ON STRIP COOLING RATE****Author(s):** PLANQUART, Philippe¹**Co-author(s):** Mr. DELSIPEE, Mathieu ¹ ; Mr. DUBOIS, MICHEL ² ; Prof. BUCHLIN, Jean-Marie ¹¹ *von Karman Institute*² *CMI INDUSTRY***Corresponding Author(s):** philippe.planquart@vki.ac.be

In order to characterise the maximum possible cooling rate for AHSS with non oxidizing gas a new test bench has been constructed at VKI, combining 1 central round jet surrounded by 6 jets. The facility allows jet Reynolds number up to 200.000, value for which very few experimental data are available in the literature. Results are obtained for different normalised standoff distances Z/D (ratio between the outlet of the jet and the plate divided by the diameter of the round jet) and for different tilt angles of the plate with respect to the array of jets. The heat transfer coefficient is obtained by application of the active quantitative infrared thermography. Plate at constant and uniform heat flux is used. The thermograms are analysed by an in-house DIP program allowing the determination of the heat transfer coefficient mapping. A mean heat transfer coefficient is defined on a characteristic cell. The evolution of the Nu-number obtained by increasing the

Reynolds number to this high value will be presented. The experimental data are compared with numerical simulation for the validation of turbulent heat transfer. The numerical simulations are afterwards performed taking into account the industrial temperature (higher temperature difference between the jets and the metal sheet). A comparison of the heat transfer coefficient and the Nusselt number is made between the laboratory and industrial context.

Coating Alloy and Modification effects on Corrosion Behaviour / 204

STUDY OF MANGANESE ADDITION ON THE CORROSION RESISTANCE OF GALVANIZED ZINC COATING

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This study investigates the effect of manganese addition in the galvanized zinc coating on steel. Manganese possesses more negative electrochemical potential than both zinc and iron. In addition, manganese can also provide sacrificial protection to iron like zinc. A stepwise process was used to prepare the required bath composition for coating due to a very high melting point of manganese than that of Zn. Initially, Zn-Mn master alloy was prepared in a resistance-heated furnace and then the master alloy was diluted in the molten zinc bath for the required coating composition. The dipping of steel sheets in zinc alloy bath was carried out after preparation of surface by degreasing, pickling, fluxing, and drying. The microstructures of the coated sheets were observed by Scanning Electron Microscopy, and the electrochemical tests were performed in 3.5wt. % NaCl solution. The results show that the Mn addition reduces the corrosion current density by half, and red rust was not observed on the Zn-Mn-Al alloy coated steels even after 336 hours of salt spray test.

Coating Alloy Corrosion Studies / 205

ELECTROCHEMICAL BEHAVIOR OF Si PHASES IN NOVEL ZnAlMgSi COATINGS

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Novel Si-alloyed coatings provide further improvement of corrosion resistance compared to commercial ZnAlMg, yet the mechanism is still a matter of research. Latest studies focused either on binary electrochemical behavior of phases present in the coating or on accelerated and outdoor tests. To provide the link between the two and help understanding the corrosion mechanism we combined the two approaches. Using selection of phases stable in the ZnAlMgSi at normal conditions (etha, alpha, MgZn₂, Mg₂Si, Si) and ZRA method in unorthodox setup (individual phases as working electrode, all other phases as counter electrode), we were able to directly show evolution of galvanic behavior of each phase over time. This was done both in diluted chloride solution, simulating contamination of fresh coating as well as in solution saturated with ZnCl₂, AlCl₃ and MgCl₂, simulating behavior in thin electrolyte after saturation with corrosion products an chloride. As a reference, data from ZnAlMg system (without Si and Mg₂Si) were used. Consumption of phases in terms of sacrificial-anode capacity can be showed directly using this method. The results also show that while Mg₂Si and Si act as a significant porization agent, their effect on galvanic current is low. This is due to high inactivity of Si and quick selective dissolution of Mg from Mg₂Si. Yet, the shift in potential of the whole coating is significant. "Real" behavior of the ZnAlMgSi was studied in accelerated corrosion test both as in form of an alloy and steel coating. Frequent inspection of corrosion products combined with SKP measurements

provides link between galvanic behavior of phases and behavior of coating/coated steel after contamination. The results show that while microstructure refinement caused by Si addition is significant, the electrochemical effect also plays major role.

Fundamentals on Surface Oxidation and Wettability / 206

IMPROVEMENT OF WETTABILITY BETWEEN STEEL AND LIQUID Zn-Al ALLOY BY FORCED WETTING

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The main objective of the present work was to investigate the forced wetting of a partly oxidized steel by a liquid Zn - Al (0.2 wt. %) alloy. The wetting experiments are performed by means of the dispensed drop technique. The wetting is shown to be reactive with the formation of Fe₂Al₅Zn_x. The evolution of the contact angle and spreading diameter is determined as a function of spreading time. The final contact angle lies between the receding and the advancing contact angle and is a decreasing function of the initial kinetic energy of the droplet. The liquid zinc drop remains pinned in a metastable position, due to the contact angle hysteresis. During the first ms, the spreading diameter increases up to its maximal value D_{max}. In good agreement with previous studies in the field of wetting at low temperatures, the maximal spreading diameter scales as \sqrt{We} , We being the Weber number which compares inertial and capillary forces. The kinetic energy of the liquid metal droplet needed to reach the minimum receding contact angle was predicted from the model based on the Weber number to describe D_{max}. This kinetic energy is in good agreement with the experimental results. As a final conclusion, an increase in the initial kinetic energy of the droplet leads to a decrease in the final contact angle. It is therefore expected that forced wetting could improve the galvanizability of steels by liquid Zn-Al alloys.

PHS-AlSi & PHS-ZnFe: Controlling Surface Properties / 207

NEW COATING FOR PRESS HARDENED STEELS: Al-SiZnMg

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The Press Hardened Steels (PHS) offer unique weight saving opportunities to the automotive market, allowing to reach extremely high mechanical properties (until 2000 MPa) on complex parts with a well-controlled geometry. Since 2001, pre-coated PHS are available. AlSi coated PHS are the mostly used worldwide with more than 75% of the hot stamping lines in the world dedicated to them. This predominance can be explained by the simplicity of the corresponding hot stamping process, the large process windows and the robustness of the product performance. Furthermore, Al based coating-alloy remains the best in class solution regarding perforating corrosion resistance. Nevertheless, Al-Si remains sensitive to the red rusting from the coating surface, especially in areas with a too thin E-coat or areas where E-coat is locally eliminated (like stone chipping). Zn based coatings can give an appropriate answer to that point, but the process-window is quite narrow due to its rapid evolution at austenitizing temperature (for Zn from 880°C to 910°C). Aiming at gathering Al-Si strengths (compatibility with direct Press Hardening Process, perforating corrosion resistance, no micro-cracks in the substrate...) with those from Zn based product (cosmetic corrosion and red rusting resistance) a new hot dip coating offer is being developed. Such new bath containing Al-Si-Zn-Mg has been developed with an innovative strategy consisting in taking profit of the austenitizing step to finish coating transformation, in particular regarding surface functionalization. Consequent improvement on corrosion resistance at painted and unpainted state will be highlighted. Moreover, product corrosion performances are constant in a wide range of press hardening conditions. Risk assessment and performance validation were done at lab scale. Industrial development is in progress. The challenge in the

development of coatings dedicated to PHS is to satisfy the main requests of the final customers by keeping a solution working in a large industrial range of production for the Hot Stamper.

HDG Coating Weight Control by Nozzle Design & Settings / 208

WIPING PILOT USE FOR BAFFLE DESIGNS AND SETUP IMPROVEMENTS

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For decades, baffles became the standard tool to limit the edge effects of wiping in the hot dip galvanizing process (overcoating, splashing). Initially designed to highly reduce the noise caused by the interaction of the two opposite air jets, baffles exhibited as well benefits to master the quality of the wiping process along the edges. Each line acquired specific designs and setup to reach their quality levels and to solve their quality issues. A wiping pilot has been developed in ArcelorMittal Maizières laboratory in 2013. The only concession on the scale is the width of the nozzle (1/3, 700mm), but still large enough for the edge effects study. This pilot trials coupled with CFD simulations allowed to: - identify the main parameters (baffles and nozzles designs) acting on the edge effects intensity, - provide baffles setup recommendations according to the wiping configurations (nozzle distance, coating weight, pressure) - test the performances of alternative designs. This experimental phase clearly reduced the need of industrial trials (time, costs and risks) while keeping the possibility to test a large number of setup and designs.

HDG Coating Weight Control by Innovative Technological Concepts / 209

THE EVOLUTION OF COATING CONTROL SYSTEMS AS THE NEED FOR NEW COATED PRODUCTS EXPANDS

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Hatch has been developing and deploying a model-based coating control system for over 20 years. The resultant physics-based gas wiping process model has been adapted to a wide variety of equipment and coatings now being produced by the major steel producers. As the coating control technology has matured and the processing ability of PLCs has increased, the process model and control system has been migrated from computers to industrially robust PLCs.

The coated product market is moving from traditional zinc and zinc/aluminium coatings and carbon steel substrates, to more advanced products with a wide range of coating and substrate properties. At the same time, the relentless demand to lower production costs and increase product quality needs to be met. The process model, through the addition of techniques such as the parameterisation of the air wiping process, has matured over time to meet these demands. Strip stabilisation and flattening at the wiping zone, have become commonplace and can be attained using Electromagnetic Stabilisation (EMS) or Air Floatation Stabilisation (AFS).

Tighter requirements, both in the processing of magnesium-dosed coatings and the introduction of Advances Hight Strength Steels (AHSS) and new 3rd Generation steels, require the implementation of even more advanced control strategies. Coating process control is now moving into the realm of managing strip shape effects. Hatch's model-based coating control system can now include passline tracking using laser measurement techniques and is being further developed to include active crossbow control.

This paper presents the current state of coating control systems and the progress towards the next evolutionary step. The use of crossbow modelling and active crossbow correction to manage the strip shape prior to the gas wiping.

HDG Coating Weight Control by Innovative Technological Concepts / 210**THE EVOLUTION OF COATING CONTROL SYSTEMS AS THE NEED FOR NEW COATED PRODUCTS EXPANDS**PEARCY, Owen¹¹ *Hatch Ltd***Corresponding Author(s):** lisa.loeschauer@asmet.at

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Plenary Talk 4 -USA / 211**NORTH AMERICAN DEVELOPMENTS AND OPPORTUNITIES FOR GALVANIZED STEEL SHEET****Author(s):** Dr. GOODWIN, Frank Erik¹**Co-author(s):** SILVA, Eduardo ²¹ *International Zinc Association*² *United States Steel Corporation***Corresponding Author(s):** fgoodwin@zinc.org

Automotive industry requirements for steels capable of enabling increasingly fuel-efficient vehicles continue to drive process technology developments for North American hot-dip and electro-galvanizing lines. Third-generation zinc and zinc alloy-coated grades have reached commercialization; higher-capability grades continue to be developed. Zinc-coated hot press forming grades have reached commercialization, tailor-processed hot press formed grades permit increasingly efficient use of steel in automobiles. A key barrier to adoption of advanced zinc-coated steels are incidences of liquid metal embrittlement (LME) that is associated in many cases with higher levels of steel retained austenite or silicon alloying and ameliorative practices are under development. Quality and productivity benchmarks also continue to be pushed to ever-higher levels. Dual phase and multi-phase grades with expanded combinations of formability and strength continue to be developed. Such steel grades should satisfy automaker requirements and ensure the dominance of steel-based vehicle manufacturing for many years to come. The processing of these steels creates challenges for steel suppliers, and the approaches being taken to meet these challenges are described. These include reactive wetting, IR pyrometry during heat treating of advanced high strength steels (AHSS), hydrogen-induced delayed cracking and cold rolling harder substrates. A new census of North American production coating lines is provided. Challenges for

the future include further improved productivity, quality and process efficiency, and flexibility in line scheduling to minimize costs.

Plenary Talk 2 - Korea / 212

RECENT PROGRESS OF ZINC AN ZINC ALLOY COATED STEEL SHEETS IN KOREA

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Recent progress of galvanizing facilities and new products activities are described regarding to automotive, appliance and construction markets in South Korea. Especially, several corrosion resistant Zn-Al-Mg coated steels have been developed for automotive, home appliance and construction. In addition new functional coated steels and PVD products will be introduced briefly.

Plenary Talk 3 - Japan / 214

RECENT DEVELOPMENTS AND OUTLOOK ON ZINC AND ZINC ALLOY COATED STEEL SHEETS IN JAPAN

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Zn and Zn alloy coated steel sheets are widely used because of their good corrosion resistance. In particular, galvanized steel sheets are mostly used for automobile manufacturing in Japan because of their good corrosion resistance after painting, weldability, and stampability. Furthermore, several innovative high Mg added Zn alloy coatings with superior corrosion resistance have been originally developed in Japan primarily for construction use. To clarify the mechanism of the excellent properties of these coatings, a series of consortiums has been organized in Japan, wherein a lot of innovative and epoch-making results were obtained.

Coating Microstructure Analysis and Steel/Coating Surface Reactivity / 215

SCANNING KELVIN PROBE TECHNIQUES FOR THE INVESTIGATION OF CORROSION, HYDROGEN UPTAKE AND PERMEATION PROPERTIES OF ZINC ALLOY COATINGS ON STEEL

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In the recent years the Kelvin probe technique found a steadily and quickly increasing usage in corrosion research. The main application initially was for through-paint monitoring of corrosion driven delamination. Soon after that, with the development and availability of Scanning Kelvin Probe Microscopy (SKPFM), an Atomic Force Microscopy based Kelvin probe technique, followed the application of the technique for the screening of possible galvanic elements on alloy surfaces and more recently Kelvin probe techniques are applied for detection of hydrogen. In this paper an overview will be given about the potential of the Kelvin probe techniques for investigating corrosion performance and the hydrogen uptake and release characteristics of zinc and zinc alloy coatings and steel. It will be shown that Kelvin probe techniques, if applied in combination with an experimental test protocol that is tailored for the question to be addressed, can provide information that would be difficult to obtain with other techniques.

Tutorial Lecture / 216

Welcome

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Continuous Hot Dip Galvanizing – A Process Tutorial from Cleaning to Galvannealing

Tutorial Lecture / 218

Galvanizing of Advanced Steel – Process Fundamentals

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Fundamentals of Corrosion Protection by Zinc Alloy Coatings