EFFECT OF SEVERAL PROCESS PARAMETERS ON INTERFACIAL ALUMINUM RICH LAYER IN GALVANIZED COATINGS

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ABSTRACT

The presence of Al in Zn bath during galvanizing completely inhibits the formation of brittle Fe - Zn intermetallic through the formation of an extremely thin interfacial Al rich barrier layer at the substrate-coating interface. This interfacial layer is adherent to both the matrix and coating, and sheet formability is not affected. This study deals with both theoretical and experimental investigations in the formation of aluminum rich inhibition layer at the interface between the steel substrate and the zinc coating. The effect of several process parameters on the interfacial layer formation is studied. The inhibition layer thickness is predicted based on material balance as well as nucleation and growth mechanisms for different process temperatures. Instantaneous strip temperature, bath temperature and arithmetical mean between instantaneous strip and bath temperatures are considered as process temperatures for the prediction of the inhibition layer. The cooling path of the strip is assumed to consist of a series of isothermal holds of infinitesimal time step and is predicted taking into consideration both the conductive and convective heat transfers. The influence of the galvanizing reaction is assessed by considering nucleation and growth mechanisms at each hold time which is used to estimate the total effect of the immersion time on formation mechanism of the inhibition layer. During the very initial stages of immersion, the temperature of the strip changes rapidly. Consequently, Al enrichment at the steel surface and liquid zinc interface is also high. Theoretical predictions are compared with the experimental findings of other researchers. Further experimental validation is carried out by characterizing the inhibition layer and it is found to corroborate well with the theoretical predictions.

INTRODUCTION

Zinc coatings on steel are of significant commercial importance. These are predominantly used to enhance the corrosion resistance of steel by two methods - barrier protection, sacrificial anode galvanic protection and secondary barrier protection. Hot dip galvanizing is a popular method of producing Zn diffusion coatings. In this method, a zinc coating is applied to the fabricated iron or steel material by immersing it in a bath consisting primarily of molten zinc. Several components used in car manufacturing are coated by hot dip galvanizing. During hot dip galvanizing, in the very short time of contact between steel and liquid zinc, brittle Fe-Zn intermetallic compounds are formed at the coating-substrate interface [1 – 3]. These phases are detrimental to sheet formability. The presence of Al in the galvanizing bath at low concentrations (about 0.2 wt %) inhibits the formation of Fe-Zn intermetallic through the formation of an extremely thin interfacial barrier layer of $Fe_2Al_5Zn_x$ at the substrate-coating interface [4 - 7]. This interfacial layer is adherent to both the matrix and coating, without affecting the sheet formability as opposed to the iron zinc intermetallics which are much more fragile. The final coating is therefore composed of a thin layer of solid $Fe_2Al_5Zn_x$ about 0.1 µm thick covered with a 10 – 15 µm layer' of Zn.

The presence of dross particles within the zinc bath is a major difficulty to overcome in the production of high quality coatings even with the presence of aluminium. A rigorous control of the bath Al content ensures a high product quality and reduces the dross formation. The effectiveness of Al in the formation of the inhibition layer of the η-$Fe_2Al_5Zn_x$ intermetallic at the substrate/bath interface is complicated by the partitioning of Al between the coating and intermetallic compounds that form within the galvanizing bath. In order to maintain the bath Al content at a targeted level, the Al content of the ingots added to the Zn bath needs to be significantly higher. This is mainly because the Al content in a galvanized coating is much higher than that in a Zn bath. However, the dross formation within the Al containing zinc bath indicates that the iron is still able to dissolve from the strip. It is necessary to evaluate the variation in iron flux at the steel/zinc bath interface as a function of process parameters in order to limit the dross formation as far as possible. Since measurements are difficult to make in industrial plants, numerical modeling can play an important role in improving the understanding of the process in order to reach an optimum setting of the parameters.

The main objective of the study is to develop a simple and realistic mathematical model based on material balance as well as nucleation and growth mechanism to predict the effect of various process parameters on the inhibition layer formation at the substrate-coating interface. The studies of the effect of temperature on the galvanizing reactions are still limited [4, 8] and the analysis by several researchers is mostly restricted to isothermal galvanizing conditions [9] (the temperatures of the bath and the immersed strip are taken as equal). In the present study, the inhibition layer formation is investigated by considering the instantaneous strip temperature, bath temperature and instantaneous arithmetical mean between strip temperature and bath temperature as the process temperature. The cooling path of the strip is assumed to be consisting of a series of isothermal holds of infinitesimal time step. The influence of each hold time on the galvanizing reaction is assessed and the total effect of the immersion time on the formation mechanism of the inhibition layer is determined. During the very initial stages of immersion, the temperature of the strip changes rapidly. Consequently, Al enrichment at the steel surface and liquid zinc interface is high. Characterization of the inhibition layer at the substrate-coating interface has been carried out in the present investigation, and theoretical predictions are compared with the experimental results obtained by other researchers.

EXPERIMENTAL PROCEDURE

Hot dip galvanizing experiments were performed using a hot dip process simulator with varying strip entry temperatures of 470^{o}C, 650^{o}C, 750^{o}C at RDCIS, Ranchi. Interstitial free (IF) steel [C: 0.0034, Mn: 0.07, S: 0.012, P: 0.01, Si: 0.008, Al: 0.034, Ti: 0.068, N: 0.0027, Nb: 0.001] sheet of thickness around 1 mm was the substrate material. This steel sheet was galvanized in a molten zinc bath containing aluminum ~ 0.2 wt% for a period of around 4 sec. The bath temperature was 460^{o}C. Figure 1 shows the sample temperature and actual position of the sample with the duration of the experiment for a strip entry temperature of 470^{o}C.

Standard metallographic techniques were followed to prepare the samples for microstructural analysis, especially the microstructure at the interface between the steel and Zn coating. For the examination of the cross sectional microstructure, the galvanized specimen was mounted on a Cu - based conductive molding compound [BUEHLER PROBEMET] and polished down to 0.1 µm diamond emulsion. The samples were observed in a Hitachi

S – 3400N scanning electron microscope (SEM) and concentration profiles were obtained with a Thermo Electron energy dispersive spectroscopy (EDS) analyzer attached to the microscope, using pure iron, aluminum and zinc standards. The nature of the phases, mainly at coating – steel interface, was identified using X – ray diffraction and transmission electron microscopy. Polished cross sections were observed in an atomic force microscope (Make: SEICO – Japan, Model No.: SPA – 400) to estimate the thickness of the inhibition layer.

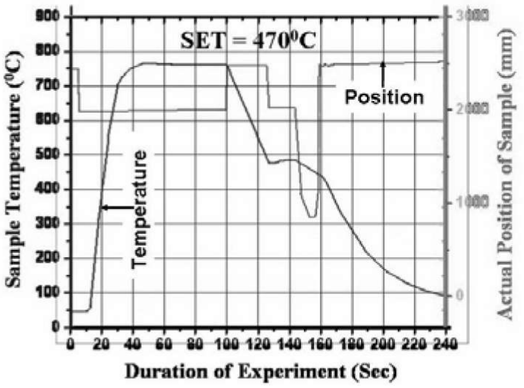

Fig. 1: Variation of sample temperature and actual position of sample with duration of experiment

THEORY

According to Tang [4], the change in temperature of a strip after it enters the bath is governed by the following equation:

$$T_S = (T_{SET} - T_b) \times \exp[(-h \times t)/(\rho \times 2a \times C_P)] + T_b \quad \ldots.(1)$$

where T_{SET} is strip entry temperature, Tb is bath temperature, h is heat-transfer coefficient at steel-metal bath interface, t is the time, ρ is density of steel, 2a is the strip thickness, and C_P is the heat capacity of the steel strip.

In the present model, the mathematical formulation of heat transfer in the strip as it enters the bath is developed by taking into consideration both the conductive and convective heat transfers. To set up the heat balance equation, a control volume with the dimensions dx and unit lengths in the y and z directions is considered. It is further assumed that the control volume is moving with the strip. Heat balance over the control volume generates the following equation:

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2} \quad \ldots.(2)$$

where, $\alpha = \dfrac{K}{\rho C_P}$, K is thermal conductivity, ñ is density, C_P is specific heat, and T is temperature of the strip.

Calculation of variation of the strip temperature with immersion time involves the solution of differential equation for a set of initial and boundary conditions. The heat flux from the strip surface to the metal bath is estimated by calculating the average heat transfer coefficient as a function of strip velocity.

As soon as the strip enters the bath, two reactions occur at the interface between the steel strip and the liquid zinc alloy, namely, the dissolution of iron and the formation of Al rich inhibition layer. Iron dissolution from the strip occurs in two distinct stages - before the nucleation of inhibition layer and after the formation of inhibition layer. Before nucleation of the Al rich inhibition layer, the dissolution of iron is the only reaction that occurs at the liquid zinc - steel interface. The diffusivity, D_{Fe} of iron atoms through the liquid zinc can be considered as a function of temperature and the dissolution of iron from strip as it enters the bath is governed by the generalized diffusion equation:

$$\frac{\partial C_{Fe}}{\partial t} = D_{Fe} \frac{\partial^2 C_{Fe}}{\partial x^2} \quad \ldots.(3)$$

where C_{Fe} is concentration of Fe in liquid Zn. The flux of Fe at the interface between steel strip and liquid Zn bath depends on the concentration of iron in the liquid zinc in metastable equilibrium with pure iron. With the initial and boundary conditions, the model enables calculation of the concentration profile of Fe as a function of time t and of a space variable in the direction x perpendicular to the plane of the strip. The partial differential equations (Eq. [2] & [3]) are solved using the Finite Volume method.

The aluminum enrichment at the coated steel interface can be predicted using a simplified material balance approach. It is assumed that as the strip enters the galvanizing bath containing Al in the range of 0.2 wt%, the precipitation of Fe_2Al_5 occur on the steel surface by the reaction between iron and aluminum. This Fe-Al intermediate layer inhibits the formation of Fe-Zn compounds. Fe_2Al_5 formed during hot dipping of steel in the zinc bath containing 0.2 wt% Al has bcc orthorhombic structure and its interplanar spacings at 450°C are a = 763.3 pm, b = 647.0 pm and c=422.9 pm [10]. This gives the unit cell volume as 209.79×10^{-30} m^3. The theoretical density of the Fe_2Al_5 compound is calculated as $\rho_{Fe2Al5} = 3920\times10^6$ mg/m^3. It is further assumed that for as-dipped galvanized interstitial free (IF) steel the overall coating thickness (1_c) is around 15 micron (15×10^{-6} m) and the total aluminum present in the coating layer reacts with iron to form the inhibition layer at the interface. Therefore, the inhibition layer thickness is roughly in the range of 90 nm.

Inhibition layer formation can be described using nucleation and growth mechanism and its thickness can be calculated by modifying the Tang equation [4] introducing a few correction factors as follows:

$$L_{in} = \int \gamma dt + B\sqrt{D_{Al}t} \quad \ldots.(4)$$

where $\int \gamma dt$ is thickness due to nucleation (m) and second term of **Equation (4)** relates to thickness of the inhibition layer due to diffusion. B is computed using the following expression:

$$B= \frac{C_0^{Al} - C_e^{Al}}{C_\eta^{Al} - C_e^{Al}} \quad \ldots.(5)$$

where C_0^{Al} = molar fraction of Al in liquid in front of interface before precipitation, C_e^{Al} = molar fraction of Al in liquid in equilibrium with Fe_2Al_5, C_η^{Al} = molar fraction of Al in Fe2Al5 and DAl is diffusion coefficient of Al in liquid zinc.

As proposed by Tang [4], the critical nucleus radius for formation of a hemispherical particle of iron aluminide from a liquid onto the liquid/solid interface is determined based on classical nucleation theory. The derivation of an equation for concentration of sub critical crystals (generally referred to as embryos) of radius r, at any instant is a complex problem. The number of embryos of radius r, n(r), can be given by

$$n(r)=\Omega\times\exp[\frac{-\Delta G^*}{k\times T}] \qquad a_0 \prec r \prec r^* \quad \ldots.(6)$$

where k is the Boltzmann constant, T is process temperature as a function of dipping time in Kelvin, a_o is the lattice parameter, ΔG* is the critical energy barrier for the formation of a supercritical particle and Ω is the factor relative to the number of nucleation sites per unit surface. The thickness of the inhibition layer due to nucleation depends on the initial velocity of aluminum incorporation in the inhibiting layer:

$$\gamma = \frac{27000\times1.829\times f\times C_{Al}\times\Omega\times\exp[-\Delta G^*/(k\times T)]}{A_0\times\rho_{Fe_2Al_5}}$$

$$\int\gamma\partial t= \int\frac{27000\times1.829\times f\times C_{Al}\times\Omega\times\exp[(-\pi/3\,\Delta\gamma^3/\{\frac{(-283470+84.8T)\times\rho_{Fe_2Al_5}}{247}\}^2)/(k\times T)]}{A_0\times\rho_{Fe_2Al_5}}\partial t \quad \ldots.(7)$$

where A0 is Avogadro’s constant, f is a complex function and it is treated as a constant equal to 1011, is the surface energy, and C_{Al} is the fraction of Al in the melt/nucleus interface. Inhibition layer thickness is computed by considering the cooling path of the strip consisting of a series of isothermal holds of infinitesimal time step at decreasing temperatures. The effect of each hold time on the formation mechanism of inhibition layer is assessed and the total effect of the immersion time is determined.

RESULTS AND DISCUSSION

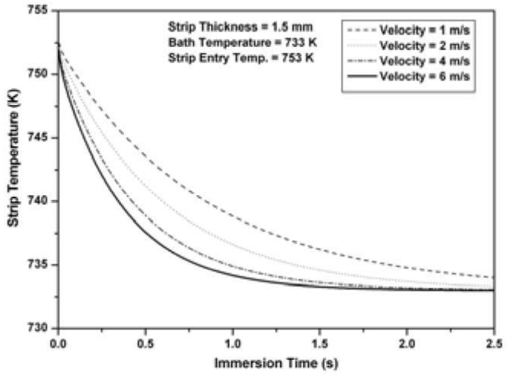

Fig. 2: The effect of strip velocity on strip cooling

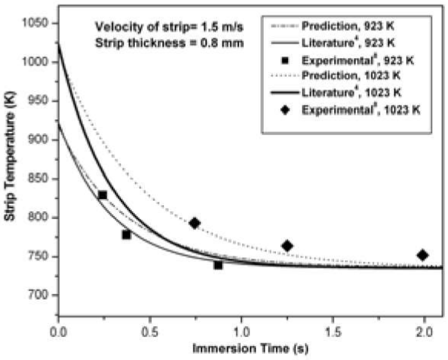

Fig. 3: The influence of strip entry temperature (SET) on strip cooling

The temperature change of the immersed strip of thickness 1.5 mm and assumed strip entry temperature of 753 K and a bath temperature of 733 K with varying strip velocity is shown as a function of immersion time in Fig. 2. As expected, the temperature of the strip decreases rather rapidly as it enters the bath. Increase in the cooling rate of the strip with increasing strip velocity is attributed to the increase in the heat transfer coefficient with strip velocity. The model also predicts the temperature changes of strips of various thicknesses as a function of immersion time. With increasing strip thickness, the cooling rate decreases. The strip-entry temperature is always higher than the metal bath temperature in a modern continuous galvanizing line. The influence of the strip entry temperature (SET) on strip cooling is shown in Fig. 3 for SETs of 923 and 1023 K. The cooling rate of the strip is increases with an increasing SET. However, for all SETs, the temperature of the strip decreased rapidly following immersion, and approached the temperature of the zinc bath within 2 sec. However, the duration of this transient has a marked effect on the nucleation and growth mechanism leading to the formation of a Al rich inhibition layer. The figure also compares the theoretically predicted temperature changes of immersed strip with those experimentally measured and reported in literature [8]. For comparison purposes, the theoretical prediction based on Tang model [4] are also included. The latter assumes a heat transfer coefficient of ~15000 $Wm^{-2}K^{-1}$, which gives strip velocity in the range 9 m/s. It may, however, be mentioned that most of the modern galvanizing plants operate in the range of 1 – 4 m/s. In this range of strip velocity, the computed average heat transfer coefficient is in the range of 5000 to 10000 $Wm^{-2}K^{-1}$. Therefore, the heat transfer co-efficient used in the literature is on the higher side. In the present investigation, the heat transfer co-efficient is calculated for the given strip velocity which is then used to predict the strip temperature. Theoretically predicted cooling curve of the strip for a strip velocity of 1.5 m/s compare reasonably well with the experimentally measured values by others investigators (Fig. 3).

Theoretically determined inhibition layer thickness with dipping time of the strip, by considering arithmetical mean between instantaneous strip and bath temperatures as the process temperature, is shown in Fig. 4. Increase in the inhibition layer thickness with immersion time in the coating–steel interface, based on nucleation controlled and long range diffusion controlled mechanisms, is predicted solving Equation (4) over the immersion time for a bath temperature of 733 K, strip velocity of 2 m/s, strip thickness of 1 mm and Al content of the galvanizing bath as 0.2 wt %. The rate of formation of Al rich inhibition layer is low after the very initial stages of immersion (fraction of second) because of diffusion controlled growth mechanism. The figure also depicts the effect of strip entry temperature (SET) on formation of interfacial layer. The inhibition layer thickness at the substrate-coating interface increases about 3 times with an increase in SET from 733 to 1023 K at a constant bath temperature of 733 K. This may be due to possible change in the rate determining mechanism of Al consumption with increasing SET.

The theoretical prediction of inhibition layer thickness matches reasonably well with those obtained by other researchers as well as the experimental findings of the present study. The mathematical model of inhibition layer formation, developed based on nucleation and growth mechanism as well as material balance, provides satisfactory results. There is an increase in process temperature for the formation and growth of Al rich inhibition layer with decreasing strip velocity and with increasing strip entry temperature, and thickness of the strip and therefore, all these process variables play an important role in galvanizing reactions at the interface.

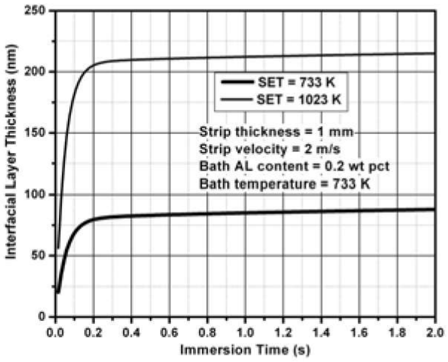

Fig. 4: Prediction of inhibition layer thickness with dipping time

SUMMARY AND CONCLUSIONS

In the present study, the role of aluminum in formation of aluminum rich inhibition layer at the interface between steel substrate and zinc coating is investigated based on material balance as well as nucleation and growth mechanism. The strip temperature is predicted based on both conductive and convective heat transfer mechanisms. Theoretically predicted cooling curve of the strip compares reasonably well with the experimentally measured values by previous investigators. Instantaneous strip temperature, bath temperature and arithmetical mean between instantaneous strip and bath temperatures are considered as process temperatures for the prediction of inhibition layer. The theoretical prediction on thickness of inhibition layer is in conformity with those obtained by other researchers. Experimental study using AFM and TEM also corroborates the theoretical prediction of the thickness of the inhibition layer.

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