Reactive wetting of high Mn steels during continuous hot-dip galvanizing

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Abstract

An electrobalance was used to study the reactive wetting of a series of Mn-containing steels ranging in composition from 0.14 wt.% to 5.1 wt.% Mn by a 0.20 wt.% dissolved Al continuous galvanizing bath as a function of immersion time, alloy Mn content and annealing atmosphere pO_2. It was found that the wetting force for the 1.4–5.1 wt.% Mn alloys was significantly less than that for the 0.14 wt.% Mn alloy due to the formation of a significant MnO layer on the higher Mn alloys. For all alloys and process atmospheres, reactive wetting and the formation of a well-developed interfacial Fe–Al intermetallic layer was achieved with the wetting force being directly related to the thickness of the external MnO layer. The wetting force was a strong function of the process atmosphere pO_2, which was in turn strongly related to the thickness of the external MnO layer. A reactive wetting model in which the motion of the triple line and the wetting force is limited by the oxide layer thickness is proposed.

1. Introduction

Dual Phase (DP) steels have found increased use in automotive structures due to their beneficial combination of strength and ductility. To meet the requirement of corrosion resistance, these steels must be protected against corrosion, for which continuous hot-dip galvanizing is the most economical method for large scale production. However, some alloying elements commonly employed in DP steels such as Mn and Si are oxidized preferentially during controlled atmosphere annealing prior to immersion in the galvanizing bath, since the conventional N_2/H_2 atmospheres used to reduce surface iron oxides in the continuous galvanizing line (CGL) remain oxidizing for these alloying additions.

It has been reported that alloy Mn additions result in the appearance of appreciable amounts of MnO on the surface

[1–3] which can limit the ability of Mn-containing steels to be galvanized [3–6]. Moreover, it has been proposed that the maximum alloy Mn content which can be successfully reactively wet by a continuous galvanizing bath should not exceed 1.5 wt.% Mn [7]. This can place restrictions on the Mn content of some of the higher strength DP grades currently being proposed by steel makers if they are subsequently to be Zn-coated. However, good reactive wetting has been observed for a dual phase steel with 2 wt.% Mn, attributed to in situ aluminothermic reduction of MnO by the dissolved Al in the zinc bath (Eq. (1)) [8].

$$3MnO_{(solid)} + 2Al_{(solution)} \rightarrow Al_2O_{3(solid)} + 3Mn_{(solution)} \qquad (1)$$
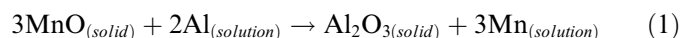
Characterization of reactive wetting kinetics in galvanizing is usually measured in one of several ways. The first is characterization of the rate of growth of the Fe–Al intermetallic layer during immersion. This is well-suited to alloys which exhibit good wettability, such as low-alloy steels, as the measurements do not offer insight into any reactions occurring before the formation of the $Fe_2Al_5Zn_x$ intermetallic layer. The second method is referred to as the

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sessile drop method and involves placing a drop of the liquid bath alloy on the steel surface after annealing while utilizing a high-speed camera to measure the contact angle as a function of time [9]. However, since the reaction is a strong function of the dissolved Al in a dilute Zn–Al–Fe liquid, this method is limited by the finite amount of solute in the drop and can result in incomplete wetting or reaction rates which are far from those seen in a CGL [5]. Moreover, there continues to be debate as to whether the contact angle has a significant meaning in reactive wetting vs. its role in physical wetting [10–12]. Due to these limitations, the effect of surface MnO on the reactive wetting of advanced steels has never been quantified – only to say that it has been associated with the formation of bare spots in the coating and is, therefore, detrimental to the production of high quality coatings in continuous galvanizing.

The reactive wetting of liquid metals has been characterized using a meniscograph, also known as the Wilhelmy plate method. Most commonly, this apparatus has been widely used in the study of soldering systems (e.g. formation of Cu_6Sn_5 or Cu_3Sn) [13,14], although it has been applied to continuous galvanizing [15–19]. In the meniscograph technique, the wettability of a specific substrate/liquid system is characterized using a electrobalance by measuring the vertical forces acting on the sample after immersion in a liquid metal bath. This technique, illustrated in Fig. 1, allows one to monitor the motion of the solid–liquid-vapour triple line as a function of time and can be used to infer the progress of reactive wetting of the substrate by the liquid metal bath. Thus, if $F_{measured}$ increases as a function of time, indicating an upward motion of the triple line and a decreasing value of θ, it implies that the solid surface is being reactively wet by the liquid. In the case of reactive wetting by an Al-containing galvanizing bath, this would also indicate that the desired η-$Fe_2Al_5Zn_x$ interfacial layer is being formed at the liquid Zn(Al,Fe)/steel interface.

A typical meniscograph cannot be used to simulate continuous hot-dip galvanizing because the sample has to be annealed in a controlled atmosphere to reduce Fe-based

oxides prior to immersion. Moreover, with advanced high strength steels (AHSS), rapid cooling, which can cause significant noise in the electrobalance signal through interactions between the cooling gas and sample, is usually required in order to obtain the desired martensite/ferrite microstructure. Although some data has been published using this technique to simulate galvanizing [15–19], it is sparse. Due to these difficulties, more subjective and qualitative analyses of the reactive wetting process is typically used in galvanizing, for example bare-spot measurement.

The objectives of the present research are to study the reactive wetting process for high Mn steels during continuous hot-dip galvanizing as a function of immersion time, steel Mn content and annealing atmosphere oxygen partial pressure (pO_2). It is also the objective of the present investigation to assess the maximum allowable alloy Mn content which can be galvanized by attempting to reactively wet steels with Mn contents greater than 2.0 wt.% Mn. This limit is of particular interest given the developing interest in the so-called third generation (3G) AHSS, whose Mn contents are often in excess of 3.5 wt.% Mn [20,21].

2. Experimental Method

The chemical compositions of the experimental steels are shown in Table 1 and comprise one low Mn (0.14 wt.%) interstitial free steel and four higher Mn dual phase steels with approximately 0.06 wt.% C. It should be pointed out that the 2.5Mn, 3.5Mn and 5.1Mn grades were custom fabricated at the CANMET Materials Technology Laboratory. The 0.14Mn and 1.40Mn steels were supplied by US Steel Canada. All steels were supplied in the form of full-hard cold-rolled sheet.

Two sets of experiments were carried out on the experimental alloys: (i) oxidation experiments, carried out in the McMaster Galvanizing Simulator (MGS) (Iwatani-Surtec, Japan) and (ii) reactive wetting experiments, carried out using a Rhesca® Force Balance Simulator. In all cases, samples were heated at 10 °C/s to their peak annealing temperature (PAT) in an atmosphere of 95% N_2/5% H_2 with four different dew points (dp) ranging from −50 °C to +5 °C (Table 2), holding at the PAT for 120 s followed by cooling at −20 °C/s to either the dipping temperature for reactive wetting experiments or to room temperature for oxidation experiments. The samples used for reactive wetting experiments were cooled to 460 °C and dipped for 10 s in the Zn(Al,Fe) bath to a depth of 8 mm at a rate of 15 mm/s (resulting in a travel time of ∼0.533 s from initial surface contact to the final depth) while the wetting force was continuously measured with the resident electrobalance. In addition, all dipping experiments employed an Fe saturated 0.20 wt.% dissolved Al bath at 460 °C, as determined using the solubility curves of McDermid et al. [22], and were run in triplicate or more to ensure repeatability.

The peak annealing temperature was chosen to produce a microstructure comprising 30%γ – 70%α for the 1.4Mn
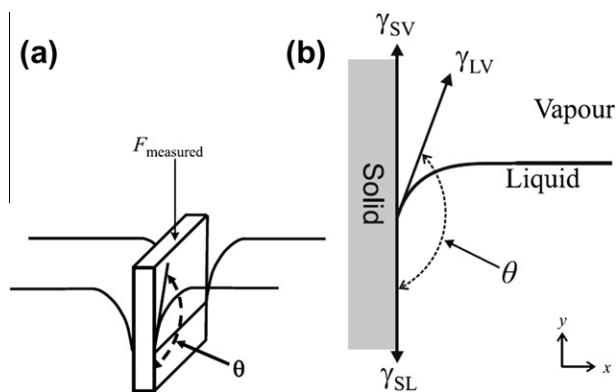

Fig. 1. (a) Schematic diagram of the meniscograph forces measured during experiments ($F_{measured}$) and (b) surface tensions acting at the triple line between the steel surface (S), experimental atmosphere (V) and Zn bath (L).