

Research Article

Aluminising of Mild Steel Plates

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Hot dip aluminising of low carbon steel was done at temperatures 690°C and 750°C for dipping time ranging from 300 to 2400 seconds. During aluminising a mixture of $ZnCl_2$ and NH_4Cl was used as flux. During aluminising components of the flux decomposed and zinc formed interacted with the Fe and Al. The aluminised samples were characterised for iron-aluminium intermetallic layer formation, morphology, and local composition. It was observed that intermetallic layer was predominantly Fe_2Al_5 and $FeAl_3$ at 690°C and at 750°C coating consisted of $FeAl_3$ layer and a layer with Al/Fe ratio greater than 3.26. For both temperatures, coating thickness increased with increase in time. For a given dipping time, deposition was less at higher temperature and this is attributed to changes in the kinetics of growth of individual layers due to dissolved zinc in the aluminium, at 750°C. Also, spalling of intermetallic layers was observed at elevated temperatures and longer dipping times.

1. Introduction

Steel remains the material of choice for numerous applications, largely because of its low cost and wide variety of properties available through alloy design, heat treatment, and amenability for forming operations [1]. The oxide layer forming on the steel substrate is a noncompact one and due to this conventional mild steel exhibits poor oxidation and corrosion resistance properties. To improve corrosion properties, the steel can be alloyed with various elements such as chromium and nickel, but this increases material cost and limits width of the processing window [1]. Alternate route is to modify the surface of the steel appropriately, so that it can replace expensive alloy steel material [2]. During surface modification, the surface of the steel material is modified over a relatively shallow depth, using an appropriate method. When a suitable technique is selected and correctly done, the following properties of the steel can be increased: resistance to wear, chemical resistance, mechanical resistance, and oxidation resistance [3, 4]. Among various surface modification methods available for steel, the hot dipping process has drawn much attention because it is an effective and inexpensive process. In this context, use of aluminium as a coating material is highly relevant because, aluminium,

when applied to steel provides corrosion resistance layer [5]. Also, aluminium bearing steels can be easily nitrided and nitrided steel has better wear and fatigue properties. Continuous alumina layer is highly resistant to oxidation, sulfidation, and degradation in chloride containing aqueous solutions [6]. Hence, hot dip aluminising is widely used for coating of steel with aluminium to increase corrosion, oxidation, and hardness of the steel components [5, 7].

Fe–Al is a complex system and its phase diagram is shown in Figure 1. It shows five types of intermetallic compounds, namely, Fe_3Al , $FeAl$, $FeAl_2$, Fe_2Al_5 , and $FeAl_3$. Beneficial application of aluminising depends on minimising detrimental brittle phases and promoting growth of relatively ductile phases. There are investigations on the formation and growth kinetics of the intermetallic phases, under both isothermal and nonisothermal conditions. Shatynski et al. [9] modelled the formation of intermetallic phases from purely diffusional perspective. They found that growth of intermetallics follows parabolic relation. In the case of Cr–Ni stainless steel, Dybkov [10] experimentally proved that the intermetallics follows parabolic (initially linear followed by parabolic) growth kinetics. Eggeler et al. [11] have studied interaction between pure solid steel with liquid aluminium and observed that near aluminium side $FeAl_3$ forms and

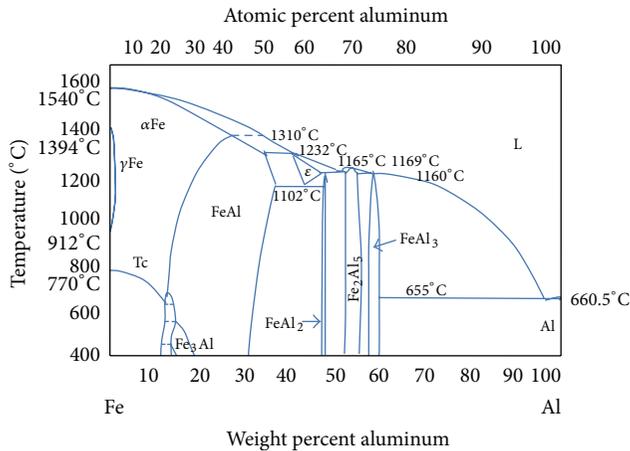


FIGURE 1: Phase diagram of Fe–Al [8].

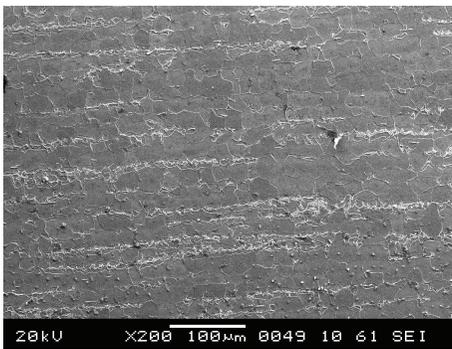


FIGURE 2: Microstructure of steel consisting of proeutectoid ferrite and pearlite.

near iron side Fe_2Al_5 intermetallic forms. Heumann and Dittrich [12] tried to explain the tongue like morphology of Fe_2Al_5 layer. Bouayad et al. [13] studied the kinetics of various intermetallic layer formation in pure solid iron and pure liquid aluminium and found that FeAl_3 follows linear growth kinetics and Fe_2Al_5 follows parabolic kinetics. They did experiments at temperatures 700, 800, and 900°C. Naoi and Kajihara [14] did Al/Fe interdiffusion experiments over temperature range 550–640°C and found that only Fe_2Al_5 forms at the interface. They did experiments for fairly long time (120 hours) before arriving at this conclusion. Springer et al. [15] concluded that Fe_2Al_5 grows faster at lower temperature. They covered a temperature range of 600–675°C to cover solid-solid and solid-liquid diffusion couples. Maki et al. [16] have observed alloying reaction in aluminised steel when it was exposed for long durations at 600°C. Kobayashi and Yakou [17] have done experiments with a view to control intermetallic layers at interface between medium carbon steel and aluminium during diffusion experiments over the temperature range from 700 to 900°C for 300 s. They observed that interface is exclusively of Fe_2Al_5 . It is stated that the growth of intermetallic layers depends on the diffusion of Fe atoms into the Al rich intermetallic layers [17]. It is also stated that intermetallic compounds with high Al content

TABLE 1: Composition of the steel strip (wt.%).

C	Mn	Si	S	P	Fe
0.186	0.47	0.23	0.027	0.018	Bal.

(namely, FeAl_2 , Fe_2Al_5 , and FeAl_3) are not desirable due to their brittleness. Hwang et al. [18] investigated the role of carbon in the dissolution of the substrate and formation of intermetallics. They concluded that carbon effectively lowers the rate of intermetallic layer formation.

Aluminium is a highly reactive metal and gets oxidised very fast, especially, when it is molten. Shielding molten aluminium is very essential. Also, the steel surface has to be cleaned for effective aluminisation of the surface. Mixture of zinc chloride and ammonium chloride is a promising one. It is a violent flux used in galvanisation [19], but its use in aluminising is less explored. Here an effort was made to understand the effectiveness of the zinc chloride and ammonium chloride as the flux and its role on the formation of Fe–Al based intermetallic layers.

2. Materials and Experimental Methods

The substrate material used in this investigation was low carbon steel, purchased in the form of a rolled strip. The composition of the strip is given in Table 1. The strip was cut into coupons of 3 cm length and 1 cm wide. Coupons were annealed at 900°C for two hours to remove the effect of prior work. Coupon surfaces were ground and polished. The coupons were precleaned using 10% HCl, washed in distilled water, and dried just before they were dipped in liquid aluminium.

Aluminium melt for hot dipping was prepared by heating aluminium ingot in a clay crucible heated by resistance heating. The aluminium was melted and the set temperature was attained. Fluxing was done using a eutectic mixture of ammonium chloride and zinc chloride. Fluxing treatment was done in order to enhance the wetting and dissolution of the oxide coating on the steel, in the molten aluminium bath. Fluxing was done by maintaining a layer on the top of the Al bath. Steel coupons were dipped in aluminium melt maintained at 690°C and 750°C for the time intervals of 300, 600, 900, 1500, and 2400 seconds.

The specimens were cut across the cross-section, metallographically polished, and etched using 3% nital solution. Microstructures were observed in scanning electron microscope (SEM) and coating morphology was studied. Intermetallic layer thickness was measured. Local composition was measured using EDS (energy dispersive spectroscopy) attached to SEM.

3. Results and Discussion

Figure 2 shows the microstructure of the low carbon steel used in the experiment. Microstructure consists of proeutectoid ferrite and eutectoid pearlite. The area fractions of these features confirm that the substrate used is a low carbon steel. Figures 3 and 4 show the microstructure of the aluminised

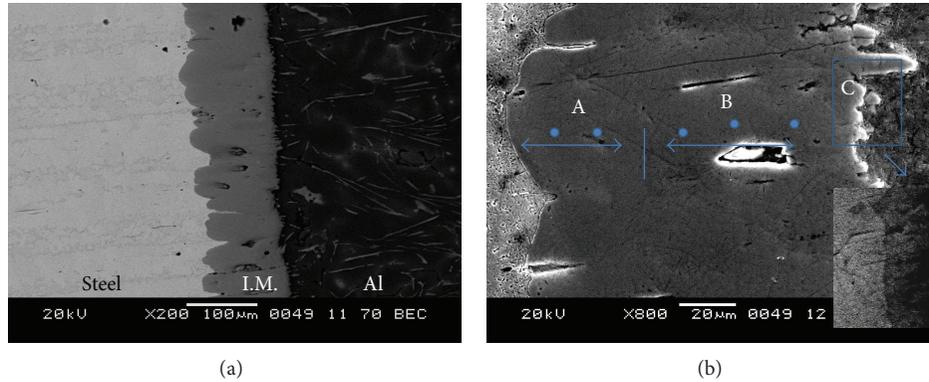


FIGURE 3: (a) Intermetallic (I.M.) formation at the interface (690°C and 300 s). (b) Magnified from (a) EDS analysis at circled points indicates 3 distinct zones: (A) Fe_2Al_5 , (B) FeAl_3 , and (C) Fe:Al~1:4.6.

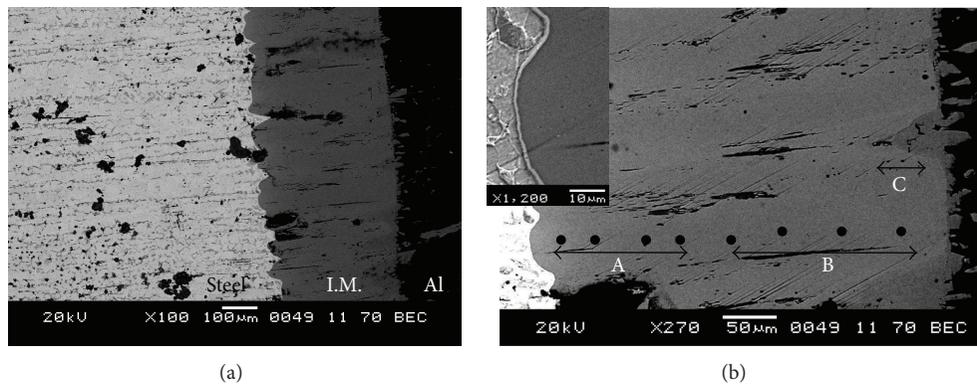


FIGURE 4: (a) Intermetallic (I.M.) formation at the interface (690°C and 2400 s). (b) Magnified from (a) EDS analysis at circled regions indicates 3 distinct zones: (A) Fe_2Al_5 , (B) FeAl_3 , and (C) Al/Fe ratio 4:1.

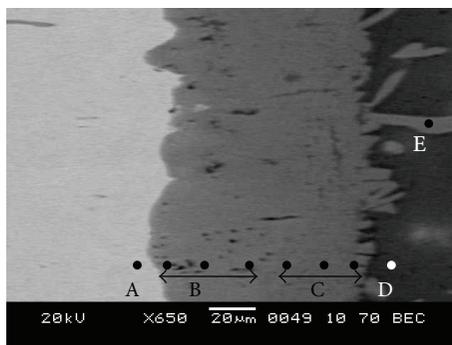


FIGURE 5: Intermetallic layer formation at 750°C for 300 s. At (%) at various locations are (A) 99.3%Fe, 0.7Al, (B) FeAl_3 ratio with Zn 3 to 3.4%, (C) Al:Fe ratio in the range 3.6:1 to 4.1:1, Zn 0.4 to 1.3, (D) 0.4Fe, 93.3Al, 5.4Zn, (E) 80.4Al, 18.8Fe, 0.9Zn.

steel, aluminised at 690°C for 300 s and 2400 s, respectively. We see a layer of intermetallic phases (I.M.) between steel and aluminium. Intermetallic layer has a characteristic morphology, which is referred to in the literature as “tongue” like morphology. Intermetallic layer is continuous but its thickness is not constant. The interface between the Al and intermetallic layer is not smooth but the unevenness is on a

smaller length scale. On the contrast, the interface between steel and intermetallic layer is more uneven and appears like wave or tongue like. Wave or tongue like morphology for intermetallic layers during aluminising is reported in the literature [15, 17]. Thickness was measured over a length of 1 mm. For 300 s exposure time, the interface thickness was in the range of 95 to 120 μm with an average value of 112 micrometers. Intermetallic layer was showing predominantly single contrast, but periodic EDS measurements on this layer showed two distinct regions A and B, whose chemistry was matching with Fe_2Al_5 and FeAl_3 , respectively.

There exists another layer C (Figures 3(b) and 4(b)) where the Al/Fe ratio was much higher than 3.26 which is the upper limit of the atomic ratio for the phase, FeAl_3 [9]. When the dipping time was large, a thin layer D at Fe/ Fe_2Al_5 interface is clearly visible (inset in Figure 4(b)). EDS analysis on it at selected places indicates Fe/Al ratio as 1:2 indicating it most probably as FeAl_2 compound. It may be mentioned that Fe_2Al_5 and FeAl_3 are not line phases (refer to phase diagram shown in Figure 1), indicating the possibility of different Fe/Al ratios at different locations. This is also observed during EDS analysis.

Figure 5 shows microstructural features under the conditions of 750°C and 300 seconds. We see two distinct regions

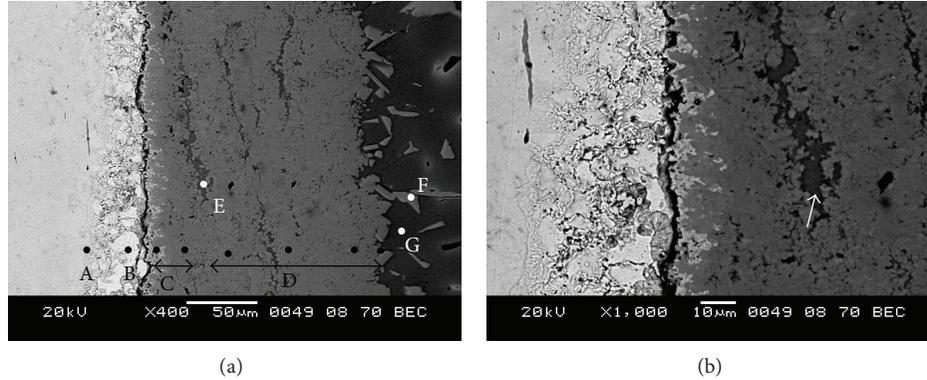


FIGURE 6: (a) Intermetallic layer formation at 750°C for 2400 s. At (%) at various locations are (A) 100Fe, (B) 93Fe7Zn, (C) FeAl₃ ratio, Zn 1.4 to 3, (D) Al: Fe ratio 3.6:1 to 4.2:1, Zn up to 1.2, (G) Fe: Al: Zn = 1: 94: 5, (F) Fe: Al: Zn = 80.4: 18.8: 0.8.3b: Enlarged at point (E). EDS at arrow point in (b) indicates a ternary system with Fe: Al: Zn = 85.5: 6.6: 7.9.

corresponding to FeAl₃ and another layer with Al:Fe ratio greater than 3.26:1. Both show dissolved zinc of various scales. There is no layer corresponding to Fe₂Al₅ which is distinctly clear in 690°C. Figures 6(a) and 6(b) show microstructures in the case of 750°C bath temperature and holding time of 2400 seconds. Here also no layer corresponding to Fe₂Al₅ is visible. A layer corresponding to solid solution of Al in iron is clearly visible. All layers show dissolved zinc in them.

We see many polyhedral crystals peeled off from the intermetallic layers in the aluminium matrix. This is due to decrease in the iron solubility in aluminium during cooling. The occurrence of these crystals is more favoured when the cooling rate is increased and the interaction time is long (Figures 4(a) and 5(a)). These crystals have a composition close to that existing in the intermetallic layer close to Al side. Such peeling off is reported by Bouayad et al. [13].

Formation of various phases in the intermetallic layer under different conditions is explained as follows. In the initial stages of dipping, the intermetallic layer forms are FeAl₃ and Fe₂Al₅ [17]. The FeAl₃ layer is initially formed at the interface between the aluminium and steel substrate by the diffusion of iron atoms into aluminium layer and the Fe₂Al₅ layer is then formed at the interface between the FeAl₃ layer and steel substrate. Formation of this layer depends on the relative values of diffusivities (iron into aluminium and aluminium into iron). Under normal conditions, diffusion of iron towards aluminium is larger [20]. It favours Fe₂Al₅ formation at Fe-FeAl₃ interface. This is happening at lower temperature. At higher temperature, the zinc increased the activity of Al in the bath (for details refer to the next paragraph). Increased activity leads to increased diffusion of Al towards iron-FeAl₃ interface. This reduced the chances of Fe₂Al₅ and increased the chances of FeAl₃ layer as well as a layer with Al/Fe ratio greater than 3.2:1.

Higher dipping temperature means higher amount of ZnCl₂ from the flux mixture reacts with metal oxides or oxygen in the environment. It gives ZnO which gets reduced by Al into Zn. This explains higher levels of Zn in the intermetallic layer formed at elevated temperatures. Higher

levels of dissolved zinc in Al favour formation of FeAl₃ intermetallic than Fe₂Al₅. The two-phase equilibrium of Fe₂Al₅ and FeAl₃ cannot appear in this study as it involves diffusion of species under chemical potential gradient. Presence of Zn in the bath increases activity of Al, leading to a layer with more Al concentration. Such observations are also reported in the literature [21]. This explains the observation of FeAl₃ and higher Al concentration layers. The eutectic reaction at 655°C in Fe–Al system [8] is bypassed during experimental investigation. Another aspect is liquid aluminium-iron layer on the surface is rapidly cooled giving metastable phases. Skinner et al. [22] have reported possibility of a number of metastable phases, namely, Al₆Fe, Al₅Fe, and Al₉Fe₂ under rapid cooling conditions. All these metastable phases have Al concentration more than that in FeAl₃. In our experiments also, the condition at the surface is rapid cooling leading to metastable phases.

Figure 7 shows variation of thickness as a function of dipping time. It shows an increase in the deposit thickness as a function of time. To explore the parabolic relationship between intermetallic layer thickness and dipping time, a plot of thickness versus square root of dipping time is drawn (Figure 8). A straight line relationship is observed indicating that total intermetallic layer follows parabolic growth behaviour. At 690°C, increase in thickness is mainly from thickness of Fe₂Al₅ and FeAl₃. Though FeAl₂ layer is visible during longer dipping times, its thickness is negligible compared to overall deposition thickness. Amongst Fe₂Al₅ and FeAl₃, Fe₂Al₅ undergoes parabolic growth behaviour and FeAl₃ follows quasilinear behaviour [13]. Gibbs free energy for formation of FeAl₃ is lower than Fe₂Al₅ and due to this FeAl₃ forms instantaneously during dipping. But from kinetics point of view Fe₂Al₅ is more favoured [23]. Diffusion of Al and Fe takes place across the FeAl₃ layer, promoting formation of Fe₂Al₅ [24]. Due to this, for lower dipping times, FeAl₃ and for longer dipping times, Fe₂Al₅ are major constituents. Because of this, thickness seems to be nonzero even at the start of the dipping. Such observations are also reported by Cheng and Wang [23] and Li et al. [25]. It is also to be mentioned the smallest experimental duration during

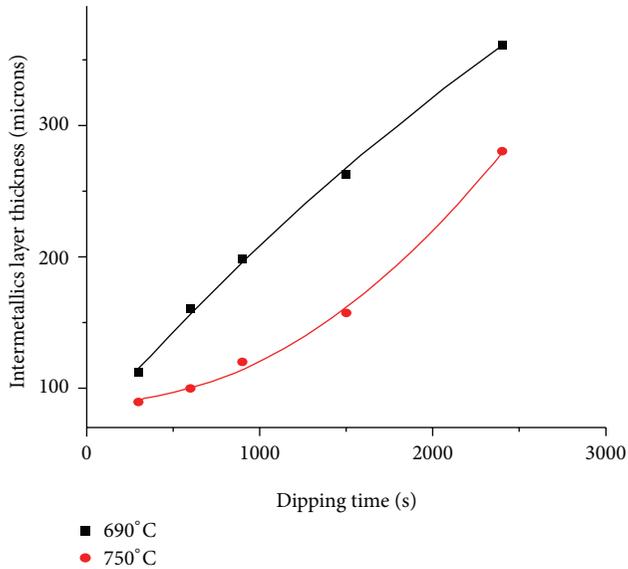


FIGURE 7: Plot shows variation of intermetallic layer thickness as a function of dipping time for temperatures 690°C and 750°C.

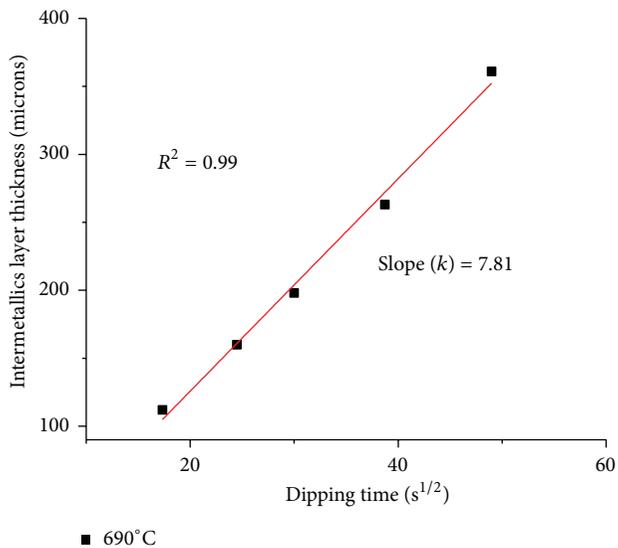


FIGURE 8: Plot showing total intermetallic layer thickness versus square root of time. A good (linear) fit indicates that the total intermetallic layer growth follows parabolic growth behaviour.

our experiments is 300 seconds. It is reported that by this time all the transient nature associated with this reactive diffusion is crossed [25].

At 750°C, the deposit consists of FeAl_3 and another layer $\text{FeAl}_{3.26+x}$ where x is a positive decimal number. These individual layers have different growth kinetics and hence at 750°C the overall thickness is less compared to that at 690°C. At long interaction times and high temperatures, the spalling of the intermetallic layer takes place and it affects the measurement of the layer thickness [11].

4. Conclusions

The experimental investigations lead to the following conclusions. Use of a mixture of ZnCl_2 and NH_4Cl as a flux for aluminizing leads to some amount of dissolved zinc in the Al bath, especially when bath temperature is high.

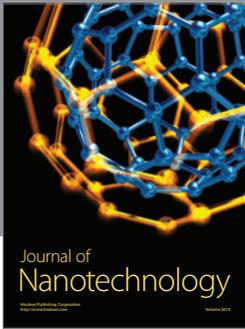
At 690°C, the intermetallic layer consisted of predominantly, Fe_2Al_5 , and FeAl_3 and at 750°C, the intermetallic layer consists of FeAl_3 , and a layer with higher levels of Al concentration (Al/Fe ratio more than 3.26) forming due to rapid cooling conditions. This change is attributed to increased Al activity due to dissolved zinc.

The growth of Fe_2Al_5 layer and total intermetallic layer follows parabolic growth behaviour with respect to dipping time.

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