Analysis of the Intermetallic Compound Formed in Hot Dip Aluminized Steel

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Abstract. A hot dip aluminising process was carried out with a 1mm steel sheet dipped into the Al-10 at.% Si melt in an automatic hot-dip simulator. When steel and liquid aluminium are in contact with each other, a thin intermetallic compound (IMC) is formed between the steel and the aluminium. The analysis and identification of the formation mechanism of the IMC is needed to manufacture the application products. Energy dispersive X-ray spectroscopy (EDX) and electron probe microanalysis (EPMA) are normally used to identify the phases of IMC. In the Al-Fe-Si system, numerous compounds with only slight differences in composition are formed. Consequently, EDX and EPMA are insufficient to confirm exactly the thin IMC with multiphases. In this study, transmission electron microscopy (TEM) analysis combined with EDX was used. The TEM sample was prepared with focused ion beam (FIB) sampling. The FIB lift-out technology is used to slice a very thin specimen with minimum contamination for TEM analysis. It is clearly shown that the IMC consists of Al\textsubscript{8}Fe\textsubscript{2}Si with a hexagonal unit cell (space group P6\textsubscript{3}3/mmc). The cell parameters are a= 1.2404\,nm and c= 2.6234\,nm.

Introduction

A hot dip aluminizing (HDA) process has been used to increase the oxidation and corrosion resistance and the hardness of the steel substrate [1,2]. The superior corrosion resistance of aluminum coated steel is provided by an approximately 20nm thick oxide film formed by exposing the surface of aluminum to the atmosphere. If the oxide film is removed by abrasion, it immediately reproduces and protects again the coating layer against corrosion [2].

The HDA process is generally carried out in three successive steps: pre-treatment for removing scales on the steel sheet, dipping in a pure molten aluminum (type II) or aluminum with 10 at. % Si (type I) for a certain period and then cooling [1]. This process forms an intermetallic compound (IMC) between the solid steel and the liquid aluminum. The phase of the IMC varies according to the melt composition, dipping time and temperature [3-10]. The type of IMC and its thickness are important parameters to obtain an improved bonding strength between the steel and the aluminum melt in HDA [3,8].

The IMC is usually analyzed by energy dispersive X-ray spectroscopy (EDX) and/or auger electron spectroscopy (AES). But, in the case of EDX and AES analysis, measuring the exact content of phases with only a slight difference in composition might cause some errors when approaching the resolution limit of the instruments. When the energetic electrons in the microscope strike the sample, the interaction volume that can also make the error in the analysis examining thick or bulk specimens can occur inside the specimen. In the Al-Fe-Si system it is not evident to determine the exact composition and phase even with the help of several established analysis technology such as EDX, AES and EPMA. Phase identification of the IMC with the help of electron microscopy (TEM), electron
diffraction and EDX is much more reliable. Thin samples for TEM have been prepared by focused ion beam (FIB).

Experimental

A hot dip aluminizing process to simulate the continuous galvanizing line (CGL) was carried out in successive steps by the automatic hot dip simulator (as shown in Fig. 1). The composition of the steel is Fe- 0.047%C -0.016%Si -0.238%Mn -0.016%Ni -0.016%Cr -0.016%Cu -0.069%Al -0.003%N -0.012%P in at. %. The steel specimens were degreased in a KOH solution at 60°C for 20min. The steel sheet was attached to an up-down sample holder and spot-welded with thermocouples to measure the temperature of the sample. The heating in the simulator was performed at 780°C for 9s in the upper zone. The heated specimen was moved to the lower zone for deoxidizing. The specimen was exposed to a N₂+H₂ atmosphere (~56.0°C dew point) to activate the surface in the lower zone, then lowered and dipped in the melt during 3s at 660°C. The dipped sample was dragged up and blown by air knife (0.3MPa) to control the thickness of the coating layer. Then, the sample was cooled in a N₂ atmosphere.

Identification of this IMC formed on the steel sheet were performed by AES, EDX and TEM. The TEM sample was carefully prepared by the focused ion beam (FIB). The FIB acceleration voltage was 30keV. The cross section of the IMC was cut and lifted out by FIB technology to analysis the IMC layer (Figure 2).

![Fig. 1. Schematic view of the device used for hot-dip aluminizing](image-url)
Results and discussion

Figure 3 shows a typical cross section of the Al-coated steel. Two distinct layers are visible on top of the steel. The black layer is the Al-Si coating layer, and the gray region is the IMC. By the line profiles of AES, the distributions of Al, Si and Fe are uniform in the IMC region. Little silicon is detected in Al-Si layer, but a large amount of silicon is present in the IMC region. EDX analysis in the three regions (1st, 2nd and 3rd from the left) shows that Fe and a very small amount of C is present in the steel (Fig. 3), and that Al, Si and Fe exist in the IMC layer (the second dot), the Al coating layer (the first dot) mostly consists of aluminum. The spectra are shown in figure 3-b). Compositions of each layer in Figure 3 (using the INCA software, in atomic %) are for the steel layer (100% Fe), for the IMC layer (Al-9~10%Si-26~28%Fe), and for the Al coating layer (Al-2~5% Si-0.5~2.5%Fe).

TEM shows that the interface layer actually consists of large grains (500nm) (figure 4). Selected area diffraction patterns of all grains examined, are consistent with the phase Fe$_3$Si Al$_9$. The unit cell is hexagonal (space group P6$_3$/mmc) with cell parameters: a= 1.2404nm and c= 2.6234nm (figure 5, Advanced Materials Research Vols. 15-17 161).
6). The Fe$_2$Si Al$_8$ has a hardness of 1147 kg/mm$^2$, a density of 3.62 g/cm$^3$ and a molar volume of 98.23 mol/cm$^3$ [1].

Fig. 4. TEM image of intermetallic compound

![TEM image of intermetallic compound](image)

Fig. 5. Electron diffraction patterns of intermetallic compound, indexed in the hexagonal unit cell of Fe$_2$Si Al$_8$.

![Electron diffraction patterns of intermetallic compound](image)

The presence of silicon inhibits the growth of the alloy layer, changes the phase constitution of the alloy layer, and results in the formation of a planar interface between the steel and the alloy layer of the aluminized steel [1]. Although the phase morphology of the aluminized steel is dependent on the silicon content of the bath, the mechanism has not been thoroughly investigated. The interface between the Al melt and the Fe$_2$SiAl$_8$ phase is generally irregular, owing to dissolution effects in the melt.

To reduce the growth of the alloy layer and improve the formability, silicon additions up to about 11 at. % are generally used in the aluminizing bath and Coburn suggests that an optimum addition of
silicon is approx. 8.5~9.5 at. % [1, 11]. In this study, EDS analysis adjacent to the interface of the Fe$_2$SiAl$_8$/steel shows that the Si content in the melt need at least 5~6 at. % in concentration.

**Summary**

A hot dip aluminizing process to simulate the continuous galvanizing line was executed. The aluminum alloying with approx. 10 at. % silicon forms a thin FeSiAl alloy. By TEM analysis coupled with FIB sample preparation, the compound is identified as Fe$_2$SiAl$_8$ with a hexagonal unit cell (space group P6$_3$/mmc). The cell parameters are a= 1.2404nm and c= 2.6234nm.

**References**