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Experimental study and thermodynamic assessment of the Al–Fe rich side of the Al–Zn–Fe system at 300 and 550 °C

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ABSTRACT

The phase relations of the Al–Zn–Fe system on the Al–Fe rich side at 300 and 550 °C were studied by means of the diffusion couple technique. The morphologies of $Al_{96.2}Zn_{3.8}$/Fe diffusion couples were observed by scanning electron microscopy (SEM) and the composition profiles were determined using energy dispersive spectroscopy (EDS). The intermetallics layer formed between the $Al_{96.2}Zn_{3.8}$ and Fe end-members were mainly Fe_2Al_5 phase. The diffusion path identified at 300 °C was (Al) $\rightarrow$ Fe_4Al_{13} $\rightarrow$ Fe_2Al_5 $\rightarrow$ bcc(Fe) $\rightarrow$ (Fe), and that was (Al) $\rightarrow$ Fe_4Al_{13} $\rightarrow$ Fe_2Al_5 $\rightarrow$ (Fe) at 550 °C. Based on the literature information and the current experimental results, the Al-Zn-Fe system was re-assessed thermodynamically with a CALPHAD approach. The calculated phase diagrams at 300, 450 and 550 °C agreed well with current experimental results as well as the data from the literature.

1. Introduction

The hot-dipping coating of Al–Zn based alloys has become one of the major methods to protect steel products from oxidation and corrosion. This approach can produce a coating with excellent corrosion resistance and adhesion due to the formation of multi-layer intermetallics between the substrate iron and the molten Al–Zn coating alloy during the hot-dipping process [1]. However, the overreaction between liquid and substrate steel will lead to a very thick layer of Fe–Al intermetallic compound that will decrease the mechanical properties and subsequent machinability of coating. The knowledge of the Al–Zn–Fe phase diagram will help us understand the equilibrium between liquid and iron substrates. Nevertheless, compared to the extensive study on the Zn-rich corner of the ternary system [2–8], little attention has been paid to the Al–Fe rich side and only one thermodynamic assessment of the whole Al–Zn–Fe system within 420–500 °C has been reported [9]. As a matter of fact, for the hot-dip 55 wt.% Al–Zn coatings, the most important part of the phase equilibrium occurs on the Al–Fe rich side at the temperature near 600 °C, because the zinc bath temperature in factory is around 600 °C. This work studied the phase equilibrium relationships on the Al–Fe rich side of the Al–Zn–Fe system.

The diffusion couple method has its advantages in the phase diagram determination since the super-cooling effect can be avoided in the directly phase diagram measurement [10,11]. The diffusion couple in this work was arranged in such a way that the Al–Zn alloy and Fe were used as the end-member alloys to investigate the phase equilibrium relationships of the Al–Fe rich side in the Al–Zn–Fe system. Combining our experimental results and the available data from the literature, the Al–Zn–Fe system was re-assessed through the CALPHAD approach. This optimized thermodynamic description would be expected to be useful in determining the phase equilibrium relationships in a wider temperature range for practical applications.

2. Review of the literature

2.1. Binary systems

The phase relationships of the Al–Zn system are relatively simple. It exhibits a miscibility gap in the Al-based face-centered cubic phase below 351.5 °C. No intermediate phase was found in this system. Mey [12] evaluated this system using Redlich–Kister polynomial description and the calculated results were in good agreement with all available experimental information. In present work, the thermodynamic data set was selected from the framework of COST Action 507 including the results reported by Mey [12].

The assessment of the Al–Fe phase diagram made by Seiersten [13] was a consistent description and has been accepted in the COST Action 507 project. Jacobs and Schmid-Fetzer [14] re-assessed the system and improved the representation of bcc(A2), bcc(B2) and fcc(Al) phases. More recently, Sundman et al. [15] have reassessed the Al–Fe system and mainly improved the modeling of the different ordered phases, B2, $D0_3$ and B32. Almost all available experimental and theoretical data for all phases in this system have been fitted within estimated uncertainties. The thermodynamic assessment by Sundman et al. [15] was accepted in this work.

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The binary Fe–Zn system has been thermodynamically modeled several times [9,16–18] based on experimental thermodynamic data and crystallographic results. Nakano et al. [9] have reported the modeling of the Fe–Zn system with the well-established thermodynamic models for the binary compounds. The updated thermodynamic description of the Fe–Zn system by Xiong et al. [19] showed not only a better agreement with the experiments but also sound physical meaning. Therefore, the thermodynamic description provided by Koester and Goedecke [20] was adopted in this work.

2.2. Al–Zn–Fe ternary system

The phase equilibria of the Al–Zn–Fe system have attracted much interest, particularly in the Zn rich corner around 450 °C due to very stringent quality control of galvanized steel sheets for automotive industry. Many studies primarily focused on experimental determinations [2–8] and CALPHAD modeling [9] of phase equilibria of the Zn rich corner in the temperature range of 450–480 °C. The isothermal section at 450 °C has been investigated several times. There is a substantial agreement between the earlier results of Koester and Goedecke [20] and Urednicek and Kirkaldy [21]. Recent significant results are due to Chen et al. [2], Perrot et al. [3] and Tang [4–6,8,22]. Chen et al. [2] did not consider Γ_1 phase in the 450 °C isothermal section. But Perrot et al. [3] reported two Γ phases, Γ_1 and Γ_2, after equilibration for 1000 h at 450 °C. Tang [5,6] labeled Γ_2 phase as Γ' and reported continuous solid solubility of Γ' in the isothermal section at 440 and 450 °C, respectively. The isothermal section by Perrot et al. is preferred because of its much longer annealing time. With respect to thermodynamic modeling, the whole Zn–Fe–Al system has been assessed by Nakano et al. [9] with the CALPHAD approach. However, this model was reliable only in the range of 420–480 °C because few experimental data were available outside this temperature range.

3. Experimental procedures

In order to investigate the phase relationships of the Al–Zn–Fe system on the Al rich side, the solid-state diffusion couples with end members of the Al–Zn alloy and Fe were prepared in this work. The starting materials used for the alloy samples were all high in purity: Al block (99.99 wt.%), Zn block (99.99 wt.%) and Fe block (99.99 wt.%). The composition of the Al–Zn master alloy was chosen as 95.0 at.% Al-5.0 at.% Zn. The temperature of annealing was chosen at 550 °C to avoid the presence of liquid. If the Al–Zn alloy melts, the liquid phase would flow away and the diffusion couple would be destroyed. The Al–Zn alloy (30 g) was re-melted at least three times to improve homogeneity in a medium frequency induction furnace under argon atmosphere with ultrahigh purity (Ar 99.999 vol.%). The melt temperature is about 650–700 °C. Then pure Fe block was put in the furnace. When the Al–Zn alloy was completely melted and held for a few seconds at this temperature, the power was switched off. The melted Al–Zn alloy flopped on the surface of the Fe block and was solidified in a water jacketed copper crucible. It should be noticed that the potential reaction between the liquid and Fe may happen at the interface during the preparation process. The fast diffusion of Fe to the liquid may lead to the formation of several acicular Fe_4Al_{13} phases in the substrate (Al) after solidification. However, the heating and cooling processes were very quick. The morphologies have no obvious difference from the diffusion morphologies (annealed at 300 °C) for 35 days and 52 days. Therefore, it can be assumed that the equilibrium was reached after long time annealing. Slices of cross-section 4 mm × 4 mm were cut from the enveloped sample, sealed in evacuated quartz capsules, and were then annealed in a tube type resistance furnace. Some of the diffusion couples were kept at 300 °C for 52 days and others were kept at 550 °C for 16 days. Finally, all the diffusion couples were quenched in water.

The inductively coupled plasma atomic emission spectrometry (ICP) was used to analyze the actual composition of Al–Zn master alloy. The composition was 96.2 at.% Al and 3.8 at.% Zn, where the Zn content was less than the nominal composition owing to volatilization of Zn during melting process. The morphologies and chemical compositions of various phases in the diffusion couples were measured by Quanta 200FEG SEM equipped with EDS (20 kV, live time is 30 s).

4. Results and discussion

4.1. The phase equilibria in $Al_{96.2}Zn_{3.8}$/Fe diffusion couple annealed at 300 °C

The diffusion zone morphologies observed in the $Al_{96.2}Zn_{3.8}$/Fe diffusion couple after annealing at 300 °C for 52 days are shown in Fig. 1. Fig. 1(b) is the enlarged view of those area marked by the square frame in Fig. 1(a). The left hand side shown in Fig. 1(a) indicates iron end-member, and the right hand side is the Al–Zn alloy with several dispersive acicular intermetallic compounds. The acicular intermetallic compounds may be formed by fast diffusion of Fe to the liquid during heating process. Some voids formed at the $Al_{96.2}Zn_{3.8}$/Fe interface were consistent with the Kirkendall effect, where different Fe and Al diffusion rates caused a net flux of vacancies on the $Al_{96.2}Zn_{3.8}$ substrate. The backscattered electron images (BSE) micrograph of the Fe–Al intermetallic layer near the $Al_{96.2}Zn_{3.8}$ substrate displays an atomic number contrast image, which reveals that the Fe–Al intermetallic layer possesses a gray outer layer about 4 μm in thickness and a major light gray inner layer, implying that the gray outer layer possesses a relatively lower iron content than the major light gray inner layer. The compositions of phases are confirmed by EDS and the concentration profile measured in the diffusion couple is also shown in Fig. 1(a). The EDS analysis showed that the composition of the acicular intermetallic compounds in the $Al_{96.2}Zn_{3.8}$ substrate, gray outer layer and light gray inner layer in the continuous Fe–Al intermetallic layer were Al-11.7 at.% Fe-2.1 at.% Zn, Al-17.1 at.% Fe-1.1 at.% Zn and Al-26.8 at.% Fe-1.5 at.% Zn, respectively. The compositions of the acicular intermetallic compound and the gray outer layer are located in the (Al) and Fe_4Al_{13} two-phase region. Both the compositions did not accord with any Al–Zn–Fe intermetallic compound, implying that the high aluminum content compounds could be attributed to the small phase area, in which case, the electron beam of SEM hit both the intermetallic compounds and the (Al) substrate during EDS analysis. The light gray inner layer is near to the compositions of Fe_2Al_5.

The morphology of dispersive acicular Fe_4Al_{13} distributed in an (Al) substrate indicates the existence of the two-phase equilibrium Fe_4Al_{13} + (Al). The interface between gray outer Fe_4Al_{13} layer and light gray inner Fe_2Al_5 layer indicates the phase equilibrium between Fe_4Al_{13} and Fe_2Al_5. Fig. 1(b) shows the enlarged image of the Fe_2Al_5 and the (Fe) interface, in which the bright thin layer is formed at the edge of the tongue-like Fe_2Al_5. Because the area is too small, the composition cannot be accurately determined by EDS analysis. The average composition of this region identified by EDS were Al-60.8 at.% Fe-0.5 at.% Zn and Al-45.0 at.% Fe-1.8 at.% Zn, which are consistent with the composition of bcc(Fe). However, the line scanning results show that a continuous change of composition was observed from the edge to the Fe_2Al_5 phase region. It may be formed due to some cooling stages. The phase relations in that region require further research. The results observed throughout the diffusion zone reveal the sequence of intermediate layers from $Al_{96.2}Zn_{3.8}$ to bcc(Fe): (Al) $\rightarrow$ Fe_4Al_{13} $\rightarrow$ Fe_2Al_5 $\rightarrow$ bcc(Fe) $\rightarrow$ (Fe).