Reactive Diffusion between Solid Fe and Liquid Zn at 723 K

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Reactive diffusion between solid Fe and liquid Zn was experimentally examined using Fe/Zn diffusion couples prepared by an immersion technique. Using this technique, a pure iron sheet was immersed in a molten pure Zn bath with a constant temperature of $T=723\text{ K}$ (450°C) for various times up to $t=7.2\times 10^3\text{ s}$ (2 h). The microstructure of the cross section of the Fe/Zn diffusion couple was observed by scanning electron microscopy, and the chemical composition of each phase was determined by electron probe microanalysis. Interface concentrations of Fe for the ζ -FeZn₁₃ and δ -FeZn₇₋₁₀ phases at the ζ/δ interface, $c^{\zeta\delta}$ and $c^{\delta\zeta}$, and for the liquid-Zn (L) phase at the ζ/L interface, $c^{\zeta\text{L}}$, determined from the diffusion couples were found to be extremely higher than the corresponding equilibrium values, especially in the early stage of $t<300\text{ s}$, and the difference gradually decreased during immersion. The deviations from the equilibrium values for the $c^{\zeta\delta}$ and $c^{\zeta\text{L}}$ were proportional to the interdiffusion flux across the ζ phase layer.

KEY WORDS: phase diagram; diffusion; interface; galvanizing.

1. Introduction

It is known that microstructural control of intermetallic compounds formed in the galvanizing and galvanealing processes of hot-immersion zinc coating is very important to improve corrosion resistance and mechanical strength of the coating layer of steels.¹⁾ Zinc melt including a small amount of Al is widely used for the coating material in steel for the body of automobiles. While the hot-dip zinc coating is applied to many kinds of practical steels, basic understanding for growth and microstructural evolution of intermediate phases, Γ -Fe₃Zn₁₀, Γ -Fe₁₁Zn₃₉, δ -FeZn₇₋₁₀ and ζ -FeZn₁₃ formed during the galvanizing and/or galvanealing processes is insufficient even in the Fe–Zn binary system.¹⁾ For instance, the growth behavior of these intermediate phases during galvanization is very complicated and still under discussion. The growth rate of an intermediate layer is sometimes interpreted by a power-law growth equation:

$$x=K\cdot t^n \dots\dots\dots(1)$$

where x is the thickness of the intermediate layer, K is the growth rate coefficient, t is the immersion time and n is the exponent. In a reaction under the parabolic law, the n value becomes equal to 0.5. However, the n values of the Γ and ζ layers formed at 450°C in the Fe/Zn binary diffusion couple are in the range between 0.1 and 0.4, while that of the δ phase is almost 0.5.^{2,3)} Furthermore, while the ζ phase layer dominates in the entire coating layer for a short immersion time, the dominant phase changes to the δ phase at $t>300\text{ s}$.^{1,3)} Recently, the present authors⁴⁾ reported that this change of the dominant phase in the diffusion layer occurs

drastically, not gradually, during the immersion time between 60 and 300 s due to the sudden appearance of the δ_p phase with a low Fe content below about 8 wt%, called the palisade delta phase,⁵⁾ and that the n values for both the δ and ζ layers are basically 0.5 each in the early stage of $t<60\text{ s}$ and in the late stage of $t>300\text{ s}$. **Figure 1** shows the typical microstructures of the diffusion couples in the early, middle and late stages and the change of layer thickness for the δ and ζ phases,⁴⁾ where the δ phase region existing from the initial stage is labeled δ_k so as to distinguish it from the δ_p phase. It is interesting to note that the δ/ζ interface becomes temporarily rough, namely, unstable, in the middle stage of $60<t<300\text{ s}$ when the δ_p phase starts to appear, as shown in Figs. 1(b) and 1(d), where the width of the “two-phase” region in the unstable interface is represented by hatching in the δ_p phase of Fig. 1(d). Thus, the appearance of the unstable interface and the drastic growth of the δ_p phase suggest the existence of some complicated and unknown characteristics even in the Fe–Zn binary diffusion couples.

In this study, the phase equilibria among the liquid Zn, ζ and δ phases appearing in diffusion couples obtained by immersing pure Fe into Zn melt were examined mainly by electron-probe microanalysis (EPMA) and the microstructural evolution focusing on the δ/ζ interface was evaluated.

2. Experimental Procedures

Iron sheet specimens with $0.4\times 5\times 40\text{ mm}^3$ were prepared by cold rolling to 85% reduction followed by mechanical- and chemical-polishing, the starting material being 99.95 wt% electrolytic pure iron. Electrolytic pure

Fig. 1. Microstructures of diffusion zone formed in Fe/Zn diffusion couples at 450°C for (a) 30 s, (b) 60 s and (c) 1 200 s, and (d) the time dependence of the layer thickness for the δ and ζ phases.⁴⁾ The unstable (namely, rough) ζ/δ interface shown typically in (b) appears in the immersion time region from about 60 to 300 s, where the width of the $\delta + \zeta$ two-phase region is shown by hatching for the δ_p as exhibited in (d).

zinc flakes (99.99 wt%) and an iron sheet specimen were sealed in a quartz tube with a diameter of 10 mm and a length of 500 mm. The tube was backfilled with argon gas, the zinc flakes being held at an end of the tube and the iron sheet being completely separated from the zinc flakes by a magnetic force applied from outside the tube with a permanent magnet. The end of the quartz tube with the zinc flakes was inserted into a vertical electric furnace with a constant temperature of 450°C, and then the iron sheet was immediately inserted into the zinc melt by removing the magnet from the tube. By this method, the iron sheet can be heated to a target temperature for less than a couple of seconds and oxidation of the iron surface layer can be prevented. The immersion starting time, $t=0$, is defined as the moment when the iron sheet was inserted into the zinc melt. After an appropriate duration, the Zn melt including the Fe sheet was quenched in ice water without breaking the quartz tube, the quenching being carefully performed to suppress mechanical convection of the Zn melt.

The obtained solid Fe/liquid Zn diffusion couples were cut in a section vertical to the iron sheet buried in the Zn and mechanically polished and then embedded in resin. For the cross-section of the Fe/Zn diffusion couple, the microstructure of the reacted zone was observed by optical microscopy (OM) and scanning electron microscopy with an electron backscattering image mode (SEM-EBS), where a 5 vol% nital was used as an etchant for the OM observation. The composition of the diffusion zone was analyzed by electron probe microanalysis (EPMA).

3. Results and Discussion

3.1. Concentration Profiles

Figure 2 shows some typical Fe concentration profiles of Fe in the vicinity of the diffusion zone of the diffusion cou-

ples immersed for durations ranging from the early to late stages. It is seen that the shape of the concentration profile gradually changes with increasing immersion time. Generally, in the diffusion couple examination, the interface concentration can be determined by extrapolation of a profile to an interface as indicated by the open circles located on the interfaces in the profiles of Fig. 2. This interface concentration obtained by this technique usually coincides with the equilibrium composition determined using conventional multi-phase alloy specimens, and the diffusion couple method is one effective experimental method used for determination of the phase equilibrium concentrations in alloys. **Figure 3** shows the interface Fe concentrations among the δ , ζ and L phases determined from all the diffusion profiles. It is very interesting to note that the interface concentrations for the δ and ζ phases at the δ/ζ interface, $c^{\delta\zeta}$ and $c^{\zeta\delta}$, and for the L phase at the ζ/L interface, $c^{L\zeta}$, are extremely large in the early stage, decreasing and converging to the values close to the equilibrium values in the assessed phase diagram,⁶⁾ while that for the ζ phase at the ζ/L interface, $c^{\zeta L}$, is almost constant throughout the immersion time. This result means that the interface concentrations determined by the present diffusion couples in the early stage are not in stable conditions, but in pseudo-equilibrium conditions. Such change of the interface concentrations seems to be related to the presence of a large amount of flux crossing through the interface in the early stage. The interdiffusion flux is obtained by Fick's first law:

$$\tilde{J} = -\tilde{D} \frac{\partial c}{\partial x} \dots\dots\dots (2)$$

where $\tilde{D}$ is the interdiffusion coefficient, c is the concentration, x is the distance and $\partial c/\partial x$ corresponds to the gradient of the concentration profile. Interdiffusion flux for every phase appearing in the diffusion zone can be evalu-

Fig. 2. Concentration profiles in the diffusion zone formed in Fe/Zn diffusion couples immersed at 450°C for (a) 10 s, (b) 60 s, (c) 600 s and (d) 7200 s.

Fig. 3. Interface concentrations of Fe among the δ , ζ and liquid Zn phases as a function of the immersion time, where the equilibrium concentrations were represented using the data for 7200 s.

Fig. 4. Interface concentrations of Fe for the $\delta/\delta+\zeta$ and $\zeta+L/L$ interfaces against the interdiffusion flux in the ζ phase layer.

ated by Fick's law using the experimental concentration profile. This method, however, is not available for the liquid phase because of convection in the liquid phase. In the present study, the interdiffusion flux in the ζ phase, which is easily evaluated, was chosen to consider that in the diffusion zone. The interdiffusion flux in the ζ phase layer can be simply evaluated based on the thickness, w_ζ , and solubility range, $\Delta c_\zeta (=c^{\zeta\delta}-c^{L\zeta})$, of the ζ phase layer obtained from the concentration profile using the modified relation of Eq. (2):

$$\tilde{J}_\zeta = -\tilde{D}_\zeta \frac{\partial c}{\partial x} \approx -\tilde{D}_\zeta \frac{\Delta c_\zeta}{w_\zeta} \dots\dots\dots (3)$$

where $\tilde{D}_\zeta$ is the interdiffusion coefficient of the ζ phase. In Fig. 4, the $c^{\delta\delta}$ and $c^{L\zeta}$, which have been exhibited in Fig. 3, are plotted again as a function of the interdiffusion flux in the ζ layer evaluated by Eq. (3), where the interdiffusion coefficient of ζ at 450°C ($\tilde{D}_\zeta = 1.4 \times 10^{-12} \text{ m}^2/\text{s}$) was estimated from the diffusion parameters, $D_0 = 4.0 \times 10^{-7} \text{ m}^2/\text{s}$ and

$Q = -75.3 \text{ kJ/mol}$, reported by Shimozaki *et al.*,⁷⁾ and the Δc_ζ was converted from the experimental mass fraction data using the density (7.15 Mg/m^3).⁸⁾ It can be seen that both $c^{\delta\delta}$ and $c^{L\zeta}$ are proportional to the amount of interdiffusion flux in the ζ phase layer and that the data obtained in the specimens immersed for $t > 2400 \text{ s}$ at least can be considered as being in the stable equilibrium conditions. This result suggests that the large deviations from the equilibrium concentrations are due to the presence of a large amount of interdiffusion flux crossing through the δ/ζ and ζ/L interfaces. Consequently, the shift of the interface concentrations due to the change of the interdiffusion flux should be taken into account for microstructural control in the hot-immersed zinc coating which is usually achieved in a very short immersion time of $t < 10 \text{ s}$. The reason for such a large shift of the $c^{\delta\delta}$, $c^{\zeta\delta}$ and $c^{L\zeta}$ is not clear at present. Some thermodynamic consideration to evaluate the non-equilibrium conditions, for instance, as performed by Speer *et al.*,⁹⁾ may be required for understanding this phenomenon. While the convection occurring in the zinc melt may

Table 1. Stable phase equilibrium concentrations obtained from the diffusion couple at 7 200 s.

	δ in Γ/δ , $c_e^{\delta/\Gamma}$	δ in δ/ζ , $c_e^{\delta/\zeta}$	ζ in δ/ζ , $c_e^{\zeta/\delta}$	ζ in ζ/L , $c_e^{\zeta/L}$	L in ζ/L , $c_e^{L/\zeta}$
wt% Fe	11.6	6.8	6.0	5.8	0.25

Fig. 5. (a) Concentration profile of Fe and (b) backscattering electron image obtained from the Fe/Zn diffusion couples immersed at 450°C for 7 200 s and 2 400 s, respectively. A pseudo-phase boundary (PPB), namely, a low diffusivity zone (LDZ), is shown in the δ phase region.

affect the shape of concentration profile of the liquid phase, a thin layer directly in contact with the solid phase is in convection-free conditions at least and the data extrapolated from the concentration profile are available to determine the interface concentration.

It is clear from the relation between the shift of interface concentrations and the interdiffusion flux in the ζ phase shown in Fig. 4 that since the interdiffusion fluxes evaluated in the diffusion couples at $t > 2\,400$ s are very small, their interface concentrations should be almost equal to the equilibrium ones in the absence of interdiffusion flux. Therefore, the phase equilibrium concentrations among the δ , ζ and liquid phases were determined using the profile at $t = 7\,200$ s shown in Fig. 5(a). In this profile, the concentration step detected in the range from 8.0 to 10.0 wt% Fe of the δ phase region is the pseudo-phase boundary (PPB), which appears as only a diffuse contrast in the SEM-EBS image, as indicated by the white broken line in Fig. 5(b). This PPB is considered to be formed by a drastic decline of the interdiffusivity in this concentration region of the δ phase¹⁰⁾; this concentration region with low diffusivity is called a low diffusivity zone (LDZ) hereafter. The equilibrium data determined from this concentration profile are listed in Table 1 and plotted in Fig. 6, where the phase dia-

Fig. 6. Phase equilibrium data obtained from the diffusion couple of 7 200 s and the Fe-Zn binary phase diagram.⁴⁾ **Fig. 7.** Schematic illustration explaining the formation mechanism of stable interface in binary diffusion couple.

gram modified by Kainuma and Ishida⁴⁾ on the basis of that evaluated by Burton and Perrot⁶⁾ is shown. The obtained data except the solubility of the liquid Zn phase were in good agreement with the previous phase diagram. The determined solubility (0.25 wt% Fe) is about ten times larger than that shown by the evaluated phase diagram (less than 0.03 wt% Fe). Recently, Tang¹¹⁾ reported that the Fe solubility in zinc melt for alloy specimens is about 0.03 wt%, which is almost the same as that of the previous report. The reason for the mismatch with our result is unclear.

3.2. Formation Mechanism of the δ/ζ Unstable Interface

It is known that an unstable phase interface with a rough

microstructure is not ideally formed in binary diffusion couples under equilibrium conditions. This is explained by the interfacial energy, namely, the Gibbs–Thomson effect, and by the constraint of the interface concentrations due to the local equilibrium. The migration velocity $v_{\delta/\zeta}$ of the δ/ζ phase interface is given by the following equation:

$$v_{\delta/\zeta} = \frac{\tilde{J}_{\delta} - \tilde{J}_{\zeta}}{\Delta c_{\delta/\zeta}} \dots\dots\dots(4)$$

where $\tilde{J}_{\delta}$ and $\tilde{J}_{\zeta}$ are the interdiffusion fluxes of the δ and ζ phases at the δ/ζ interface, respectively, and $\Delta c_{\delta/\zeta} = c^{\delta\zeta} - c^{\zeta\delta}$. Instability of an interface is sometimes discussed with the scheme using promotion or disappearance of a microstructural fluctuation of the interface given for an initial condition as illustrated in **Fig. 7**. In a usual binary diffusion couple under the local equilibrium conditions, the interface concentrations for the two phases in the unstable interface region are basically invariable. Furthermore, as demonstrated in **Fig. 7**, since the Gibbs–Thomson effect yields a slight change of the local equilibrium conditions at the tip in the A–A' section and at the bay in the B–B' section of the unstable interface, the slope of the concentration profile in both the phases becomes positive and the direction of the interdiffusion fluxes, $\tilde{J}_{\delta}^{A-A'}$ and $\tilde{J}_{\zeta}^{B-B'}$, would be opposite to the normal direction from the Fe sheet to the liquid Zn. Consequently, the interfaces in the sections A–A' and B–B' migrate towards opposite directions each other due to the flux balance expressed in Eq. (4), and the unstable interface finally disappears. This feedback mechanism, which always makes the interface stable, may be valid in the δ/ζ interface of the present diffusion couples except those in the middle stage of $60 < t < 300$ s.

On the other hand, in the first half of the middle stage where formation of the unstable interface starts as shown in **Fig. 1(b)**, the difference of the migration rates of the δ/ζ interface at the tip and bay parts has to increase with immersion time and the amplitude of the interface roughness must increase as indicated by arrows in **Fig. 8**. In a binary system, although such a phenomenon does not usually occur under the local equilibrium conditions, if the interface concentrations $c^{\delta\zeta}$ and $c^{\zeta\delta}$ depend on the amount of the interdiffusion flux crossing through the interface as discussed in the previous section, the feedback mechanism for keeping the interface stable may be affected. Furthermore, it is worthy noting that the $c^{\delta\zeta}$ at around $t=100$ s has a value of about 8 wt% Fe, which is the border of LDZ in the δ phase, as shown in **Fig. 3**. That is, at around $t=100$ s the border concentration of the LDZ is located near the δ/ζ interface as shown in **Fig. 8**, and the diffusivity of the δ phase may drastically change just in the two-phase region. Conse-

Fig. 8. Schematic illustration showing the formation of unstable interface.

quently, the mass balance of solute at the δ/ζ interface may be strongly affected and the feedback mechanism may be temporarily disabled. Further investigations will be required to confirm the origin of the unstable interface.

4. Conclusions

Phase equilibria and reaction diffusion between solid Fe and liquid Zn were investigated using the diffusion couples fabricated by immersing a pure iron sheet in a pure zinc bath at 450°C. The results obtained are as follows:

(1) In the early stage of immersion time, $t < 300$ s, the interface concentrations of Fe for the δ and ζ phases at the ζ/δ interface, $c^{\delta\zeta}$ and $c^{\zeta\delta}$, and for the L phase at the ζ/L interface, $c^{L\zeta}$, determined by the diffusion couples show extremely high iron contents and those values gradually decrease with increasing immersion time. Since the deviations from the equilibrium values for the $c^{\zeta\delta}$ and $c^{L\zeta}$ are proportional to the interdiffusion flux in the ζ phase layer, this relationship may be brought about by the presence of a large amount of interdiffusion flux crossing through the interfaces.

(2) Stable phase equilibrium concentrations among the Γ , δ , ζ , and L phases were estimated from the diffusion couple at $t=7200$ s. Except for the solubility of the liquid phase, the obtained results are in good agreement with the previous data.

(3) The formation of unstable morphology in the ζ/δ interface, which was reported by Kainuma and Ishida, was examined based on the concepts of the Gibbs–Thomson effect and the local equilibrium. The origin of the unstable interface may be related to the remarkable immersion time dependence on the $c^{\delta\zeta}$ and $c^{\zeta\delta}$ and the drastic change of interdiffusivity of the δ phase in the vicinity of 8.0 at% Fe.

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