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LETTER

Growth kinetics of intermediate phase layers in an early stage of hot dip galvanizing at 450 °C

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The hot dip galvanizing technique has been widely used as a surface treatment to prevent corrosion of steels [1]. Figure 1 shows the Fe–Zn binary phase diagram assessed by Burton and Perrot [2]. Four intermediate phases, ζ ($FeZn_{13}$), δ ($FeZn_{7-10}$), Γ_1 ($Fe_{11}Zn_{39}$), and Γ (Fe_3Zn_{10}), in the Zn-rich side are shown. After an adequate diffusion time below 530 °C, the formation of all these intermediate phase layers are predicted in the diffusion zone of the solid iron and liquid zinc couple (melting temperature of Zn is 419.6 °C). However, from the viewpoint of surface technology, the thick growth of intermediate phase layers sometimes leads to peeling off the layers because of their brittleness. Such problems were resolved through technical developments leading to industrial practices for galvanizing sheet steels. For example, the addition of small amount of aluminum to liquid zinc is effective in retarding the growth of intermediate layers. Recently, it has been recognized that the composition of the top layer is a key to plastic deformation of sheet steel for automobiles, because the ζ layer is soft and easily adheres to a metal pattern for plastic deformation whereas the Γ and Γ_1 layers are hard and brittle. As a result, the δ phase is suitable to the top layer of sheet steel for plastic deformation. To obtain the suitable surface composition of sheet steel, an annealing treatment with appropriate temperature and time has been used after galvanizing [3].

The growth kinetics of intermediate phase layers in the diffusion reaction zone between solid iron and liquid zinc has been studied by many research groups [1]. Furthermore, the difference in the growth kinetics of the layers in solid/liquid couples and solid/solid couples of iron and zinc has been studied [4, 5]. However, the growth kinetics of the layers in an early stage has not been addressed [4, 5]. The thickness d of the intermediate phase layer formed during reaction diffusion is represented by

$$d = k\,t^{n} \tag{1}$$

where k is the constant, t the diffusion time, n the index. For the layer growth which obeys the parabolic law, n has a value of 0.5 [6]. From the theoretical view points of diffusion reaction, the various phases will form when the local concentration of solute reaches the appropriate level for the nucleation of the phase. However, it has been generally observed that in the solid metal couple the formation of all intermediate phases shown in the phase diagram starts simultaneously at the beginning of the diffusion reaction and the growth of the phase layers obeys the parabolic law with $n = 0.5$, although an incubation time for the growth is often observed [6]. The composition of the intermediate phase is consistent with that of the phase diagram. Therefore, the diffusion reaction for the solid metal couple is often used to determine the phase diagram [6]. However, various values of n for the growth of intermediate phase layers formed in the solid iron and liquid zinc couple have

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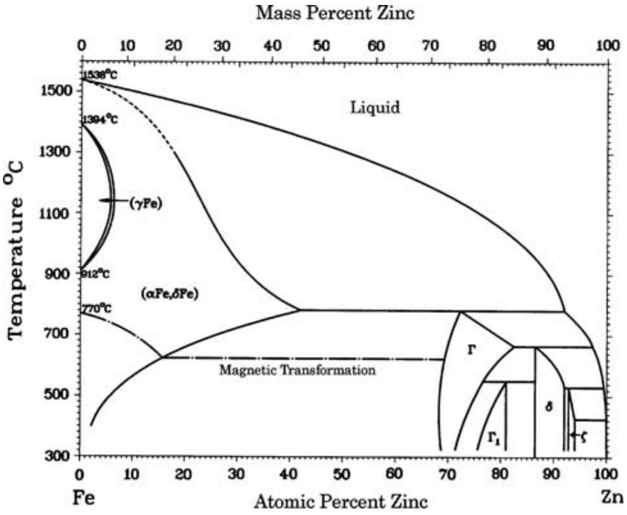

Fig. 1 Phase diagram of the Fe–Zn system

been obtained [1]. Wakamatsu and Onishi [4] have summarized the values of n obtained by many research groups including them in the temperature ranges from 430 °C to 490 °C and concluded that $n = 0.4 \sim 0.5$ for total thickness of layers, $n = 0.2 \sim 0.25$ for (Γ plus Γ_1) layers, $n = 0.58 \sim 0.64$ for δ layer, and $n = 0.2 \sim 0.3$ for ζ layer. From the metallographic observations, the δ layer has been recognized to consist of the δ_k and δ_p layers [4]. On the other hand, Jordan and Marder [7] have obtained $n = 0.31 \sim 0.37$ for the growth of the total layer at 450 °C which is a typical temperature of hot dip galvanizing in industry.

Recently, Kainuma and Ishida [5] investigated the diffusion reaction between solid iron and liquid zinc, and also between solid iron and solid zinc. They observed the thickness of intermediate phase layers formed in the solid iron and liquid zinc couple at 450 °C from 10 to 1200 s. At 10 s only ζ layer appeared. The δ_k and δ_p layers appeared after 30 and 60 s, respectively. Finally, the Γ layer appeared after 180 s. The magnitude of thickness is in the order: $\zeta \gg \delta_p > \delta_k \gg \Gamma$. The Γ_1 layer could not be distinguished from the Γ layer. According to their study [5], the growth kinetics of the layers were divided into two regions at about 100 s, although all the layers grew with $n = 0.5$. The value of k for the layer ζ after 100 s was less than that before 100 s. This was somewhat strange diffusion reaction behavior. Therefore, in the present work, the early stage layer growth of intermediate phases in the solid iron and liquid zinc diffusion couple at 450 °C has been examined.

A pure iron specimen, 0.35 mm in thickness, was dipped into molten pure zinc in a pure argon gas atmosphere. After a dipping for a period of 30–600 s, the specimen was removed and cooled rapidly. The cross section of the specimen was examined by optical microscopy and scanning electron microscopy (SEM). The concentration of the diffusion zone was measured using an electron probe microanalyzer (EPMA).

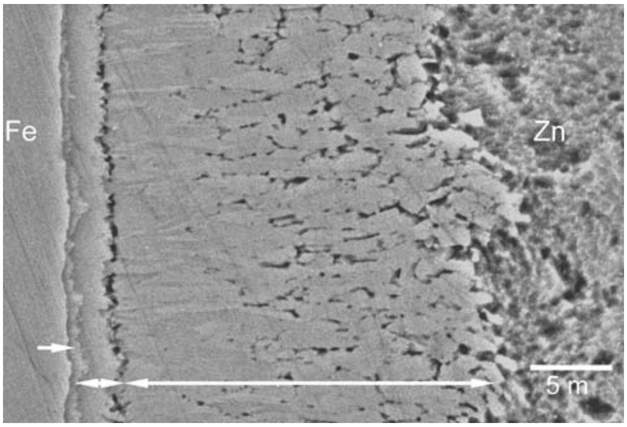

Fig. 2 Diffusion zone in the solid iron and liquid zinc couple dipped at 450 °C for 300 s

Figure 2 shows the diffusion zone in the solid iron and liquid zinc couple at 450 °C for 300 s. Three layers of the ζ, δ, and Γ phases are observed, where most of the diffusion zone is occupied by the ζ layer. Figure 3 shows the layer growth of intermediate phases formed in the diffusion zone. At 30 s, three layers of ζ, δ, and Γ are formed, although the thicknesses are in the order: $\zeta \gg \delta \gg \Gamma$. In the present experiments, the Γ_1 layer could not be distinguished from the Γ layer, and the total layers of δ_p and δ_k are denoted as the δ layer. The growth of three layers is very slow until about 150 s. Since both the vertical and horizontal axes in Fig. 3 are represented by the logarithmic scale, the slope indicates directly the value of n in equation 1. From the beginning to 150 s, n for all the three layers can be recognized as 0.25. After 200 s, n increases to 0.5 for all the three layers. In particular, for the growth of the δ layer a visible transition at about 200 s is observed.

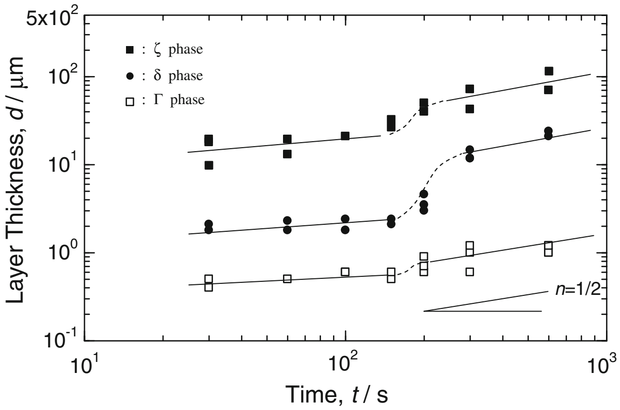

Fig. 3 Layer growth of intermediate phases formed in the diffusion zone at 450 °C

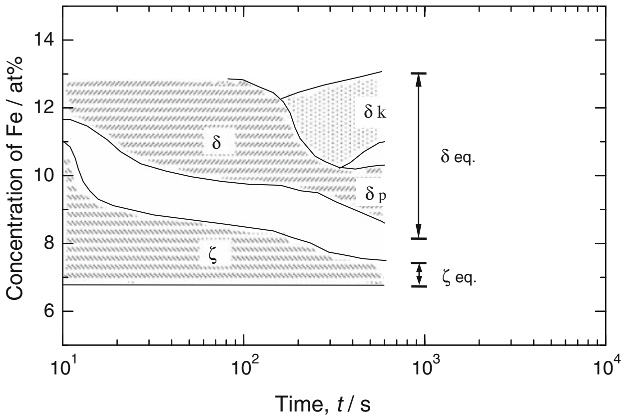

Fig. 4 Time dependence of Fe concentration at the phase boundaries in the diffusion zone at 460 °C, quoted from a paper of Wakamatsu and Onishi. ζ_{eq} and δ_{eq} are the concentrations of Fe in the ζ and δ phases shown in the equilibrium phase diagram

To understand this particular growth behavior shown in Fig. 3, other information on the variation with diffusion time is certainly useful. Figure 4 shows the time dependence of iron concentration observed by Wakamatsu and Onishi [4] for the intermediate phases formed at 460 °C. Wakamatsu and Onishi [4] have observed that at the beginning of 5 s the ζ layer already appears and the concentration of iron in the ζ phase is 6.7 $\sim$ 11.5 at% which is strongly shifted to the iron-rich side from the equilibrium concentration of 6.5 $\sim$ 7.2 at% [2]. As shown in Fig. 4, the concentration of iron in the ζ phase at the boundary with the ($\zeta + \delta$) phases decreases markedly with diffusion time and approaches the equilibrium value at about 300 s. Non-equilibrium behavior of the concentration of the δ phase is also shown in Fig. 4. These facts suggest that the formation and growth of the intermediate phases in the early stage of the diffusion between solid iron and liquid zinc starts under non-equilibrium conditions and gradually approaches the ordinary behavior with diffusion time. This is also true for the present experiment, although the temperature of the present experiments was 450 °C which was 10 °C lower than that of Wakamatsu and Onishi [4].

The value of $n = 1/4$ observed until about 150 s in Fig. 3 means that the layer growth is controlled by a mechanism of grain boundary diffusion [8]. At the beginning of the diffusion between solid iron and liquid zinc, iron dissolves into liquid zinc and immediately intermediate phase layers are formed at the phase boundary, although these layers are very thin with non-equilibrium compositions. This is a particular phenomenon of the diffusion reaction between solid metal and liquid metal, which is not the case for the solid metal diffusion couple. In the present experiment, the temperature of 450 °C is too low for the solid intermediate phase layers to grow via the volume diffusion mechanism. The diffusion reaction proceeds via the grain boundaries till about 150 s where the concentration of the phase boundary approaches the equilibrium one. Then, the chemical potential of each phase approaches the equilibrium value, and the driving force for the growth of each phase layer attains the ordinary value as in the case of the solid metal diffusion couple. Therefore, after 200 s the intermediate phase layers grow via the volume diffusion mechanism with $n = 0.5$.

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References

1. Marder AR (2000) Prog Mater Sci 45:191. doi:10.1016/S0079-6425(98)00006-1
2. Burton BP, Perrot P (1993) In: Okamoto H (ed) Phase diagrams of binary iron alloys. ASM International, Materials Park, Ohio, p 459
3. Sagiyama M (2001) Jpn Surf Sci 22:86. doi:10.1380/jsssj.22.86
4. Wakamatsu Y, Onishi M (1978) Tetsu-to-Hagané 64:2215
5. Kainuma R, Ishida K (2005) Tetsu-to-Hagané 91:349
6. Philibert J (1991) Atom movements diffusion and mass transport in solids, Les Editions de Physique, p 421
7. Jordan CE, Marder AR (1997) J Mater Sci 32:5593. doi:10.1023/A:1018680625668
8. Corcoran YL, King AH (1990) J Electron Mater 19:1177. doi:10.1007/BF02673330