Formation and Growth Kinetics of Intermediate Phases in Fe–Zn Diffusion Couples*

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The iron-electrodeposited zinc diffusion couples were annealed at temperatures from 240 to 410°C. In the diffusion zone, intermediate phases appear in the order of ζ , δ_1 and Γ phases. Kirkendall markers exist always at the interface between the ζ and zinc phases. This pronounced Kirkendall effect means that there is a one-sided diffusion of zinc atoms by a vacancy mechanism.

The compact and palisade δ_1 layers and the thin double layer between the compact δ_1 and iron phases were observed in the same manner as in the case of hot dip galvanizing. It appears that the existence of the thin double layer causes the formation of the compact δ_1 . For the ζ phase layer, the growth rate was decreased by the formation of the δ_1 layer and by the subsequent rapid growth of the δ_1 which occurred twice. From the results of this experiment growth kinetics of the intermediate phases in hot dip galvanizing were discussed.

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I. Introduction

It is known that three intermediate phases ζ , δ_1 and Γ are formed by ordinary hot dip galvanizing at temperatures from 440 to 460°C. In 1970 Horstmann⁽¹⁾ summarized hot dip galvanizing reactions reported in more than two hundred papers in the past four decades and has tabulated the values of the exponents “ n ” when the thickness of the intermediate phase layers (W) is represented as a function of time (t) according to the form

$$W = kt^n$$

where k is a constant. In his table the exponents for the δ_1 and the total thickness of each intermediate phase layer are evaluated to be around 0.5 with a few exceptions, but those for the ζ and Γ phases are smaller than 0.5. It is well established that if the growth of intermediate phases is controlled by diffusion, the exponent should be 0.5. Hence, it has been suggested that the diffusion is not the rate-determining process for a certain or all intermediate phase growth in hot dip galvanizing⁽²⁾⁽³⁾.

In the equilibrium diagram of the Fe–Zn binary system⁽⁴⁾ as shown in Fig. 1, the ζ , δ_1 , Γ phases are stable in the range of 530 to 200°C and the boundary concentration of each phase, except for the ζ , is at least kept constant in the same temperature range. For interpretation of the phase growth in the galvanizing, therefore, the knowledge of the reaction diffusion of iron with solid zinc is very useful. In a diffusion zone between two pure metals whose equilibrium phase diagram has some intermediate phases, all phases are not always formed at the same time⁽⁵⁾. If the phase

Fig. 1 Equilibrium phase diagram of the Fe–Zn binary system.

which appears with a delay has a larger diffusivity, the phase formed previously is consumed, decreasing its width, and consequently the growth rate does not obey the parabolic law. From this point of view, the formation and growth of the intermediate phases were investigated on Fe–solid Zn diffusion couples and the phase growth kinetics in the galvanizing of iron was discussed on the basis of the observations in this work.

II. Experimental Procedures

Iron specimens containing 0.004% C, 0.04% Mn, 0.010% Si, 0.002% P, 0.013% S, 0.009% Cu, 0.01% O and 0.004% N were used as the diffusion couple halves. As previously reported⁽⁶⁾, the growth of the intermediate phases in Fe–Zn diffusion couples does not depend on the grain size of iron specimens. Consequently, fine grain iron specimens of about 30 μ grain diameter were used in this experiment, and the disks of 10 mm diameter and 2 mm thickness were machined from the iron sheet. The surfaces of the disks were polished metallographically and then electroplated with zinc. The electrolyte of 1 l contains 360g ZnSO₄, 30g NH₄Cl and 15g NaC₂H₃O₂ · 3H₂O. With use of a

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Pt anode, the Zn deposited layer of 700μ thickness was obtained by the electroplating with a current density of $2A/dm^2$ at $25^\circ C$ for 24 hr. In order to remove the hydrogen absorbed during the electroplating the electroplated iron specimens were annealed in a vacuum of 5×10^{-6} mmHg at $150^\circ C$ for 3 hr. The Fe-electrodeposited Zn couples thus obtained were mainly used in this experiment. Another type of couples consisting of iron and zinc disks was also used. In this case the surfaces of the two metals were joined together at room temperature and kept in contact with a clamp.

Molybdenum powder of about 4μ diameter was employed as markers for the detection of Kirkendall effect in these two types of couples. All of the couples were clamped always during annealing, because the couples without clamps surely separated at the interfaces between the intermediate phases and the zinc couple halves. Annealing was carried out in argon at a temperature between 240 and $410^\circ C$ which was controlled within $\pm 1^\circ C$. An electron probe micro-analyzer (JXA-5) was used to determine the concentration penetration curves by counting either the zinc or iron K_α radiation. An accelerating voltage of 25 kV was employed with a sample current of $0.03\mu A$ in pure zinc. The conversion of the intensity into chemical composition was made using the calibration curve obtained from standard specimens.

III. Experimental Results

1. Formation sequences of the intermediate phases

In the couples consisting of iron and zinc disks, an intermediate phase in a conical shape appeared at the interface between the iron and the zinc on the early stage of annealing. The conical crystals are analogous to the cones which were observed by Rig⁽⁷⁾ and remarked subsequently by Seith⁽⁸⁾. By further anneal-

Photo. 1 Photomicrograph of the conical ζ phase formed at the interface between the iron and zinc plates. Annealed at $300^\circ C$ for 3 hr. ($\times 800 \times 9/10$)

ing, the conical crystals joined together as shown in Photo. 1 and then developed into a layer.

In the Fe-electrodeposited Zn couples, a stratiform intermediate phase appeared immediately after annealing. The formation of either the conical or the stratiform intermediate phase seems to depend on the condition in which both couple halves come into contact. Because the Fe-electrodeposited Zn couples are more appropriate to investigate the formation kinetics of the intermediate phases than the couples consisting of iron and zinc disks, we will describe the formation and growth of the intermediate phase for the Fe-electrodeposited Zn diffusion couples annealed isothermally.

Photograph 2 shows the development of the intermediate phases in the Fe-electrodeposited Zn couples annealed at $300^\circ C$. In each photomicrograph, the upper and lower parts correspond to the zinc and iron couple halves, respectively. In Photo. 2(a) a single intermediate phase layer was observed between the zinc and the iron. As shown in Photo. 2(b), the second intermediate phase particles were detected in the Fe

Photo. 2 Photomicrographs of Fe-electrodeposited Zn diffusion couples annealed at $300^\circ C$ for various periods of time. (a) 1 hr, $\times 800 \times 2/3$ (b) 5 hr, $\times 800 \times 2/3$ (c) 9 hr, $\times 600 \times 2/3$ (d) 16 hr, $\times 400 \times 2/3$ (e) 25 hr, $\times 250 \times 2/3$ (f) 40 hr, $\times 250 \times 2/3$

side of the phase layer at first formed and then developed to a layer shown in Photo. 2(d) by way of that in Photo. 2(c). From those stages the intermediate phases were observed as three-phase layers. Figure 2 shows the line analysis curves obtained by electron probe microanalysis from the iron to the zinc side; the analysis curves for the iron and zinc regions were omitted, because the α solid solution of zinc in iron and the η solid solution of iron in zinc were not detected at all.

The curve A shows the line analysis of the single intermediate phase layer as presented in Photo. 2(a). It is clear that the intermediate phase first formed varies continuously in the concentration from the ζ to the δ_1 composition. In the mixed powder compacts consisting of iron and zinc powders, the ζ phase was first formed as reported in a previous paper⁽⁹⁾. Because such a phase has the same concentration range as in the intermediate phase in Photo. 2(a), the intermediate phase first formed in the Fe-Zn couple can be regarded as the ζ . The B and C curves were obtained by E.P.M.A. analysis of the single phase and two-phase regions in Photo. 2(c) respectively. Although they show a continuous change in concentration in the single phase region, the C curve has a concentration jump dividing into ζ and δ_1 phases. It appears that there are three intermediate phases in Photo. 2(e), but D curve obtained from the same couple as Photo. 2(e) does not show the existence of the Γ phase. The Γ phase is first detected in the E curve obtained from a couple shown in Photo. 2(f). Figure 3 shows the relation between iron concentration and annealing time at 300°C for the intermediate phases. For the shortest annealing time, the ζ phase has a wide composition range which deviates from the equilibrium composition to the iron-rich side. Such a nonequilibrium phase layer is divided into two layers in the zinc and iron sides by the formation of the stratiform δ_1 phase. The former has the equilibrium concentra-

Fig. 2 E.P.M.A. line analysis for Fe-electrodeposited Zn diffusion couples annealed at 300°C for various periods of time. A: 1 hr, B and C: 9 hr, D: 25 hr, E: 40 hr.

Fig. 3 Time dependence of Fe concentration in the ζ , δ_1 and Γ intermediate phase layers formed in Fe-electrodeposited Zn diffusion couples annealed at 300°C.

tion, and the latter denoted by ζ' in Fig. 3 for convenience has a higher Fe concentration than that of the δ_1 phase layer. Further annealing resulted in disappearance of the ζ' phase, replaced by the Γ phase.

2. Growth of the intermediate phases

Figure 4 shows the relation between the layer width of the ζ , δ_1 , Γ as well as the total width of the three intermediate phases and the square root of annealing time at 300°C. The ζ phase existing as a single intermediate phase layer in an initial stage of the anneal grows according to the parabolic law. Diffusion coefficients in

Fig. 4 Width of the ζ , δ_1 and Γ phase layers and of the total phase layers vs square root of annealing time. The Fe-electrodeposited Zn diffusion couples were annealed at 300°C.

the ζ at this stage, therefore, can be obtained in the limited cases where the compositions at both interfaces of the ζ phase layer are approximately constant, respectively, as reported in a previous paper⁽¹⁰⁾. The appearance of the δ_1 and Γ phases affects the total width and the width of each intermediate phase which has existed prior to the δ_1 and Γ formation. The time of appearance of the δ_1 and Γ phases can be roughly estimated by extrapolating the growth curves of each phase to the abscissa.

Figure 5 shows the isothermal growth of the diffusion layers at 340°C, in which the δ_1 phase begins to grow rapidly after about 8 hr annealing. This causes an increase of the growth rate for the total width and a decrease of the growth rate for the ζ layer. By annealing at 380°C, a compact⁽²⁾ or adherent⁽¹¹⁾ δ_1 that is well established by the studies on the galvanizing

Fig. 5 Width of the ζ , δ_1 and Γ phase layers and of the total phase layers vs square root of annealing time. The Fe-electrodeposited Zn diffusion couples were annealed at 340°C.

Fig. 6 Width of the ζ , Γ , compact δ_1 , total δ_1 and of the total phase layers vs square root of annealing time. The Fe-electrodeposited Zn diffusion couples were annealed at 380°C.

Photo. 3 Photomicrographs of Fe-electrodeposited Zn diffusion couples annealed at 380°C for various periods of time. (a) 4 hr, $\times 400 \times 2/3$ (b) 9 hr, $\times 250 \times 2/3$ (c) 16 hr, $\times 200 \times 2/3$

reaction appears at the interface between the δ_1 and Γ phases after about 7-hr annealing as shown in Fig. 6.

Photograph 3 shows a series of photomicrographs for the diffusion layers in the couples annealed at 380°C. In Photo. 3(a) small particles were observed at the interface between δ_1 and Γ phases; they joined together to develop into a layer as shown in Photo. 3(c). Such a new layer was also detected by many investigators on galvanizing, and the layer together with the Γ has been called the double Γ layer by Bablik et al.⁽¹²⁾, and the thin double layer by Harshmann⁽²⁾. The formation of the compact δ_1 layers which are shown in Photo. 3(b) and (c) may possibly start after the formation of the thin double layer.

Figure 7 shows the line analysis curves obtained by E.P.M.A., where the couples at the various annealing stages as shown in Photo. 3 were used. The curve C for Photo. 3(c) has a concentration jump by which it is divided into the palisade and compact δ_1 layers. Figure 8 shows the analysis curves obtained from the Γ region in Photo. 3(a) and from the thin double layer region in Photo. 3(c). The thin double layer is clearly divided into the Γ phase and the new layers by a concentration jump; the new layer is called as the Γ' for convenience. The variation in composition of the intermediate phases with annealing time at 380°C is summarized in Fig. 9. Although there is a concentration jump between the palisade and compact δ_1 layers,

Fig. 7 E.P.M.A. line analysis for Fe-electrodeposited Zn diffusion couples annealed at 380°C for various periods of time. A: 4 hr, B: 9 hr, C: 16 hr

Fig. 8 E.P.M.A. line analysis for Fe-electrodeposited Zn diffusion couples annealed at 380°C for various periods of time. A: 4 hr, B: 16 hr.

these δ_1 layers cannot be thought to have different crystal structures, because the interface between the palisade and compact layers is extremely obscure as shown in Photo. 3(c) and the concentrations of the two layers are in the composition range of the δ_1 phase in equilibrium. On the contrary, the Γ' layer may possibly be a new phase that is not seen in the equilibrium phase diagram of the Fe-Zn system, because the Γ' layer has clearly distinguishable interfaces and a nonequilibrium composition as shown in Photo. 3(c) and Fig. 9, respectively.

Figure 10 shows the isothermal growth of the intermediate phases at 410°C. It appears from Fig. 10 that the rapid growth of the palisade δ_1 occurring during about 27-hr annealing allows to increase the rate of growth of the total width and to decrease that of the ζ phase again. The rapid growth of the palisade δ_1 layer seems to be the last characteristic process of the reaction diffusion in the Fe-Zn system. As the result of this process, the palisade δ_1 layer occupies the greater part of the diffusion zone after a prolonged

Fig. 9 Time dependence of Fe concentration in the ζ , palisade δ_1 , compact δ_1 , Γ' and Γ intermediate phase layers formed in Fe-electrodeposited Zn diffusion couples annealed at 380°C.

Fig. 10 Width of the ζ , Γ , compact δ_1 , total δ_1 and of the total phase layers vs square root of annealing time. Fe-electrodeposited Zn diffusion couples were annealed at 410°C.

annealing. The same situation was also observed by Sjoukes⁽¹³⁾ in his study on galvanizing at 460°C.

3. Kirkendall effect and interface movements

Photograph 4 shows a photomicrograph of the marker position in the couple annealed at 410°C for 16 hr. After annealing the markers always existed at the interface between the ζ and zinc phases. This means that zinc atoms one-sidedly diffuse into the intermediate phases. Figure 11 shows the movements of the interfaces between distinct intermediate phases, where the movements were measured relative to iron ends of the couples. The Zn- ζ and ζ - δ_1 interfaces moved towards the Zn side and the Γ -Fe interface

Photo. 4 Photomicrograph of the marker position in a Fe-electrodeposited Zn diffusion couple annealed at 410°C for 16 hr. ($\times 400 \times 9/10$)

Fig. 11 Movements of the interfaces between individual intermediate phases in Fe-electrodeposited Zn couples annealed at 300°C.

moved towards the Fe side.

IV. Discussion

As shown in Figs. 4 to 6 and in Fig. 10, it is self-evident that the intermediate phases in the Fe-Zn diffusion couples do not grow according to the parabolic law. As an approximation, however, the total width of all phases can be drawn by a straight line passing through an origin against the square root of annealing time. If the relation between the width of the ζ , δ_1 , Γ phases and the square root of annealing time is approximated by straight lines, the lines for the ζ , Γ phases and the line for the δ_1 phase tend to intersect the ordinate and the abscissa, respectively, without passing through the origin of the coordinates.

Figure 12 shows the relation between logarithm of the width of the intermediate phase and logarithm of the annealing time at 410°C, as replotted Fig. 10. Logarithm of the width could be approximately represented by the straight line against the logarithm of the

Zn

ζ

Fig. 12 Logarithms of the thickness of the ζ , total δ_1 , Γ and total intermediate phase layers vs logarithms of annealing time. The Fe-electrodeposited Zn diffusion couples were annealed at 410°C.

- 1

Fe	ζ	Zn
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 ζ Formation, Parabolical Growth
- 2

Fe	ζ'	δ₁	ζ	Zn
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 δ₁ Formation
- 3

Fe	Γ	δ₁	ζ	Zn
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 Γ Formation
- 4 Rapid Growth of δ₁
- 5

Fe		δ₁	ζ	Zn
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 Formation of Thin Double Layer (Double Γ Layer)
- 6

Fe		c. δ₁	p. δ₁	ζ	Zn
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 Formation of Compact δ₁
- 7 Rapid Growth of Palisade δ₁

Fig. 13 Modes of formation and growth of the intermediate phases. In the second to the fifth processes the δ_1 phase can be regarded as the palisade δ_1 .

annealing time, and the tangents of the lines for the total width of all phases and for the δ_1 , ζ and Γ phases were 0.43, 0.49, 0.36 and 0.23 respectively. For the ζ phase, the growth obeys the parabolic law as long as the ζ exists as a single phase in the diffusion zone, but it is disturbed by the formation of the δ_1 phase and by the rapid growth of the δ_1 phase which occurred twice. Hence, the fact that the n value for the ζ is 0.36 does not always mean that the growth of the ζ is not diffusion-controlled.

The formation and growth processes obtained in this experiment are summarized in Fig. 13. Although these processes were separately detected at four different anneal temperature, it is appropriate to consider that the seven processes should occur in the numerical order at a given temperature. For the purpose of estimating the times to initiate some of the seven processes at a given temperature, the relation between the logarithms of t_i and the reciprocal of the absolute temperature is shown in Fig. 14, where t_1 , t_2 , t_3 , t_4 and t_5 are the beginning times of the formation of the δ_1 and Γ , the rapid growth of the δ_1 , the formation of the compact δ_1 and the rapid growth of the palisade δ_1 , respectively. Although the t_5 were obtained only at two of the temperatures, it appears from Fig. 14 that

Fig. 14 Logarithms of t_i vs reciprocal of the absolute temperature.

Table 1 Values of A_i and B_i .

t_i	A_i	B_i
t_1	4.79×10^{-14}	2.35×10^4
t_2	2.95×10^{-15}	2.59×10^4
t_3	2.95×10^{-15}	2.68×10^4
t_4	7.24×10^{-17}	3.09×10^4
t_5	5.50×10^{-20}	3.80×10^4

t_i varies with temperature according to the form

$$t_i = A_i \exp(B_i/T)$$

where A_i and B_i are constants. The values of A_i and B_i are summarized in Table 1.

As characteristic phenomena in the galvanizing reaction, the existence of the palisade and compact δ_1 layers and the thin double layer were also detected in this experiment. Horstmann⁽¹⁾ classified the formation processes of the intermediate phases by galvanizing into seven possible ways, and reported that a first process in which the phases were formed in the order of the ζ , δ_1 and Γ phases and α solid solution of zinc in iron would be the most reliable one. The α solid solution was not detected at all in this experiment, but the processes shown in Fig. 13 do not contradict the prediction by Horstmann.

Because of the analogy between the reaction of the galvanizing and that of iron with solid zinc, kinetics of the galvanizing reaction can be discussed by extrapolating the results obtained in this experiment to the galvanizing temperature. In Fig. 14 we find that the times t_1 to t_4 at 460°C are less than 2 min and t_5 is about 30 min. If the same type of the graph as Fig. 10 is obtained by the studies on galvanizing at 460°C, the growth curves for the intermediate phases at the time up to t_4 would be reduced to an indistinguishable extent and the greater part of the graph would be occupied by the growth curves after t_5 . In the same type of the graph as Fig. 12, the exponents for the δ_1 and ζ ought to be larger and smaller, respectively, than the values obtained in Fig. 12. Because of the dissolution

of the ζ into molten zinc, it may be predicted that the exponent for the ζ is less than 0.3. In fact, 0.65 for the δ_1 at 450°C⁽²⁾, 0.58 for the δ_1 and 0.26 for the ζ at 460°C⁽¹³⁾ were reported. According to the experimental results by Blickwede⁽¹⁴⁾, Horstmann described that the δ_1 phase layer tended to grow slowly at the early stage of the galvanizing reaction and rapidly at the late stage, while the ζ , Γ layers tended to grow rapidly at the early stage and slowly later. It can be considered that such trends will be always observed in the galvanizing reaction in the lower parabolic temperature range⁽¹¹⁾ from the m.p. of zinc to 480°C.

V. Summary

The formation and growth kinetics of the intermediate phases in the Fe-Zn diffusion couples can be represented by the characteristic processes which appeared in the following numerical order; (1) ζ , (2) δ_1 and (3) Γ phase formation, (4) rapid growth of δ_1 , (5) formation of the thin double layer, (6) formation of the compact δ_1 and (7) rapid growth of palisade δ_1 . As a result of the last process, the palisade δ_1 occupied most of the diffusion zone in the couple annealed for a long period of time at 410°C.

By extrapolating the results of this experiment to the galvanizing temperature, the intermediate phase growth by the galvanizing reaction could be predicted as follows. At 460°C, the first to sixth processes are completed within about 2 min after dipping of iron into molten zinc. The last process that appears after dipping for about 30 min greatly affects the growth of the intermediate phases. When the width of each phase is represented by a simple exponential function of the dipping time, the exponents for the δ_1 and ζ phases are expected to be about 0.6 and less than 0.3 respectively.

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