# The Grain-Boundary Diffusion of Zn in α-Fe

### Jonathan S. Dohie, J.R. Cahoon and W.F. Caley

**Using semi-infinite amounts of pure Zn and pure Fe as the diffusing media and maintaining constant boundary conditions, the diffusion of Zn into αFe has been experimentally studied at temperatures of 400, 500, and 725 °C. Long diffusion times (4 days) were used to allow the various intermetallic phases to become well developed. It was determined that diffusion of Zn into Fe is not "anomalously rapid," but follows normal diffusion behavior for polycrystalline metals in that both lattice diffusion and grain-boundary diffusion contribute to mass transport for the temperatures investigated. The grain-boundary diffusion coefficients determined are consistent with those for many other metal systems.**

## 1. Introduction

Hot dip Zn coating or galvanizing has been employed as a method of protecting steel from corrosion for more than 100 years and remains a popular corrosion prevention technique. In 1985, the production of galvanized steel in the United States was estimated at $5.9 \times 10^5$ Mg ($6.5 \times 10^6$ tons),[1] and innovative applications for galvanized products are continually being developed.[2]

Despite the large use of galvanized steel products, the reaction of molten Zn with solid Fe is not fully understood. Several previous studies[3-6] have shown that at temperatures from 300 to 620 °C, Zn diffuses rapidly into Fe. Some authors have called this "anomalously fast" diffusion of Zn in Fe.[3] Several of the diffusion studies have used thin Fe foils ($\sim 100\,\mu m$ thick) with Zn vapor sources.[4-6] In the thin-foil studies, grain-boundary migration often occurs that obscures diffusion results. Also, it has been suggested that grain-boundary migration rates may be limited by the transport of Zn vapor to the Fe surface and not by diffusion in the grain boundaries.[6] Further, the Zn sources in these studies did not maintain a constant Zn vapor pressure with time, and therefore the boundary conditions in these studies could be changing.

Some studies were conducted using commercial galvanized steel where the thickness of the Zn layer measured only about 0.1 mm.[3,7] The Fe-Zn binary system has four intermetallic compounds.[8] These are $\Gamma(Fe_3Zn_{10})$, $\Gamma1(Fe_{11}Zn_{40})$, $\delta(FeZn_{10})$, and $\zeta(FeZn_{13})$. In these studies, the Zn layer as well as some of the intermetallic phases were consumed during the diffusion anneals, resulting in contin-

ually changing boundary conditions. Also, some commercial Zn coatings may contain aluminum additions, ostensibly to hinder the nucleation of $\Gamma$ phase.[3]

The possibility of Zn vapor transport controlling grain-boundary migration in thin-film studies and the continually changing boundary conditions in the commercial galvanized steel studies render quantitative results concerning the grain-boundary diffusion of Zn in Fe difficult (if not impossible). Therefore, the present investigation was conducted to study the nature of the diffusion of Zn in Fe. Semi-infinite amounts of both Zn and Fe were used to keep the boundary conditions essentially constant during the diffusion anneal. Also, the use of semi-infinite couples permits long diffusion anneals that should allow the various intermetallic phase layers to become well developed. The diffusion studies were conducted at temperatures where the Zn was solid, and at temperatures where the Zn was liquid, to determine if liquid Zn penetration into the Fe grain boundaries was a factor in the diffusion of Zn into Fe. For the liquid Zn studies, the number and composition of intermetallic phases formed was varied by changing the temperature of the diffusion anneal to determine if the nature of the intermetallic phases affected the diffusion of Zn into Fe. The major objective of this work was to clarify the nature of the diffusion of Zn into Fe during the galvanizing of steel, thus providing a better understanding of the galvanizing process.

## 2. Experimental

The materials used for the diffusion couples were 99.95 wt.% Fe rod 3.2 mm in diameter and 610 mm long, and 99.99 wt.% Zn pellets ~7 mm in diameter. The Fe rods were received in the as-rolled condition and exhibited greatly elongated grains. They were therefore annealed at 725 °C for 90 min, achieving an equiaxed grain size of $20 \pm 3\,\mu m$.

Tapered alumina crucibles (99 wt.% purity) with a 36 mm maximum outer diameter, a 45 mm height, and a wall thickness of ~3 mm were used to hold the diffusion couples. An alumina silicate ceramic insert 9 mm long with a 3.2 mm diameter central hole to secure the Fe portion of the diffusion couple was machined to fit tightly into the

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bottom of the crucible. The ceramic insert also contained three holes 3.2 mm in diameter and 5 mm deep that filled with Zn during the diffusion anneal and served to maintain the integrity of the Fe/Zn interface following the diffusion anneal. A schematic of the crucible assembly is shown in Fig. 1.

A diffusion couple was made by spark machining a 9 mm segment from an annealed Fe rod, sanding one end of the segment to 600 grit paper and inserting the segment into a ceramic insert with the sanded end flush with the end of the insert. A liquid-Zn/solid-Fe diffusion anneal was initiated by preheating a crucible to 525 °C in a flowing argon atmosphere and placing the ceramic insert holding the Fe segment into the preheated crucible. Approximately 45 g of liquid Zn at 525 °C melted in a separate crucible furnace was immediately poured into the crucible assembly containing the Fe segment. The assembly was held at 525 °C for 15 min and then transferred to the diffusion anneal furnace, which was controlled at the diffusion temperature, either 500 or 725 °C. For the 400 °C experiments, the assembly was removed from the 525 °C furnace and allowed to solidify before being placed in the diffusion anneal furnace controlled at 400 °C. The temperature of the diffusion anneal furnace was controlled to ±2 °C. The sample remained in the furnace, in an argon atmosphere, for the duration of the diffusion anneal (96 h), after which it was removed from the furnace and air cooled.

Sample ingots were removed from the crucible and carefully sectioned to expose the central cross section of the Fe rod. The samples were mounted in bakelite, sanded through 600 grit SiC paper, and polished to 1 μm diamond abrasive. The Zn penetration into the Fe was measured using an Oxford energy dispersive spectrometer (EDS) on a JEOL 5900 scanning electron microscope (SEM), JEOL Ltd, Tokyo with INCA standardless correction software, Oxford Instruments NanoAnalysis, High Wycombe. Fe/Γ interface determined using the standardless software always agreed to within ±5 at.% of the value taken from the phase diagram, which is well established.[8] Therefore, further
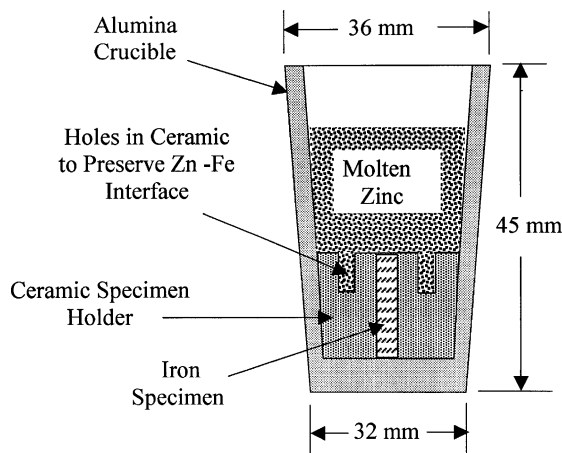
calibration with other standards was not required. Samples were always analyzed in an as-polished, unetched condition to minimize errors in the EDS measurements.

Concentration profiles in the Fe portions of the samples were established by scanning for a length of 0.19 mm parallel to the Zn/Fe interface at measured distances from the interface with an electron beam about 1 μm in diameter. The profiles were measured in the central 2 mm of the 3.2 mm diameter Fe rods to avoid surface effects. Portions of at least 10 grains were included in each scanned section. Two specimens were annealed at 725 and 500 °C, and five specimens were annealed at 400 °C. Seven to nine concentration profiles were obtained for each of the specimens. All of the results for a given temperature were averaged to obtain a single concentration profile for each of the diffusion anneal temperatures.

The composite concentration profiles for the three diffusion anneal temperatures are given in Fig 2. The error bars in Fig. 2 are ±2% of the amount present for concentrations above 2 at.% Zn and a constant value of ±0.1 at.% Zn for compositions below 2 at.% Zn, where the signal-to-background ratio decreases significantly.

## 3. Results and Discussion

A micrograph exemplifying grain-boundary diffusion of Zn into nonrecrystallized Fe after 96 h at 400 °C is given in Fig. 3, which shows Γ phase (Fe$_3$Zn$_{10}$), as identified by EDS analysis, extending over 90 μm into the Fe from the Fe/Zn alloy interface. Using the lattice interdiffusion coefficient for Zn (2 at.%) in Fe, $D_L = 5.0 \times 10^{-23}$ m$^2$/s,[9] it is easily calculated that Zn would penetrate only about 3 μm into the Fe in the absence of grain-boundary diffusion. All diffusion samples exhibited some Γ phase in the Fe grain boundaries and a thin ($\sim 5\,\mu$m) layer of Γ at the interface. The diffusion samples for both 400 and 500 °C showed all of the phases in the Fe-Zn binary system. Figure 3 also illustrates the need for recrystallized Fe to be used for all the diffusion studies since the Fe would otherwise recrystallize during the diffusion anneals conducted at the higher temperatures and render quantitative comparison of the diffusion results impossible. Microstructures taken near the (Fe)/Γ interface of diffusion couples made using recrystallized Fe for diffusion temperatures of 400, 500, and 725 °C are shown in Fig 4.

Grain-boundary diffusion is described by the equation:[9,10]

$$\delta D_{gb} = \left[ \frac{\partial \ln C_{av}}{\partial y^{6/5}} \right]^{-5/3} \left[ \frac{4D_L}{t} \right]^{1/2} \left[ \frac{\partial \ln C_{av}}{\partial (\eta \beta^{-1/2})^{6/5}} \right]^{5/3} \quad \text{(Eq 1)}$$

where δ is the width of the grain boundary, $D_{gb}$ is the grain-boundary diffusion coefficient, $D_L$ is the lattice interdiffusion coefficient, $t$ is the time of the diffusion anneal, and $C_{av}$ is the average concentration in at.% at depth $y$ parallel to the interface in the region where grain-boundary diffusion dominates. In Eq 1, η and β are dimensionless parameters given by:[9]



**Fig. 1** Diffusion couple arrangement

Alumina Crucible
36 mm
Holes in Ceramic to Preserve Zn -Fe Interface
Molten Zinc
45 mm
Ceramic Specimen Holder
Iron Specimen
32 mm

**Fig. 3** Diffusion of Zn into nonrecrystallized iron after 96 h at 400 °C (etched with 2% nital)
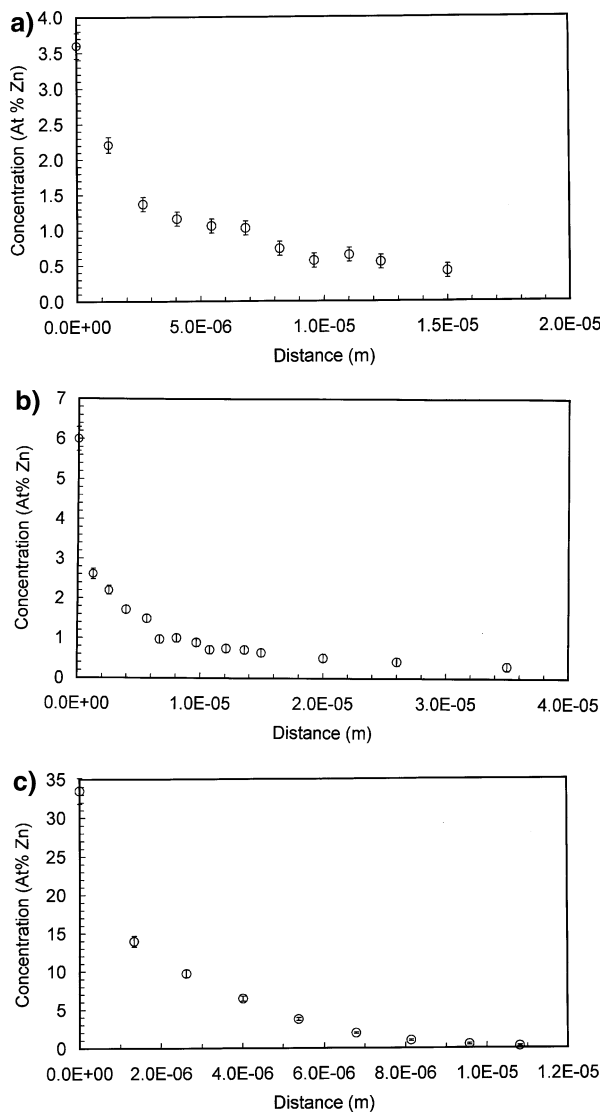


**Fig. 2** Concentration profiles after four days at the diffusion anneal temperatures. (a) Diffusion at 400 °C. (b) Diffusion at 500 °C. (c) Diffusion at 725 °C

$$\eta = \left[ \frac{y}{(D_{\mathrm{L}}t)^{1/2}} \right], \text{ and } \beta = \left\{ \frac{\delta D_{\mathrm{gb}}}{2D_{\mathrm{L}}(D_{\mathrm{L}}t)^{1/2}} \right\}$$

The grain-boundary width is estimated to be only $\delta \approx 5 \times 10^{-10}$ m.[10-13] With the uncertainty of the value for $\delta$, only the product $\delta D_{\mathrm{gb}}$ can be accurately determined from Eq 1. In Eq 1, a segregation factor, $s$, is sometimes included to account for the situation where the solute solubility in the grain boundary is higher than that in the grain at the grain boundary. Figure 4 does show some $\Gamma$ phase in the grain boundaries for the diffusion anneals conducted at 400 and 500 °C, but the $\Gamma$ phase is discontinuous and is not present in appreciably more quantities near the (Fe)/$\Gamma$ interface than at further distances. It is concluded that the $\Gamma$ phase in the grain boundaries
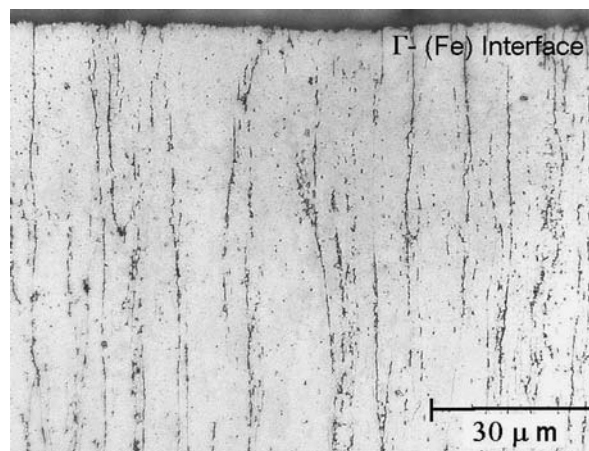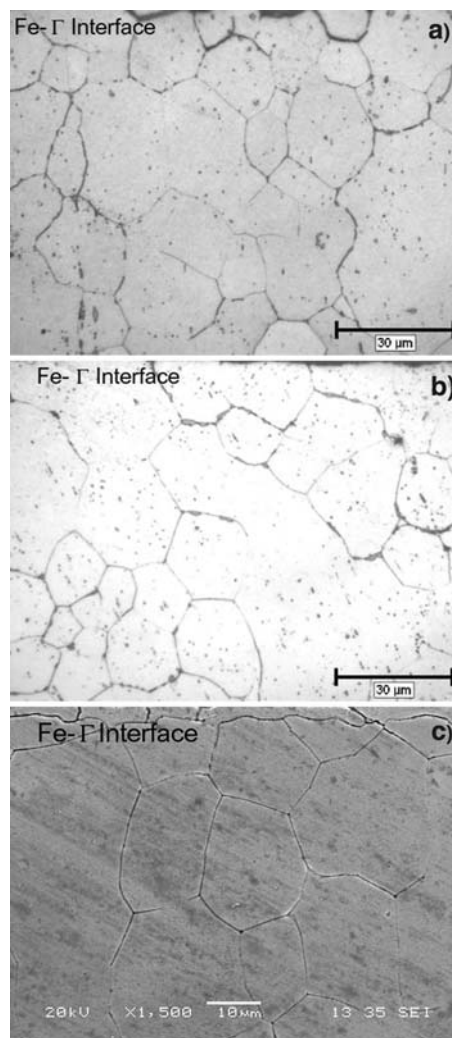


**Fig. 4** Microstructures near the Fe/$\Gamma$ interface after four days at the diffusion anneal temperatures. (a) After four days at 400 °C. (b) After four days at 500 °C. (c) After four days at 725 °C

precipitates out during cooling after the diffusion anneal and is not present during the diffusion anneal. The segregation factor is therefore considered to be unity and is not included in Eq 1.

In calculating $\delta D_{gb}$ from Eq 1, the first term of the right hand side (RHS) is determined from the slope of the plot of on $C_{av}$ versus $y^{6/5}$. This plot is shown for the diffusion anneal temperatures of 400, 500, and 725 °C in Fig 5. The calculations of $\eta$, $\beta$, and the second term of the RHS of Eq 1 require the value of the lattice diffusion coefficient, $D_L$. The lattice interdiffusion coefficient for Zn in Fe has been reported by Richter and Feller-Kniepmeier[14] to vary considerably with concentration. For example, at 725 °C, the interdiffusion coefficient increases from $6 \times 10^{-17} \text{m}^2/\text{s}$ at 0% Zn to $6 \times 10^{-14} \text{m}^2/\text{s}$ at 33.6 at.% Zn if the data of

Richter and Feller-Kniepmeier[14] are extrapolated linearly. Further, diffusion in the (Fe) phase at 725 °C occurs in the ferromagnetic region for concentrations below about 14 at.%[8] and in the paramagnetic region for higher concentrations, which also influences the interdiffusion coefficient.[15] However, for purposes of this investigation, the lattice diffusion coefficient used was that for a concentration of half the solid solubility of Zn in Fe at the diffusion temperature ($1/2$ $C_{(Fe)}$ in Table 1) as calculated from the results of Richter and Feller-Kniepmeier.[14] The lattice interdiffusion coefficients used are included in Table 1.

For the conditions employed in most grain-boundary experiments, the third term of Eq 1 is often nearly constant and has a value of $-0.661$.[9] In the present case, however, the large variation of $D_L$ with concentration and the large difference in concentration ranges for the three temperatures studied will probably result in deviations from the value of $-0.661$. Therefore, the value of the third term was calculated from the Suzuoka instantaneous source solution:[9]

$$\left[ \frac{\partial \ln C_{av}}{\partial (\eta \beta^{-1/2})^{6/5}} \right]^{5/3} = -0.578 \beta^{0.013}$$

This term contains the slope of the graph of $\ln C_{av}$ versus $[\eta (\beta)^{-1/2}]^{6/5}$ in the region where grain-boundary diffusion is predominant, and these are shown in Fig 6. The values of the entire term are included in Table 1.

As mentioned previously, only the product $\delta D_{gb}$ can be determined. It is, however, instructive to estimate the value of $D_{gb}$ using a value of $\delta = 5 \times 10^{-10}$ m for the grain-boundary width. The values of $D_{gb}$ are included in Table 1, and the Arrhenius plot is shown in Fig 7 where the error limits are the sums of the standard deviations of terms one and three in Eq 1. The best fit line through the points in Fig 7 yields

$$D_{gb} = 0.0034 \ \exp(-162,000/RT) \text{m}^2/\text{s}$$

The activation energy of 162 kJ/mole for the grain-boundary diffusion of Zn in α Fe seems reasonable in that it is close to the activation energies for the grain-boundary diffusion of Fe (174 kJ), Co (174 kJ), and Ni (181 kJ) in α Fe.[16] Also, the activation energy for the grain-boundary diffusion of W in ferritic Fe-8 wt.%Cr alloys ranges from 192 to 252 kJ depending on the carbon content.[17] It appears that the grain-boundary diffusion of Zn in Fe is consistent with normal grain-boundary diffusion. The experimental results shown in Fig 7 are not perfectly linear, which could be a result of analytical errors, the variation of the lattice diffusivity with concentration, or a combination of both these factors.

Further, Fig 8 compares the present results for grain-boundary diffusion of Zn in α Fe with a compilation of some 60 results by Hwang and Balluffi[18] for grain-boundary diffusion at temperatures above about 0.4 of the melting temperature. Figure 8 shows that the present results lie in the middle of the range of grain-boundary diffusion coefficients given by Hwang and Balluffi.[18] The range is defined as ± one standard deviation from the "average"
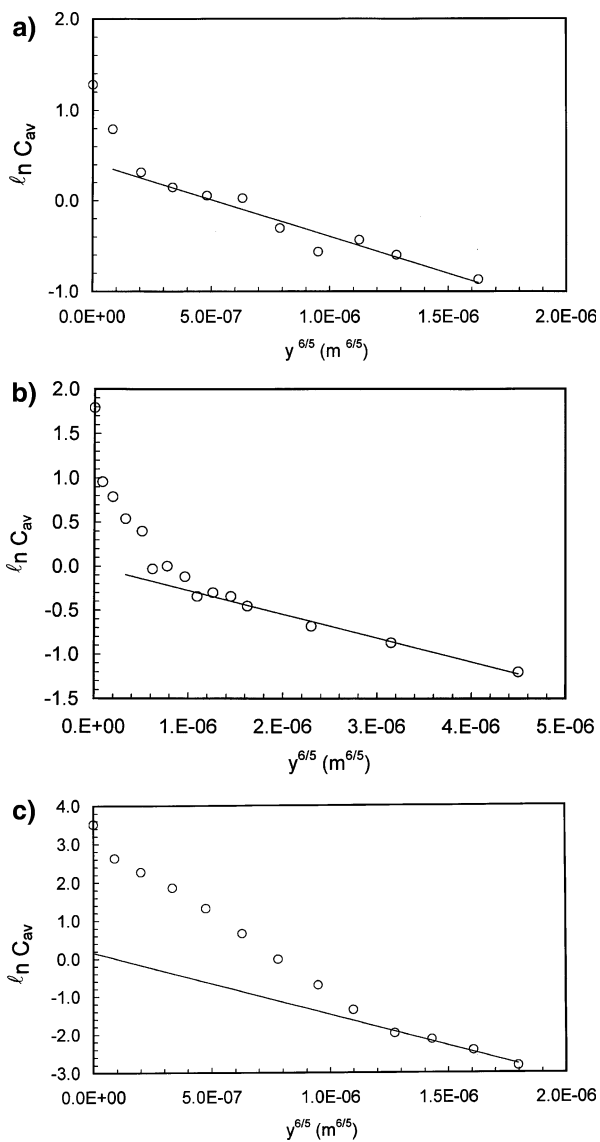


**Fig. 5** Plots for the determination of the first term in Eq 1 at the three diffusion anneal temperatures. (a) Diffusion at 400 °C. (b) Diffusion at 500 °C. (c) Diffusion at 725 °C

**Table 1  Concentrations and lattice diffusion coefficients used in calculating the grain-boundary diffusion coefficients**

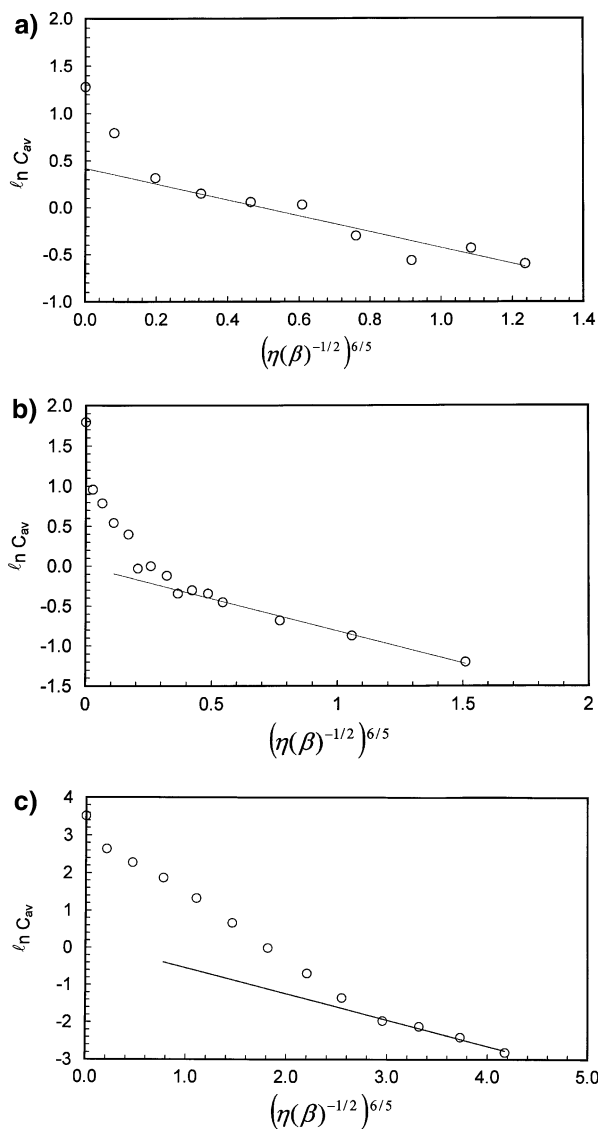| Temperature, °C | Time, s | $C_{(Fe)}$, at.% Zn | $D_L$, m²/s | 0.578 $\beta^{0.013}$ | $\delta D_{gb}$, m³/s | $D_{gb}$, m²/s |
|---|---|---|---|---|---|---|
| 400 | 345,600 | 3.6 | $4.5 \times 10^{-25}$ | $-0.753$ | $2.43 \times 10^{-25}$ | $4.86 \times 10^{-16}$ |
| 500 | 345,600 | 6.0 | $9.8 \times 10^{-22}$ | $-0.701$ | $6.56 \times 10^{-23}$ | $1.31 \times 10^{-13}$ |
| 725 | 345,600 | 33.5 | $2.0 \times 10^{-15}$ | $-0.553$ | $3.76 \times 10^{-21}$ | $7.51 \times 10^{-12}$ |



**Fig. 6**  Plot for the third term in Eq 1 at the three diffusion anneal temperatures. (a) Diffusion at 400 °C. (b) Diffusion at 500 °C. (c) Diffusion at 725 °C



**Fig. 7**  Arrhenius plot for the grain-boundary diffusion of Zn in α Fe
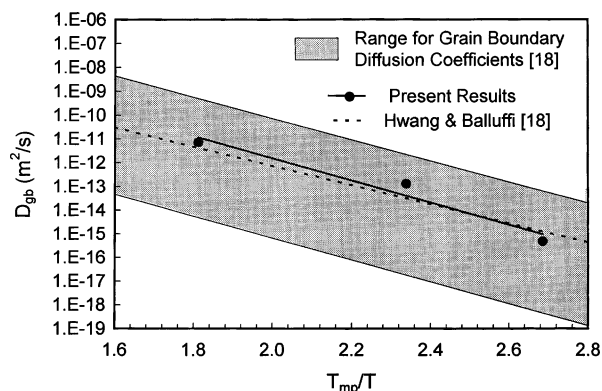


**Fig. 8**  Comparison of present results with the compilation of results by Hwang and Balluffi[18]

results. The "average" results are given by $D_{gb} = 1.0 \times 10^{-4} \exp(-9.35 T_m/T) \text{m}^2/\text{s}$, where $T_m$ is the melting temperature of solvent metal and is plotted as the dashed line in Fig. 8. The present results are very close to the "average" results of Hwang and Balluffi, which
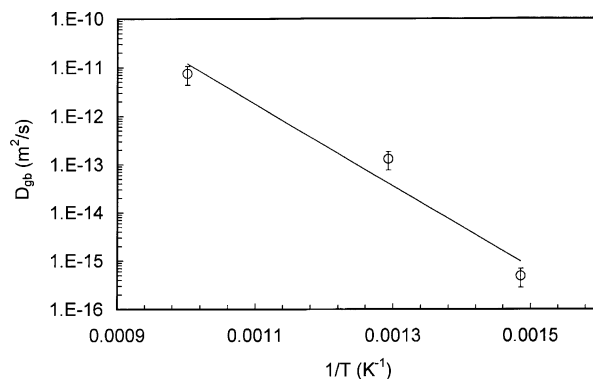
provides further evidence that grain-boundary diffusion of Zn in α Fe is normal and characteristic of grain-boundary diffusion in many metals.

The results of the present investigation have shown that for semi-infinite diffusion couples where one end remains as pure Fe and the other essentially as pure Zn, diffusion in the range of 400 to 725 °C is adequately described by the normal combination of lattice and grain-boundary diffusion. The results are consistent with normal diffusion whether the Zn source is molten or solid. The presence of all the intermetallic phases in the Fe-Zn system or just the Γ phase ($Fe_3Zn_{10}$) alone does not significantly influence the results. The large concentration dependence of the lattice diffusivity,

may result in nonlinear Arrhenius plots for the grain-boundary diffusivity.

## 4. Conclusions

With the use of semi-infinite diffusion couples in which the end concentrations remain at pure Fe and essentially pure Zn, respectively, it has been demonstrated that:

- The grain-boundary diffusion of Zn in $\alpha$ Fe is described by the Arrhenius equation $D_{gb} = 0.0034 \exp(-162,000/RT)\text{m}^2/\text{s}$. The activation energy for the grain-boundary diffusion of Zn in $\alpha$ Fe is consistent with that for the grain-boundary diffusion of Fe, Co and Ni in $\alpha$ Fe.
- The grain-boundary diffusion of Zn in $\alpha$ Fe is not "anomalously fast," but is consistent with normal grain-boundary diffusion
- The nature of the source of Zn, liquid or solid, has little influence on the diffusion of Zn in $\alpha$ Fe; that is, there is no significant grain-boundary grooving or penetration by the liquid Zn.
- The presence of all the phases in the Fe-Zn system or that of $\Gamma$ phase ($Fe_3Zn_{10}$) alone has little influence on the diffusion of Zn into $\alpha$ Fe.

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