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FIGURE

ABSTRACT

Self-diffusion coefficients have been determined from sintering data for α-Fe at 885°C and for γ-Fe at 935°C. The respective values are $D_{885} < 6 \times 10^{-14}$ cm^2/sec and $D_{935} = 3.5 \times 10^{-13}$ cm^2/sec. These values have been compared with results obtained previously from radioactive tracer measurements and it has been concluded that a ring mechanism of diffusion is dominant in α-Fe and a vacancy mechanism is dominant in γ-Fe.

I. INTRODUCTION

Several years ago, Kuczynski[1] introduced a method for determining self-diffusion coefficients without the aid of radioactive tracers. An expression was derived which relates the dimensions of a sintered interface between two particles to D, the coefficient of volume self-diffusion. Although this method will never supplant the tracer method for determining diffusion parameters, the importance of its use should not be overlooked in diffusion studies (a) where no suitable isotopes are available and (b) where it is desired to distinguish various diffusion phenomena which have different causal origins. As long as 50 to 100 measurements of separate fillets are made for each point on the ln D vs 1/T curve, the statistics will be favorable to enable the determination of D within a factor of two or three with about an 80% confidence limit for most metals.

An adaptation of this method has been used to determine the self-diffusion parameters in both face-centered-cubic (fcc) and body-centered-cubic (bcc) thorium,[2] where no suitable isotope for tracer studies is available. In this latter work, it was found that near the transition temperature, D in bcc thorium is approximately a factor of five less than D in fcc thorium. In contrast, radioactive tracer studies[3,4] show that D in bcc iron is approximately 400 times larger than D in fcc iron, when near the transition temperature. It was therefore suggested[2] that sintering studies be conducted on iron in an attempt to determine the cause of this extremely large difference in D for the fcc and bcc structures.

It is important to note that the volume diffusion mechanism responsible for sintering phenomena must involve lattice defects, e.g., interstitials or vacancies, since a net transport of matter must take place to establish the sintered fillet. On the other hand, the total diffusion which is observed through use of radioactive tracers may have occurred either by such a defect mechanism or by a direct interchange or ring mechanism,[5] or possibly by a combination of both kinds of mechanisms. The direct interchange mechanism cannot contribute to the formation or growth of the sintered fillet since it does

not result in any net mass transport. Consequently, a comparison of diffusion data obtained from tracer and sintering studies should allow one to determine the relative contributions of those diffusion mechanisms which can produce net mass transport and those mechanisms which cannot.

II. EXPERIMENTAL PROCEDURE AND RESULTS

In the present study, 0.020 inch diameter wires were fabricated from Johnson-Matthey (99.99% pure) iron. These wires were wrapped in four spools, each containing about four layers, in such a way that approximately 100 possible sintered interfaces were available for examination for each cross-sectional cut. These spools were pre-sintered in hydrogen at 950°C for one hour. Two of the spools were sectioned and measurements were made on the sintered interfaces. These results established the dimensions of the fillets at "zero" time; this procedure also eliminates errors due to distortion of the interface region during wrapping of the spools. One of the sectioned spools and one of the whole spools were then heated in vacuum ($<10^{-5}$ mm Hg) for 100 hours at 935°C; the other spools were treated similarly at 885°C. Following these treatments, final measurements of the sintered interfaces were made and the growth of each fillet in this time period was determined by subtracting the initial from the final values. Approximately 100 separate fillets were measured for each temperature and these values were averaged to obtain the value from which D was determined. The previously derived formula[2] relating D to the fillet measurements is

$$D = ka^3T(2\delta^3t\gamma)^{-1}y^5f(y) \quad ,$$

where

k = Boltzmann constant,

a = wire radius,

δ = interatomic distance,

T = absolute temperature,

t = time,

γ = surface energy,

y = ratio of fillet width to wire diameter, and

$f(y) = 0.0637 + 0.1096y + 0.1426y^2 + 0.1668y^3 + \ldots$.

For γ = 2000 dynes/cm, the values of D determined from this expression for the two temperatures are:

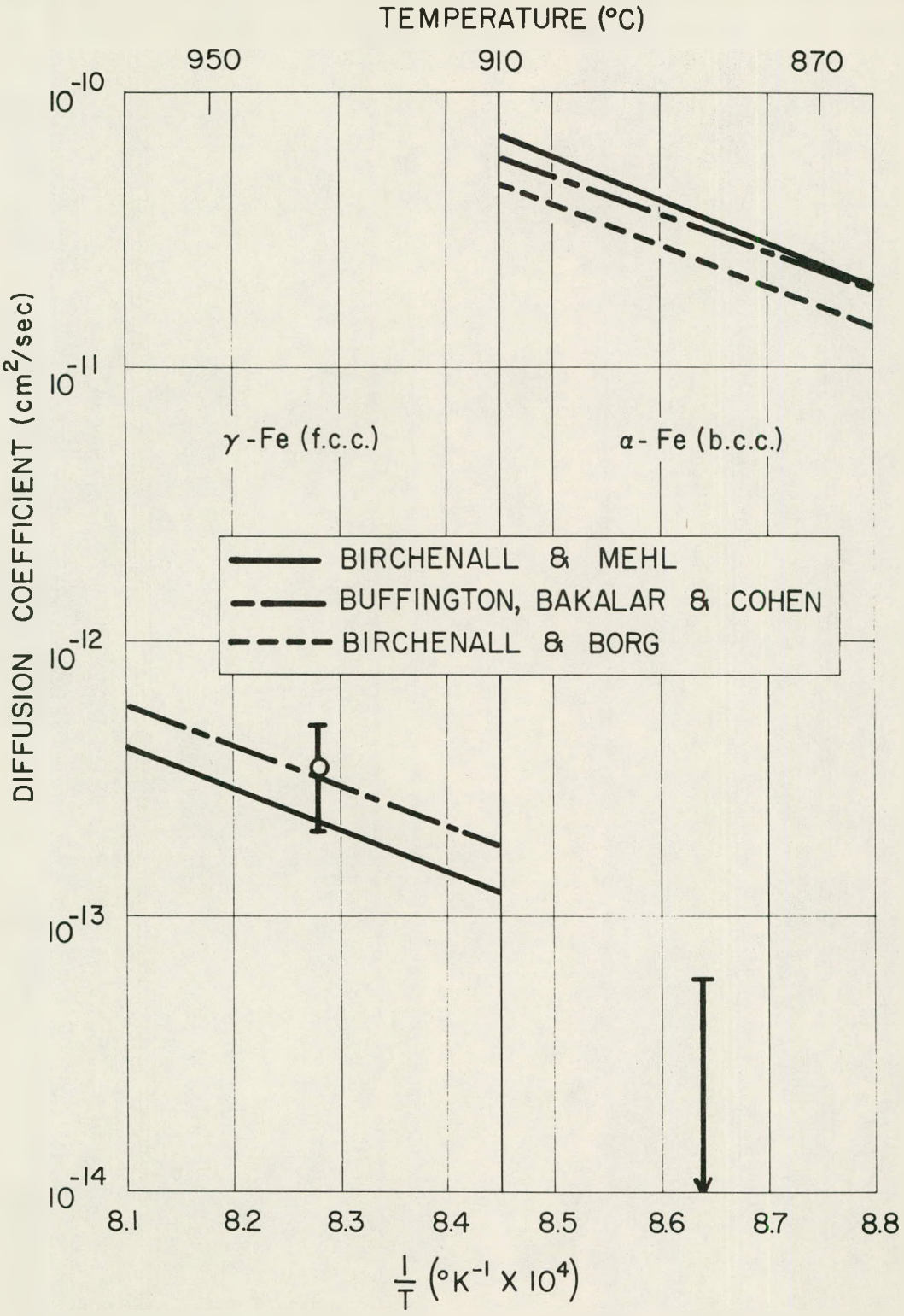
$$D_{935} = 3.5 \times 10^{-13} \text{ cm}^2/\text{sec (fcc)},$$

$$D_{885} < 6 \times 10^{-14} \text{ cm}^2/\text{sec (bcc)}.$$

Although some sintering did occur at 885°C, the diffusion rate was so slow that after the 100 hour treatment, it was only possible to place an upper limit on D_{885}. These values are plotted in the figure along with the previously mentioned data obtained using radioactive tracers. More recent tracer data[6] on α-iron are also shown. Approximately 85% of the present individual measurements of D_{935} fall within the error bar shown in the figure.

III. CONCLUSIONS

From the preceding discussion and a consideration of the fact that the value of D_{935} obtained from sintering data is in good agreement with the value obtained from the tracer data, it is concluded that (a) the sintered fillets in the fcc structure were established by volume self-diffusion via a defect mechanism, presumably vacancies, and (b) a diffusion mechanism which does not involve lattice defects is primarily responsible for volume diffusion in bcc iron. This latter mechanism is presumed to be a ring mechanism such



Plot Showing Comparison of ln D vs 1/T for α-Fe and γ-Fe as Determined From Radioactive Tracer Data and the Present Sintering Data (⊻, ⊺)

as proposed by Zener, where two or more neighboring atoms exchange positions simultaneously. The contribution from a four-atom ring seems most favorable from theoretical energy considerations.[7] Therefore, it is concluded that the large change in D, which occurs when iron is heated through the α-γ critical temperature, is caused by a change in the dominant diffusion mechanism. It seems most likely that this change is from a four-atom ring mechanism in bcc iron to a vacancy mechanism in fcc iron. This conclusion is further substantiated by recent diffusion studies on α-iron in a high-temperature gradient,[8] and is direct experimental support for the theoretical treatment of Le Claire[9] on diffusion mechanisms in bcc metals.

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