

coarser, and its content increased to about 30 pct in the weld metal, as shown in Figure 3. This type of microstructure was named vermicular austenite (VA). In addition to the vermicular morphology mentioned above, some ferrites with spiky outlines are also observed through close examination, as shown in Figure 4. The ferrite in the type LA microstructure, having a zig-zag appearance instead of the roundish outline observed in the typical vermicular appearance, possesses the similar description of lacy ferrite (LF) observed in the welds of duplex Ni-Cr stainless steels.^[3] In general, the amount of type LF is much less than that of type VF in the weld of these alloys.

Figure 5, taken from a weld of Fe-30Mn-9Al-0.3C alloy, shows typical acicular austenite (AA) at low magnification. The ferrite content is in the range of 45 to 55 pct. It is difficult to describe the characteristic morphology of the type AA microstructure. Generally, welds consisted of tail-like (or leaflike) austenite and the ferrite matrix. But detailed observation of type AA microstructure revealed that the appearance of austenite could be divided into two subcategories, in accordance with the Dubé morphological classification.^[6] As can be seen from Figure 2, the matrix of weld metal is ferrite, and austenites were precipitated from ferrite as grain boundary allotriomorph and Widmanstätten sideplate morphology. Some grainlike austenites found within the ferritic matrix might come from Widmanstätten sideplate austenite when viewed by transverse cross-section.

The Widmanstätten austenite (WA) microstructure type, having a ferrite content in the range of 65 to 80 pct, was observed in the lower carbon-containing weld metal (0.1 wt pct). As can be seen in Figure 6, some needle-like WA grew from the grain boundary allotriomorph austenite into ferrite along a distinct direction. In addition, the WAs formed within ferrite were lying along two to three distinct directions. It might imply that the austenite has a distinct orientation relationship with ferrite as the WA observed in high Creg/Nieq (>1.95) duplex stainless steel, in which austenite forms from the ferrite in the solid state. Furthermore, a Kurdjumov-Sachs (K-S) or Nishiyama-Wasserman (N-W) relationship exists between WA and ferritic matrix.^[4]

In the conventional Cr-Ni stainless steel system, the hot-crack susceptibility is more closely related to the solidification process or microstructural morphology during weld solidification than residual δ -ferrite content at room temperature.^[3] In the Fe-30Mn-9Al-XC alloy system, the hot-cracking susceptibility was associated with the microstructural morphology mentioned above. In our previous studies,^[1] the type VA microstructure with 25 to 35 pct ferrite has the maximum resistance to hot cracking during welding.

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Interdiffusion Coefficients in the Zeta Phase of the Fe-Al System

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Interdiffusion is an important mechanism in the formation and degradation of coatings on iron-based superalloys. Interdiffusion data for the FeAl₂ (ζ) phase are particularly scarce, with the only sources being R. Drewitt^[1] and J. Ling;^[2] a comparison of their results shows a discrepancy of an order of magnitude at 1000 °C. Moreover, the source of Drewitt's data is uncertain, since the reference he gives does not contain the diffusion data quoted, and J. Ling measured \bar{D}_{ζ} only at 1000 °C. It was the purpose of this work to determine \bar{D}_{ζ} values from 900 °C to 1050 °C in order to complete the set of interdiffusion data for the first three phases of the Fe-Al system.

Average values of \bar{D}_{ζ} from 900 °C to 1050 °C were determined using vapor-solid diffusion couples prepared using aluminizing packs. Cylindrical iron specimens (99.9 wt pct pure, 0.97 ± 0.01 cm in diameter, and 0.66 ± 0.01 cm in thickness) were annealed in alloy packs consisting of a 50:50 ratio by weight of Fe + Al to Al₂O₃ + AlF₃ powders. At 900 °C and 950 °C, the Al content of the Fe + Al powder was 73 at. pct, at 1000 °C, 71.0 to 71.5 at. pct, and at 1050 °C, 72.5 to 73 at. pct. The Al₂O₃ to AlF₃ ratio was always 48.73:1.25 by weight. The Al activity of the pack was high enough to form a thin layer of η , as well as the ζ phase, at the surface of the iron. Details of the construction of diffusion couples using the pack cementation method are given elsewhere.^[3]

After removal from the pack, samples were Ni plated to protect the edges, cut along their diameters, mounted in epoxy, and metallographically prepared for microprobe examination of the exposed surfaces by polishing down to a finish, ending with 0.3- μ m alumina polishing solution.

Concentration profiles, measured by straight traverses from the end of the cylinders toward the center, were determined using a Cameca electron microprobe. The electron probe was operated at an accelerating voltage of 15 KV with a current of 30 mA; the spot size was 1 μ m. An Fe-Al alloy with a composition of 74 at. pct Fe and 25.64 at. pct Al (measured by wet chemical analysis) was used as a standard. Al and Fe K α lines were

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counted; the raw intensities were corrected to Al and Fe atomic percentages by the Z.A.F. correction program. Data for which wt pct Fe + wt pct Al were less than 90 or greater than 102 were rejected. Successive traverses along the same line indicated concentration values were reproducible to 0.5 to 1.0 at. pct. A typical concentration profile used in calculating D is given in Figure 1. The data for the ζ and η phases were fitted to straight lines using linear regression.

Interdiffusion coefficients were extracted from concentration profiles using the version of Wagner's equation suitable for a solid-vapor couple of the type utilized:^[4]

$$\bar{D}(N_2^*) = \frac{Vm(N_2^*)}{2t(dN_2/dx)_{x=x^*}} \left[N_2 \int_0^{x^*} \frac{(1-N_2)}{Vm} dx + (1-N_2) \int_{x^*}^{\infty} \frac{N_2}{Vm} dx \right] \quad [1]$$

Here, $\bar{D}(N_2^*)$ is the diffusion coefficient at composition N_2^* , N_2^* is the concentration of Al at a distance x^* , t is the time in seconds, and Vm is the molar volume. The lattice parameter data of Nishida and Narita^[5] were

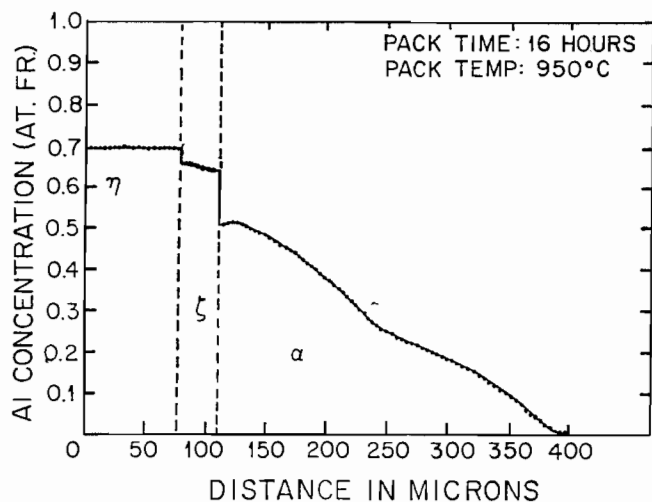


Fig. 1—Typical concentration profile.

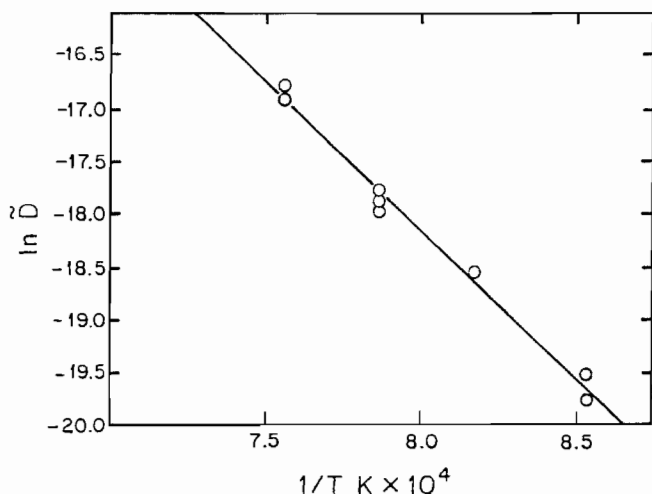


Fig. 2—Arrhenius plot of interdiffusion coefficients.

Table I. Interdiffusion Coefficients in the Zeta Phase

Temp. (°C)	\bar{D} Drewitt (cm ² /s)	\bar{D} Ling (cm ² /s)	\bar{D} Present Study (cm ² /s)
900	2.1×10^{-10}	—	2.8×10^{-10}
950	8.4×10^{-10}	—	9.2×10^{-10}
1000	2.3×10^{-9}	3.2×10^{-8}	1.9×10^{-9}
1050	5.7×10^{-9}	—	5.1×10^{-9}

used to determine the average molar volumes of the ζ , α , and η phases as 8.67 cc/mol, 7.42 cc/mol, and 8.88 cc/mol, respectively.

A plot of $\ln \bar{D}$ vs $1/T$ K for \bar{D} values from 900 °C to 1050 °C (Figure 2) gave linear regression values of 58.4 Kcal/mol for the activation energy of diffusion and

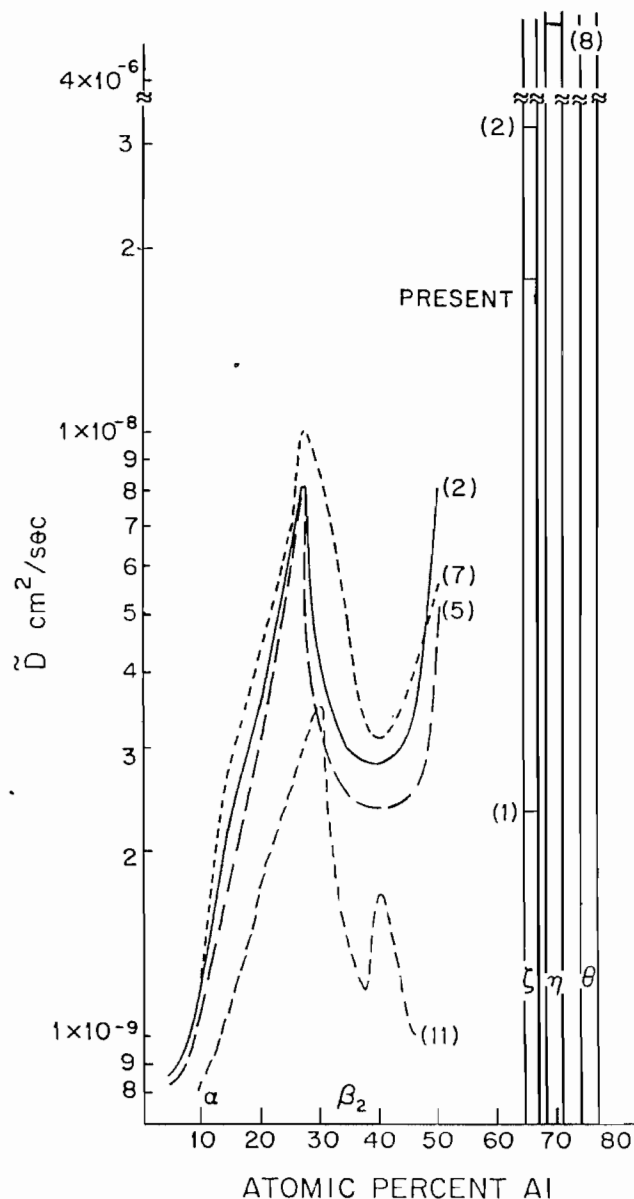


Fig. 3—Interdiffusion coefficients at 1000 °C in the Fe-Al system.

$\cdot 219 \text{ cm}^2/\text{s}$ for the frequency factor. The temperature dependence of \bar{D}_ζ was found to obey

$$\bar{D}_\zeta = (219 \pm 3) \exp [(-29,400 \pm 1200)/T] \text{ cm}^2/\text{s} \quad [2]$$

Table I compares the \bar{D}_ζ values obtained in this study with that determined by Ling^[2] and those presented by Drewitt.^[1] Our \bar{D}_ζ values are an order of magnitude higher than those given by Drewitt for temperatures between 900 °C and 1050 °C but only slightly lower than Ling's value at 1000 °C. Figure 3 presents data for the mutual diffusion coefficients of the $\alpha(\beta_2)$, ζ , and η phases of the Fe-Al system at 1000 °C obtained from various sources. Akuezue and Whittle's^[11] values for $D\alpha(\beta_2)$ and that of Neverov and Pimenov^[8] for \bar{D}_η were calculated from their data using Arrhenius relationships. For the θ phase, a value of $\bar{D}_\theta \sim 10^{-7} \text{ cm}^2/\text{s}$ at 1000 °C can be calculated from Darken's equation using the Al and Fe tracer diffusion coefficients of Larikov, *et al.*^[9,10] and the thermodynamic data of Eldridge and Komarek.^[12] Due to uncertainty over the exact width of the homogeneity range of θ , however, this value can only be considered as a rough estimate and is not shown in Figure 3.

Ling's values for $\bar{D}\alpha(\beta_2)$ were obtained by the same pack aluminization technique used in our experiments, and the good agreement of his values with those of Neverov, Pimenov, and Gurov,^[7] who used conventional solid-solid diffusion couples, and those of Nishida, Yamamoto, and Nagata,^[6] who used another type of vapor-solid couple, leads us to believe that the \bar{D}_ζ values obtained by the pack aluminization method are fairly reliable. Therefore, it appears that the \bar{D}_ζ values quoted by Drewitt are questionable, although little can be said on the subject, since the original source could not be located. The $\bar{D}\alpha(\beta_2)$ values calculated from the data of Akuezue and Whittle plotted in Figure 3 are significantly lower than those of the other investigators and show some other differences as well. A discussion of the possible reasons for the discrepancies, however, goes beyond the scope of this short communication.

Possibly the most outstanding feature of the mutual diffusion coefficient values for the various phases of the Fe-Al system collected in Figure 3 is the extraordinarily high value of \bar{D}_η , which, at 1000 °C, is about two orders of magnitude greater than the diffusion coefficients of the other phases. This accounts for the extremely rapid rate of aluminization of iron, which is observed in packs in which the Al activity is high enough to induce the formation of η on the surface.

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An Investigation on the Mechanism of 475 °C Embrittlement in High-Cr Ferritic Stainless Steel

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High-Cr ferritic stainless steel has been used widely over a broad temperature range, but its application is restricted because of the so-called 475 °C embrittlement. The cause of this embrittlement was first recognized by Fisher, Dulis, and Carroll^[1] as the precipitation of a Cr-rich α' phase. Later on, Grobner's experiments^[2] showed that such Cr-rich α' phase preferentially precipitated on dislocations. Recently, one of the authors found that such embrittlement always leads to twin formation in the vicinity of crack flanks,^[3] but the real effect of such twins on 475 °C embrittlement was still obscure. Besides, since the Cr content in the ferritic stainless steel used was more than 18 pct, the α' phase formed in this steel should be a product of spinodal decomposition. Though much research has been done on spinodal decomposition by field-ion microscopy,^[4-8] Mössbauer spectrum,^[9,10] and neutron diffraction,^[11,12] the mechanism of spinodal decomposition was also obscure. In this report, the mechanism of 475 °C embrittlement associated with this spinodal decomposition was studied in detail.

The composition of the steel used is listed in Table I. The steel was induction-melted in an argon atmosphere, cast, hot rolled, and then cold rolled and was supplied in the form of a 1.5-mm strip. Pieces of the material were solution-treated in air for 10 minutes at 950 °C, water quenched, aged at 475 °C for time periods from 10 to 4500 hours and water quenched. The resultant grain size, independent of the aging treatment, was 8 μm . Substandard size vee-notched Charpy impact specimens with dimensions 1.5 \times 9 \times 55 mm were prepared from the heat-treated material.

The spinodal decomposition kinetics were shown by

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