

A review of recent developments in Fe₃Al-based alloys

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Fe₃Al-based iron aluminides have been of interest for many years because of their excellent oxidation and sulfidation resistance. However, limited room temperature ductility (<5%) and a sharp drop in strength above 600 °C have limited their consideration for use as structural materials. Recent improvements in tensile properties, especially improvements in ductility produced through control of composition and microstructure, and advances in the understanding of environmental embrittlement in intermetallics, including iron aluminides, have resulted in renewed interest in this system for structural applications. The purpose of this paper is to summarize recent developments concerning Fe₃Al-based aluminides, including alloy development efforts and environmental embrittlement studies. This report will concentrate on literature published since about 1980, and will review studies of fabrication, mechanical properties, and corrosion resistance that have been conducted since that time.

I. INTRODUCTION

Iron aluminides have been of interest since the 1930's when their excellent oxidation resistance was first noted.^{1,2} They offer relatively low material cost, conservation of strategic elements, and a lower density than stainless steels (with potentially a better strength-to-weight ratio). These property advantages have led to the consideration of iron-aluminum alloys for many applications including those listed in Table I.³ However, limited ductility at ambient temperatures and a sharp drop in strength above 600 °C have been major deterrents to their acceptance for structural applications. More recent studies have demonstrated that adequate engineering ductility (10–15%) can be achieved in Fe₃Al-based alloys through control of composition and microstructure.^{4–7} Because of these advances and the renewed interest in the Fe₃Al system (as well as the FeAl system), it seems appropriate at this time to review recent developments which have led to property improvements in the Fe₃Al-based alloys.

Since the 1930's, efforts have been made to understand and improve the metallurgical properties of iron aluminides, with the aim of producing strong, ductile, corrosion resistant materials for structural applications. Especially noteworthy are the studies conducted at the Naval Ordnance Laboratory (1950's),^{3,8–10} Ford Motor Co. (1950's and 1960's),^{11–13} Iowa State University (~1965–75),^{14–19} and, more recently (1980's), work at Pratt and Whitney (P & W),⁴ TRW,⁵ and Oak Ridge National Laboratory (ORNL).^{6,20–24} All of these studies (as well as less extensive studies in other laboratories) have resulted in significant contributions to the understanding of the fabrication and mechanical properties of iron aluminides, as well as selected demonstrations of the excellent corrosion resistance of these alloys. Although a short background will summarize the major early development efforts, we will not attempt to provide a comprehensive review of all the literature on iron aluminides since the 1930's. Several excellent reviews of this type already exist.^{25–29} This report will concentrate mostly on literature published since about 1980, and will review studies of fabrication, mechanical properties, and corrosion resistance that have been conducted since that time. Special emphasis will be given to those studies at ORNL which have led to improvements in room temperature (RT) ductility and high temperature (HT) strength in Fe₃Al-based alloys and to an understanding of the factors affecting ductility in iron aluminides.

TABLE I. Applications for ductile iron aluminides.³

- | | |
|------|---|
| (1) | jet engine compressor blades and housings |
| (2) | structural members in aircraft |
| (3) | heating elements |
| (4) | furnace fixtures |
| (5) | heat exchangers |
| (6) | pipng and tubing for automotive applications |
| (7) | pipng and tubing for fossil energy applications |
| (8) | food handling equipment |
| (9) | chemical processing equipment |
| (10) | magnetic and electronic parts |
| (11) | nuclear reactor components |

II. BACKGROUND

Phase relationships in the Fe–Al system are shown in Fig. 1.³⁰ Near Fe₃Al, the following equilibrium phases have been confirmed: a disordered solid solution (α), an Fe₃Al with an imperfectly ordered B2 structure, an ordered Fe₃Al with the D0₃ structure, and the two phase

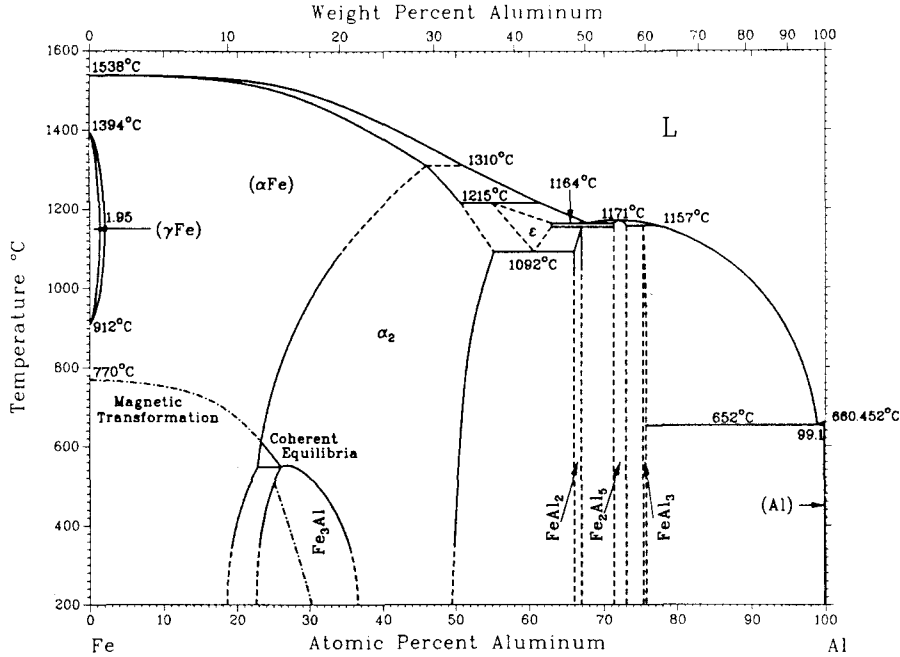


FIG. 1. Iron-aluminum phase diagram.³⁰

regions, $\alpha + D0_3$ and $\alpha + B2$, with the boundaries shown in Fig. 2.³¹⁻³³ Two versions of the phase boundaries in this region have been proposed. These versions are in agreement with respect to the relative temperature dependence of the various phase fields, but disagree on the location of the boundaries. Allen and Cahn^{34,35} concluded from thermodynamic considerations and critical experiments that both versions presented in Fig. 2 are correct, the diagram according to Oki *et al.*³¹ being the metastable one, while Okamoto and Beck's version³³ is the true equilibrium diagram. The ordered $D0_3$ and $B2$ crystal structures, the unit cells for which are presented in Fig. 3,³⁶ are body-centered-cubic derivative structures. These structures have high crystal symmetries and slip behavior similar to bcc iron, indicating that Fe₃Al should be intrinsically ductile at ambient temperatures. The transition temperature (T_c) between the two structures is at approximately 550 °C.

The first large-scale study to improve the properties of alloys near Fe₃Al was conducted at the Naval Ordnance Laboratory in the 1950's and 1960's.^{3,8-10} Nachman and Buehler studied fabrication extensively and developed methods for rolling iron aluminides of up to 30% Al (*unless otherwise noted, all compositions will be given in atomic percent*) to thin sheet (reportedly as thin as 0.1 mm). This program resulted in the development of an alloy called Thermenol, which contained 28% Al and approximately 1.5-2% Mo, plus small amounts (<1%) of zirconium and carbon (from addition of mischmetal). It was reported to have excellent oxidation and aqueous corrosion resistance, good stress-rupture and tensile strength at elevated temperatures, soft

magnetic characteristics similar to some nickel-based alloys, high electrical resistivity, and a RT ductility of 8-10%.^{3,8-10} However, there was no significant commercialization (although a few cast products were available from the Duraloy Company and wrought products from Universal Cyclops Steel Corp.) because of difficulties with processing and control of microstructure.

At approximately this same time, an extensive study was conducted by the Scientific Laboratory at Ford Motor Company under sponsorship of the United States Air Force.¹¹⁻¹³ This study included alloy development, oxidation, fabrication, mechanical properties, and welding studies on recrystallized alloys containing up to approximately 32% Al. They were able to improve the hot strength of 18-22% Al binary alloys with additions

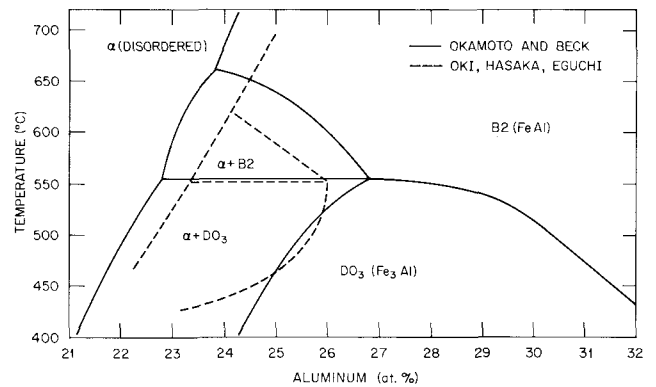


FIG. 2. The iron-aluminum phase diagram showing the phases of interest to this review. Phase boundaries defined as per Refs. 31 and 33.

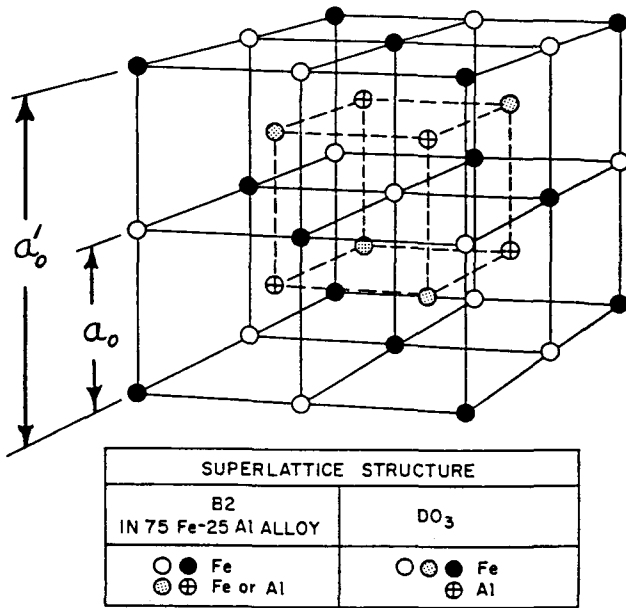


FIG. 3. Unit cell of the Fe₃Al (D0₃) and FeAl (B2) superlattices. The B2 superlattice is a bcc cell with iron on one sublattice and aluminum on the other. The D0₃ superlattice is eight B2 superlattices stacked to allow for the maximum distance between aluminum atoms.³⁶

of titanium. They also investigated some Fe–Al–Cr alloys with about 14% Al and 7–8% Cr and found them to have good oxidation resistance to 1200 °C.

With the evolution of the transmission electron microscope (TEM) and the application of dislocation theory, the 1960's and 1970's saw an emphasis on the study of ordering and formation of antiphase domains (APD's) and boundaries (APB's) in long-range ordered alloys, the study of superlattice dislocations in ordered systems (twofold and fourfold superdislocations), and the development of TEM techniques for observing superlattice dislocations and measuring APB energies. The works of Lawley *et al.*,³⁷ Marcinkowski *et al.*,^{19,38} Stoloff and Davies,¹³ Davies,³⁶ and Crawford *et al.*³⁹ are noteworthy for their studies of ordering reactions, superlattice dislocations (see Fig. 4), and the effect of order and superlattice dislocation movement on mechanical properties of iron aluminides. The work at Iowa State University in the 1960's^{14–19} also contributed much to our understanding of the nature of D0₃ and B2 ordering and the effect of ordering on the mechanical properties of Fe₃Al. An excellent review of these studies has already been compiled²⁵ and will not be repeated here.

As of about 1980, the understanding of the properties of Fe₃Al-based aluminides included the following:

Fabrication—Fabrication procedures had been extensively studied. Alloys of reproducible quality could be produced by either vacuum or air melting techniques. It was recognized that alloys could be hot-worked readily at temperatures up to 1000 °C and could be warm

worked at 575–700 °C, but the alloys were difficult to work at ambient temperature. Good hot workability required a fine, equiaxed ingot grain structure. Processing also required control of the alloy composition and the processing environment. It was recognized that, owing to its inherently low thermal conductivity, the material was subject to cracking from thermal stresses during cooling from the melt or after hot working.^{25,28}

Mechanical properties—In general, for binary alloys, RT brittleness and lack of HT strength become more problematical as aluminum concentration increases. Hot strength could be improved by solid solution strengthening (e.g., with silicon) or precipitation strengthening (e.g., using titanium).²⁸ However, both these additions decreased RT ductility dramatically, and it was found that most alloying additions that increased strength were detrimental to RT ductility. Ductility enhancements were noted for alloy additions that led to a finer grain size. Creep rupture strength was shown to increase with aluminum content²⁸ and was better above 25% Al than below. Creep resistance could also be increased through precipitation strengthening.²⁸ Tensile tests produced mainly intergranular fractures, which were believed to be intrinsic to ordered Fe₃Al and which suggested that failure was predominantly due to the

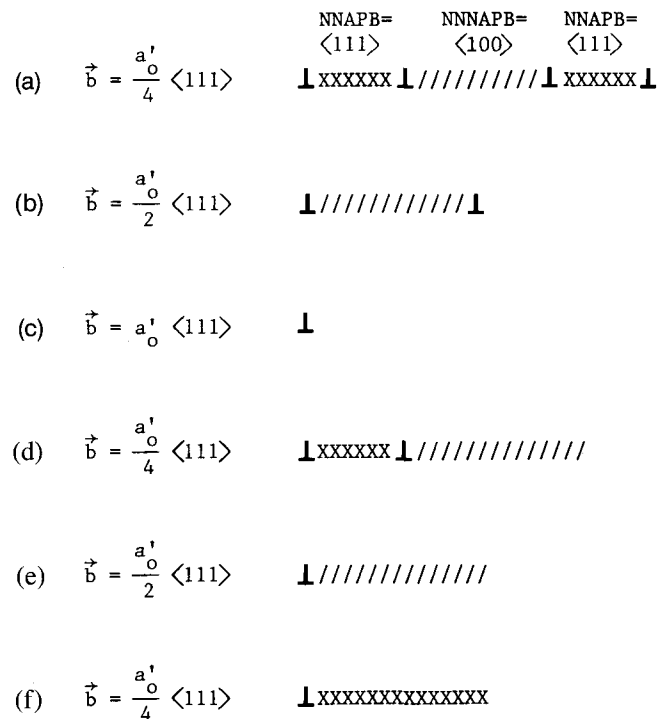


FIG. 4. Schematic illustration of possible D0₃ superlattice dislocations (a–c) and their imperfect variants (d–f). NNAPB and NNNAPB represent nearest-neighbor and next-nearest-neighbor antiphase boundaries enclosing the B2 and D0₃ antiphase domains, respectively.^{15,38,46,54}

weakness of disordered grain boundaries.^{14,19} The low ductility and resulting brittle fracture with aluminum content above 20% were believed to be associated with the retardation of cross-slip due to the onset of long-range atomic order.¹⁹

Oxidation/sulfidation resistance—Good oxidation and sulfidation resistance in binary iron aluminides require an aluminum content in excess of 15%. The study of Thermenol^{9,10} indicated that iron aluminides had excellent resistance in the following corrosive media: (1) 20% NaCl solution at 90 °C, (2) NaOH solutions, (3) organic acids, (4) concentrated NH₄OH, (5) food and food products, (6) sulfur vapors to 700 °C, and (7) concentrated nitric acid at room temperature. Thermenol was attacked at ambient temperatures by chloride-containing solutions such as ferric chloride and hydrochloric acid. Oxidation tests at the Ford Motor Co.^{11,25} showed that additions of up to 7% Cr did not harm the oxidation resistance of Fe–14% Al at 1200 °C for 500 h. They also showed that, although silicon was detrimental to the RT ductility, it was better for oxidation resistance than the same amount of aluminum.

Most of the alloy development efforts up to recent times involved alloys of less than 20% Al, for which sufficient ductility often could be achieved. However, for many applications, higher aluminum contents were desired for better oxidation and sulfidation resistance (see below). The principal obstacles to increasing the aluminum level remained lack of RT ductility, a drop in strength above 600 °C, and the need for special melting procedures to prevent cracking from thermal shock and to control impurities.

III. RECENT DEVELOPMENTS IN MECHANICAL PROPERTIES

Over the last decade, major developmental work on iron aluminides has been performed at three laboratories: Pratt and Whitney (P & W), TRW, Inc., and Oak Ridge National Laboratory (ORNL). The work at P & W and TRW has been sponsored by the Materials Laboratory at the Air Force Wright Aeronautical Laboratories (AFWAL) and has addressed the development of iron-aluminum based alloys using rapid solidification.^{4,5,40} For the most part, the work at ORNL has been sponsored by the Fossil Energy Office of the United States Department of Energy with the aim of producing wrought material for fossil energy applications.^{6,7,21–24}

A. P & W, TRW

At P & W, iron aluminide powders, some containing titanium diboride (TiB₂) precipitates, were produced by a rapid-solidification-rate (RSR) process developed in-house and were then consolidated by hot extrusion. Following consolidation, specimens for study were pro-

duced by hot and warm working. One of the most important developments to come from this program was the result that Fe₃Al alloys containing TiB₂ precipitates produced by RSR processing could achieve RT tensile elongation values in the range of 15 to 20% with tensile strengths of 965 MPa (140 ksi) (Fig. 5).^{4,40} The creep rupture strength at 982 °C (Fig. 6) was about equal to that of Hastelloy X.⁴ It was noted that changes in consolidation and working conditions and the use of fine versus coarse powder caused variations in microstructure that were found to be the major reason for differences in strength and ductility. In general, the finer grain structures produced the best combination of mechanical properties.⁴

Concurrent with the work at P & W, and as a separate task of the total iron-aluminum alloy effort sponsored by AFWAL, a development program was begun at TRW, Inc., to improve the properties of Fe₃Al-based aluminides through ternary additions. The final report⁵ presents the effects of ternary additions of Ti, V, Cr, Mn, Ni, Nb, Mo, Ta, Cu, or Si on mechanical properties, workability, and oxidation resistance. Binary alloy powders of FeAl and Fe₃Al were prepared by the Linde Division of Union Carbide Corporation by conventional inert gas atomization. Ternary alloy powders based on Fe₃Al were produced by the Plasma Rotating Electrode Process (PREP) at Nuclear Metals, Inc. The alloy powders were then mixed to produce the desired alloy composition and consolidated by hot extrusion. As a check on the properties of the powder-produced alloys, several ternary alloys were also prepared by conventional ingot metallurgy. Workability testing, involving upset isothermal forging at 954 °C, indicated no adverse effects in any of the alloys tested. Improvements in room temperature yield strength, as measured by tensile testing, were obtained with additions of up to 5% Nb or Ta. At 600 °C, significant increases in yield strength were produced by additions of Si, Ta, Mo, Nb, or Cr. However, with one exception, every alloy containing solid solution additions of chromium and molybdenum exhibited a significant drop in room temperature ductility, compared to the 4.8% ductility of Fe₃Al. The alloy containing chromium and molybdenum produced the optimum tensile properties, with 1.3 times the 600 °C yield strength and RT ductility equivalent to that of Fe₃Al. The strengthening was attributed to the potent solid-solution strengthening capability of chromium and molybdenum.⁵

The potential for further strengthening via refinement of precipitate size, especially in niobium- or tantalum-containing alloys, was noted.⁵ However, during preparation of this material, a sensitivity to quench-cracking was observed and later identified as contributing to the poor fatigue properties.⁵ The studies indicated that attention to processing techniques,

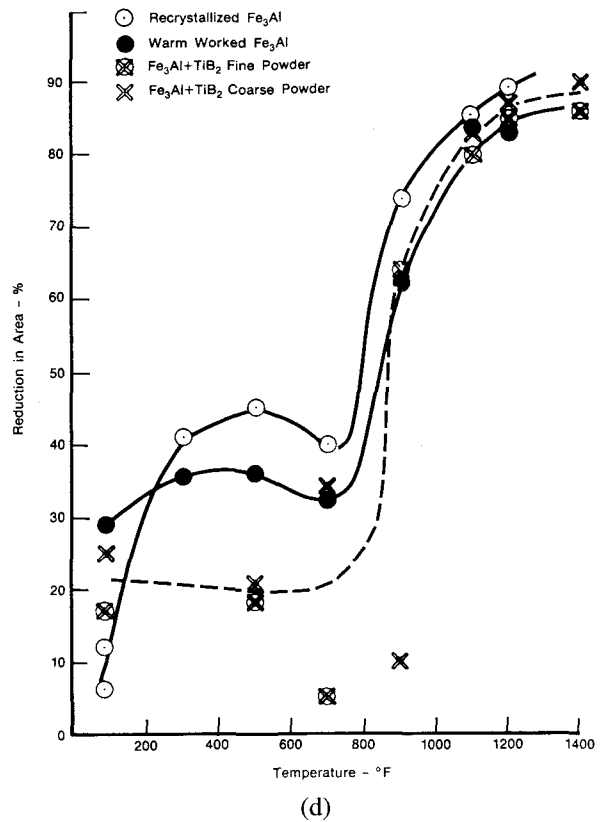
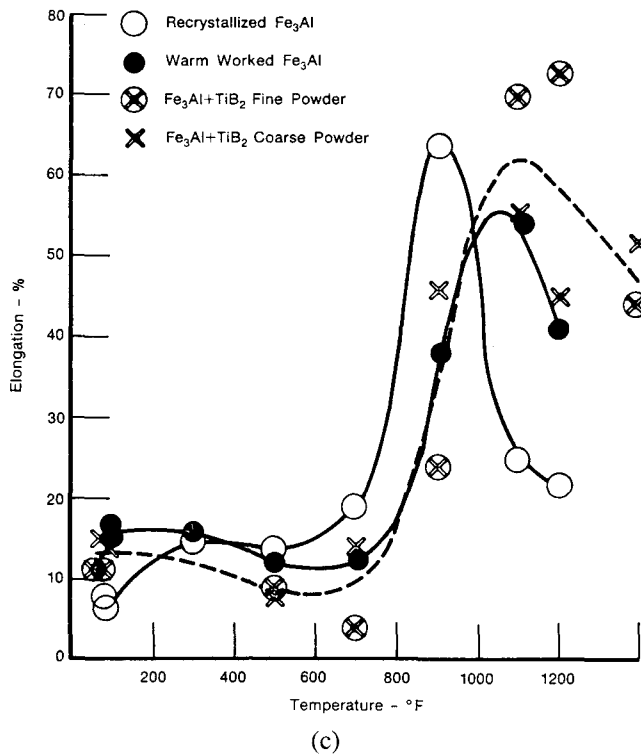
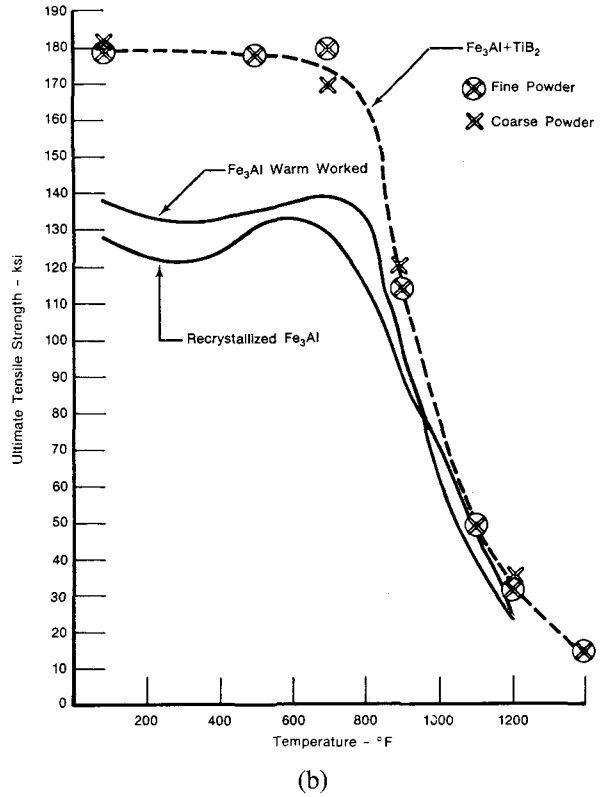
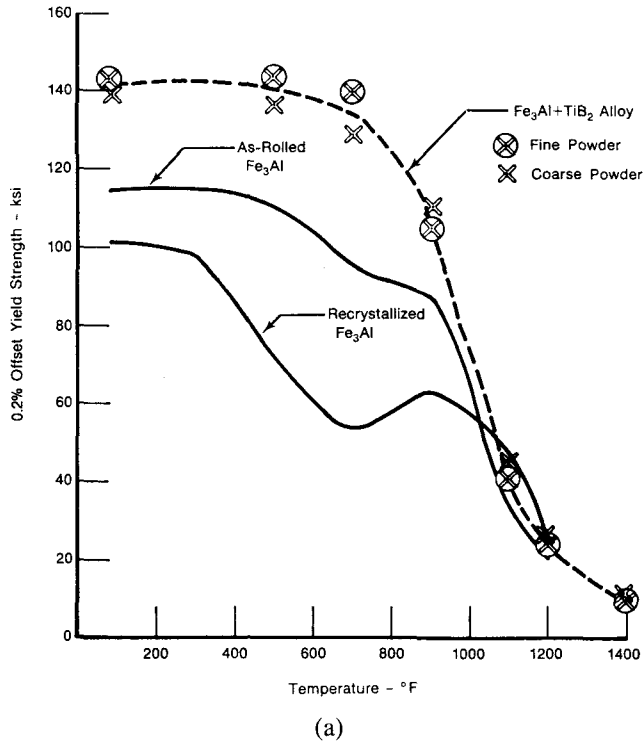


FIG. 5. Tensile properties versus test temperature of extruded and rolled Fe₃Al with and without TiB₂: (a) yield, (b) ultimate, (c) elongation, and (d) reduction in area.⁴

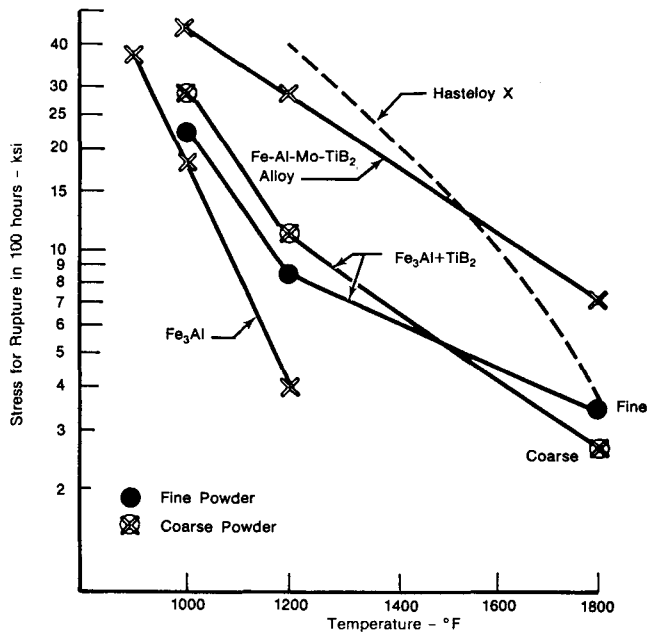


FIG. 6. Stress rupture in 100 h for extruded and rolled Fe₃Al with and without TiB₂.⁴

especially with regard to quench-cracking sensitivity, would be necessary to produce material with optimum properties.

The development programs at both P & W and TRW, which have been extensively reviewed in Ref. 25, were supported with in-depth TEM characterization of the microstructures (including APB's and precipitates) and dislocation morphologies of the alloys under study through a collaboration with Systems Research Laboratories, Inc. (SRL).⁵ By selecting the proper superlattice reflections, either both D0₃ and B2 domains or only B2 domains can be revealed. Examination of the size and morphology of the domains in the ternary alloys after heat treating at selected temperature followed by quenching indicated that ternary additions of Mn, Ni, or Mo increased T_c moderately, while titanium or silicon increased T_c significantly.^{5,41-43} However, little correlation between change in T_c and strength at 600 °C was noted for any of the alloys tested, suggesting that stabilizing the D0₃ phase to higher temperatures was not the only factor controlling strength in these alloys.

The collaboration between AFWAL and SRL resulted in several open-literature publications dealing with both microstructures and dislocation character⁴¹⁻⁴⁵ and their effect on tensile behavior.⁴⁶⁻⁵¹ A number of alloying additions increased strength through both solid-solution and precipitation-strengthening effects. In particular, a potential exists for increasing HT strength through control of precipitate size, morphology, and composition. Although thermal stability was not encouraging, precipitation of a coherent L2₁ phase in Fe-25% Al-2% Nb

after solutionizing at 1350 °C and heat treating at 700 °C produced a significant improvement in tensile strength at all temperatures to 700 °C (Fig. 7).⁴¹⁻⁴⁴ Studies of well-controlled compositions indicated that fracture in pure Fe₃Al was by transgranular cleavage.⁵¹ This result supported the conclusions of Horton *et al.*,⁵² who had earlier refuted the theory of weak grain boundaries (see below) and suggested that brittleness of Fe₃Al is due to poor cleavage strength. The general conclusion from the work sponsored by AFWAL was that iron aluminides are not inherently brittle as earlier believed, since the powder-processed alloys with TiB₂ produced reasonable ductilities at ambient temperatures. They also indicated the need for generating a database of properties, including tensile, fatigue, fracture toughness, elastic modulus, and creep data, as well as the importance of the effects of processing, fabrication techniques, and interstitial impurities on mechanical properties.

B. ORNL

1. Alloy development

The efforts at P & W and TRW were based on the production of iron aluminide alloy powders by RSR processing, the steps for which are very expensive and time-consuming if large quantities of material are produced. Work at ORNL has concentrated on producing alloys by conventional arc-melting and casting procedures, followed by fabrication by hot-forging, rolling, or extruding. Initial work (1982-84) was sponsored by the Office of Naval Research and involved alloying effects on microstructures and tensile properties,⁵² effects of D0₃-B2 transitions on the yield behavior,⁵³ and dispersion hardening with TiB₂.²⁰

Fe₃Al was alloyed with ternary additions of B, Si, Cu, or Ni for study of its alloying behavior and associated microstructures.⁵² Alloying with additions of

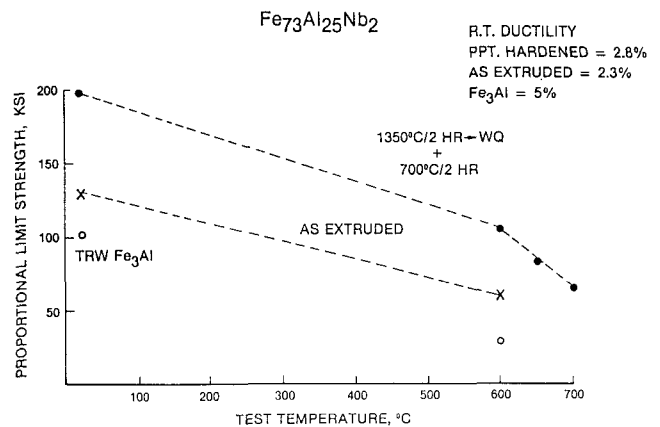


FIG. 7. Proportional limit bend strength of Fe-25% Al-2% Nb alloy containing coherent L₂₁ particles as a function of test temperature. Data for as-extruded alloy and for Fe₃Al also shown for comparison.⁴¹

0.24% B had virtually no effect on the ductility and cleavage fracture behavior of Fe₃Al. Although silicon and copper increased the yield stress and hardness, both elements were found to embrittle the alloy by a process of second phase precipitation. Nickel additions resulted in two-phase alloys and brittle grain boundary fracture. The general conclusion from this study was that pure Fe₃Al fails by transgranular cleavage (as noted above), but that grain boundaries are susceptible to embrittlement by many alloying agents, often resulting in an intergranular failure mode.⁵² This study disproved the theory of weak grain boundaries in Fe₃Al, indicating that the observations of intergranular fracture in earlier studies were probably due to impurities in the alloys.

To study the age-hardening behavior of Fe₃Al alloys, sheet tensile specimens of Fe–24% Al and Fe–26% Al were annealed at 400 °C, then aged and tested at 450, 500, and 540 °C.⁵³ The results of tensile tests showed that the yield strength of Fe–24% Al increased by a factor of two or more (from 186 to 413 MPa) within 60 min of aging at 500 °C, while Fe–26% Al showed a small decrease. The yield strength response of Fe–24% Al was due to the precipitation of α during aging at 400–500 °C, a reaction which did not occur in Fe–26% Al. For aging temperatures of 540 °C, Fe–24% Al attained its maximum yield strength in about 10–15 min but required about 30 000 min at 450 °C. Thus, when metastable alloys with an initial Fe₃Al structure were reheated, their yield strength increased with the test temperature to a maximum at the optimum combination of quantity and size of the α precipitates in the ordered phase. This proposed strengthening mechanism was in contrast to previous studies that attributed the yield behavior to a change in degree of order and a transition of unit dislocations to superdislocations.¹³

The effects of TiB₂ additions (up to 15 wt.%) on the structure and tensile properties of Fe₃Al (25% Al) were studied.^{20–22} Alloy ingots were prepared by melting and drop-casting using elemental titanium and boron, and were fabricated into sheet materials by repeated rolling at 650 to 1000 °C. The dispersion of TiB₂ was shown to be very effective in refining grain structure. TEM studies revealed that TiB₂ particles are rod-shaped, with dimensions of about 0.4 by 2 μ m, and well dispersed throughout the material. TiB₂ additions moderately strengthen Fe₃Al at temperatures to 600 °C. Dispersoid refinement through quenching from above 1300 °C provided additional particle strengthening at 700 °C. Ductility increases for alloys with 2 wt. % TiB₂ additions were observed at both room and elevated temperatures.

The effects of thermomechanical treatment on the microstructure and RT ductility of the TiB₂-modified Fe₃Al were also examined.²⁰ It was found that the degree of recrystallization had a strong influence on

the ductility: a partially recrystallized sample showed a ductility of as high as 11% as opposed to a fully recrystallized ductility of 3%. Recrystallization also shifted the fracture mode from mainly transgranular to intergranular. A maximum beneficial effect was noted with the addition of 2 wt. % TiB₂; above this concentration RT ductility decreased.

In 1985, the development of iron aluminide alloys at ORNL was reinitiated under the sponsorship of the Fossil Energy Program of the Department of Energy.^{6,7,21–24,54} Experimental-size alloys (0.5–7 kg) for this program have all been produced by arc-melting under argon and drop-casting into 500-g ingots, homogenizing at 1000 °C for 5 h, then hot-rolling at 1000–600 °C to 0.76-mm-thick sheet. Initial efforts involved the study of alloys containing 24 to 30% Al with titanium and boron added to produce a dispersion of 0.5 wt. % TiB₂.^{21,54}

The as-rolled microstructure of the TiB₂-containing alloys [Fig. 8(a)] showed elongated grains of less than 50 μ m width.²¹ The recrystallized grain size [Fig. 8(b)] was stable at 40–60 μ m even to temperatures as high as 1000 °C, indicating that the TiB₂ dispersion was effective in retarding grain growth in these alloys. Although the TiB₂ dispersion produced some strengthening at RT, HT strengths and RT ductilities were not increased, while the fracture mode was shifted from transgranular cleavage to intergranular failure. TiB₂ also proved detrimental to the weldability, resulting in hot cracking along the fusion line.⁵⁵

Figure 9 shows the 0.2% yield strength as a function of temperature for two of the compositions studied.²² The results for Fe–28% Al show the anomalous yield behavior near the D0₃-B2 transformation temperature as reported by other researchers,^{13,56} while the results for Fe–24% Al indicate significant strengthening at low temperatures caused by precipitation of the disordered α phase, as reported by Inouye.^{20,53} This figure also presents a favorable comparison of the yield strength of the iron aluminides with that of type 316 stainless steel and modified 9Cr–1Mo alloy.

From a consideration of all the properties of the binary alloys, with and without TiB₂, the Fe–28% Al alloy without TiB₂ was chosen as the base for alloy development efforts. To this binary were added small amounts (usually less than 2%) of Mo, Mn, Cr, Nb, Ti, Zr, B, Ce, Y, C, V, or Si, and tensile properties were measured at RT and 600 °C after recrystallization at 850 °C for 1 h followed by D0₃ ordering at 500 °C for 3–5 days. Only chromium was found to increase RT ductility, while improvements in tensile strength were noted for additions of Mo, Nb, Ti, Si, or Zr.²² Small additions of Nb, Mo, and Zr were found to improve creep rupture life at 593 °C (1100 °F) and 207 MPa from the 2–3 h of binary Fe₃Al to as much as 200 h.⁷ Although producing significant strengthening,

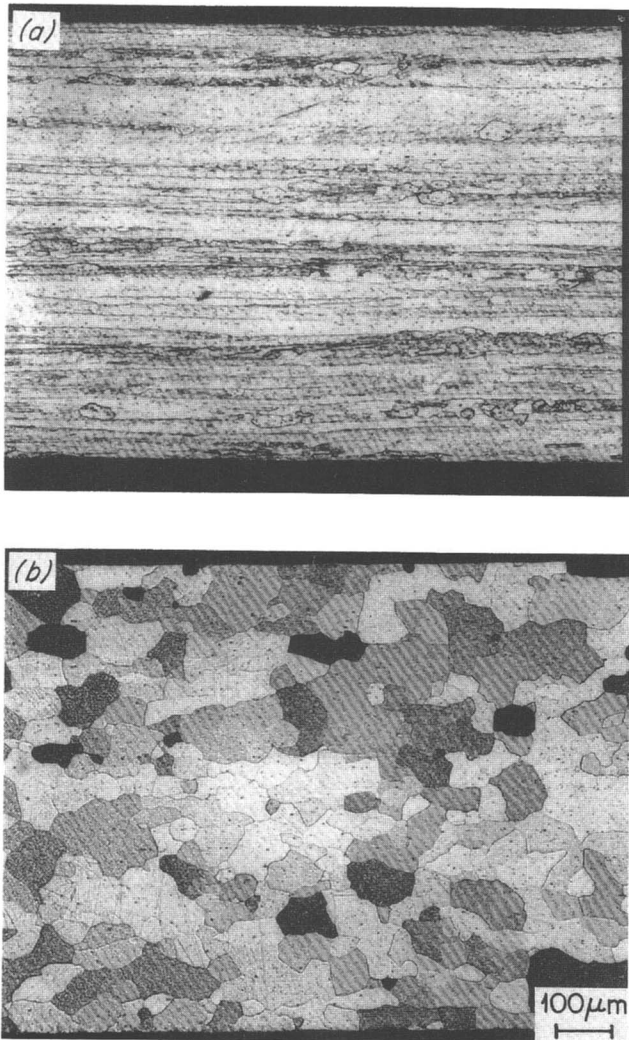


FIG. 8. Optical microstructures of Fe-27% Al with 0.5 wt. % TiB₂: (a) as-rolled, (b) after annealing 1 h at 850 °C plus 7 d at 500 °C.²¹

Ti and Si reduced the RT ductility so severely that they were not considered for further development efforts. A study of tensile fracture surfaces (Fig. 10) supported the previous findings of Horton *et al.*⁵² that the binary alloy fractures in a transgranular cleavage mode, while many elemental additions can lead to some degree of intergranular fracture.

Preliminary investigations on the weldability of Fe₃Al-based alloys were conducted.^{55,57-59} Thin sheets (0.76 mm thick) were autogenously electron beam (EB) and gas tungsten arc (GTA) welded at different speeds and power levels. The results indicated that the weldability of these alloys is sensitive to the type of welding process and welding parameters, as well as to

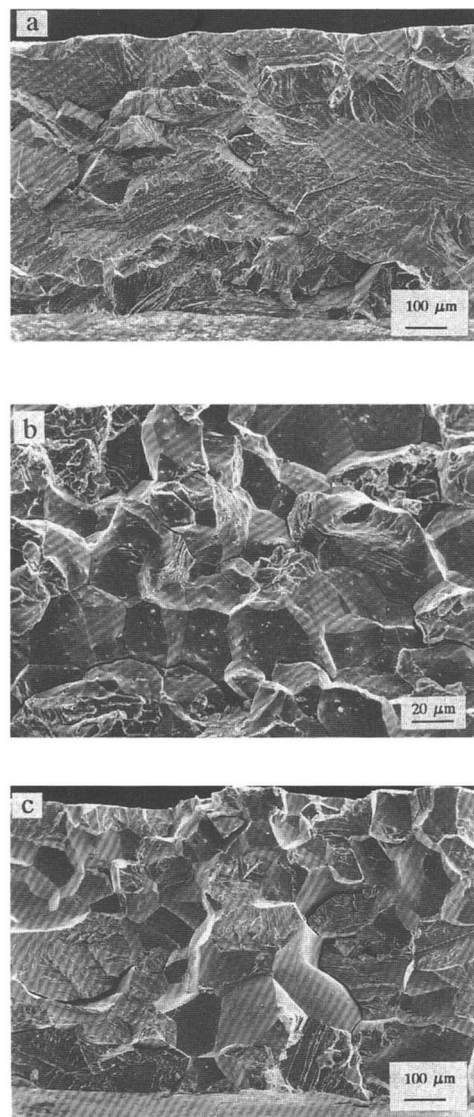


FIG. 10. Fracture mode of Fe₃Al-based alloys produced in tension at room temperature: (a) transgranular cleavage in Fe-28% Al, (b) mostly intergranular failure in Fe-28% Al with TiB₂, and (c) mixed transgranular cleavage and intergranular failure in Fe-28% Al-4% Cr.^{22,60}

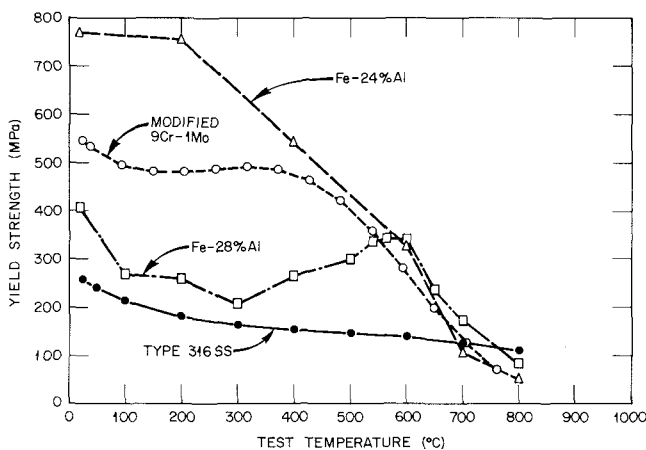


FIG. 9. Yield strength of iron aluminides versus test temperature and comparison to other alloys.²²

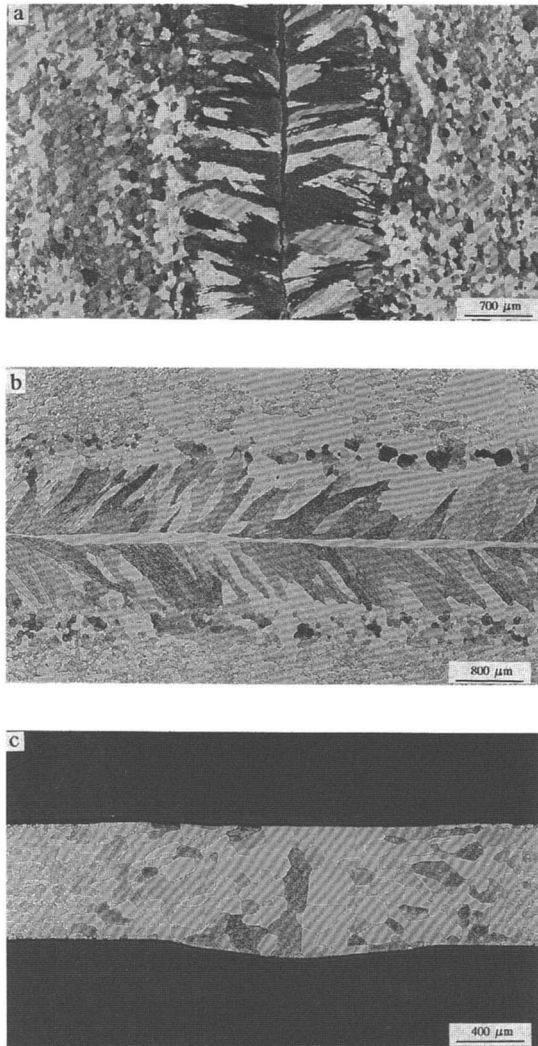


FIG. 11. Effect of alloying additions on electron beam weldability of Fe-28% Al: (a) hot cracking along the fusion line with addition of TiB₂, (b) no cracking with addition of niobium, and (c) through the thickness of the weld in (b).^{22,55}

composition, but is not sensitive to the microstructure of the starting material. Depending on the process and process parameters, welds with and without cracks were produced. Successful welds with minimum cracking were produced in an alloy modified with Cr, Nb, and C. In general, niobium and chromium were found to enhance weldability, while zirconium, boron, and TiB₂ were found to be detrimental to weldability (Fig. 11).

Table II divides the alloying elements under study at P&W, TRW, and ORNL into those which produce solid solution effects and those which have little or no solubility, and summarizes their effects on the properties.^{5,7,22,60-62} Many of the elements which go into solution in the binary alloy will readily form precipitates when other elements such as boron or carbon are also added. Only chromium was found to improve the RT

tensile ductility of Fe₃Al (Table III).^{5,22,60,61} Additions of 2-6% Cr resulted in a doubling of the RT ductility; however, no improvement was noted with 6% over 2%.^{61,63} A study to determine the mechanism(s) by which chromium affected RT ductility was initiated using the binary 28% Al alloy with and without chromium.^{60,61} The results indicated that, with the addition of chromium, the transgranular fracture was often accompanied by some degree of intergranular failure (see Fig. 10), suggesting that chromium enhanced cleavage strength and partially suppressed cleavage fracture. It was also noted that APB energies were lowered, as indicated by increased spacing among the four dislocations which make up the superdislocation. This suggested that dissociation of the superdislocation and cross-slip would be easier. Dissociation and easier cross-slip were, in fact, observed in a TEM.⁶¹

Room-temperature strengthening in these alloys is produced by precipitates, while high-temperature strength is provided by either precipitate-formers or solid solution additions. The most potent ternary addition for producing improved creep resistance is niobium, but this improvement is severely reduced by additions of other elements such as chromium.⁷ Molybdenum, on the other hand, although it improves the creep resistance as a ternary addition in comparison to the binary,^{4,7} appears to have a maximum beneficial effect on the creep resistance when added along with a small amount of zirconium.⁷

A detailed study was conducted on the effects of addition of molybdenum,⁶² which was found to be important in increasing the tensile and creep strengths. Molybdenum goes into solution to at least 6% but will also readily form precipitates with other elements such as boron and carbon.^{22,62} Grain sizes were reduced owing to grain boundary pinning by precipitates, and T_c was seen to increase approximately 25 °C for each atomic percent of molybdenum added. Additions of 1-2% produced some improvement in tensile strength at all temperatures to 800 °C, but reduced the RT ductility. Its most significant effect was on creep strength.⁷

2. Environmental embrittlement

At RT, FeAl and Fe₃Al characteristically exhibit limited ductility and brittle fracture. Their fracture mode depends on aluminum content; those alloys containing <40% Al fracture by transgranular cleavage while those with >40% Al fracture intergranularly. The vexing question concerning iron aluminides has always been why they are brittle at room temperature when they apparently have all the intrinsic characteristics required for good ductility. For example, they deform by {110} {111} slip; that is, like disordered bcc metals, they have more than five independent slip systems. They are not particularly strong at room temperature,

TABLE II. Effect of elemental additions on properties of Fe₃Al.^a

Element	Workability	RT tensile		HT tensile strength	Creep resistance ^b	D0 ₃ -B2 temperature ^c	Oxidation resistance ^d
		Elong.	Yield				
<u>Precipitate-forming additions</u>							
Nb	—	↓↓	↑↑	↑↑	↑↑	—	—
Cu	—	↓↓	↑↑	↓	—	—	—
Ta	↓↓	↓	↑↑	↑↑	—	—	—
Zr	↓↓	↓↓	—	—	↑	—	—
B	—	↑	↑	—	—	—	—
C	—	—	↑	—	↓	—	—
<u>Solid-solution additions</u>							
Cr	↓	↑	↓	↑	—	—	—
Ti	—	↓↓	↑	↑	↑	↑	↓
Mn	—	↓	↓↓	↑	—	↑	—
Si	—	↓↓	↓↓	↑↑	—	↑↑	—
Mo	↓	↓↑	↓	↑↑	↑↑	↑	—
V	—	—	—	—	—	—	↓↓
Ni	—	↓↓	↓	↑↑	—	—	—

^aInformation taken from Refs. 5, 7, 22, 52, and 60–62. Up-arrow signifies increasing effect, down-arrow decreasing effect, and dashes equal no effect. Two arrows together signify two different references.

^bTested to rupture at 593 °C and 207 MPa.

^cRaises or lowers from ~540 °C.

^dTested at 800–816 °C for 240–500 h in laboratory air.

with yield strengths on the order of 345 MPa, and, because they do not fracture intergranularly, they do not appear to have weak grain boundaries (like, for example, Ni₃Al). Until recently, the poor ductility of these materials was assumed to reflect an intrinsically low cleavage strength.⁵¹ However, Liu *et al.*⁶⁴ have now shown that the ductility of both FeAl and Fe₃Al significantly increases when the alloys are tested in vacuum rather than air. Further testing has pointed to the interaction of water vapor with aluminum in the alloy as a major contributor to the low RT ductility of this class of alloys. The removal of water vapor leads to the expected intrinsic plastic deformation prior to fracture.^{64–67}

Figure 12 and Table IV show the effect of test environment on the tensile properties of binary Fe₃Al

TABLE III. Tensile properties of Fe–Al–Cr alloys.⁶¹

Property	Fe–28% Al	Fe–28% Al + Cr		
		2%	4%	6%
<u>Room temperature</u>				
Yield (MPa)	279	247	228	232
Ultimate (MPa)	514	638	553	535
Elongation (%)	3.7	9.4	8.2	8.4
<u>600 °C</u>				
Yield (MPa)	345	349	347	358
Ultimate (MPa)	383	401	409	415
Elongation (%)	33	43	32	34

and FeAl (36.5% Al).^{64–67} When tested in air, the FeAl alloy has a tensile ductility of 2.2%, which increases to 5.4% when tested in vacuum (pressure $<1 \times 10^{-4}$ Pa). This indicates that some gaseous species in air is causing embrittlement, and when its effect is avoided (e.g., by testing in vacuum), ductility is improved. The embrittling agent was identified as water vapor by first evacuating the test chamber to a pressure $<1 \times 10^{-4}$ Pa, and then individually leaking various gaseous species into the chamber (including oxygen, hydrogen, and water vapor). As shown in Table IV and Fig. 12, the water vapor tests reproduced the low ductility obtained in the air tests. The best ductility for FeAl (17.6%) is obtained in dry oxygen (Fig. 12), indicating either that the higher oxygen content promotes faster oxide formation (which acts as a barrier against water vapor), or that even the residual moisture in the vacuum test is sufficient to cause some embrittlement of FeAl relative to the dry oxygen test. These studies were extended to Fe₃Al (Table IV), and the results confirmed that Fe₃Al is also susceptible to environmental embrittlement in the presence of water vapor,⁶⁶ although the degree of sensitivity appears to be less. The phenomenon does not appear to be structure-dependent, occurring in both D0₃ and B2 structures. Table IV shows vacuum and oxygen ductilities to be equal for Fe₃Al, indicating that any water vapor left in the vacuum is not detrimental to Fe₃Al. These results on environmental embrittlement have recently been substantiated by Kasul and Heldt on Fe–24.6% Al by tensile testing in air, oxygen, and vacuum.⁶⁸

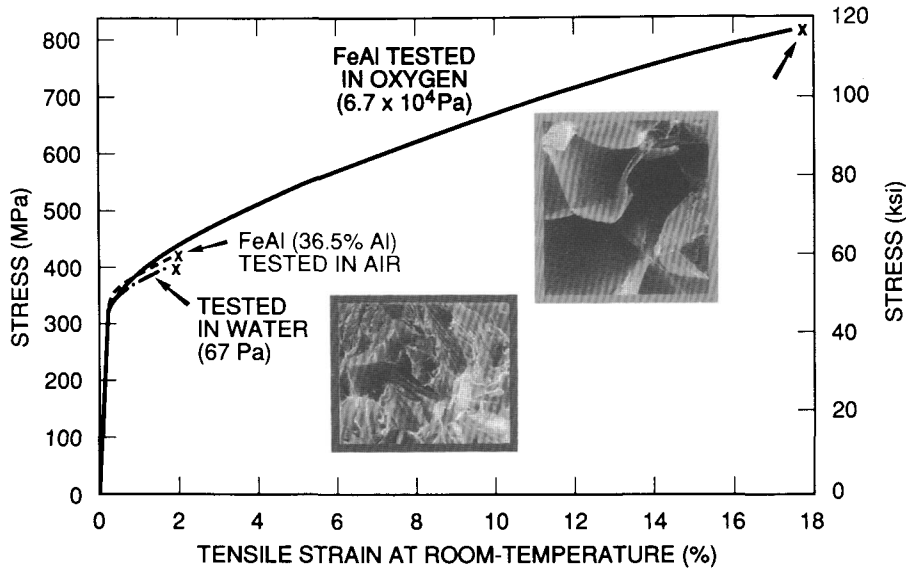
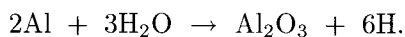


FIG. 12. The effect of test environment on ductility and fracture behavior of FeAl (36.5% Al) tested at room temperature.^{65,67}

The mechanism that has been proposed⁶⁴⁻⁶⁷ for this type of environmental embrittlement is similar to that which is observed in aluminum and its alloys.^{69,70} The embrittlement is thought to involve the chemical reaction⁷⁰



Because iron aluminide alloys contain relatively large concentrations of aluminum, it is postulated that the alu-

minum reacts with the water vapor molecule, producing alumina (or a precursor oxide) and chemisorbed atomic hydrogen, which induces classic hydrogen embrittlement at crack tips where fresh surfaces are created due to stress concentrations. Table IV shows that the yield strength is insensitive to test environment, a common observation in other studies of hydrogen embrittlement in ordered intermetallics.⁷¹⁻⁷⁵ Much more work needs to be done to unravel the details of environmental

TABLE IV. Effect of test environment on room-temperature tensile properties of FeAl (36.5% Al) and Fe₃Al (28% Al).⁶⁴⁻⁶⁷

Test environment (gas pressure)	Elongation (%)	Yield strength (MPa)	Ultimate tensile strength (MPa)
<u>Annealed 1 h/900 °C + 2 h/700 °C</u>			
FeAl			
Air	2.2	360	412
Vacuum ($< 1 \times 10^{-4}$ Pa)	5.4	352	501
Oxygen (6.7×10^4 Pa)	17.6	360	805
Ar + 4% H ₂ (6.7×10^4 Pa)	6.2	379	579
H ₂ O vapor (67 Pa)	2.4	368	430
Fe ₃ Al			
Air	4.1	387	559
Vacuum ($\sim 1 \times 10^{-4}$ Pa)	12.8	387	851
Ar + 4% H ₂ (6.7×10^4 Pa)	8.4	385	731
Oxygen (6.7×10^4 Pa)	12.0	392	867
H ₂ O vapor (1.3×10^3 Pa)	2.1	387	475
<u>Annealed 1 h/850 °C + 5 d/500 °C</u>			
Fe ₃ Al			
Air	3.7	279	514
Vacuum ($\sim 1 \times 10^{-4}$ Pa)	12.4	316	813
Oxygen (6.7×10^4 Pa)	11.7	298	888
H ₂ O vapor ^a	2.1	322	439

^aAir saturated with water vapor was leaked into the vacuum chamber.

embrittlement in iron aluminides. What is clear from these recent results, however, is that Fe₃Al and FeAl (<40% Al) alloys are intrinsically ductile, and that the low ductility commonly observed at RT is the result of an extrinsic factor, namely moisture-induced environmental embrittlement. This discovery, and the understanding of the mechanisms involved, will aid alloy development efforts in all aluminide systems.

Evidence for this hydrogen effect are available from the results of recent experiments in aqueous environments.^{68,76} Kasul and Heldt exposed Fe-24.6% Al to aqueous solutions under conditions of controlled electrochemical potential and pH and found that conditions producing a high fugacity of hydrogen at the specimen surface caused a significant loss of ductility.⁶⁸ Conversely, testing in neutral or low hydrogen fugacity conditions had little effect on ductility. They also found that cathodically precharging with hydrogen in acid solutions for times as short as 5 min could produce embrittlement. The ductility could be restored by heat treatment at 800 °C for 1 h, but vacuum degassing at room temperature for up to 30 days did not restore the ductility. Buchanan and Kim also reported some embrittlement in aqueous solutions when hydrogen is generated at the specimen surface (see below).⁷⁶

In the light of these new findings concerning the embrittling mechanism in Fe₃Al-based alloys, new studies of the effects of chromium additions were initiated at ORNL.⁷⁷ Table V shows the results of tensile tests in air at room temperature for Fe-28Al and Fe-28Al-4Cr as a function of annealing treatment and surface condition. The lower yield strength of the chromium-containing alloy is due to a solid-solution softening effect produced by the chromium addition.^{60,61} Several observations can be made concerning the ductilities of the chromium-containing specimens: (1) The specimens which were electropolished to remove oxide and then annealed in

vacuum to minimize oxide formation (EP) showed elongations comparable to the binary alloy. (2) Leaving the as-rolled oxide coating on the specimens (AR) resulted in an observable increase in ductility for the chromium-containing alloys compared to both the binary and to chromium-containing specimens that had been electropolished. (3) The chromium-containing specimens which were annealed for 1 h at 850 °C and 96 h at 500 °C in air had comparable ductilities whether they were electropolished (EP + OC) or left with the as-rolled oxide coating. This suggests that the heat treatment in air produced a thin protective oxide coating on previously electropolished specimens. (4) In the AR condition, the ductility values for the chromium-containing specimens annealed in air were comparable to values from the same alloy annealed in vacuum; however, in the EP condition, higher ductilities were observed by annealing in air, again suggesting the formation of a protective oxide coating during the air anneal. These observations suggest that, although chromium may affect APB energies and fracture strength as noted earlier,^{60,61} it may also reduce environmental embrittlement through some kind of effect on the composition or properties of the oxide coating. Recent x-ray diffraction studies of the effect of chromium addition on the D0₃-B2 transition also indicate that as a ternary addition chromium tends to stabilize the B2 structure all the way to room temperature.^{63,78} This means that the 28% Al with 4% Cr exists in a highly "imperfect" B2 structure, with little long-range order, allowing the superdislocations to dissociate and cross-slip much more easily.

Improvements in alloy ductility have been achieved at ORNL by macroalloying with chromium and by using thermomechanical techniques to produce highly elongated grains with fewer transverse boundaries to permit the entry of hydrogen. These techniques have resulted in RT ductilities in air of 15–20% in experimental-

TABLE V. Effect of surface condition and heat treatment on tensile properties of Fe₃Al and Fe₃Al + Cr tested in air at room temperature.⁷⁷

Heat treatment (h/°C)	Surface condition at testing ^a	Fe-28Al			Fe-28Al-4Cr		
		Yield (MPa)	Ultimate (MPa)	Elong. (%)	Yield (MPa)	Ultimate (MPa)	Elong. (%)
1/900 + 2/700 vac	EP	387	559	4.1	256	364	4.0
1/900 + 2/700 vac	AR	398	587	4.3	199	433	7.8
1/900 + 96/500 vac	EP	267	515	5.4	192	356	5.8
1/900 + 96/500 vac	AR	277 ^b	551 ^b	5.6 ^b	196	423	7.2
1/850 + 96/500 air	EP + OC	270	429	3.6	236	483	8.2
1/850 + 96/500 air	AR	285	466	3.6	248	461	7.0

^aEP = electropolished; AR = as-rolled; OC = oxide coating produced by annealing in air.

^bData from different ingot of same composition.

size castings (0.5–7 kg).^{6,7} Macro- and microalloying techniques have also produced improvements in creep and tensile strength compared to the binary Fe₃Al (see Table VI).⁷ Charpy impact properties and studies of the protective oxide may also contribute to our understanding of the water vapor phenomenon.^{79,80}

3. Fabrication

Melting and fabrication of commercial size heats will be necessary for the successful application of iron aluminides. Early studies of melting and fabrication are reviewed in Refs. 25, 28, and 29. In the recent literature, no information regarding their fabricability, other than the work carried out at ORNL in cooperation with several commercial producers,^{6,81–83} is available. Melting of iron aluminides at ORNL and at commercial vendor facilities has been accomplished by many different methods. These have included air induction melting (AIM), vacuum induction melting (VIM), vacuum arc remelting (VAR), and electroslag remelting (ESR). Large heats (~250 kg) produced by the AIM process showed good surface quality but were found to contain some gas-type porosity, believed due to the reaction of aluminum in the melt with moisture in the air or moisture adsorbed on the surface of the charge material. Melting by the AIM process using dry melt stock and a dry argon gas cover resulted in a significant reduction of the porosity.⁶ However, to avoid gas porosity and control microstructure, vacuum melting techniques such as VIM and VAR are recommended. Examples of Fe₃Al-based alloys produced in heats of up to 250 kg by the VIM, VAR, and ESR processes are shown in Fig. 13.^{82,83} The ingot sizes in these photographs are 100 mm for VIM and 150 mm for VAR and ESR. The surface quality of the VIM, VAR, and ESR ingots is significantly better than that of AIM ingots.

An unanswered question in the scale-up of Fe₃Al-based alloys is the sequence by which commercial melting will be most economical. The question specifically relates to the exact steps by which up to 30 at. % (16 wt. %) aluminum will be added to the alloy. Experience gained at ORNL has indicated that two approaches are possible.⁸⁴ In the first, alloying additions (such as

chromium, niobium, etc.) are added to scrap iron that has been refined by an argon-oxygen decarburization process to the correct levels of carbon, sulfur, etc. This metal of correct composition is then added to the aluminum in a ladle that has been preheated to 500 °C. The final homogenization of the alloy is accomplished by blowing argon through the ladle. This method is expected to produce the alloy at the lowest cost, will use current technology, and will result in minimum reaction of the aluminum with the crucible material. In the second approach, the alloy is prepared by vacuum induction melting, where all of the alloy ingredients are added simultaneously. In this case, aluminum will melt first and will start dissolving the iron and other alloying elements. The first method is expected to be more economical, with VAR and ESR processes used for further refining of the alloy.

As noted above,^{4,5} Fe₃Al-based powders can be produced by either nitrogen- or argon-gas atomization.^{85–89} Subsequent consolidation to full density can be accomplished by extruding at 1000 °C to an area reduction ratio of ≥9:1, resulting in fully dense alloys with a grain size of approximately 70 μm (Fig. 14). Tensile tests at ORNL indicated that alloys produced from the nitrogen-gas atomized powder gave slightly enhanced properties over the argon-gas atomized powder.⁸⁶

Studies to determine satisfactory techniques for conversion of ingots into various product forms have been conducted.^{6,83} Hot or warm working of the as-cast ingot by rolling, forging, or extruding at temperatures of 600–1100 °C were used to produce billets, rod, wire, sheet, and tube (Fig. 15). Iron aluminide seamless tubing may be produced by three fabrication methods: centrifugal casting from the liquid metal, hot rotary piercing of the bar, and hot extrusion of the bar over a mandrel.^{6,82} The combination of working temperatures developed at ORNL has yielded highly elongated grain structures that can be recrystallized into equiaxed fine-grained structures by annealing between 750 and 850 °C.

C. Other studies

A program to study the effect of ternary additions of Mo, Ti, Si, Hf, and Ta on properties of Fe₃Al-

TABLE VI. Creep rupture and tensile properties of Fe₃Al-based alloys.⁷

Alloy	Composition (at. %)	Creep rupture		RT tensile		600 °C tensile	
		Life (h)	Elong. (%)	Yield (MPa)	Elong. (%)	Yield (MPa)	Elong. (%)
FA-61	Fe–28Al	2	34	393	4.3	345	33.4
FA-122	Fe–28Al–5Cr–0.1Zr–0.05B	13	49	480	16.4	474	31.9
FA-91	Fe–28Al–2Mo–0.1Zr	208	55	698	5.7	567	20.9
FA-130	Fe–28Al–5Cr–0.5Nb–0.5Mo–0.1Zr–0.05B	202	61	554	12.6	527	31.2

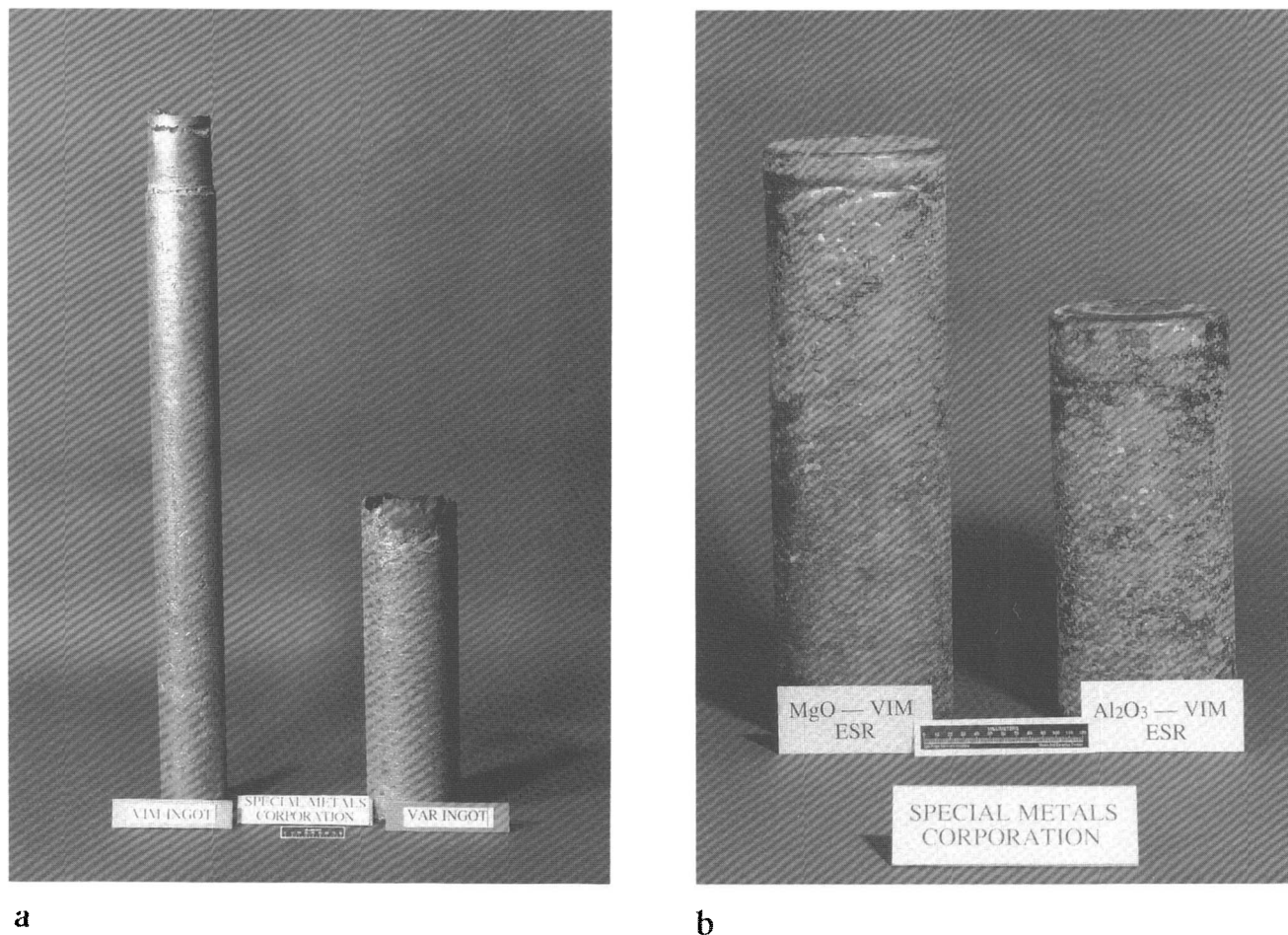


FIG. 13. Photographs of Fe₃Al-based alloy ingots commercially produced at Special Metals Corp.: (a) 100-mm diameter VIM and 150-mm diameter VAR ingots. (b) VIM and ESR ingots, one each using MgO and Al₂O₃ crucibles, respectively.⁸³

based aluminides is currently being pursued at Michigan Technological University.^{88,90-92} Much of this work involves the use of x-ray diffraction and TEM to determine the site occupancy of each of these elements and to study their effect on the D0₃-B2 transition, including the domain structures, ordering kinetics and energies, and dislocation characters.⁹⁰⁻⁹² Compression strengths at temperatures to 800 °C were increased with additions of molybdenum and titanium to a total of <10%. This increase was attributed to the increase in T_c (to 785 °C for 9% addition) produced by these elemental additions.⁹⁰ Chromium was found to mitigate the embrittling effects of the molybdenum and titanium additions, but generally decreased yield strength.⁸⁸

Rapid solidification processing (RSP) has been used extensively during recent years to enhance the strength and ductility of intermetallics. This method of fabrication produces grain refinement, increases chemical homogeneity, extends the solid solubility of elemental additions, and in some cases produces nonequilibrium structures.^{93,94} Most RSP iron aluminides have been produced by powder processes, with consolidation by

hot extrusion or pressing. Examples include the work of P & W and TRW.^{4,5,40} Another method for RSP is melt-spinning, which involves ejecting the molten alloy onto a rotating wheel, producing quench rates on the order of 10⁶ °/s. Décamps *et al.*⁹⁵ reported that the addition of 0.5 wt.% TiB₂ to Fe-28% Al-5% Cr resulted in a stabilization of the grain size, tensile properties, hardness, and Young's modulus for anneals of up to 4 h at 1000 °C. TEM studies revealed diffraction patterns characteristic of D0₃ ordering but dislocations typical of the B2 structure. The predominant slip system was [111] {110}, but [100] slip, characteristic of slip at high temperatures,^{96,97} was observed in the as-melt-spun material, suggesting that these high-temperature dislocations were quenched-in by the rapid solidification process.

Studies into the effects of rapid solidification and ternary (Cr, Mo) substitution on the structure and properties of ordered Fe-Al alloys have recently been initiated at the University of Sheffield.⁹⁸⁻¹⁰⁰ In particular, these studies concentrate on the dislocation character, formation and stability of APD's, and the effect of

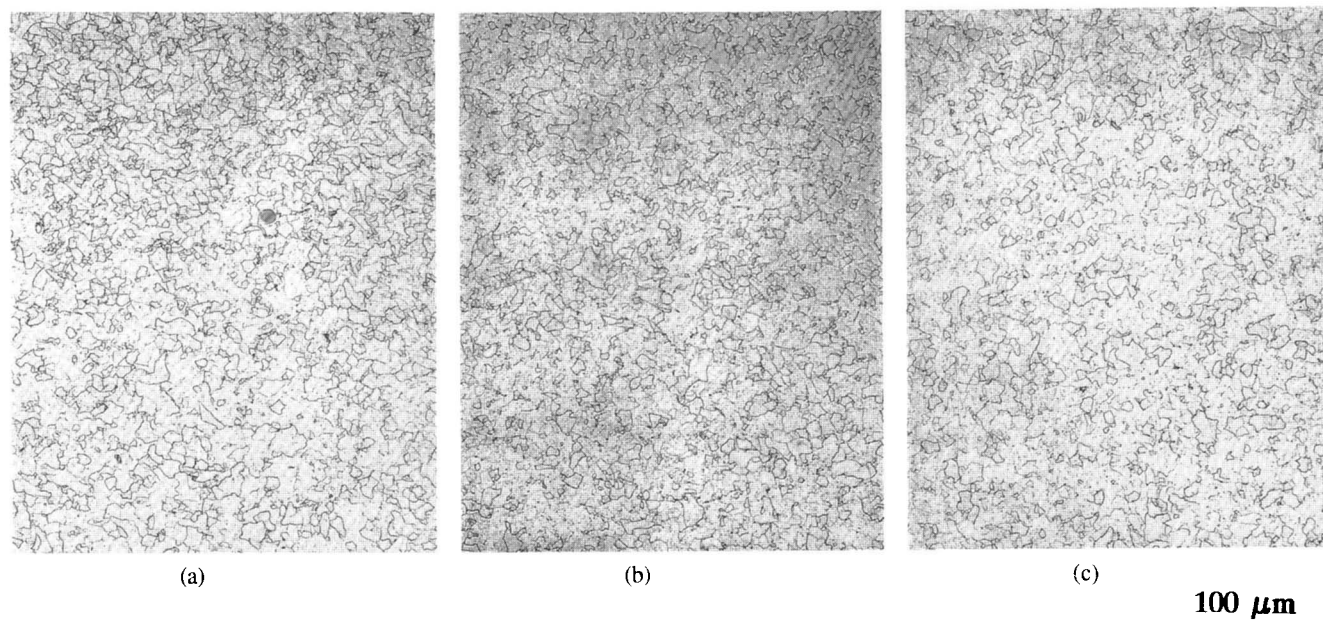


FIG. 14. Optical microstructure of as-extruded bar of Fe₃Al-based alloy powder prepared by nitrogen gas atomization at Ametek. The powder was sealed in a mild steel can and extruded to 9:1 area reduction at 1000 °C. Microstructures are from (a) edge, (b) one-half radius, and (c) center of the extruded bar.^{6,86}

dislocation-APB interactions on mechanical properties. Strengthening and fracture in ordered alloys with additions of chromium and molybdenum are explained in terms of dislocation-APB interactions that are believed to reduce stress concentrations at the grain boundaries and thereby prevent intergranular failure.¹⁰⁰

Fe₃Al-based alloys with the D0₃ superlattice exhibit a peak in yield stress near the B2-D0₃ transition temperature (T_c). The effect of varying degrees of order on the peak in flow stress was investigated by Lawley, Vidoz,

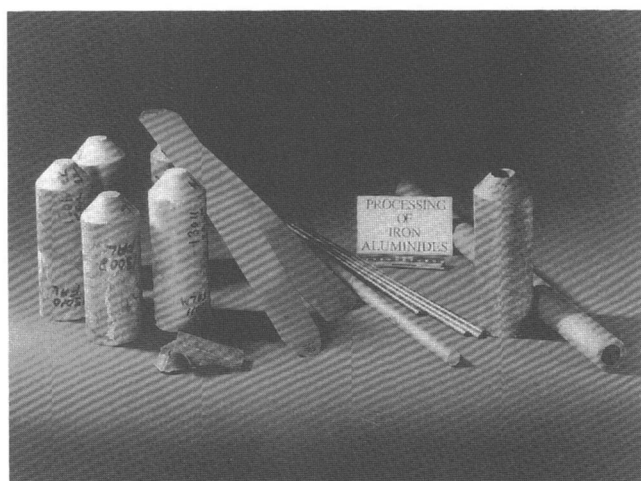


FIG. 15. Photograph showing various product forms produced from Fe₃Al-based alloy.

and Cahn,¹⁰¹ who also discussed several physical processes which have been proposed to explain the presence of the peak. Studies by Stoloff and Davies¹³ interpreted this peak in terms of a mechanism involving a transition from the interaction of unit dislocations in a partially ordered lattice to the interaction of superdislocations in a nearly perfect ordered lattice, suggesting that the position of the peak with respect to T_c and the deformation behavior near the peak depend on the temperature dependence of the degree of long-range order (S). The study of the presence and meaning of the anomalous yield peak continues. The temperature dependence of S can vary significantly with composition near Fe₃Al,¹⁰² resulting in the appearance of peaks at temperatures either below or above T_c . Therefore, conflicting results concerning the peak temperature can be explained in terms of a slight difference in alloy composition: <1 at.% difference in the composition of Fe₃Al can result in a shift of as much as 70° in the temperature of the same degree of S.¹⁰³ Hanada *et al.*¹⁰³ indicated that a peak in yield stress at a temperature below T_c is controlled by both the Stoloff and Davies¹³ mechanism and the ease of cross-slip of D0₂ superdislocations, while the peak above T_c is interpreted in terms of the ease of cross-slip of B2 superdislocations.¹⁰³ Recent studies have indicated that the precipitation of α phase significantly affects the anomalous yield behavior in hypostoichiometric alloys, where a first-order transition occurs from the α phase to the D0₃ structure.¹⁰⁴ In contrast, only the change in the degree of order was a dominant factor in the anomalous

yield behavior and the second order transformation from B2 to D0₃ in hyperstoichiometric alloys.¹⁰⁵

In order to explain the anomalous yield behavior and to determine the effect of the change in order from B2 to D0₃ on the metallurgical properties of iron aluminides, several studies of ordering transitions have been initiated. These include both experimental and theoretical studies, beginning with the works of Swann *et al.*,³² Okamoto and Beck,³³ Allen and Cahn,^{34,35} and Oki *et al.*³¹ Most of the recent studies have dealt with reaffirming the presently-accepted phase diagram¹⁰⁶ or the kinetics of the second order transition between B2 and D0₃.¹⁰⁷⁻¹⁰⁹ Also, several studies during the last ten years have involved the measurement of other properties of Fe₃Al-based alloys, including magnetic properties, specific heat, elastic modulus, thermal expansion, and further phase diagram studies.¹¹⁰⁻¹¹² In the interest of completeness, these references are cited but will not be discussed further.

Since the alloys of interest to this review have "imperfect" B2 structures above approximately 550 °C and many heat treatments will leave some degree of B2 order in the specimens under study, we include a short review of recent work being done on B2 iron aluminides. Several recent reviews on B2 aluminides already exist.¹¹³⁻¹¹⁵ With increasing aluminum content, RT ductility decreases, suggesting that the environmental embrittling mechanism is more effective in producing premature fracture.^{65,67} However, there is some evidence to suggest that below approximately 30% Al, the B2 structure, in a very "imperfect" state at these compositions, provides some improvement in RT ductility.⁶ Also, many of the metallurgical properties and mechanisms are similar for all compositions.

Most of the recent studies on B2 iron aluminides¹¹⁶⁻¹³³ have been conducted at three laboratories: NASA Lewis Research Center, Dartmouth College, and, more recently, ORNL. The work at NASA Lewis has involved identifying alternate materials to the commonly used nickel-base superalloys used in gas turbine engines. Their study has concentrated on alloys of 40-50% Al produced by either powder fabrication techniques¹¹⁶⁻¹²⁰ or melt spinning,^{121,122} fabrication techniques which produce fine grain sizes and increased RT ductility. In general, work is aimed at understanding the mechanisms controlling both elevated temperature deformation, where the materials may find applications, and the near RT deformation behavior, where limited ductility is a serious deterrent to their eventual use. Studies involve improving HT strength through control of fabrication,¹¹⁶ alloying,^{117,120} and grain size effects.¹¹⁶ Strengthening is noted for grain sizes of approximately 10 μm,¹¹⁶ and by alloying with many different elements to produce solid-solution, second-phase, or grain-boundary strengthening.^{117,118,120} Increased RT ductility

with transgranular fracture was noted with addition of boron, indicating that boron is effective in strengthening grain boundaries.¹¹⁸⁻¹²⁰ Melt-spun ribbons produced low ductilities with intergranular failure, which could be improved somewhat by heat treating.¹²¹ Other researchers have indicated that intergranular failure in melt-spun FeAl may be due to segregation of carbon or oxygen on the as-solidified grain boundaries.¹²³ Recently, Gaydos and Nathal have also confirmed the effects of water vapor on embrittlement of FeAl-based iron aluminides.¹²⁴

The studies by Baker *et al.* have included TEM studies of the flow and fracture characteristics and microstructures of alloys from approximately 34-50% Al.¹²⁵⁻¹³¹ They note a change to transgranular cleavage with decreasing aluminum content, and a change from $\langle 111 \rangle$ to $\langle 100 \rangle$ slip with increasing temperature for FeAl,^{125,127} both of which have been noted by other researchers.^{47,66,67,96,97} The presence of $\langle 100 \rangle$ dislocations was also observed in specimens deformed in compression at room temperature.¹²⁸ They suggest that the $\langle 100 \rangle$ dislocations form as a result of energetically favorable reactions between $\langle 111 \rangle$ dislocations, resulting in transgranular cleavage on $\{100\}$ planes (see Fig. 16). Annealing studies indicated that differences in cooling rate can have dramatic effects on the hardness of FeAl, even at compositions near 34% Al.^{127,131} Air cooling produced hardness values just as high as water quenching (see Fig. 17). Even after slowly cooling, retained vacancies resulted in increased RT hardness, and presumably increased yield strength.¹³¹ This suggests that reported data on strengths of B2 iron aluminides can vary significantly, depending on the cooling treatment used.

The FeAl alloy development effort at ORNL has helped in elucidating the embrittlement mechanisms at room temperature. The understanding of environmental embrittlement through the reaction of aluminum with water vapor in the atmosphere is a direct consequence of the effort to improve room temperature ductility in FeAl-based alloys.⁶⁴⁻⁶⁶ Additionally, alloys of 40% Al and higher were found to be less sensitive to test environment than lower aluminum alloys.^{132,133} The reason for the different behavior was found to be the intrinsically weak grain boundaries in the higher aluminum alloys. Table VII and Fig. 18 show that these weak boundaries result in low ductility and brittle grain boundary fracture (GBF), but that the grain boundaries can be strengthened by the addition of boron, as noted earlier by Crimp *et al.*^{118,119} When boron is added to the 40% Al alloy as a grain-boundary strengthener, the environmental effect becomes the dominating embrittlement mechanism. Tensile tests of the boron-doped 40% Al alloy produced a ductility of 4.3% in air, but 16.8% in oxygen.¹³³

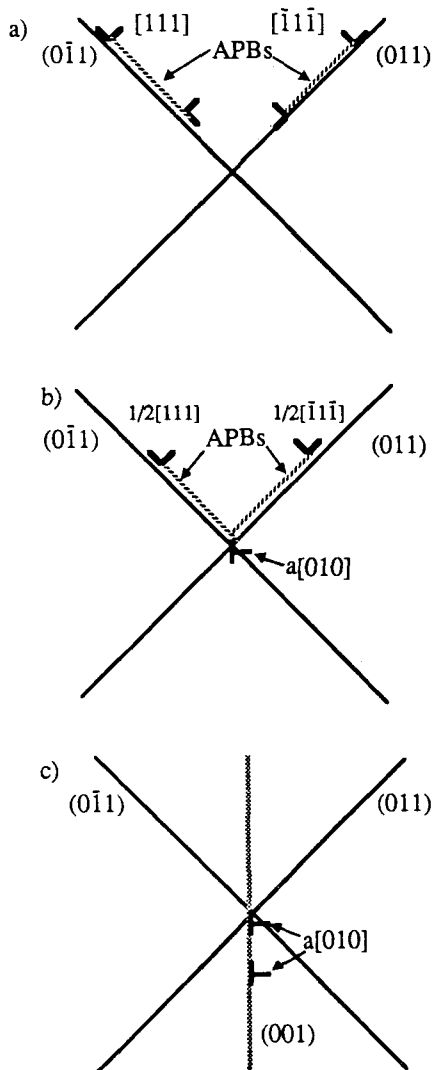


FIG. 16. Schematic illustration of the formation of an $a\langle 001 \rangle$ dislocation: (a) two $\langle 111 \rangle$ dislocations, each consisting of two $a/2\langle 111 \rangle$ dislocations separated by an APB glide on intersecting $\{011\}$ planes. (b) The leading $a/2\langle 111 \rangle$ dislocations interact to form an $a\langle 001 \rangle$ dislocation (it is still connected to the trailing $a/2\langle 111 \rangle$ partials). (c) The trailing $a/2\langle 111 \rangle$ partials interact to form a second $a\langle 001 \rangle$ dislocation. (This repels the $a\langle 001 \rangle$ dislocation already present, which curves away from the second $a\langle 001 \rangle$ dislocation.)¹²⁸

IV. RECENT DEVELOPMENTS IN CORROSION OF IRON ALUMINIDES

An important attribute of iron aluminides is their corrosion resistance to oxidizing environments, particularly at elevated temperatures. This resistance derives from the thermodynamic stability and relatively slow growth of the alumina surface product formed in the presence of oxygen. In this section, recent results on the corrosion of iron aluminides in gaseous, salt, and aqueous environments are briefly described and are compared with earlier work on corrosion properties.

Until recently, most of the corrosion studies of iron aluminides were concerned with their high tempera-

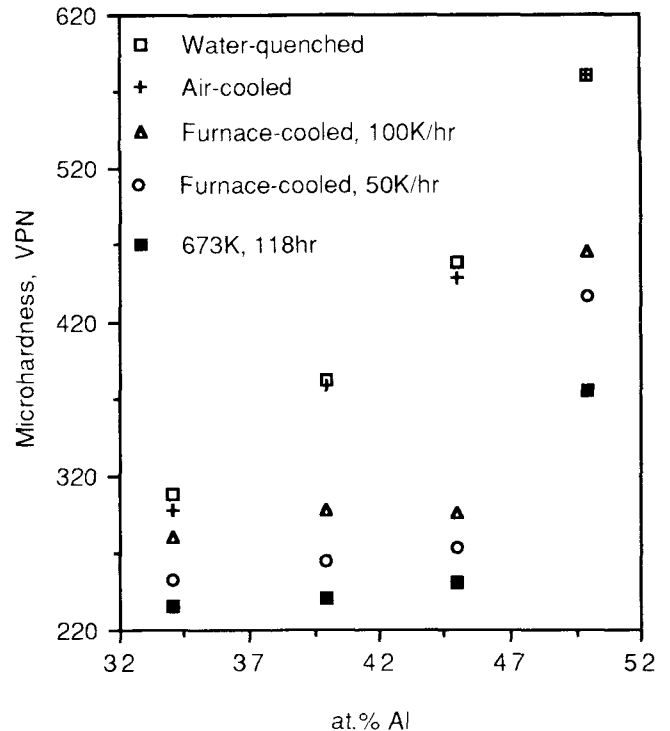


FIG. 17. Graph of microhardness versus atomic percent aluminum for FeAl after various heat treatments.¹³¹

ture oxidation properties in air or pure oxygen. They usually were studied in combination with more dilute aluminum-containing alloys, many of which contained more chromium than aluminum. Accordingly, previous reviews have addressed the properties of a spectrum of iron-aluminum alloys, considering the effect of aluminum on the corrosion of an iron or iron-chromium matrix. At present, the focus will primarily be on alloys of ≥ 22 at. % Al with chromium concentrations at or below 6%. As will be seen, the inferences drawn from this review relate more to effects of the different environments on these alloys as a class rather than to differences from alloy to alloy.

In many of the studies covered below, the test temperatures are well above those that are practical for structural applications, considering the alloy's expected strength capabilities. Nevertheless, where the iron aluminides show superior resistance to aggressive environments at higher temperatures, the possibility exists for using the alloys as coatings or claddings on higher strength but less resistant materials. Initial results on the high temperature corrosion of steels coated with iron aluminide have recently been reported.¹³⁴

A. High temperature oxidation

The oxidation resistance of iron aluminides at high temperatures depends on the formation of a chemically stable Al_2O_3 surface layer upon exposure to an oxidizing environment. The rate of formation and growth

TABLE VII. Effect of test environment on room-temperature tensile properties of FeAl (40 at. % Al), with and without boron.¹³³

Test environment	Strength (MPa)		Ductility (%)	Fracture Mode ^a
	Yield	Ultimate		
<u>No boron</u>				
Air	390	405	1.2	GBF
Oxygen ^b	402	537	3.2	GBF
<u>Doped with 300 wt ppm boron</u>				
Air	391	577	4.3	TF
Oxygen ^b	392	923	16.8	TF

^aGBF = grain-boundary fracture; TF = mainly transgranular fracture (cleavage).

^bOxygen pressure: 6.7×10^{-4} Pa.

of this scale, its soundness, and its adherence to the underlying alloy all are important in determining the actual corrosion resistance of an iron aluminide under specific environmental conditions. Studies of the phase stabilities in the Fe–Al–O system (reviewed in Ref. 27) demonstrate that Al₂O₃ will form on the iron aluminide class of alloys even at relatively low oxygen partial pressures. For a pure binary Fe–Al alloy, approximately 14% is the minimum aluminum concentration needed to suppress internal oxidation and overgrowth of the alumina scale by iron oxides at 800 °C.^{27,135} The addition of chromium reduces this critical aluminum concentration, while nickel increases it.²⁷ Obviously, the aluminum levels present in Fe₃Al and its alloys are well in excess of these critical concentrations and, as expected, alumina forms readily above approximately 500 °C upon exposure of such aluminides to an oxidizing environment. However, in many cases, the scale is very thin and difficult to analyze in a simple manner.¹³⁶ Despite its thinness, the scale on Fe₃Al is subject to spallation as an oxidized specimen is cooled.^{136,137} Alumina scales grown on iron aluminides containing 40% Al at 900–1100 °C spall extensively.¹³⁸ Interestingly, spallation resistance tended to improve under thermal cycling conditions; it appeared that, for the Fe–40% Al alloys, the strength of the scale metal interface increased by continued cycling, spallation, and fragmentation of the scale.¹³⁸ Possible reasons for this include thinner, more compliant scales under cyclic oxidation conditions, microcracked scales failing in small pieces instead of massively (as in the case of isothermally grown scales), fewer voids at the interface, and purging of bond-weakening segregants from the interfacial region.¹³⁸

The amount of available oxidation data on Fe–Al and Fe–Cr–Al alloys containing between 8 and 19% Al (principally 8–10%) is more extensive than the corresponding data on Fe₃Al-based iron aluminides. Thus, it is instructive to consider the former database when

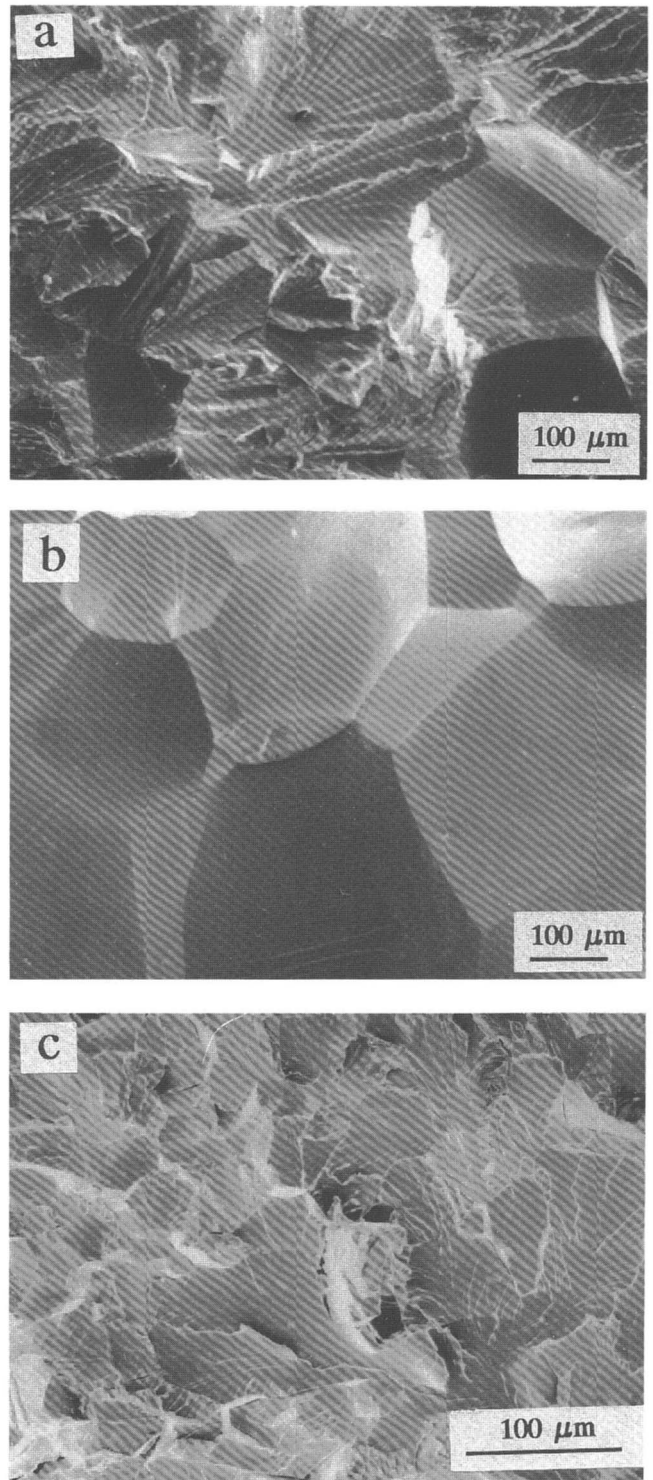


FIG. 18. Fracture modes of FeAl alloys tested in air at room temperature: (a) 36.5% Al, (b) 40% Al, and (c) boron-doped 40% Al.¹³³

examining the oxidation properties of Fe₃Al. The addition of as little as 4% Al to iron alloys significantly lowers the oxidation rate, particularly above 800 °C.²⁷ Above a level of 14% Al, binary Fe–Al alloys match or surpass the oxidation resistance of iron alloys containing

chromium and aluminum in combination. Thus, alloys with the Fe₃Al base composition are expected to have very low rates of oxidation in air or oxygen, and this expectation has been confirmed in cyclic air tests and thermogravimetric experiments at 800–900 °C (see, for example, Fig. 19).^{136,137,139, 140} Parabolic rate constants (defined as the slopes of the square of the weight change versus exposure time curves) for the Fe–28% Al binary composition measured over a 200 h period in dry air at 800 °C are on the order of 10^{-5} mg² cm⁻⁴ h⁻¹ and are lower than the rate measured for the Fe₃Al with 4% Cr.^{136,140} Other results for Fe–28% Al alloys containing 0.07% Zr and 2% and 5% Cr, respectively, over shorter times at 800 °C,¹⁴¹ showed slightly less weight gain for the higher chromium alloy, and yielded rates of about the same magnitude as, but somewhat higher than, that for the aforementioned 4% Cr alloy. Weight gains remain small at 800–900 °C even with periodic thermal cycles to room temperature,⁸⁰ and the effects of alloying additions appear very minor in this temperature range. Although the presence of larger concentrations of chromium at lower aluminum concentrations is beneficial in promoting the growth of protective Al₂O₃ scales, this effect is negligible at the higher aluminum levels in iron aluminides. (Chromium does have a deleterious effect on oxidation/sulfidation, as described below.)

No significant effects of minor alloying elements on the oxidation of Fe₃Al and Fe₃Al + Cr have yet been observed. There is no consistent influence of small additions of Zr, Hf, or Mo on weight gain behavior,^{136,137,140} nor has any effect on scale properties been detected¹⁴⁰ (although this has not yet been examined in any detail). However, substantial additions of Ti (5%), V (10%), and Mo (2.3%) to Fe₃Al degrade its oxidation resistance in air at 816 °C (particularly the Ti and V).⁵ Hafnium (at

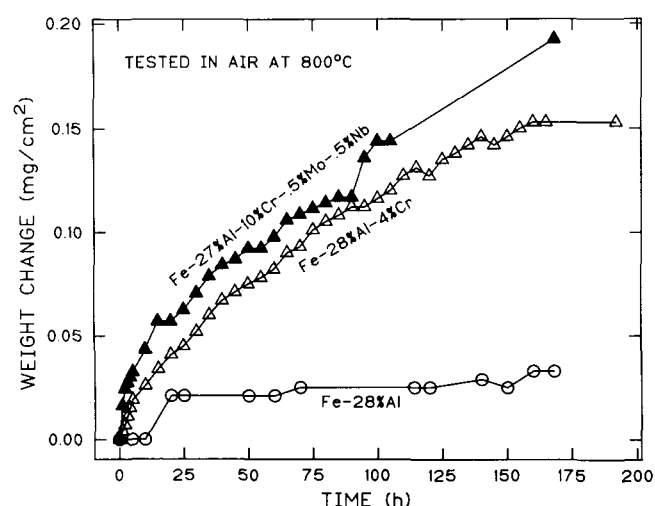


FIG. 19. Weight change versus time for Fe₃Al binary and 4% Cr alloy in air at 800 °C.¹³⁶

the 1% level) in Fe–40% Al had a deleterious effect on oxidation and scale spallation at 900–1100 °C.¹³⁸ Zirconium, hafnium, and yttrium (in small concentrations) have been observed to influence scale morphology, stress, and adherence for Fe–(8–19)% Al alloys (see, for example, Refs. 142–145). In these cases, the additions had beneficial effects on the protectiveness of the alumina scale. It remains to be seen whether similar effects will occur for Fe₃Al alloys when more substantial information is available, particularly for higher oxidation temperatures (>900 °C). Indeed, much greater characterization of scale behavior under conditions where thicker products are formed is needed for these aluminides.

B. High temperature sulfidation

Effects of chromium and aluminum additions on the sulfidation of iron alloys have been examined by several investigators.^{146–150} These studies have shown that aluminum additions to iron and iron-chromium alloys significantly improve sulfidation resistance in sulfur vapor or H₂S/H₂ mixtures and that the corrosion rate decreases as the Al/Cr ratio increases. In reviewing the design of sulfidation resistant alloys, Strafford and Datta¹⁵¹ noted that aluminum is a very beneficial alloying element because of (1) the thermodynamic stability of aluminum sulfide, (2) the relatively low rate of sulfidation of aluminum compared to iron and chromium, and (3) the relatively large molecular volume of aluminum sulfide (that is, a large Pilling–Bedworth ratio). These properties would be expected to support the selective sulfidation of aluminum to form a barrier sulfide layer with an acceptably low reaction rate at elevated temperatures.

Several studies^{147,149,150,152} have verified that binary iron aluminide alloys containing $\geq 18\%$ Al afford relatively good resistance in sulfur vapor or H₂S/H₂ mixtures up to ~ 750 °C. Reaction rates are parabolic and are below 1 mg² cm⁻⁴ h⁻¹ at 800 °C at an effective $p_{S_2} \leq 1$ Pa. However, at 800–1000 °C, the ability of the aluminum to suppress iron sulfide formation at sulfur pressures > 133 Pa (1 Torr) is lost and sulfidation rates increase rapidly with time. Depending on the sulfur and aluminum activities, the scales formed are multilayered, composed of Al₂S₃ at the alloy surface, FeS at the gas/scale interface, and a transition product of (Fe, Al)₃S₄ between these layers. Internal Al₂S₃ precipitates sometimes mixed with FeAl₂S₄ were also observed below this external scale in alloys containing 18–20% Al at 750 and 900 °C in sulfur vapor at 10^{-3} Pa.¹⁵⁰ However, under the same conditions, an alloy containing 28% Al formed only an Al₂S₃ external scale. (An analysis of the aluminum content required to suppress internal sulfidation in iron-aluminum alloys has been reported by Smeltzer and Patnaik.¹⁵³) Marker measurements indicate

that growth of the outer FeS layer of external scale is controlled by outward diffusion of iron and growth of the inner layer by inward sulfur migration.^{147,150} The breakdown in protection at higher temperatures is associated with the production of a porous scale near the alloy surface and mechanical fracturing of the alloy surface by internal sulfide precipitates.

C. Corrosion in mixed gases

1. Oxidation/sulfidation

As discussed above, aluminum provides an effective addition to iron-based alloys for resistance to sulfur-containing environments in the absence of oxygen. Nevertheless, the diffusion rates of aluminum and iron through the aluminum sulfide reaction product formed in such environments are considerably faster than the corresponding rates in aluminum oxide. Therefore, it is fortunate that the alumina tends to predominate over the sulfide in mixed oxidizing/sulfidizing gases, even when the partial pressures of oxygen are relatively low. The phase stability diagram shown in Fig. 20¹⁵⁴ shows that alumina is thermodynamically favored over sulfides at oxygen partial pressures that are many orders of magnitude lower than those typical of many service (particularly coal-derived) environments. The predominance of alumina is borne out by the difficulties encountered in conducting sulfidation tests of iron aluminide, where trace impurities in sulfur vapor lead to oxide rather than sulfide reaction products.¹⁵³ Although the weight gains of Fe₃Al in mixed oxidizing/sulfidizing gases are generally higher than those in oxygen or air at comparable temperatures, the corrosion product scales are relatively thin and compact and contain no measurable sulfur.¹³⁶ The spalling tendencies of these scales also tend to be greater than in air, but

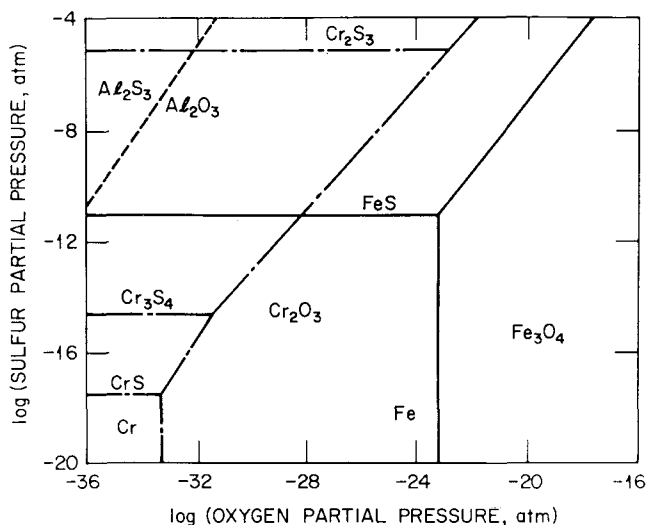


FIG. 20. Thermochemical M-S-O stability diagram at 650 °C.¹⁵⁴

repeated thermal cycling tests showed the continued regrowth of alumina as opposed to any sulfur-containing products.^{80,136} Figure 21 compares 800 °C weight gain results for Fe₃Al in an H₂S–H₂–H₂O mixed gas with that of a stainless steel and an Fe–Cr–Al alloy and clearly indicates the significantly better resistance of the aluminide. Preoxidation enhances further the corrosion resistance of Fe₃Al to H₂S–H₂–H₂O at 800 °C,⁸⁰ as has also been observed for Fe–Cr–Al alloys exposed to simulated coal gasifier environments.¹⁵⁵ The resistance of Fe₃Al to H₂S–H₂–H₂O mixtures, in which p_{O_2} is below 10^{-15} Pa, indicates that the alloy should perform well even in highly reducing mixed gas service environments. Initial results from an actual coal gasifier at 600–900 °C have, in fact, verified its excellent resistance to the product gas.⁸⁰

The addition of chromium to the Fe₃Al (28% Al) base composition adversely affects the corrosion resistance to H₂S–H₂–H₂O ($p_{O_2} \approx 10^{-15}$ Pa, $p_{S_2} \approx 10^{-1}$ Pa) at chromium concentrations above 2%.¹³⁶ This marked effect is shown in Fig. 22, which compares 800 °C weight changes for ternary iron aluminide alloys containing 2, 4, and 10% Cr with those for the binary Fe₃Al composition. The corrosion products formed on the 4 and 10% Cr alloys were considerably thicker than on the binary and 2% Cr aluminides.¹³⁶ X-ray diffraction patterns showed the existence of Cr₂S₃ and Al₂S₃. No Al₂O₃ was detected and it was concluded that alumina must have comprised less than 10% of the product mass, consistent with the observation of the formation of very thin scales in the absence of sulfur effects. The deleterious effect of chromium at the 4% level can be offset by increasing the aluminum concentration of the iron aluminide to 40%.¹³⁶ Comparable weight changes were measured for the binary Fe₃Al and Fe–40%

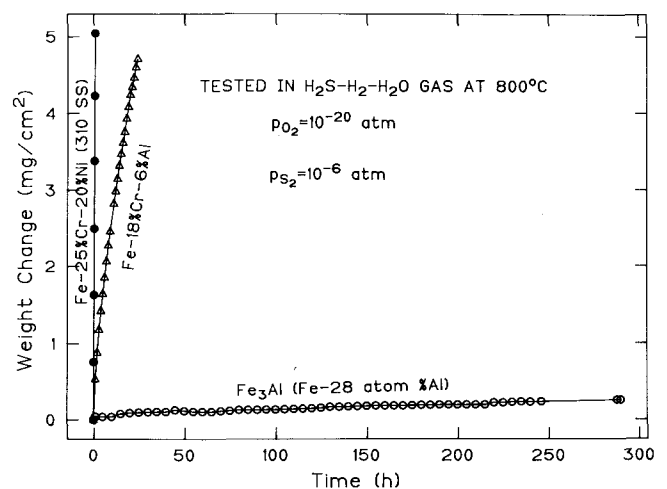


FIG. 21. Weight change versus time for Fe₃Al and Fe–Cr–Ni and Fe–Cr–Al alloys exposed to an oxidizing/sulfidizing gas at 800 °C.¹³⁶

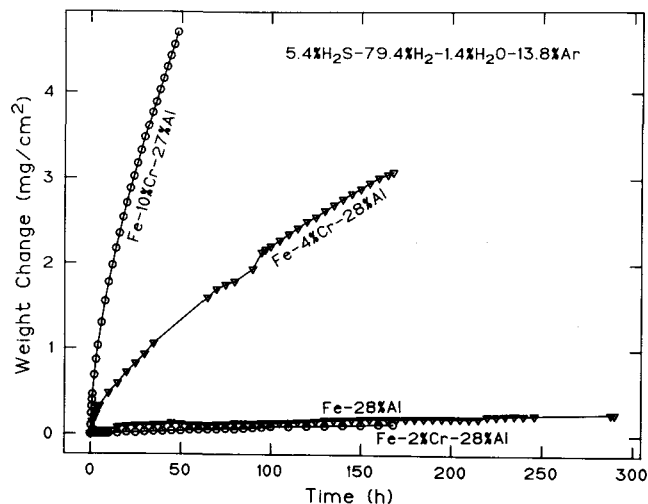


FIG. 22. Effect of chromium additions on weight change versus time for Fe₃Al exposed to an oxidizing/sulfidizing gas at 800 °C.¹³⁶

Al-4% Cr when these alloys were exposed in the oxidizing/sulfidizing gas at 800 °C and similar scales were observed.

Preoxidation in air at 800 °C also significantly lowers the weight gains of the chromium-containing Fe₃Al alloys in H₂S-H₂-H₂O at 800 °C.⁸⁰ Like the binary Fe₃Al, the corrosion product scales on the alloys with chromium spall back to the base metal on cooling from 800 °C to room temperature. This results in a significant weight loss in the case of Fe₃Al with more than 2% Cr. However, on repeated 800 °C exposures with intermediate thermal cycles, the weight gains and subsequent spallation losses decreased dramatically (see Fig. 23).⁸⁰ Since the corrosion rates ultimately approach those of the binary Fe₃Al, it appears that the improvement with repeated spalling of the corrosion product results from the depletion of chromium at the surface. This result, combined with studies of corrosion product scales on oxidized specimens, indicates that the presence of chromium acts to accelerate the growth of iron sulfide at the expense of alumina.

The effects of niobium and molybdenum alloying additions on corrosion in an oxidizing/sulfidizing environment were evaluated at 800 °C.¹³⁶ Additions of 1% Nb and 2% Mo to Fe₃Al reduced corrosion rates over the first 100 h of exposure by factors of 2 and 4, respectively. Some reduction in weight change of Fe₃Al with 4% Cr were reported when 0.3% Y, 0.1% Zr, and 0.1% B were present in the alloy, but the beneficial effect was greater for a 1% Nb addition. In both of these cases, however, the scale was still primarily composed of sulfides. Therefore, it appears that these minor alloying additions are not promoting the growth, nor improving the protective properties, of the oxide scale, as has been observed for hafnium additions to Fe-19% Al, which enhanced the ability of a scale formed during

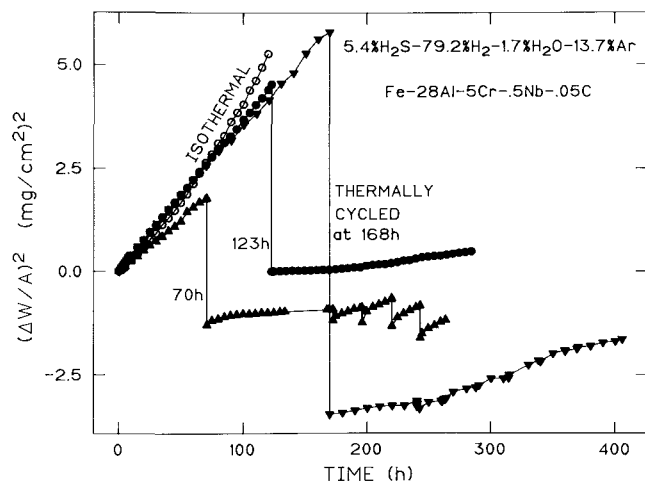


FIG. 23. Effect of thermal cycling on the square of the weight change versus time for Fe-28% Al-5% Cr alloy exposed to an oxidizing/sulfidizing gas at 800 °C.⁸⁰

preoxidation to resist subsequent sulfidation (without the presence of oxygen).¹⁴³

To date, there has been very little work on the exposure of iron aluminides to more oxidizing mixtures of oxygen and sulfur, which are typical of combustion atmospheres. Lee and Lin conducted a limited study of the corrosion of Fe₃Al alloys containing 0.075% Zr and 2 and 5% Cr in air containing 1% SO₂.¹⁴¹ Exposures at 605, 800, and 1000 °C for 24 h produced weight changes of the same order as those in uncontaminated air. Such results are not surprising given the good resistance of the low-chromium Fe₃Al alloys in oxidizing/sulfidizing gases with much lower oxygen (and higher sulfur) pressures, as described above.

2. Oxygen/chlorine

As with sulfur, the presence of chlorine in an oxidizing environment can degrade the resistance of a normally oxidation-resistant material at high temperatures (see, for example, Ref. 156). No controlled experiments on the mixed oxidation of iron aluminides in high temperature environments containing chlorine have been performed. However, the good resistance of Fe₃Al in a coal gasifier oxidizing/sulfidizing atmosphere with 100–300 vppm of HCl⁸⁰ is encouraging in this regard. No effect attributed to the chlorine could be detected when the gasifier results were compared to laboratory experiments with a mixed (oxygen/sulfur-bearing) gas containing no chlorine.

D. Salt corrosion

1. Sulfates

Molten sulfate-induced corrosion of iron aluminides has been studied at 605, 800, and 1000 °C.¹⁴¹ The presence of the liquid Na₂SO₄-Li₂SO₄ on the surface of iron aluminides exposed in a oxidizing/sulfidizing

gaseous environment (1% SO₂ in air) led to corrosion rates that were at least a factor of ten higher than rates measured in the absence of the sulfate product. In contrast to oxidation/sulfidation results discussed above, increased chromium concentrations (from 2 to 5%) somewhat mitigated the degradation by hot corrosion, as did a higher aluminum concentration (36 versus 28%). The relative resistance of types 310 and 321 stainless steel were significantly better than that of the iron aluminides.¹⁴¹ Preliminary findings from a corrosion study in a simulated flue gas (14% CO₂, 10% H₂O, 4% O₂, 0.2% SO₂, balance of N₂) with an ash deposit chemistry more typical of coal-fired boilers (Fe₂O₃, K₂SO₄, Na₂SO₄) showed relatively poor behavior of Fe₃Al (with 2% Cr) at 650 °C compared to some stainless steels and Ni-base alloys, but comparable resistance at 700 °C.¹⁵⁷ However, the Fe₃Al was exposed with ash that was highly corrosive,¹⁵⁷ and its resistance using an ash composition like that for deposits found on superheater tubes from a boiler burning a moderately aggressive coal is currently being evaluated.

The corrosion of iron aluminide under conditions where the surface deposit was a solid CaSO₄, typical of fluidized coal combustors, has been studied by Natesan and Podolski.¹⁵⁸ They found that a Fe₃Al (with 1 wt. % TiB₂) had good resistance to attack when coated with deposits of either reagent CaSO₄ or circulating-fluid-bed ash and held at 870–900 °C in a mixed oxidizing/sulfidizing gas ($p_{\text{O}_2} = 3 \times 10^{-7}$, $p_{\text{S}_2} = 10^{-2}$, $p_{\text{SO}_2} = 2 \times 10^2$, $p_{\text{SO}_3} = 1 \times 10^{-4}$ Pa).

2. Nitrates

A study of the corrosion of iron aluminides by a highly aggressive, oxidizing molten NaNO₃(–KNO₃)–Na₂O₂ at 650 °C has shown that such aluminides are relatively resistant compared to many other metallic materials (stainless steels, nickel-base alloys, refractory metals), particularly when the aluminum concentration exceeds 30% Al.¹⁵⁹ The corrosion of the iron aluminides proceeded by oxidation and a slow release of metal ions from an aluminum-rich product layer into the salt such that the compositions with higher aluminum concentrations yielded significantly better resistance.¹⁶⁰ However, it appears that Fe₃Al-type aluminides would offer excellent resistance in NaNO₃(–KNO₃)–Na₂O₂ at lower temperatures (<600 °C) or in nitrate salts that do not contain Na₂O₂ (which severely exacerbates the corrosivity of the melt).¹⁵⁹

E. Aqueous corrosion

The resistance of iron aluminides to corrosion in aqueous environments often depends on the ability of a protective aluminum-rich surface film to remain sound under various chemical and electrochemical conditions.

The corrosion of a series of iron-aluminum compositions was studied in ambient and boiling seawater.¹⁶¹ It was found that a minimum of 19% Al was necessary to maintain a protective oxide film under these conditions. For alloys containing between 12 and 19% Al, additions of molybdenum up to about 4% were found to significantly reduce corrosion losses. Recent experiments in simulated seawater (ambient temperature) showed that a Fe–28% Al–4% Cr alloy with 2% Mo had better resistance to pitting corrosion than a 5% Cr aluminide without molybdenum and comparable resistance to that of type 304L stainless steel (albeit worse than type 316L stainless steel).¹⁶² Exposures of weldments in seawater showed that the high aluminum (27–30% Al) suffered no apparent degradation of corrosion properties relative to the base metal.¹⁶¹

Electrochemical characterization of iron aluminides showed relatively high corrosion rates in strong acid, low corrosivity in a highly basic solution, and low to average rates, but definite susceptibility to localized attack, in a neutral chloride environment.^{162,163} Experiments in a 200 ppm chloride, pH = 4 solution (to somewhat simulate an aggressive acid-rain-type atmospheric corrosion situation) revealed increasing resistance to corrosion with chromium concentration (up to 6%) in Fe₃Al¹⁶³ and a beneficial effect of increasing molybdenum levels (investigated up to 2%) on chloride-induced pitting corrosion.^{162,163} On the basis of electrochemical and immersion tests in the acid chloride solution, the Fe–28% Al–4% Cr–2% Mo alloy exhibited the best corrosion resistance of the aluminides with many of the rates being fairly low (<0.03 mm/y).^{163,164} The corrosion behavior of iron aluminides in solutions containing sulfur compounds (simulating possible conditions encountered in ambient exposures of components to burning fossil fuels) has also been reported.¹⁶⁴ Fe₃Al with 2 and 5% Cr had high corrosion rates (1.1–7.8 mm/y) in both thiosulfate and tetrathionate solutions.

Results from U-bend tests under freely corroding conditions indicated that Fe₃Al with 2 and 5% Cr are highly susceptible to stress corrosion cracking in sulfur-bearing (thiosulfate and tetrathionate) solutions.^{76,164} In an acid-chloride environment, no cracking of U-bend specimens of these aluminides was observed under freely-corroding and applied anodic potential conditions.⁷⁶ However, at cathodic potentials sufficient to generate the necessary amount of hydrogen, the 2% Cr–Fe₃Al, but not the 5% Cr–Fe₃Al, failed by cracking. This result indicates that stress corrosion cracking in such solutions is probably related to hydrogen embrittlement rather than effects associated with anodic dissolution (that is, direct corrosion) and that higher chromium levels are beneficial in minimizing this cracking. (Such susceptibility to hydrogen in aqueous solutions is consistent with the results of

Kasul and Heldt⁶⁸ and the observed ambient temperature embrittlement of iron aluminides by water vapor,⁶⁴⁻⁶⁷ as discussed above.) The ability of the 5% Cr alloy to resist stress corrosion cracking under U-bend conditions does not necessarily mean that it is not susceptible in aqueous environments under slow-strain-rate tensile testing conditions. In fact, very preliminary results from slow-strain testing of Fe₃Al alloys under freely corroding conditions indicated a more severe environmental embrittlement effect for the 5% Cr aluminide (versus the 2% Cr aluminide).¹⁶² At a hydrogen-producing cathodic potential, both alloys had significantly reduced elongations under slow strain conditions, which is consistent with the hydrogen embrittlement mechanism.¹⁶²

V. SUMMARY

The unique advantages of iron aluminides have been known for many years. However, these alloys have not been used extensively because of their limited ductility at ambient temperatures. Recent advances in the understanding of environmental embrittlement in intermetallics, and particularly in iron aluminides, have indicated that iron aluminides are not inherently brittle as previously believed, but are embrittled by atomic hydrogen as a result of a reaction between moisture in the air and aluminum on the surface of the specimen. Alloy development efforts have resulted in improved Fe₃Al-based alloys with room temperature ductilities of over 10% and strengths comparable to many presently-used structural alloys. Additions of chromium have been found to improve cleavage strength, to lower antiphase boundary energies (resulting in easier cross-slip of dislocations), and possibly to have an effect on the composition and/or properties of the protective oxide film. Together, these effects result in a minimization of environmental embrittlement and increased ductilities. Additions of niobium, molybdenum, zirconium, and other elements have improved the hot strength through both precipitation and solid-solution mechanisms. Melting and fabrication techniques that result in controlled compositions and microstructures are being developed, making it possible to produce commercial-size heats of Fe₃Al-based alloys. Advances are also being made in welding techniques. These improved properties have resulted in increased interest in these alloys as structural material for many applications.

The most important attribute of iron aluminides is their corrosion resistance to oxidizing environments, particularly at elevated temperatures. This resistance derives from the thermodynamic stability and relatively slow growth of the alumina surface product formed in the presence of oxygen. This alumina product also protects the iron aluminide from gaseous sulfidation, even at low

oxygen partial pressures. In the total absence of oxygen, iron aluminides sulfidize in gaseous environments at significantly higher rates than under strictly oxidizing conditions, but not catastrophically. Fe₃Al alloys are not particularly resistant to hot corrosion in the presence of aggressive liquid sulfates, but show good behavior under solid CaSO₄ deposits. In aqueous environments, iron aluminides tend to corrode rapidly in strong acids and sulfur-bearing media. They typically have low corrosion rates in highly basic and neutral chloride solutions, but there is a definite susceptibility to localized corrosion in the latter environment. There is some indication of stress corrosion cracking under conditions where hydrogen is evolved. For Fe₃Al, the addition of chromium appears to (1) degrade oxidation/sulfidation resistance when above 2%, (2) improve the corrosion behavior of Fe₃Al in molten sulfates, and (3) beneficially influence dissolution in acid chloride solutions. To date, no other major effects of any alloying elements on the corrosion resistance of iron aluminides have been found except for an improvement in pitting resistance in certain aqueous environments with the addition of molybdenum.

ACKNOWLEDGMENT

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