

BRITTLE FRACTURE AND DUCTILITY IMPROVEMENT IN NICKEL AND IRON ALUMINIDES

CONF-900632--1

E. P. GEORGE and C. T. LIU

DE90 017319

1 8 1990

The submitted manuscript has been authored by a contractor of the U.S. Government under contract No. DE-AC05-84OR21400. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes.

Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6093, USA

Nickel and iron aluminides are two potentially useful ordered intermetallic alloy systems that share a problem common to many ordered intermetallics, namely brittle fracture and poor ductility at room temperature. However, recent developments have shown that it is possible to overcome this problem and get significantly improved room-temperature ductilities in both these alloy systems by employing a combination of micro- and macro-alloying techniques. Concurrently, our understanding of the underlying causes of brittle fracture in ordered intermetallics has improved dramatically. We review here recent results related to the ductility and fracture behavior of two nickel aluminides (Ni_3Al and NiAl), and two iron aluminides (FeAl and Fe_3Al). We will show that the major difference between Ni_3Al and the two iron aluminides is the following: in the former, brittle fracture is a result of intrinsically weak grain boundaries, whereas in the latter, brittle fracture is a result of an extrinsic factor, namely moisture-induced environmental embrittlement. The brittleness of Ni_3Al can be overcome by microalloying with boron and carefully controlling the alloy stoichiometry, whereas the ductilization of iron aluminides requires modification of their surface composition (or environment) to minimize the chemical reaction with moisture in air. NiAl also has weak grain boundaries (like Ni_3Al), which can be strengthened by the addition of small amounts of boron. However, because of its other problems, like poor cleavage strength and insufficient number of deformation modes, the ductility of NiAl is not significantly improved even after intergranular fracture is totally suppressed.

1. INTRODUCTION

There is considerable interest in ordered intermetallics based on aluminides and silicides because of their potential for use in high-temperature structural applications.¹⁻³ Among their attractive properties are superior oxidation and corrosion resistance, good high-temperature strength and stiffness, and relatively low density (especially if their constituent atoms are light elements). Unfortunately, most ordered alloys are plagued by brittle fracture and poor ductility at ambient temperatures. As a result, these potentially useful materials have yet to find widespread engineering application. It is heartening to note, however, that our under-

standing of brittle fracture in ordered alloys is progressing rapidly, and significant advances have been made recently in the alloy design of ductile intermetallics.

Table 1 lists the various ordered intermetallic alloys of current interest, along with some of their physical properties and fracture behavior. We will restrict our present discussion to two nickel aluminides (Ni_3Al and NiAl), and two iron aluminides (Fe_3Al and FeAl). The nickel aluminide, Ni_3Al , is the so-called γ' phase in Ni-base superalloys, and is the most extensively studied of the ordered intermetallics listed in Table 1. It is also a good model material for the study of intrinsic grain-boundary brittleness in

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

ordered alloys, and a striking example of the successful use of microalloying to produce ductile alloys.⁴⁻⁶ NiAl has recently received considerable attention because of its relatively high melting point and low density. It has the potential of replacing the heavier Ni-base superalloys if its twin problems of room-temperature brittleness and poor high-temperature strength are overcome. The iron aluminides are targeted for slightly lower-temperature applications: they possess several potentially unique properties for structural applications at temperatures to 800°C, especially in harsh environments. For example, they are highly oxidation and sulfidation resistant at elevated temperatures

because of their ability to form protective aluminum oxide scales.⁷⁻¹⁰ In fact, iron aluminides can exhibit corrosion rates that are dramatically lower than those of even the best existing iron-base alloys (including coating materials) when tested in a severe sulfidizing atmosphere at 800°C.¹¹ In addition, iron aluminides containing > 30 at.% Al are very resistant to corrosion in molten nitrate-salt environments at 650°C.¹² When these potentially unique capabilities are coupled with the low cost, low density, and good fabricability of the iron aluminides, it is clear that they have considerable development potential as new-generation structural materials.

Table 1. Ordered Intermetallic Alloys of Current Interest

Alloy	Crystal Structure	Tc/Tm	Density (g/cc)	Brittleness
Ni ₃ Al	L1 ₂ , fcc	1400	7.50	GB
Ni ₃ Si	L1 ₂ , fcc	1140	7.30	GB
TiAl ₃	DO ₂₂ , tetra.	1350	3.20	Cleavage
ZrAl ₃	DO ₂₃ , tetra.	1580	3.70	Cleavage
NbAl ₃	DO ₂₂ , tetra.	1605	4.54	Cleavage
Fe ₃ Al	DO ₃ , bcc	1540	6.72	Cleavage
FeAl	B ₂ , bcc	1300	5.56	GB and Cleavage
NiAl	B ₂ , bcc	1640	5.86	GB and Cleavage
Ti ₃ Al	DO ₁₉ , hexag.	1600	4.20	Cleavage
TiAl	L1 ₀ , tetra.	1460	3.91	Cleavage
NbCr ₂	C ₁₅ , comp. cubic	1770	7.60	Cleavage
MoSi ₂	C _{11b} , tetra.	2020	6.24	Cleavage and GB
Ti ₅ Si ₃	D8 ₈ , hexag.	2130	4.32	Cleavage

2. GRAIN-BOUNDARY FRACTURE AND MICROALLOYING EFFECTS OF BORON

2.1. Ni₃Al

Although single crystals of Ni₃Al are quite ductile, polycrystalline Ni₃Al fractures intergranularly with very little ductility.^{4,13,14}

Detailed Auger studies^{5,15,16} have shown that the grain boundaries in sufficiently pure Ni₃Al are extremely clean and free of impurities, implying that they are intrinsically brittle. Takasugi and Izumi^{17,18} concluded that the major factor controlling the propensity for intergranular fracture in L1₂ com-

pounds was the valency difference between the constituent atoms: those alloys which had large valency differences were more prone to grain-boundary fracture than those with relatively small valency differences. Taub et al.,¹⁹⁻²¹ on the other hand, found that better correlation could be obtained if the electronegativity difference rather than the valency difference was used. King and Yoo²² attributed the intrinsic intergranular brittleness of Ni₃Al to the considerably fewer dislocation reactions that are permissible at strongly ordered grain boundaries than at those that are compositionally disordered. Vitek et al.^{23,24} found that the atomic structure of grain boundaries in strongly ordered L1₂ compounds like Ni₃Al contained columns of atomic size cavities, which could act as nuclei for intergranular cracks, thereby weakening the grain boundaries and resulting in intrinsic grain-boundary brittleness.

Researchers attempting to understand and overcome the brittleness of ordered intermetallics in general and Ni₃Al in particular got a big boost when it was discovered⁴⁻⁶ that small amounts of boron (on the order of 0.1 wt.%) not only eliminated intergranular fracture in Ni₃Al but also made it extremely ductile, with room-temperature tensile elongations as high as 50%, see Fig. 1. As shown in this figure, boron is most effective in 24 at.% Al alloys: with increasing Al content, the fracture mode becomes increasingly intergranular and ductility decreases. Both Auger microprobe,⁵ and imaging atom probe²⁵⁻²⁸ studies have shown that boron segregates strongly to grain boundaries in Ni₃Al. An example of this is shown in Fig. 2 which is an atom probe image of a high-

angle ($\Sigma 27$) grain boundary in Ni₃Al densely covered with boron atoms (bright spots).

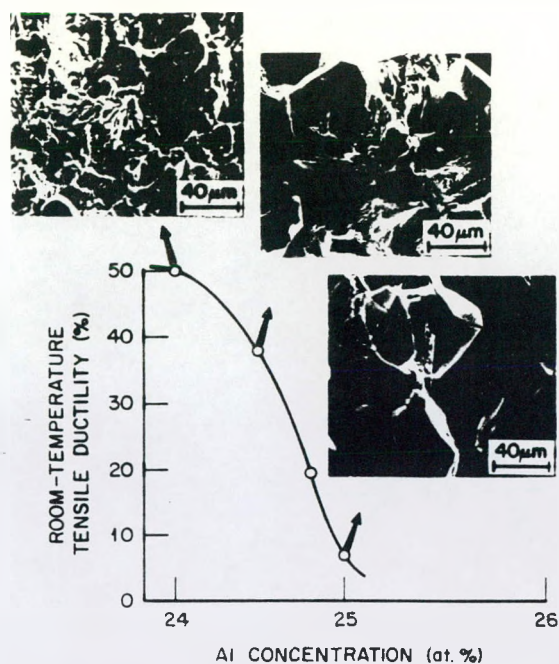


FIGURE 1

The effect of Al concentration on the room-temperature ductility and fracture mode of Ni₃Al doped with 0.1 at. % B.⁵

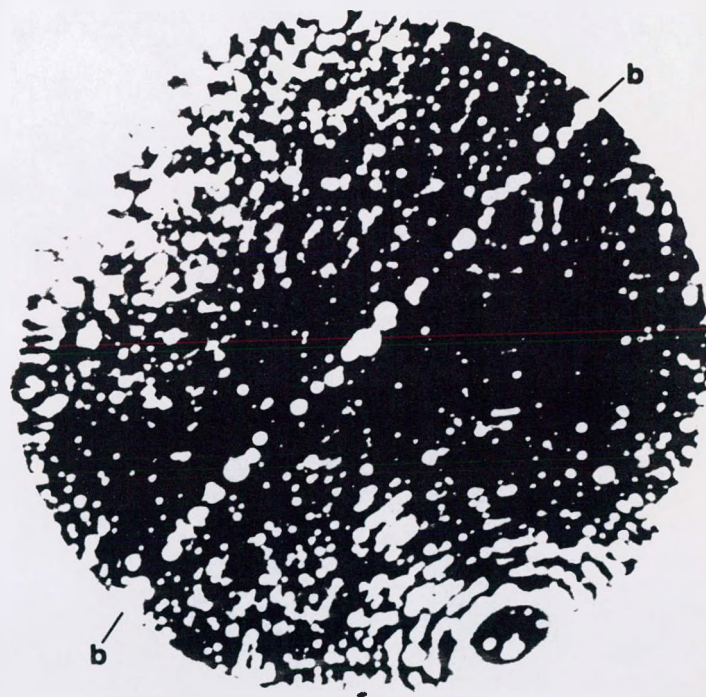


FIGURE 2

Field ion image of a high angle ($\Sigma 27$) grain boundary in B-doped Ni₃Al showing extensive boron segregation along the boundary marked "b-b".²⁷

Considerable effort has gone into understanding this remarkable ductilizing effect of boron in Ni_3Al , but we are not yet in a position to identify a unique mechanism. There is evidence in support of both currently favored theories: the boron-enhanced cohesive strength theory as well as the boron-facilitated slip transfer theory. Because of space limitations we will only briefly discuss these two points of view here; the interested reader who needs additional information may consult another recent review²⁹ in which we have dealt with these subjects in considerably more detail.

The first possibility is that boron improves ductility by enhancing the cohesive strength of the grain boundaries.⁵ There is some indirect experimental evidence to support this argument: unlike the well-known behavior of sulfur and other embrittling impurities, which tend to segregate much more strongly to free surfaces than grain boundaries, it was found that boron tended to segregate strongly to grain boundaries but not to free surfaces.^{5,30,31} Additionally, sulfur is known to exacerbate grain-boundary fracture in Ni_3Al ,³² whereas boron suppresses it.^{4,5} These results are consistent with the thermodynamic theory of Rice,³³ who many years ago predicted that those solutes which segregate more strongly to grain boundaries than free surfaces should enhance grain-boundary cohesion, whereas those that segregate more strongly to free surfaces than grain boundaries should embrittle. There is also considerable theoretical evidence, based on first-principles cluster calculations,³⁴ cluster calculations of density of states,³⁵ and embedded atom calculations,³⁶ that confirms that boron does, in fact, enhance the cohesive

strength of Ni_3Al grain boundaries. Whether that is enough to account for the dramatic ductilizing effect of boron is still unclear, although it is worth remembering that embrittling impurities can have similarly large effects on fracture mode and ductility (in the opposite direction) through changes principally in the grain-boundary energies.

The second possibility is that boron improves ductility by facilitating slip transfer across grain boundaries.³⁷⁻⁴⁰ There is some indirect experimental evidence (based on the lowering of the Hall-Petch slope³⁷⁻³⁸) to support this point of view, but the exact mechanism by which boron facilitates slip transmission across grain boundaries remains unknown. For example, it has been suggested that boron facilitates slip transfer by enhancing grain-boundary dislocation mobility.⁴¹ However, recent dislocation spreading experiments in the TEM⁴² have shown that the mobilities of grain-boundary dislocations in both boron-doped and undoped Ni_3Al are negligibly low at room temperature; at higher temperatures ($> 300^\circ\text{C}$), when there is a difference, the dislocations in the boron-doped alloy actually have *lower* mobilities than those in the undoped alloy.

Another possible mechanism was proposed by King and Yoo²² who suggested that the real role of boron might be to disorder boundaries in Ni_3Al and thus enable more dislocation reactions to take place. Unfortunately, it is not easy to directly image grain-boundary structures by high-resolution TEM, and there is evidence both for⁴³ and against^{44,45} the existence of a *very thin* ($< 20 \text{ \AA}$) disordered layer at the grain boundaries. Clearly, additional experiments are

needed before this question can be satisfactorily resolved.

Because of the difficulty in directly imaging grain boundaries, several attempts have been made to obtain indirect evidence of disorder. For example, Sieloff et al.^{28,46} used atom probe microanalysis and found that the grain boundaries in B-doped Ni₃Al were considerably Ni-enriched (by as much as 7 at. % relative to the bulk), whereas those in the undoped alloy had the bulk composition, suggesting B-induced disorder. However, their undoped alloy was rapidly solidified, and analyzed in the as-solidified condition (without annealing), so that the observed differences between the undoped and B-doped alloys might primarily be the result of differences in processing and not really indicative of B-Ni cosegregation. Baker et al.⁴⁷ used STEM analysis on undoped and B-doped powder-metallurgy Ni₃Al and reported that the grain boundaries in the latter were Ni-enriched (by about 6 at.% relative to the bulk), whereas those in the former had the bulk composition. However, only three boundaries in each sample were analyzed and it is not clear that their limited results are of a general nature. To overcome some of these deficiencies, George et al.⁴⁸ used Auger electron spectroscopy and analyzed a large number of grain boundaries in similarly processed (arc melted and well recrystallized) undoped and B-doped Ni₃Al. Their results are summarized in Fig. 3, and indicate that although the grain boundaries in Ni-rich Ni₃Al are slightly Ni-enriched relative to the bulk, there was no significant difference between the undoped and B-doped alloys, i.e., there was no indication of strong B-Ni cosegregation. However, this does not

rule out B-induced disorder because grain-boundary chemistry can only indirectly tell us about disorder: large B-induced deviations from stoichiometry probably mean that there is B-induced disorder, but the opposite is not necessarily true.

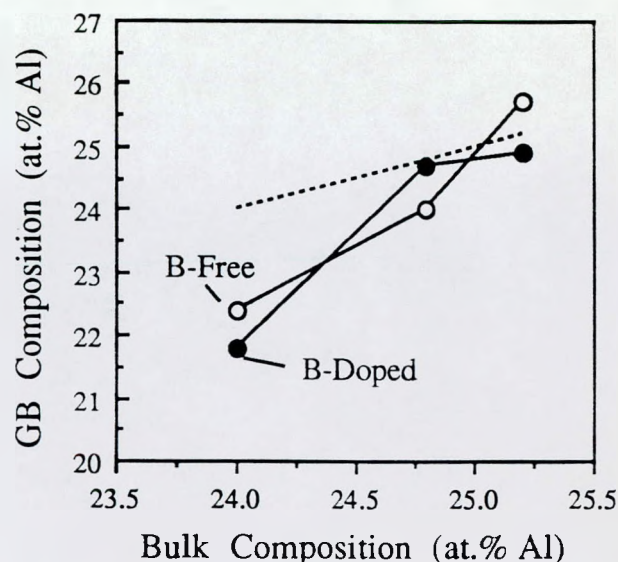


FIGURE 3

Comparison of grain-boundary and bulk compositions in B-free and B-doped Ni₃Al. (The grain-boundary composition is the same as the bulk composition along the dotted line).⁴⁸

2.2. NiAl

After an early report in 1966 of limited (2%) room-temperature tensile ductility in polycrystalline NiAl,⁴⁹ numerous later attempts to reproduce this ductility were unsuccessful, until Hahn and Vedula⁵⁰ recently showed that it was possible to obtain room-temperature plastic elongation of 2.5% in nearly stoichiometric, cast and extruded NiAl. Although it is not completely clear why the previous attempts were unsuccessful, it is now routinely possible to obtain plastic elongations of 2-3% in cast and extruded stoichiometric NiAl [e.g., Refs. 51,52].

Perhaps some of the earlier unsuccessful attempts, especially those using the powder-metallurgy approach,⁵³ were plagued by interstitial element problems. For example, our recent work⁵¹ has shown that as little as 300 wppm of carbon can embrittle NiAl, mainly by dramatically increasing its yield strength.

The fracture mode of polycrystalline NiAl is predominantly intergranular,⁵⁰⁻⁵² but detailed Auger analyses have shown that the grain boundaries in NiAl are extremely clean and free of impurities.⁵¹ This implies that the grain boundaries in NiAl are intrinsically brittle, like those in Ni₃Al. Microalloying with boron is able to almost completely suppress this intergranular fracture, and Auger analysis confirmed that the beneficial effect of boron is due to its strong segregation at the grain boundaries.^{51,52} Unlike in Ni₃Al, however, the suppression of grain-boundary fracture is not accompanied by an increase in ductility.^{51,52} On the contrary, because of its strong solid solution strengthening effect in NiAl, addition of too much boron can actually cause embrittlement.⁵¹ Fig. 4(a) is a plot of yield strength as a function of boron concentration showing the potent strengthening effect of boron. A least-squares fit of the data yields a value of ~4500 MPa/at.% B for the increase in yield strength due to boron addition. Note that if greater than about 100 wppm boron (0.04 at.% B) is added to NiAl, it fractures by transgranular cleavage before macroscopic yielding takes place,⁵² and that is why the fracture stress is plotted instead of the yield strength in the case of the 300 wppm (0.12 at.%) boron alloy. Associated with this strong solid solution strengthening effect is a

concomitant decrease in tensile ductility, as shown in Fig. 4(b).

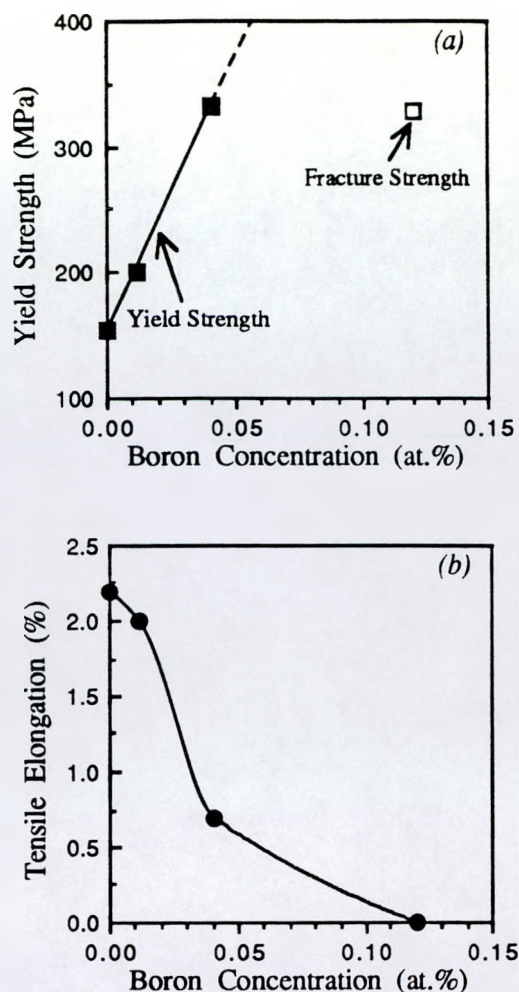


FIGURE 4

Effect of boron on (a) yield strength, and (b) ductility of stoichiometric NiAl at room temperature.⁵²

Of particular interest is the behavior of the alloy doped with 30 wppm (0.012 at.%) boron. It has a tensile ductility of 2%, which is about the same as that of undoped NiAl. In addition, this alloy has enough boron on its grain boundaries to almost completely suppress intergranular fracture.⁵² Further additions of boron appear to increase slightly the grain-boundary concentration of boron, with saturation (~10 at.% B on the grain boundaries) apparently occurring at a bulk boron concen-

tration of ~ 100 wppm (0.04 at.%).⁵² However, as we have seen above, further additions of boron cause strong solid solution strengthening, which in turn lowers the ductility. Therefore, the optimum boron level seems to be on the order of 30 wppm. At this level, boron is able to strengthen the grain boundaries and prevent intergranular fracture, without simultaneously hardening the lattice and thereby causing premature cleavage fracture.

Of course, although weak grain boundaries are part of the problem in NiAl, they are not the only problem (because single crystals of NiAl are also brittle^{54,55}). That is why even after intergranular fracture is suppressed, the B-doped alloys still have rather limited ductilities. The other problem is the lack of sufficient deformation modes in NiAl (a consequence of $\langle 100 \rangle$ slip). Recently, considerable effort has gone into finding suitable macroalloying elements that will promote additional slip systems in NiAl. It has been reported that additions of Cr,⁵⁴ Mn,⁵⁴ and V⁵⁵ promote $\langle 111 \rangle$ slip in NiAl, which should in principle result in the availability of more than 5 independent slip systems. However, no improvement in ductility was observed, indicating the need for additional study into the details of dislocation generation and motion in these alloys. Specifically, one needs to address the issue of whether macroalloying is able to create sufficient numbers of $\langle 111 \rangle$ dislocations, and also whether these dislocations are sufficiently mobile at room temperature. Additionally, since single crystals of NiAl are also brittle, it is possible that the intrinsic cleavage strength of NiAl is quite low, another point that needs detailed investigation.

3. ENVIRONMENTAL EMBRITTLEMENT IN IRON ALUMINIDES

3.1. FeAl

At room temperature, FeAl alloys exhibit poor ductility and brittle fracture. Their fracture mode depends on aluminum content: those alloys containing < 40 at.% Al fracturing by transgranular cleavage, while those with $> 40\%$ Al fracture intergranularly. The present discussion is limited to those alloys that fracture by transgranular cleavage (for information on alloys that fracture intergranularly, the reader may consult Ref. 56).

Perhaps the most important question concerning FeAl that has puzzled researchers for more than 45 years is this: why are they so brittle at room temperature when they apparently have all the *intrinsic* characteristics required for good ductility? For example, they deform by $\{110\}\langle 111 \rangle$ slip, i.e. like disordered bcc metals they have more than 5 independent slip systems. They are not particularly strong at room temperature, with yield strengths on the order of only 345 MPa. And, because they do not fracture intergranularly, they do not appear to have weak grain boundaries (like, for example, Ni₃Al). Therefore, until recently, it was thought that the poor ductility of FeAl was due to its intrinsically low cleavage strength. However, Liu et al.⁵⁷ have recently shown that FeAl is intrinsically quite ductile, and the poor ductility usually obtained in air tests is the result of an extrinsic factor, namely water vapor, which when removed permits extensive plastic deformation prior to fracture.

Fig. 5 and Table 2 show the effect of test environment on the tensile properties of FeAl (36.5% Al). 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 specie(s) in air is causing embrittlement, and when its effect is avoided (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 test chamber (including oxygen, hydrogen, and water vapor). As shown in Table 2, the water vapor tests reproduced the low ductility obtained in the air tests. Interestingly, the best ductility (17.6%) is obtained in a *dry* oxygen environment, 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 enough to cause some embrittlement relative to the dry oxygen test.

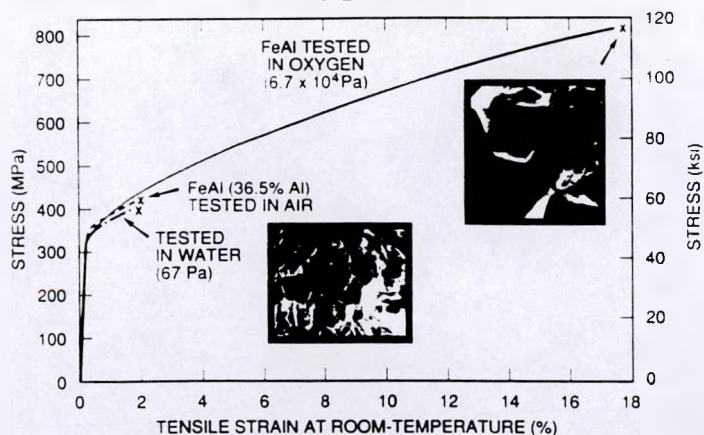
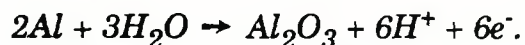


FIGURE 5

Effect of test environment on the tensile properties of FeAl (36.5 at. % Al).⁵⁷

The mechanism that has been postulated⁵⁷ for this type of environmental embrittlement is similar to that which is observed in aluminum and its alloys.^{58,59} In general, aluminum alloys are not embrittled by dry hy-

drogen; sometimes, however, they can be severely embrittled by moist air. The chemical reaction that is thought to cause this embrittlement is shown below:⁵⁸



It is believed that the high-fugacity atomic hydrogen that is produced in this reaction between the aluminum atoms and moist air, is forced into the metal at the crack tips, causing hydrogen embrittlement. Since FeAl alloys contain relatively large concentrations of aluminum, it is postulated that a reaction similar to the one described above for aluminum alloys, takes place also in FeAl.⁵⁷ Preliminary experiments using nuclear reaction analysis have shown that FeAl does, in fact, react with heavy water (presumably in a reaction analogous to the H_2O dissociation shown above), producing deuterium which is then absorbed into FeAl.⁶⁰ In the case of aluminum alloys, Speidel⁵⁸ has concluded that the role of moisture is to produce atomic hydrogen, rather than dissolution of the metal by condensation at the crack tip. If this is true also in FeAl, then the underlying mechanism of environmental embrittlement in FeAl may be similar to hydrogen embrittlement in other ordered intermetallics like Co_3Ti , $\text{Ni}_3(\text{Al}_{0.4}\text{Mn}_{0.6})$, $(\text{Fe,Ni})_3\text{V}$, and B-doped Ni_3Al ,⁶¹⁻⁶⁵ with the principal difference being the manner in which atomic hydrogen is generated and absorbed in the different studies (e.g., reaction with moist air⁵⁷ vs cathodic hydrogen charging⁶⁵). Consistent with this, Table II shows that the yield strength of FeAl is insensitive to test environment, a common observation in other studies of hydrogen embrittlement.⁶¹⁻⁶⁵ Nevertheless, despite these simi-

larities, it has to be realized that hydrogen embrittlement in metals is a complicated phenomenon, with many possible mechanisms.⁶⁶ Clearly, additional work needs to be done to unravel the details of environmental embrittlement in FeAl. What is clear

from these recent results, however, is that FeAl (36.5 at.% Al) alloys are intrinsically quite ductile: the low ductility that is commonly observed in air tests is the result of an extrinsic factor, namely moisture-induced environmental embrittlement.

Table 2. Effect of Test Environments on Room-Temperature Tensile Properties of Iron Aluminides^a [57, 67]

Test Environment (Gas Pressure)	Elongation (%)	Yield Strength (MPa)	Ultimate Strength (MPa)
<u>Fe₃Al (28% Al)</u>			
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>FeAl (36.5% Al)</u>			
Air	2.2	360	412
Vacuum ($< 1 \times 10^{-4}$ Pa)	5.4	352	501
Ar + 4% H ₂ (6.7×10^4 Pa)	6.2	379	579
Oxygen (6.7×10^4 Pa)	17.6	360	360
H ₂ O vapor (67 Pa)	2.4	368	430

^aAll specimens were annealed 1 h / 900°C + 2 h / 700°C.

3.2. Fe₃Al

As in the case of FeAl, it was only recently⁶⁷ that moisture was identified as the principal cause of poor ductility and brittle fracture in Fe₃Al (28 at.% Al). When tested in air, the alloy fractured by transgranular cleavage with a ductility of only 4%, see Table 2. When tested in vacuum ($\sim 10^{-4}$ Pa), the tensile elongation increased three-fold to about 12%. Similarly high values of ductility ($\sim 12\%$) were obtained in dry oxygen, and somewhat lower values ($\sim 8\%$) in a mixture of Ar + 4% H₂. The water vapor tests, on the other hand, resulted in ductilities even lower than those obtained in the air tests, although

the pressure in the water vapor tests was comparable to the vapor pressure of moisture in the air tests. These results clearly indicate that the Fe₃Al alloys are also susceptible to moisture-induced environmental embrittlement, just like the FeAl alloys. The postulated mechanism of embrittlement⁶⁷ is the same as that presumed to occur in the FeAl alloys, namely the generation of atomic hydrogen by the reaction of aluminum atoms in Fe₃Al with moisture in air, which then enters the metal at the crack tip and causes hydrogen embrittlement.

Recently, McKamey et al.^{68,69} have shown that the ductility of Fe₃Al alloys can be sub-

stantially improved by increasing the aluminum content from 25 to 28-30 at.%, and by adding 2-6 at.% chromium. The beneficial effect of the increased aluminum comes from the attendant sharp decrease in yield strength. In contrast, the beneficial effect of Cr has been shown to be a result mainly of Cr modifying the surface composition and reducing the reaction with water vapor, thereby reducing the susceptibility of the alloy to environmental embrittlement.⁷⁰ These Cr-modified alloys can be further improved by thermomechanical treatment, and by alloying with molybdenum and niobium.⁷¹ Some of these alloys have room-temperature tensile ductilities *in air* in excess of 15%, and yield strengths of about 500 MPa at 600°C, making them much stronger than conventional austenitic and ferritic steels such as 304 SS and 9Cr-1Mo steel.

4. CONCLUSIONS

Ordered intermetallics generally show brittle fracture and poor ductility at ambient temperatures, and their brittleness is related to both grain-boundary and bulk properties. During the past ten years, significant progress has been made in understanding brittle fracture and improving ductility. In this review, we have summarized recent results on two important classes of ordered intermetallics: nickel and iron aluminides.

Grain boundaries in both Ni₃Al and NiAl are intrinsically brittle (i.e. not caused by impurities), and their brittleness is related to the electronic and atomic structures of the grain boundaries themselves. Boron segregates strongly to the grain boundaries in both alloys, and suppresses intergranular fracture. As a result, ductility increases dra-

matically in Ni₃Al, but not in NiAl. The reason for this is that NiAl has additional problems such as poor cleavage strength and insufficient number of deformation modes.

The major cause of poor ductility and brittle fracture in iron aluminides is moisture-induced environmental embrittlement. The mechanism involves the reaction of aluminum atoms in the alloy with moisture in the air, producing atomic hydrogen which is forced into the metal at the crack tips, resulting in hydrogen embrittlement. The embrittlement can be avoided by modifying the surface composition so as to minimize the reaction of moisture with the alloy.

ACKNOWLEDGEMENTS

We thank C. G. McKamey and J. J. Liao for reviewing this paper. Thanks also to Gwen Sims for help with manuscript preparation. This research was sponsored by the Division of Materials Sciences, U.S. Dept. of Energy under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

REFERENCES

1. High-Temperature Ordered Intermetallic Alloys (Proc. Mater. Res. Soc. Symp.), Vol. 39, eds. C. C. Koch, C. T. Liu, and N. S. Stoloff (Mater. Res. Soc., Pittsburgh, PA, 1985).
2. High Temperature Ordered Intermetallic Alloys II (Proc. Mat. Res. Soc. Symp.), Vol. 81, eds. N. S. Stoloff, C. C. Koch, C. T. Liu, and O. Izumi (Materials Research Society, Pittsburgh, PA, 1987).
3. High-Temperature Ordered Intermetallic Alloys III (Proc. Mater. Res. Soc. Symp.), Vol. 133, eds. C. T. Liu, A. I. Taub, N. S. Stoloff, and C. C. Koch (Mater. Res. Soc., Pittsburgh, PA, 1989).

4. K. Aoki and O. Izumi, *Nippon Kinzoku Gakkaishi*. 43 (1979) 1190.
5. C. T. Liu, C. L. White, and J. A. Horton, *Acta Metall.* 33 (1985) 213.
6. A. I. Taub, S. C. Huang, and K. M. Chang, *Metall. Trans.* 15A (1984) 399.
7. B. Schmidt, P. Nagpal, and I. Baker, p. 755 in Ref. 3.
8. J. L. Smialek, J. Doychak, and D. J. Gaydos, *Oxidation Behavior of FeAl + Hf, Zr, B*, NASA TM-101402, NASA Lewis Research Center, Cleveland, OH, September 1988.
9. C. G. McKamey et al., *Evaluation of Mechanical and Metallurgical Properties of Fe₃Al-Based Aluminides*, ORNL TM-10125, Oak Ridge National Laboratory, Oak Ridge, TN, September 1986.
10. J. H. DeVan, in: *Oxidation of High-Temperature Intermetallics*, eds. T. Grobstein and J. Doychak (The Minerals, Metals and Materials Society, Warrendale, PA, 1989), p. 107.
11. P. F. Tortorelli, J. H. DeVan, and J. R. Distefano, presented at the "High Temperature Intermetallics Symposium," WESTEC '89, Los Angeles, CA, March 21-23, 1989.
12. C. T. Liu, F. H. Froes, and J. O. Stiegler, to be published in: *Metals Handbook: Heat Treating* (American Society for Metals, Metals Park, OH, 1990), 10th edition, Vol. 3.
13. C. T. Liu and C. C. Koch, *proc. of a public workshop on Trends in Critical Materials Requirements for Steels of the Future: Conservation and Substitution Technology for Chromium*, NBSIR-83-2679-2, National Bureau of Standards, Washington, D.C., June 1983.
14. E. M. Grala, in: *Mechanical Properties of Intermetallic Compounds*, eds. J. H. Westbrook (Wiley, New York, 1960), p. 358.
15. T. Takasugi, E. P. George, D. P. Pope and O. Izumi, *Scripta Metall.* 19 (1985) 551.
16. T. Ogura, S. Hanada, T. Masumoto, and O. Izumi, *Metall. Trans.* 16A (1985) 441.
17. T. Takasugi and O. Izumi, *Acta Metall.* 33 (1985) 1247.
18. T. Takasugi, O. Izumi, and N. Masahashi, *Acta Metall.* 33 (1985) 1259.
19. A. I. Taub, C. L. Briant, S. C. Huang, K. M. Chang, and M. R. Jackson, *Scripta Metall.* 20 (1986) 129.
20. A. I. Taub and C. L. Briant, p. 343 in Ref. 2.
21. A. I. Taub and C. L. Briant, *Acta Metall.* 35 (1987) 1597.
22. A. H. King and M. H. Yoo, p. 99 in Ref. 2.
23. V. Vitek, S. P. Chen, A. F. Voter, J. J. Kruisman, and J. Th. M. De Hosson, in: *Grain Boundary Chemistry and Intergranular Fracture*, eds. G. S. Was (Trans. Tech. Publications, 1989).
24. J. J. Kruisman, V. Vitek, and J. Th. M. De Hosson, *Acta Metall.* 36 (1989) 2729.
25. J. A. Horton and M. K. Miller, *Acta Metall.* 35 (1987) 133.
26. M. K. Miller and J. A. Horton, *J. de Phys. C7* (1986) 263.
27. J. A. Horton and M. K. Miller, p. 105 in Ref. 2.
28. D. D. Sieloff, S. S. Brenner, and M. G. Burke, p. 87 in Ref. 2.
29. E. P. George and C. T. Liu, to be published in: *Alloy Phase Stability and Design* (Proc. Mater. Res. Soc. Symp.), Vol. 186, eds. G. M. Stocks, D. P. Pope, and A. F. Giamei (Mater. Res. Soc. Pittsburgh, PA, 1990).

30. C. T. Liu, C. L. White, C. C. Koch and E. H. Lee, in: *Proc. Symp. High-Temperature Materials Chemistry II* (Electrochem. Soc., Inc., 1983), p. 32.
31. C. L. White, R. A. Padgett, C. T. Liu, and S. M. Yalisove, *Scripta Metall.* 18 (1984) 1417.
32. C. L. White and D. F. Stein, *Metall. Trans.* 9A (1978) 13.
33. J. R. Rice, in: *The Effect of Hydrogen on the Behavior of Metals* (AIME, New York, 1976), p. 455.
34. G. S. Painter and F. W. Averill, *Phys. Rev. Lett.* 58 (1987) 234.
35. M. E. Eberhart and D. D. Vvedinsky, *Phys. Rev. Lett.* 58 (1987) 61.
36. S. P. Chen, A. F. Voter, R. C. Albers, A. M. Boring, and P. J. Hay, *Scripta Metall.* 23 (1989) 217.
37. E. M. Schulson, T. P. Wiehs, D. V. Viens, and I. Baker, *Acta Metall.* 33 (1985) 1587.
38. P. S. Khadkikar, K. Vedula, and B. S. Shale, *Metall. Trans.* 18A (1987) 425.
39. I. Baker, E. M. Schulson, and J. A. Horton, *Acta Metall.* 35 (1987) 1533.
40. E. M. Schulson, I. Baker, and H. J. Frost, p. 195 in Ref. 2.
41. E. M. Schulson, T. P. Wiehs, I. Baker, H. J. Frost, and J. A. Horton, *Acta Metall.* 34 (1986) 1395.
42. W. A. Swiatnicki and M. W. Grabski, *Acta Metall.* 37 (1989) 1307.
43. R. A. D. Mackenzie and S. L. Sass, *Scripta Metall.* 22 (1988) 1807.
44. M. J. Mills, *Scripta Metall.* 23 (1989) 2061.
45. J. E. Krzanowski, *Scripta Metall.* 23 (1989) 1219.
46. D. D. Sieloff, S. S. Brenner, and Hua Ming-Jian, p. 155 in ref 3.
47. I. Baker, E. M. Schuslon, and J. R. Michael, *Philos. Mag.* B57 (1988) 379.
48. E. P. George, C. T. Liu, and R. A. Padgett, *Scripta Metall.* 23 (1989) 979.
49. A. G. Rozner and R. J. Wasilewski, *J. Inst. Met.* 94 (1966) 169.
50. K. H. Hahn and K. Vedula, *Scripta Metall.* 23 (1989) 7.
51. E. P. George and C. T. Liu, *J. Mater. Res.* 5 (1990) 754.
52. E. P. George, C. T. Liu, and J. J. Liao, to be published in: *Alloy Phase Stability and Design* (Proc. Mater. Res. Soc. Symp.), Vol. 186, eds. G. M. Stocks, D. P. Pope, and A. F. Giamei (Mater. Res. Soc. Pittsburgh, PA, 1990).
53. K. Vedula and J. R. Stephens, p. 381 in Ref. 2.
54. D. B. Miracle, S. Russell, and C. C. Law, p. 225 in Ref. 3.
55. R. Darolia, D. F. Lahrman, R. D. Field, and A. J. Freeman, p. 113 in Ref. 3.
56. C. T. Liu and E. P. George, *Scripta Metall.* 24 (1990) 1285.
57. C. T. Liu, E. H. Lee and C. G. McKamey, *Scripta Metall.* 23 (1989) 875.
58. M. P. Speidel, in: *Hydrogen Damage*, ed. C. D. Beachem (American Society for Metals, Metals Park, OH, 1977), p. 329.
59. R. J. Gest and A. R. Troiano, *Corrosion* 30(8) (1974) 274.
60. E. P. George, M. B. Lewis, and C. T. Liu, unpublished research, Oak Ridge National Laboratory (1989).
61. T. Takasugi and O. Izumi, *Acta Metall.* 34, (1986) 607.

62. N. Masahashi, T. Takasugi, and O. Izumi, *Metall. Trans.* 19A (1988) 353.
63. O. Izumi and T. Takasugi, *J. Mater. Res.* 3 (1988) 426.
64. A. K. Kuruvilla, S. Ashok, and N. S. Stoloff, in: *Proc. Third Intl. Congress on Hydrogen in Metals*, Vol. 2 (Pergamon, Paris, 1982) p. 629.
65. A. K. Kuruvilla and N. S. Stoloff, *Scripta Metall.* 19 (1985) 83.
66. J. P. Hirth, *Metall. Trans* 11A (1980) 861.
67. C. T. Liu, C. G. McKamey, and E. H. Lee, *Scripta Metall.* 24 (1990) 385.
68. C. G. McKamey, J. A. Horton, and C. T. Liu, *Scripta Metall.* 22 (1988) 1679.
69. C. G. McKamey, J. A. Horton, and C. T. Liu, *J. Mater. Res.* 4 (1989) 1156.
70. C. G. McKamey and C. T. Liu, submitted to *Scripta Metall.* (1990).
71. C. G. McKamey et al., *Development of Iron Aluminides for Gasification Systems*, ORNL TM-10793, Oak Ridge National Laboratory, Oak Ridge, TN, July 1988.