MECHANICAL PROPERTIES OF Ni3Al AND FeAl: RECENT DEVELOPMENTS

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JUL 28 1989

Abstract

Recent developments in our understanding of the ductility and fracture behavior of Ni3Al and FeAl are reviewed. Both intrinsic factors (e.g., alloy stoichiometry), and extrinsic factors (e.g., environment) have been shown to affect their mechanical properties. Of all the recent developments, perhaps the most significant is the realization that Ni3Al and FeAl are intrinsically ductile (at least on the Al-deficient side of stoichiometry); their brittleness when tested in ambient air is due mainly to environmental embrittlement. Another intriguing discovery is that boron embrittlement of Ni3Al in gaseous hydrogen (until recently, B was thought to have only beneficial, or at most neutral, effects). We review these and other recent discoveries and discuss, wherever possible, the underlying physical mechanisms giving rise to the observed mechanical behavior.

Introduction

A major drawback of many otherwise attractive ordered intermetallics is their poor room-temperature ductility and tendency to brittle fracture. Often the brittleness is a consequence of their complex, non-cubic crystal structures, which do not provide the requisite 5 independent slip systems and in which dislocation motion is usually extremely difficult. But even intermetallics with relatively simple crystal structures are often brittle. For example, at room temperature, Ni3Al undergoes brittle intergranular fracture, and FeAl brittle intergranular fracture or transgranular cleavage depending on the Fe/Al ratio. Until recently, the behavior of these latter compounds was quite puzzling because there seemed to be no obvious reason for their brittleness. For example, slip occurs on [111]<110> in Ni3Al and [110]<111> in FeAl, providing both alloys with 5 independent slip systems. Additionally, neither is particularly strong at room temperature, suggesting that dislocation generation and motion are relatively easy. For lack of anything better, it was assumed that their ordered nature somehow made them intrinsically brittle.

Then, in 1989, Liu et al [1] discovered that an extrinsic factor, the moisture in ambient air, was responsible for the brittleness of FeAl (36.5 at. % Al). They proposed that the water vapor in air reacted with the Al atoms in FeAl, generating atomic hydrogen which embrittled the crack-tip regions:

\[ 2\text{Al} + 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 6\text{H} \]

When this “environmental embrittlement” was suppressed—by conducting the tests in dry oxygen—high tensile elongations were obtained, indicating that FeAl was intrinsically ductile. The following reaction between aluminum and oxygen to form protective aluminum oxide was proposed as an explanation for the high ductilities obtained in oxygen [1]:

\[ 4\text{Al} + 3\text{O}_2 \rightarrow 2\text{Al}_2\text{O}_3 \]

The discovery of environmental effects in FeAl sparked widespread interest, not least because it offered the hope that other high-symmetry intermetallics may also be intrinsically ductile. Not long after the initial discovery in FeAl, environmental effects similar to those in FeAl were discovered in a whole host of other ordered intermetallics [2]. The basic reactions listed above (or their equivalents if other reactive elements are involved) have since been used to rationalize environmental effects in many different intermetallics.

The goal of the present paper is to review recent developments in our understanding of environmental effects by focusing on two model alloy systems, Ni3Al and FeAl. As we shall presently see, considerable progress has been made in elucidating the phenomenological aspects of environmental embrittlement; nevertheless, much remains to be done to uncover the detailed micromechanisms.

Environmental Effects

H2O-Containing Environments

As mentioned earlier, it was in FeAl (36.5 at. % Al) that Liu et al. [1] first discovered environmental embrittlement. Table 1 summarizes the reported effects of environment on the room-temperature tensile properties of this alloy.

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The ductility in air is 2.2%, which increases to 5.4% in vacuum and 17.6% in (dry) oxygen. In H₂O vapor (at a pressure of 67 Pa, which is 5% of the water vapor pressure in ordinary ambient air), the ductility is similar to that obtained in air, indicating that moisture in air can severely embrittle FeAl. Interestingly, when environmental embrittlement was suppressed (by testing in oxygen), the fracture mode of FeAl (36.5% Al) changed from transgranular to intergranular, suggesting that, in the absence of environmental effects, the grain boundaries, at least in this FeAl alloy, are weaker than the bulk. This intrinsic brittleness of the grain boundaries becomes more severe the closer one gets to the stoichiometric composition (more on this later).

### TABLE 1. Effect of test environment on room-temperature tensile properties of Fe-36.5Al [1].

<table>
<thead>
<tr>
<th>Environment (Pressure)</th>
<th>Elongation (%)</th>
<th>Yield strength (MPa)</th>
<th>Ultimate strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air (1 atm)</td>
<td>2.2</td>
<td>360</td>
<td>412</td>
</tr>
<tr>
<td>Vacuum (&lt;10⁻¹ Pa)</td>
<td>5.4</td>
<td>352</td>
<td>501</td>
</tr>
<tr>
<td>Ar + 4% H₂ (6.7 × 10¹⁴ Pa)</td>
<td>6.2</td>
<td>379</td>
<td>579</td>
</tr>
<tr>
<td>Oxygen (6.7 × 10¹⁴ Pa)</td>
<td>17.6</td>
<td>360</td>
<td>805</td>
</tr>
<tr>
<td>H₂O Vapor (67 Pa)</td>
<td>2.4</td>
<td>368</td>
<td>430</td>
</tr>
</tbody>
</table>

Shortly after environmental embrittlement was discovered in FeAl, several research groups decided to investigate whether a similar mechanism might also be responsible for the notorious brittleness of Ni₃Al, another intermetallic whose brittleness had long mystified researchers. Unfortunately, polycrystalline Ni₃Al is brittle at both low and high temperatures, making it extremely difficult to break down its cast structure and obtain equiaxed, recrystallized grains without introducing microcracks. Liu [3] attempted to minimize microcracking by carefully cold forging conventionally cast Ni₃Al alloys (Ni-23.5Al and Ni-24Al) which were then recrystallized to obtain equiaxed microstructures. However, room-temperature ductility increased from ~3% in air to only about 8% in (dry) oxygen, suggesting that moisture-induced embrittlement was not the sole reason for the poor ductility of Ni₃Al [3], or that the specimens contained internal flaws which compromised the measured ductility despite the care taken during preparation [4].

### TABLE 2. Effects of test environment, specimen orientation, and grain size on the room-temperature tensile properties of Ni-23.4Al.

<table>
<thead>
<tr>
<th>Grain size (μm)</th>
<th>Specimen orientation</th>
<th>Test environment (pressure)</th>
<th>Elongation to fracture (%)</th>
<th>Yield strength (MPa)</th>
<th>Ultimate strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>0°</td>
<td>Air (10¹⁰ Pa)</td>
<td>3.1</td>
<td>308</td>
<td>392</td>
</tr>
<tr>
<td></td>
<td>0°</td>
<td>Vacuum (1.3 × 10⁴ Pa)</td>
<td>7.9</td>
<td>323</td>
<td>519</td>
</tr>
<tr>
<td></td>
<td>0°</td>
<td>Vacuum (3.8 × 10⁴ Pa)</td>
<td>12.8</td>
<td>301</td>
<td>602</td>
</tr>
<tr>
<td></td>
<td>0°</td>
<td>Oxygen (6.7 × 10⁴ Pa)</td>
<td>15.8</td>
<td>336</td>
<td>681</td>
</tr>
<tr>
<td></td>
<td>0°</td>
<td>Vacuum (3.6 × 10⁴ Pa)</td>
<td>23.4</td>
<td>--b</td>
<td>--b</td>
</tr>
<tr>
<td>32</td>
<td>0°</td>
<td>Air (10³ Pa)</td>
<td>4.8</td>
<td>327</td>
<td>401</td>
</tr>
<tr>
<td></td>
<td>45°</td>
<td>Oxygen (6.7 × 10⁴ Pa)</td>
<td>12.6</td>
<td>345</td>
<td>642</td>
</tr>
</tbody>
</table>

*Relative to rolling direction.

*Not measured.

George et al [4,5] realized that the way to obtain defect-free polycrystals of Ni₃Al was to cold work and recrystallize single crystals of Ni₃Al (because single crystals are ductile and can be deformed extensively without cracking). When polycrystalline specimens produced in this manner were tensile tested [6], it was found that their ductilities increased dramatically from around 3% in air, to more than 23% in ultrahigh (10⁻¹⁰ Pa) vacuum (Table 2). They concluded, therefore, that the intrinsinc ductility of Ni₃Al was quite high, and that (by analogy with the earlier work on iron aluminides [1,7]) moisture-induced embrittlement was what was responsible for the low ductilities commonly measured in air. With increasing amounts of air in the test environment, ductility dropped progressively, until in ordinary ambient air at atmospheric pressure it was only 3%—which is comparable to values commonly reported for the ductility of recrystallized fine-grained Ni₃Al.

### H₂-Containing Environments

The reaction of H₂O with Al is not the only way to generate atomic H₂; dissociative adsorption of H₂ on active metal surfaces can also produce it. In principle, therefore, some intermetallics may be embrittled by both H₂O and H₂. The degree to which each environment would produce embrittlement would depend on, among other factors, the relative efficiencies of H₂ and H₂O dissociation.

In their 1989 study, Liu et al. [11] investigated the effect of H₂ by testing Fe-36.5Al in a gas mixture consisting of Ar + 4% H₂. Their results, listed in Table 1, suggest that molecular hydrogen (at a partial pressure of 2.7 × 10¹³ Pa, which is about twice the partial pressure of the residual water vapor in atmospheric air) does, indeed, cause embrittlement, although not to the same degree as H₂O. However, their experiments were conducted...
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in an unbaked, turbo-pumped vacuum chamber (base pressure: \( -6 \times 10^{-4} \) Pa) in which trace amounts of water vapor were undoubtedly present as contamination. In order to measure the true effects of \( \text{H}_2 \), without the confounding effects of \( \text{H}_2\text{O} \), experiments should be performed in very dry \( \text{H}_2 \).

Recently, Cohron and George [8] tensile tested Fe-37Al in an ultrahigh vacuum (UHV) chamber (base pressure, \( 10^{-4} \) Pa) into which high-purity (99.9999\%) \( \text{H}_2 \) gas that had been dried by flowing through a liquid nitrogen cold trap was introduced at various pressures. Figure 1 shows the results of their study. In UHV, the ductility is around 16\%, which is similar to the ductility measured by Liu et al. [1] in oxygen (see Table 1).

With increasing hydrogen pressure, ductility decreases gradually, reaching a value of \(-9\%\) at a hydrogen pressure of \( 6.7 \times 10^{-2} \) Pa. This decrease is somewhat less than that observed by Liu et al., indicating that part of Liu et al.'s decrease may have been due to moisture. Despite this minor difference, however, both studies clearly indicate that molecular hydrogen does embrittle FeAl. The embrittlement mechanism is expected to be similar to that discussed earlier except that the atomic \( \text{H} \) in this case is a result of the dissociative adsorption of \( \text{H}_2 \) (rather than \( \text{H}_2\text{O} \)). Interestingly, the embrittling effect of \( \text{H}_2 \) is not as severe as that of \( \text{H}_2\text{O} \).

Another point to note is that over the entire pressure range tested, ductility is independent of whether the ion gage (a common device used to measure gas pressures) is turned on or off (Fig. 1). The significance of the ion gage is that, when it is turned on, its hot tungsten filament dissociates molecular \( \text{H}_2 \) into atomic \( \text{H} \). Since this source of atomic \( \text{H} \) does not have any effect on the measured ductility, it must mean that the surfaces of FeAl are themselves effective in dissociating \( \text{H}_2 \) into \( \text{H} \). As discussed below, this behavior is quite different from that of NiAl.

![Fig. 1](image1.png)

**FIG 1** Effect of \( \text{H}_2 \) pressure on the room-temperature tensile ductility of Fe-37Al [8]. Open symbols represent data obtained with gage on; filled symbols represent data obtained with gage off.

Unlike its effect on FeAl, molecular \( \text{H}_2 \) does not embrittle otherwise ductile NiAl (Fig. 2, "Gage OFF" data), at hydrogen pressures as high as \( 1.3 \times 10^{-1} \) Pa (which is roughly the partial pressure of \( \text{H}_2\text{O} \) responsible for the severe embrittlement caused by ambient air. Table 2). Since the partial pressure of hydrogen in atmospheric air is considerably lower, \( -5 \times 10^{-2} \) Torr, it is clearly moisture and not hydrogen that is the cause of the observed embrittlement in air. Furthermore, since molecular \( \text{H}_2 \) has to first dissociate into atomic \( \text{H} \) before it can enter the metal and cause embrittlement, the fact that gaseous hydrogen does not embrittle NiAl must mean that the surfaces of NiAl do not dissociate \( \text{H}_2 \) into \( \text{H} \) very effectively. Thus inference needs to be verified in the future by experiments that directly measure \( \text{H}_2 \) dissociation on NiAl surfaces. So far, such experiments have been performed only on NiAl surfaces, where it was shown that \( \text{H}_2 \) does not in fact dissociate readily [10,11].

![Fig. 2](image2.png)

**FIG. 2** Effect of \( \text{H}_2 \) pressure on room-temperature tensile ductility of Ni-23.4\% Al [9]. Gage OFF and Gage ON refer to experiments conducted with the ionization gage turned off and on, respectively.

When the tensile tests were performed with the ion gage turned on (which produces atomic \( \text{H} \)), ductility dropped dramatically (Fig. 2), and the fracture mode changed from mostly transgranular to intergranular (Fig. 3). The "ion-gage effect" persists down to pressures in the UHV range (Fig. 2), indicating that even minute traces of atomic \( \text{H} \) in the test environment are deleterious to the ductility of NiAl. When the availability of atomic \( \text{H} \) (from all sources, including \( \text{H}_2\text{O} \) and \( \text{H}_2 \)) is carefully limited, B-free NiAl can be quite ductile, with elongations approaching 40\% and mostly (>70\%) transgranular fracture.

![Fracture surfaces of Ni-23.4Al tested in H2 with the gage on (top) and off (bottom) [9].](image3.png)

**FIG. 3** Fracture surfaces of Ni-23.4Al tested in \( \text{H}_2 \), with the gage on (top) and off (bottom) [9].

**Mechanisms**

Details of the atomic level interactions occurring during the dissociative adsorption of \( \text{H}_2\text{O} \) on aluminide surfaces were studied recently by Chia and Chung [12,13] and Gleason et al. [14] who performed thermal
desorption studies in conjunction with photoelectron and Auger electron spectroscopy on the surfaces of Ni$_3$(Al, Ti) and FeAl, respectively. Their results confirm that Al is the active species responsible for the dissociation of water. When water is adsorbed at cryogenic temperatures on clean Ni$_3$(Al, Ti) and FeAl surfaces, and the surfaces then slowly heated, molecular hydrogen (rather than water) is seen to desorb (Fig. 4). This indicates that the adsorbed water reacts with the Al-containing surfaces and dissociates into atomic H and O (or H and OH). Upon heating the atomic H recombines and desorbs as H$_2$.

![Graph](image1)

Consistent with the above dissociation scheme, the oxygen 1s core level peak broadened and shifted to lower binding energies (relative to its position in water) [12]. Upon heating, the atomic H desorbed as H$_2$, and was detected in the thermal desorption experiments, whereas the oxygen stayed on the surface as a remnant of the water dissociation, and was detected by Auger electron spectroscopy performed after the desorption [12]. The oxygen produced during water dissociation appears to bind with the Al atoms because photoelectron spectroscopy [13,14] detected a component of the Al 2p peak at a higher binding energy than that normally associated with metallic Al (indicative of aluminum oxide formation). Hydrogen, on the other hand, resides on the transition metal atoms [14], but appears to be weakly bound because the Ni and Fe 2p peaks did not shift after the dissociation, remaining instead at the values corresponding to those of metallic Ni and Fe, respectively.

Interestingly, the reactivity of Ni$_3$(Al, Ti) depended on which particular surface plane was examined [12]. The results noted above were for the (100) plane; on the (111) surface, in contrast, the adsorbed water remained unreacted, and desorbed upon heating as intact water molecules (i.e., no atomic H was generated). Fig. 5. Consistent with this desorption result, only the metallic Al 2p peak was observed on the (111) surface, indicating that the Al atoms on (111) do not react with water to form the oxide. The oxygen 1s binding energy also remained unchanged on (111), confirming that the adsorbed water molecules remained unreacted on this surface.

Since water dissociation is observed on the (100) planes of Ni$_3$(Al, Ti) but not on (111), it suggests that the chemistry and/or structure of a grain boundary (or cleavage plane) may affect its susceptibility to moisture-induced embrittlement. In other words, some grain boundaries (and cleavage planes) may be more active than others for the dissociation of water. Consistent with this, Nishimura et al. [15] have shown that stoichiometric Ni$_3$Al produced by a special directional solidification technique that results in mainly low-angle and (111) boundaries [16,17] is essentially immune to the harmful effects of H$_2$O: ductility remained high (Fig. 6), and the fracture mode predominantly transgranular, in vacuum, air, and water. In contrast, Ni$_3$Al alloys containing fewer special boundaries are severely embrittled by water vapor [18]. In the case of FeAl, while there is no direct evidence of certain planes being more active than others for the dissociation of water (the thermal desorption experiments discussed earlier were performed on polycrystals), fracture toughness studies have shown that the cleavage planes in FeAl change from (111) to (100) as a result of H$_2$O-induced embrittlement [19]. However, tensile tests of monocristalline Fe-40Al resulted in (100) cleavage in both air and oxygen [20], suggesting that additional studies are needed to resolve this issue. Li and Liu [21] proposed that hydrogen may accelerate the formation of (111) mixed dislocations (the so-called Cotrell mechanism), as well as their subsequent combination to form microcracks on the (100) plane, thus providing a mechanism for the observed (100) cleavage in hydrogen-containing environments.

![Graph](image2)
water vapor. However, it is not clear how this hydrogen then causes embrittlement. Two of the mechanisms proposed for the hydrogen embrittlement of conventional metals are H-induced decohesion or H-enhanced local plasticity [see, e.g., 22]. These are candidate mechanisms also for the embrittlement of intermetallics. Unfortunately, there is insufficient evidence at present to discriminate between the two. Robertson and Birnbaum [23] performed in situ crack propagation experiments in a transmission electron microscope and found that both crack growth rate and dislocation activity in Fe₃Al were higher in wet hydrogen (or helium) than in vacuum. Tests in dry hydrogen (or helium) did not show this acceleration relative to vacuum, suggesting that the atomic hydrogen generated in the reaction with moisture somehow enhanced local plasticity which in turn increased the crack growth rate. No such experimental results are available to support hydrogen-induced decohesion; however, first-principles quantum-mechanical calculations by Fu and Painter [24] showed that the ideal cleavage energy of Fe₃Al can be reduced by 20-70% depending on the dissolved hydrogen concentration (Fig. 7). Additional research is clearly needed, but given the lack of consensus in conventional metals despite decades of debate, it appears unlikely that this matter will be settled any time soon.

**Strain Rate Effects**

The proposed mechanisms of environmental embrittlement in Ni₃Al and Fe₃Al involve many individual steps (e.g., surface adsorption of H₂O / H₂, their dissociation to form H, absorption of H into the metal, and transport of H to some critical location ahead of the crack tip) any of which may be rate limiting. Consequently, room-temperature ductility is expected to be a function of strain rate. Indeed, both Fe₃Al (Fig. 8) and Ni₃Al (Fig. 9) exhibit such a strain rate dependence, with ductility increasing as the strain rate increases. A common explanation for such strain rate dependencies is that, as the strain rate increases, it becomes increasingly difficult for the environmental reactions to keep up with the growing crack, and the ductility increases. If, instead of being limited by extrinsic environmental factors, ductility is limited by intrinsic factors (e.g., dislocation mobility and cross slip), strain rate usually has the opposite effect, i.e., ductility decreases with increasing strain rate.

**Temperature Effects**

The ductilities of alloys exhibiting environmental effects are expected to also show a temperature dependence. For example, with decreasing temperature, the free energies and kinetics of the various steps in the embrittlement process should decrease, whereas with increasing temperature, the sticking probability of the H₂O (or H₂) molecules on the intermetallic surfaces should decrease and the tendency for oxide formation should increase.

Consistent with this reasoning, the ductility of Ni₃Al in air is seen to go through a local minimum at room temperature, with ductility increasing at both lower and higher temperatures [26]. In oxygen, the ductility is high at room temperature (because oxygen suppresses the embrittlement caused by H₂O) but it decreases with increasing temperature because of the well-known embrittlement effect of oxygen at elevated temperatures [29,30]. In vacuum, ductility remains high over the entire temperature range. Very high elongations to fracture were obtained recently by George et al. [31] when fine-grained (~15 μm) Ni₃Al was tested in liquid nitrogen (77 K). Table 3 lists the tensile properties of two such
specimens. Consistent with these high ductilities, the fracture mode was found to change from intergranular at room temperature to >60% transgranular at 77 K, indicating that the grain boundaries in Ni₃Al are not necessarily weak (provided that environmental embrittlement is suppressed). Chiba et al. [32] also obtained high ductilities (approaching 50%) in liquid nitrogen, but their specimens were produced by a special strain-annealing technique and had very large grain sizes (670 μm). Lee and White [33], for reasons that are not entirely clear, obtained considerably lower ductilities in Ni-24Al specimens tensile tested in liquid nitrogen. Additional research is needed to better understand these differences. Nevertheless, it is clear that the ductility of Ni₃Al increases when it is tested at cryogenic temperatures—as it should, if environmental effects are responsible for its room-temperature brittleness.

**TABLE 3** Tensile properties of polycrystalline Ni-23.4Al at 77 K [31].

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Elongation to fracture (%)</th>
<th>Yield strength (MPa)</th>
<th>Ultimate strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K-3</td>
<td>31.8</td>
<td>254</td>
<td>762</td>
</tr>
<tr>
<td>K-4</td>
<td>31.3</td>
<td>269</td>
<td>672</td>
</tr>
</tbody>
</table>

The behavior of FeAl is broadly similar to that of Ni₃Al. When tested in air, the ductility of FeAl (36.5% Al) goes through a minimum at around room temperature: in oxygen, on the other hand, its ductility remains relatively high over the entire temperature range (Fig. 10). Li and Liu [34] considered several thermodynamic and kinetic factors and produced a quantitative model of the effect of temperature on the ductility of FeAl that successfully reproduced the shape of the experimental curve (Fig. 10). They concluded that the dip in ductility due to environmental embrittlement was satisfactorily explained by a kinetic effect at low temperatures and an equilibrium effect at high temperatures.

![FIG. 10](image-url) Effect of temperature on the tensile ductility of FeAl (36.5% Al) in air and oxygen [34]. Curves calculated by Li and Liu [34] using a thermodynamic model.

**Boron Effects**

**H₂O-Containing Environments**

Nearly two decades ago, Aoki and Izumi [35] discovered that macralloying with ppm levels of B suppressed grain boundary fracture and improved the ductility of Ni₃Al in ambient air. A few years later, Liu et al. [36] showed that the beneficial effect of B resulted from its segregation to the grain boundaries, but that B improved ductility only on the Ni-rich side of stoichiometry. Until recently, B was believed to either increase grain boundary cohesion [36,37] or aid in slip transfer across grain boundaries [38,39]. However, more recent data indicate that the role of B is mainly to suppress environmental effects [40]. In general, if the amount of B is high enough, then Ni₃Al appears to be immune to embrittlement by water or its vapor [41]. If, however, there is a limited amount of B present, Ni₃Al is to some degree susceptible to H₂O-induced embrittlement [26,42].

Fig. 11 shows the effect of strain rate on the room-temperature tensile ductility of B-doped Ni₃Al (24% Al) in air and water [26]. The ductility of the 100 wppm B alloy is high and relatively insensitive to strain rate both in air and water, whereas the 50 wppm B alloy, while it is relatively ductile in air, undergoes a ductile-to-brittle transition in water as the strain rate is decreased. Except for the 100 wppm B alloy tested in air at the highest strain rate, which showed transgranular fracture with microvoid coalescence, all the other conditions resulted in some degree of intergranular fracture [26]. Taken together, these results suggest that, if the amount of B added to Ni₃Al, and therefore the amount segregated at the grain boundaries [43], is less than some “optimal” level, environmental embrittlement is only partially alleviated and, only when environmental effects are well and truly suppressed, do we get completely transgranular fracture. Additionally, a major role of boron appears to be the suppression of environmental embrittlement because virtually the same improvement in ductility can be obtained by increasing the strain rate, increasing the boron concentration, or decreasing the aggressiveness of the test environment.

![FIG. 11](image-url) Effect of strain rate, environment, and B doping on room-temperature ductility of Ni-24Al [26].

A possible mechanism [44] for the suppression of H₂O-induced embrittlement is that B inhibits the diffusion of H atoms along the grain boundaries of Ni₃Al. There is evidence to suggest that the apparent diffusivity of H along the grain boundaries of Ni₃Al is decreased in the presence of boron [45]. Other authors [46], have proposed that the role of B is to slow down the kinetics of the reaction of H₂O with the exposed grain boundaries of Ni₃Al, resulting in reduced hydrogen production. Fig. 12 shows Auger spectra taken from the grain boundaries of B-free and B-doped Ni₃Al alloys as a function of exposure (pressure x time) to H₂O vapor. The build-up of oxygen (which is mostly the result of water dissociation into H and O) is greater on the B-free grain boundaries than on the B-doped grain boundaries, indicating that B enrichment at the grain boundaries slows down the reaction of water vapor with Ni₃Al, and therefore the production of atomic H.
The behavior of B on FeAl surfaces appears to be somewhat different: Gleason et al. [47] using temperature-programmed desorption, in conjunction with Auger and photoelectron spectroscopy concluded that the amount of hydrogen product desorbing from boron-doped FeAl is very similar to that desorbing from clean FeAl surfaces after equivalent water exposures. They concluded, therefore, that B had little effect on the reactivity of FeAl surfaces to water dissociation.

**H₂ Containing Environments**

Cohron et al. [47] recently investigated the effects of boron doping on the room-temperature ductility and fracture behavior of Ni₃Al (24 at. % Al) in dry H₂ gas. As shown in Fig. 13, there is little change in ductility with increasing H₂ pressure at first, until the pressure reaches a critical value, at which point the ductility drops precipitously. At all H₂ pressures employed, the higher the B concentration the higher the elongation to fracture. An important observation is that, over the entire pressure range tested, ductility is independent of whether or not the ion gage is on (unlike the case in B-free Ni₃Al, Fig. 2). Accompanying the dramatic drop in ductility with increasing H₂ pressure is a change from predominantly (>60%) transgranular fracture to predominantly (70%) intergranular fracture in all three alloys [47]. Consistent with the lack of dependence of ductility on the state of the ion gage, the fracture mode was also independent of whether the gage was on or off [47]. Together, these observations imply that the surfaces of B-doped Ni₃Al—unlike those in B-free Ni₃Al—are active for the dissociation of H₂ into atomic H (the surfaces referred to here are the freshly created fracture surfaces which, prior to fracture, are the grain boundaries where the B atoms have segregated).

Transition metal surfaces are usually active for the dissociation of H₂. The mechanism is thought to involve the promotion of electrons from the partially filled d-band of the transition metal to the anti-bonding s-orbital of the H₂ molecule, thereby destabilizing the H₂ molecule [e.g., 48]. It is not clear why the grain boundaries of B-free Ni₃Al are not as effective as those of B-doped Ni₃Al in dissociating H₂. One possibility is that Ni₃Al is less able to make the charge transfer to the H₂ molecule than, say, Ni. By extension, if B facilitated this charge transfer it might catalyze the hydrogen dissociation reaction and cause embrittlement. Both these possibilities need additional investigation.

A consequence of this difference in the surface reactions of the B-doped and B-free alloys is that, in dry H₂ gas, at pressures in the range 1 to 10¹⁹ Pa, Ni₃Al doped with 50 or 100 ppm B is significantly more brittle than B-free Ni₃Al (Fig. 14). Consistent with these elongation data, the two B-doped alloys exhibited predominantly grain boundary fracture at the higher H₂ pressures, whereas B-free Ni₃Al exhibited a significant amount (~60%) of transgranular fracture [47]. This is an unexpected embrittling effect of B: until recently, B was thought to have exclusively beneficial effects in Ni₃Al.

![Auger spectra from grain boundaries of B-free (left) and B-doped (right) Ni₃Al after exposure to H₂O [46].](image1)

**FIG. 12** Auger spectra from grain boundaries of B-free (left) and B-doped (right) Ni₃Al after exposure to H₂O [46]. (Exposures increasing from top to bottom.)

![Effect of hydrogen pressure on the room-temperature tensile ductilities of Ni-24Al alloys doped with 50, 100, and 500 ppm B [47].](image2)

**FIG. 13** Effect of hydrogen pressure on the room-temperature tensile ductilities of Ni-24Al alloys doped with 50, 100, and 500 ppm B [47].

![Comparison of the room-temperature tensile ductilities of B-doped and B-free Ni₃Al in H₂ [47].](image3)

**FIG. 14** Comparison of the room-temperature tensile ductilities of B-doped and B-free Ni₃Al in H₂ [47]. Note that the doping with 50 or 100 ppm B severely embrittles Ni₃Al at the higher hydrogen pressures.

It is important to note, however, that B causes embrittlement over only a specific range of H₂ pressures: at low pressures, B clearly improves ductility. Interestingly, H₂ is more detrimental to the ductility of B-doped alloys than H₂O, whereas the opposite is true in the case of B-free Ni₃Al. This means that, although atomic H is the underlying cause of room-
temperature embrittlement, the kinetics of dissociation (from $\text{H}_2\text{O}$ or $\text{H}_2$) play an important role in determining the ductility and fracture mode of $\text{Ni}_3\text{Al}$. For example, the 50 wppm B alloy, which is fairly ductile (>20% elongation) when tested in water or in ordinary ambient air [26], is nevertheless severely embrittled (<5% elongation) in dry $\text{H}_2$ environments. Even the 500 wppm B alloy, which has been considered to be immune to environmental effects [41], suffers embrittlement at $\text{H}_2$ pressures above $10^3$ Pa. These observations highlight the different roles of B in $\text{H}_2\text{O}$- and $\text{H}_2$-containing environments: in the former B suppresses embrittlement whereas in the latter it promotes embrittlement.

Choudhury et al. [43] have shown that the concentration of B on the grain boundaries of $\text{Ni}_3\text{Al}$ increases as its concentration in the bulk increases. Consequently, the grain boundary concentration of B in the B-doped alloys is expected to increase (and eventually saturate) in the order 50, 100, 500 wppm. Therefore, the data in Fig. 13 imply that, as the amount of B on the grain boundaries increases, it becomes increasingly difficult for H to penetrate into the grain boundaries of $\text{Ni}_3\text{Al}$. That B hinders the uptake of hydrogen can also be seen by comparing the ductilities of the B-doped alloys with those of B-free $\text{Ni}_3\text{Al}$ with the gage on (Fig. 15): when there is an external source of atomic H available, the ductilities of the B-doped alloys are always higher than those of the B-free alloy.

FIG 15 Comparison of the room-temperature tensile ductilities of B-free $\text{Ni}_3\text{Al}$ (gage on) with those of B-doped $\text{Ni}_3\text{Al}$ (gage on or off) [47].

At pressures in the ultrahigh vacuum (UHV) range, B has a clear beneficial effect on the ductility of $\text{Ni}_3\text{Al}$ (Fig. 13): ductility increases with increasing B concentration. If one assumes for the moment that extrinsic (i.e., environmental) effects are minimal in UHV when the ion gage is off, then the UHV results suggest that one effect of B is to strengthen the grain boundaries of $\text{Ni}_3\text{Al}$. Consistent with this, at a given level of ductility, the B-doped alloys tend to have greater amounts of transgranular fracture than the B-free alloy [47]. Thus, there appear to be three main effects of B in $\text{Ni}_3\text{Al}, two of which are beneficial while the third is harmful: (i) B enhances grain boundary cohesion (seen most clearly at low H$_2$ pressures), (ii) it hinders the uptake of hydrogen (seen best at intermediate pressures), and (iii) it promotes the dissociation of H$_2$ into H thereby embrittling $\text{Ni}_3\text{Al}$ (at higher pressures).

Gleason et al. [14], showed that the amount of hydrogen product desorbing from B-doped FeAl surfaces was significantly less than that from clean FeAl surfaces after equivalent exposures to molecular hydrogen. They concluded, therefore, that B reduced the reactivity of FeAl toward H$_2$ (recall that B has little effect on H$_2$O dissociation on FeAl). The different effects of B on the dissociation of H$_2$O and H$_2$ on FeAl were ascribed by Gleason et al. [14] to the fact that the interaction of B was primarily with the Fe site, which is also the site responsible for H$_2$ dissociation. Water dissociation, on the other hand, takes place on the Al site, which is unaffected by B. Similar experiments have not yet been performed on $\text{Ni}_3\text{Al}$. If B is found to reduce the reactivity of $\text{Ni}_3\text{Al}$ surfaces for H$_2$ dissociation it would contradict the mechanism proposed [47] for the B-induced embrittlement of $\text{Ni}_3\text{Al}$ (Fig. 14) and an alternative explanation would have to be proposed.

**Alloy Stoichiometry Effects**

**FeAl**

With increasing aluminum concentration, the grain boundaries in FeAl become increasingly more brittle [49-54]. In these high-alumina alloys, therefore, there are two reasons for poor ductility and brittle fracture: (a) weak grain-boundary cohesion, and (b) environmental embrittlement (which may be inter- or trans-granular). Weak grain-boundary cohesion can be overcome by the addition of boron [49,55-57], which segregates to the grain boundaries [49] and suppresses intergranular fracture. Table 4 shows the effect of boron doping and test environment on the room-temperature ductility and fracture behavior of Fe-40Al.

**TABLE 4. Effect of environment and B doping on the room-temperature tensile properties of Fe-40Al [49].**

<table>
<thead>
<tr>
<th>Environment</th>
<th>No Boron</th>
<th>Doped with 300 wppm B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>390 405</td>
<td>391 577 4.3</td>
</tr>
<tr>
<td>Oxygen</td>
<td>402 337</td>
<td>392 923 16.8</td>
</tr>
</tbody>
</table>

GBF: grain boundary fracture; TF: transgranular fracture.

Without boron the alloy fractures predominantly intergranularly regardless of test environment. Suppression of environmental embrittlement (by testing in dry oxygen) results in a small increase in tensile ductility indicating an environmental effect on the grain boundaries, but the next brittle fracture mode (intrinsic grain boundary fracture) intervenes before significant plastic deformation can occur. If boron is added to the alloy, and it is tested in air, there is some improvement in ductility (suggesting that B counteracts intrinsic and/or extrinsic intergranular brittleness). However, the next brittle fracture mode (this time moisture-induced transgranular fracture) intervenes before significant plastic deformation can take place, and once again only limited ductility is obtained. Extensive ductility requires that all brittle fracture modes be suppressed, and when that is done (by testing B-doped FeAl in oxygen), it is seen that as much as 17% ductility is obtained. With further increases in aluminum concentration above 40 at.% Al, the grain boundaries become progressively more brittle, until in Fe-48Al they become so brittle that even boron segregation is unable to enhance grain boundary cohesion and suppress intergranular fracture [58]. Figure 16 shows the effect of test environment and aluminum concentration on the tensile ductility of B-doped and B-free FeAl alloys. In the low-alumina alloys, boron doping overcomes grain-boundary brittleness, so a big improvement in ductility is seen when the test is conducted in oxygen instead of in air. As the aluminum concentration increases, however, boron becomes progressively less effective in overcoming grain-boundary brittleness, so there is progressively less difference in ductility between the air and oxygen tests. Note that the
fracture mode in alloys containing more than ~43% Al is predominantly intergranular, despite the fact that boron segregates just as strongly to the grain boundaries in these alloys as to those in the more Fe-rich alloys.

\[ \text{Ni}_{31}\text{Al} \]

As mentioned earlier in this review, B is effective in suppressing grain boundary fracture only on the Ni-rich side of stoichiometry [36]. In light of the discovery of environmental effects in Ni₃Al, Liu and George [59] recently examined the effects of B concentration and alloy stoichiometry on the environmental susceptibility of Ni₃Al. As shown in Table 5, Ni₂₋₄Al doped with 500 ppm B shows virtually no environmental embrittlement: ductility remains high (and fracture predominantly transgranular) independent of test environment and strain rate. This indicates that B at a level of 500 ppm is able to effectively suppress environmental embrittlement in Ni₂₋₄Al. At lower concentrations (50 ppm), B is unable to completely suppress environmental effects, as evidenced by the strain rate dependence of ductility in water (Fig. 8). This is due presumably to the decrease in grain boundary concentration of B with decreasing bulk concentration [43]

With increasing Al concentration in Ni₃Al, the effectiveness of B in suppressing environmental embrittlement decreases (Table 5): the ductility in water is less than that in air, which in turn is lower than that in oxygen. A possible reason for this behavior is that the amount of B that segregates to the grain boundaries of Ni₃Al decreases with increasing Al concentration [36]. Consistent with this, an increase in the amount of bulk B from 500 to 1000 ppm (which presumably forces more B to segregate to the grain boundaries) increases the ductility of the 25.2% Al alloy significantly. Nevertheless, the best ductilities of the 24.8 and 25.2% Al alloys are substantially lower than those of the Ni₂₋₄Al alloy, suggesting that the intrinsic properties of the Ni₃Al grain boundaries may be deteriorating with increasing Al concentration. As in Fe₃Al (Fig. 16), even though B can be made to segregate to the grain boundaries, it is increasingly unable to overcome the intrinsic brittleness of the Ni₃Al grain boundaries in the near-stoichiometric alloys.

**Concluding Remarks**

We limited this review to ductility and fracture issues. Environmental embrittlement, a result of the atomic H generated during the dissociative adsorption of H$_2$O or H$_2$ on fresh fracture surfaces, is now known to be the major factor limiting the ductility of several otherwise ductile intermetallics. However, the susceptibility of an intermetallic to environmental embrittlement is often determined by other intrinsic and extrinsic factors. The roles of some of these factors were discussed with the help of two examples: Ni₃Al and Fe₃Al of the L₁₅ and B₂ crystal structures, respectively.

Despite the considerable progress made in recent years much remains to be done. Among the issues still to be resolved are the following. How does H actually cause embrittlement? Are the grain boundaries in near stoichiometric and Al-rich Ni₃Al intrinsically brittle? Why? What is the mechanism by which B suppresses environmental embrittlement in Ni₃Al? Since environmental embrittlement affects the cleavage planes in Fe₃Al, trace element additions (like B in Ni₃Al) are not effective; what other mechanisms can one use to overcome environmental effects? Why is boron, even though it segregates, not effective in strengthening the grain boundaries of the near-stoichiometric Fe₃Al alloys?

**Acknowledgments**

The authors thank J. H. Schneibel and L. M. Pike for reviewing the paper. This research was sponsored by the Division of Materials Sciences, U.S. Department of Energy under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp.

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58. Y. Liu and E. P. George, Oak Ridge National Laboratory, unpublished results.
59. C. T. Liu and E. P. George, Oak Ridge National Laboratory, unpublished results.

### TABLE 5. Effect of B doping and alloy stoichiometry on environmental embrittlement of Ni_3Al alloys [59].

<table>
<thead>
<tr>
<th>Strain rate (s⁻¹)</th>
<th>Environment</th>
<th>Elongation (%)</th>
<th>Yield strength (MPa)</th>
<th>Ultimate strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-24Al + 500 ppm B</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.3 × 10⁻⁴</td>
<td>oxygen</td>
<td>39.4</td>
<td>289</td>
<td>1316</td>
</tr>
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<td>41.2</td>
<td>290</td>
<td>1261</td>
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<td>3.3 × 10⁻⁴</td>
<td>water</td>
<td>39.4</td>
<td>270</td>
<td>1233</td>
</tr>
<tr>
<td>Ni-24.8Al + 500 ppm B</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.3 × 10⁻⁴</td>
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<td>25.4</td>
<td>306</td>
<td>801</td>
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<td>air</td>
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<td>290</td>
<td>671</td>
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<tr>
<td>3.3 × 10⁻⁴</td>
<td>water</td>
<td>12.7</td>
<td>297</td>
<td>561</td>
</tr>
<tr>
<td>Ni-25.2Al + 500 ppm B</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.3 × 10⁻⁴</td>
<td>air</td>
<td>8.4</td>
<td>221</td>
<td>300</td>
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<tr>
<td>3.3 × 10⁻⁴</td>
<td>water</td>
<td>4.7</td>
<td>219</td>
<td>270</td>
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<tr>
<td>Ni-25.2Al + 1000 ppm B</td>
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<td>3.3 × 10⁻⁴</td>
<td>oxygen</td>
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<td>301</td>
<td>566</td>
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<td>552</td>
</tr>
<tr>
<td>3.3 × 10⁻⁴</td>
<td>water</td>
<td>6.1</td>
<td>304</td>
<td>398</td>
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</table>