ENVIRONMENTAL EFFECTS IN ADVANCED INTERMETALLICS

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Abstract

This paper provides a comprehensive review of environmental embrittlement in iron and nickel aluminides. The embrittlement involves the interaction of these intermetallics with moisture in air and generation of atomic hydrogen, resulting in hydrogen-induced embrittlement at ambient temperatures. Environmental embrittlement promotes brittle grain-boundary fracture in Ni3Al alloys but brittle cleavage fracture in Fe3Al-FeAl alloys. The embrittlement strongly depends on strain rate, with tensile-ductility increase with increasing strain rate. It has been demonstrated that environmental embrittlement can be alleviated by alloying additions, surface modifications, and control of grain size and shape. Boron tends to segregate strongly to grain boundaries and is most effective in suppressing environmental embrittlement in Ni3Al alloys. The mechanistic understanding of alloy effects and environmental embrittlement has led to the development of nickel and iron aluminide alloys with improved properties for structural use at elevated temperatures in hostile environments.

1. INTRODUCTION

Ordered intermetallics based on aluminides and silicides constitute an interesting class of metallic alloys for structural use [1-5]. This is because these intermetallics generally possess good strength at elevated temperatures, excellent oxidation and corrosion resistance, and relatively low material density (as compared with Ni-base superalloys). However, a major drawback of these intermetallics is their poor tensile ductility and tendency for brittle fracture at ambient temperatures. For the past two decades, considerable effort has been devoted to both the understanding of brittle fracture and alloy design of intermetallic alloys with improved mechanical and metallurgical properties for structural applications. Among these studies, one of the most important findings is the discovery of environmental embrittlement of intermetallic alloys when tested in air at ambient temperatures. Intermetallic alloys were previously considered to be mainly intrinsically brittle until the discovery of environmental embrittlement in iron aluminides in 1989 [6]. The embrittlement involves the reaction of intermetallic alloys with moisture in air during tensile testing, and the generation of atomic hydrogen, resulting in moisture-induced hydrogen embrittlement at ambient temperatures. Since then, the environmental embrittlement has been observed in many intermetallic alloys with L12 and B2 crystal structures [1-5]. This paper provides a comprehensive review of environmental embrittlement in iron aluminides based on FeAl- Fe3Al and nickel aluminides based on Ni3Al.

2. ENVIRONMENTAL EMBRITTLEMENT IN IRON ALUMINIDES

Fe3Al and FeAl alloys were previously considered to be intrinsically brittle at room temperature because of their poor cleavage strength and difficulty in cross slip in ordered lattices. In 1989, Liu, Lee and McKamey first reported that FeAl alloys containing less
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than 40% Al are intrinsically quite ductile, and that the low tensile ductility and cleavage fracture were caused mainly by environmental embrittlement involving moisture in air [6]. The environmental effect is demonstrated in Fig. 1. An FeAl alloy (36.5% Al) showed brittle cleavage fracture and only 2.2% tensile elongation when tested in air at room temperature. The same alloy tested in a conventional vacuum had a ductility of 8%. Ultimately, the alloy exhibited a tensile ductility as high as 18% when tested in a dry oxygen environment. The same embrittlement effect was also observed in single-crystal FeAl alloys [7] and polycrystalline Fe3Al alloys (see Fig. 2) [8].

Mechanistically, the environmental embrittlement is explained by a chemical reaction involving the interaction of Al atoms with moisture in air and the subsequent generation of hydrogen [6,9]. The penetration of atomic hydrogen at crack tips results in hydrogen-induced embrittlement in iron aluminides and other intermetallic alloys. Systematic studies of the embrittling effect as functions of test temperature, strain rate, and shielding gas have indicated that the severity of the embrittlement depends on two kinetic parameters: the moisture/aluminide reaction kinetics and the hydrogen transport to crack tips. The embrittlement can be substantially reduced by controlling test environments, increasing strain rates and using shielding gases [9-12]. As shown in Fig. 1, the room-temperature tensile ductility increased from 2.2% in ambient air to 18% in dry oxygen.

The effect of strain rate on the room-temperature tensile ductility of FeAl (45% Al) is indicated in Fig. 3 [11]. The ductility shows a general increase with strain rate and reaches a maximum when the strain rate is above a critical value. The strain-rate dependence can be explained from kinetic considerations. With the increase in strain rate, it becomes increasingly difficult for the environmental reactions to keep up with the growing crack and the ductility increases. Similar results are obtained in Fe3Al and other FeAl alloys [8-12]. Recently, an environmental softening effect was detected in Fe-40% Al, where samples tested in air had the yield strength 15 to 20% lower than those tested in vacuum or dry oxygen [12]. Additional studies are certainly required to confirm this unusual behavior.
The hydrogen-induced environmental embrittlement affects not only tensile ductility but also cleavage planes [7,13-15]. Table 1 summarizes the effect of Al concentration on cleavage fracture planes of iron aluminides tested in different test environments at room temperature. This table shows that FeAl aluminides fractured mainly by {100}-type cleavage when tested in moist air. With increasing Al concentration from 35 to 50 %, the cleavage fracture gradually changed from {100} to {111} types in vacuum. These observations suggest that moisture-induced hydrogen promotes {100} cleavage fracture in FeAl alloys with high Al concentrations.

Table 1. Effect of Test Environment and Al Level on Cleavage Fracture Plane in FeA Alloys

<table>
<thead>
<tr>
<th>Al concentration (at. %)</th>
<th>Vacuum</th>
<th>Air</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>(100)+others</td>
<td>(100)+others</td>
<td>7</td>
</tr>
<tr>
<td>40</td>
<td>(100)+others</td>
<td>More (100)</td>
<td>13, 14</td>
</tr>
<tr>
<td>50</td>
<td>(111)</td>
<td>(100)</td>
<td>15</td>
</tr>
</tbody>
</table>

First-principles calculations were used to understand the electron concentration and atomic bonding in FeAl. The calculations by Fu and Painter [16] showed that interstitial hydrogen absorbs electrons from iron atoms and reduces the cleavage strength of {100} planes by as much as 70 %. This result is consistent with the observed {100} cleavage when FeAl is tested in moist air. Li and Liu [17] suggest that interstitial hydrogen in FeAl alloys also promotes crack nucleation on {100} planes. The $a<010>$ dislocations stabilized by
hydrogen segregation can serve as crack nucleus for the \{100\} cleavage fracture in FeAl alloys. The \langle010\rangle dislocations were observed in a FeAl alloy by Munroe and Baker [18].

3. ENVIRONMENTAL EMBRITTLEMENT IN Ni₃Al ALLOYS

Ni₃Al, like many other L₁₂ intermetallics, showed brittle grain-boundary fracture with limited tensile ductility at room temperature[19,20]. After extensive studies, it became clear that the brittle intergranular fracture is caused by two major factors: poor grain-boundary cohesion (intrinsic factor)[1-5], and environmental embrittlement (extrinsic factor) [10,21,22]. Previous studies suggested that the grain boundaries in Ni₃Al might be intrinsically brittle. This was based mainly on the auger analyses which showed no appreciable segregation of impurities on fractured grain boundary facets [19]. During the past several years, however, sufficient evidence has evolved to assert that moisture induced hydrogen is a major cause of brittle grain boundary fracture when Ni₃Al alloys are tested in air [10,21,22].

In 1991, Liu et al. [21,23] made a first attempt to link brittle intergranular fracture with environmental embrittlement in binary Ni₃Al and Ni₃Si with the L₁₂ structure. Table 2 shows the tensile properties of recrystallized polycrystalline Ni₃Al (24% Al) produced by repeated cold forging and 1000°C annealing of alloy ingots [21]. The binary aluminate showed only 2.6% elongation in air but 7.2% in dry oxygen, an increase in ductility by a factor of about 3. Later, George et al. [22] reported a surprisingly larger environmental effect in polycrystalline Ni₃Al (23.4%) prepared by recrystallization of cold worked single crystal material. This polycrystalline material also showed a tensile ductility of 3% in air. However, its ductility increases steadily as the vacuum improves, and it reaches as high as 23% in an ultra-high vacuum of 10⁻⁶ Pa. Their work clearly demonstrated the dominant role of environmental effect on tensile ductility of Ni₃Al at room temperature [22,24]. Recently, Hanada et al. [25] showed that polycrystalline Ni₃Al with both on- and off-stoichiometric compositions exhibited extensive tensile ductilities in dry oxygen at room temperature, in agreement with the result from George et al. [22,24].

Table 2. Effect of Boron Additions on Environmental Embrittlement of Ni₃Al (24% Al) Tested at Room Temperature

<table>
<thead>
<tr>
<th>Strain Rate (s⁻¹)</th>
<th>Test Environment</th>
<th>Elongation (%)</th>
<th>Yield Strength (ksi)</th>
<th>Ultimate Tensile Strength (ksi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IC-2: Ni₂₄ at. % Al</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.3 x 10⁻³</td>
<td>Oxygen</td>
<td>7.2</td>
<td>40.5</td>
<td>63.7</td>
</tr>
<tr>
<td>3.3 x 10⁻³</td>
<td>Air</td>
<td>2.6</td>
<td>40.6</td>
<td>48.3</td>
</tr>
<tr>
<td>IC-19: Ni₂₄₈Al + 100 wt ppm B</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.3 x 10⁻³</td>
<td>Oxygen</td>
<td>39.5</td>
<td>31.4</td>
<td>189.3</td>
</tr>
<tr>
<td>3.3 x 10⁻³</td>
<td>Air</td>
<td>18.2</td>
<td>31.2</td>
<td>101.4</td>
</tr>
<tr>
<td>3.3 x 10⁻³</td>
<td>Water</td>
<td>12.6</td>
<td>30.1</td>
<td>75.2</td>
</tr>
<tr>
<td>IC-15: Ni₂₄₈Al + 500 wt ppm B</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.3 x 10⁻³</td>
<td>Oxygen</td>
<td>39.4</td>
<td>41.9</td>
<td>190.8</td>
</tr>
<tr>
<td>3.3 x 10⁻³</td>
<td>Air</td>
<td>41.2</td>
<td>42.1</td>
<td>182.9</td>
</tr>
<tr>
<td>3.3 x 10⁻⁵</td>
<td>Air</td>
<td>39.4</td>
<td>39.1</td>
<td>177.3</td>
</tr>
<tr>
<td>3.3 x 10⁻³</td>
<td>Water</td>
<td>38.7</td>
<td>41.8</td>
<td>174.0</td>
</tr>
</tbody>
</table>
Fig. 5. Stress strain curves for Fe-Cr-Zr-C at 25°C [8].

Fig. 6. Effect of boron additions on tensile elongation and fracture behavior of Ni₃Al (24 at. % Al) tested at room temperature [19].

Gleason et al. [26] first reported the possible release of hydrogen from water decomposition on surfaces of aluminide alloys using a temperature-programmed-desorption technique. Later, Chia and Chung [27] studied the reaction of D₂O molecules with single crystal Ni₃(Al,Ti) and discovered that the reaction kinetics strongly depend on the crystallographic orientation of the surfaces. Their results indicate that D₂O chemically adsorbed reacts with (100) planes and generates deuterium during heating of the specimens to 200°K and above. This confirms the suggested reaction of moisture with aluminides at ambient temperatures. On the other hand, no D₂ was detected during thermal desorption from (111) surfaces on which D₂O had been chemically adsorbed. These results provide evidence that the moisture reaction is highly dependent on the atomic arrangement and chemical composition of crystallographic planes. Furthermore, Zhu et al. [28] successfully detected atomic hydrogen produced by the reaction of moisture with an iron aluminide, using laser desorption mass spectrometry. All these results provide direct support for the proposed reaction that moisture-induced hydrogen is the cause of severe embrittlement in aluminide alloys when tested in moisture containing environments at ambient temperature.

The effect of strain rate on the room-temperature tensile ductility of Ni₃Al alloys tested in air and moist Ar is shown in Fig. 4, as compiled by George et al. [10]. Ni₃Al alloys, just like iron aluminides, exhibit a steady increase in tensile ductility with strain rate. The ductility appears to reach a maximum value when the strain rate approaches 10⁰ s⁻¹. At this strain rate, the environment embrittlement is virtually suppressed presumably because of insufficient hydrogen being generated and transported to the tip of moving cracks.

4. ALLOY DESIGN OF IRON ALUMINIDES
The understanding of environmental embrittlement and alloying effects had led to the development of physical metallurgy principles for design of ductile iron aluminide alloys for structural use. The general principles deduced from these studies include:

1. Controlling the Al level <38% (to avoid intergranular brittleness [9]),
2. Producing wrought/fibrous/elongated grain structures,
3. Refining grain size,
4. Forming protective surface coatings/layers (e.g. oxide coating),
5. Adding beneficial alloying elements, including
   - Boron: to strengthen grain boundaries,
   - Carbon: to improve weldability and form carbides,
   - Zr borides/carbides: to refine grain size and retain fibrous grain structure, and
   - Mo: to improve strength and creep resistance.
   - Cr: to form protective Cr oxides on alloy surfaces during processing of Fe$_3$Al alloys

It has been reported that environmental embrittlement can be alleviated by alloying additions, control of surface conditions, and control of grain size and shape [1-5] in iron aluminides. Recently, Alven and Stoloff [8] reported that the moisture-induced hydrogen embrittlement can be completely eliminated by alloying Fe$_3$Al alloys with 0.5Zr and 0.05C. This is indicated in Fig. 5, where the tensile ductility of Fe-28Al-5Cr-0.5Zr-0.05C is not sensitive to test environment, moist air or dry oxygen. The beneficial effect of the alloying additions is due to the formation of Zr-rich particles, which pin grain boundaries and produce elongated grain structures during alloy processing [29].

An example of substantial improvement of the ductility of a FeAl alloy is shown in Table 3 [9]. The refinement of grain size by adding 0.05Zr and 0.24B increased the room-temperature ductility of FeAl (35.8% Al) from 2.2 to 10.7%. The addition of B also enhanced the grain-boundary cohesion and suppressed intergranular fracture of the alloy. Usually, preoxidation leads to a decrease in the ductility of metals and alloys. However, the formation of protective oxide scales by preoxidation at 700°C alleviated moisture-induced environmental embrittlement and further improved the tensile ductility of the FeAl alloy from 10.7% to 14.2%, i.e. a 33% increase in room temperature ductility. A series of FeAl alloys based on Fe-(36-40)Al-0.2Mo doped with 0.01-0.15% C and B, with improved mechanical properties at room and elevated temperatures, had been developed for structural use in oxidizing and sulfidizing environments [30].

5. ALLOY DESIGN OF Ni$_3$Al ALLOYS

The tensile ductility of Ni$_3$Al alloys can be improved by substitutional and interstitial alloying elements [31]. Among these elements, boron is found to be most effective in eliminating brittle grain-boundary fracture and increasing the tensile ductility of Ni$_3$Al with
Table 3. Influence of Alloy Addition and Preoxidation on Room-Temperature (RT) Tensile Ductility of FeAl Alloys [9]

<table>
<thead>
<tr>
<th>Alloy composition (at. %)</th>
<th>Elongation (%)</th>
<th>Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Yield</td>
</tr>
<tr>
<td>FeAl (35.8Al)</td>
<td>2.2</td>
<td>356</td>
</tr>
<tr>
<td>FeAl+0.05Zr+0.24B</td>
<td>10.7</td>
<td>332</td>
</tr>
<tr>
<td>FeAl+0.05Zr+0.24B+</td>
<td>14.2</td>
<td>357</td>
</tr>
<tr>
<td>preoxidation</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*To form protective oxide scales at 700°C.*

hypostoichiometric compositions (<25% Al) [9]. This is because boron is able to enhance grain boundary cohesion and suppress environmental embrittlement. The beneficial effect of boron is shown in Fig. 6. Unalloyed Ni$_3$Al containing 24% Al showed brittle grain boundary fracture with little tensile ductility when tested in air at room temperature. The ductility increased sharply with boron doping and reached >40% when doped with >200 wppm B. The increase in ductility was accompanied with a change in fracture mode from brittle intergranular to ductile transgranular.

The effect of boron additions on environmental embrittlement is also shown in Table 2. Ni$_3$Al (24% Al) doped with 100 wppm B showed a ductility as high as 40% in dry oxygen at room temperature. The ductility, nevertheless, decreased to 18.3% in air and 12.6% in water, indicating that doping with 100 wppm B is sufficient to take care of the problem of poor grain boundary cohesion but insufficient to suppress environmental embrittlement. The aluminide doped with 500 wppm B, on the other hand, showed a high ductility of 40% and transgranular fracture, independent of test environment and strain rate. These results suggest that both poor grain boundary cohesion and environmental embrittlement have been overcome by doping with 500 wppm B. Apparently, boron at levels >100 wppm is required to suppress moisture-induced hydrogen embrittlement along the grain boundaries. Furthermore, it is found that doping with more boron is necessary in order to ductilize Ni$_3$Al with stoichiometric and hyperstoichiometric compositions [19,31].

The study of environmental embrittlement and alloying effects has led to the development of a number of Ni$_3$Al alloys with improved mechanical properties for structural applications [31]. In these alloys, chromium at a level of 7 to 9 at. % is added for reducing environmental embrittlement at elevated temperatures. Zirconium and hafnium additions are most effective in improving the high temperature strength via solid-solution hardening effects. Molybdenum additions are used for improving strength at ambient and elevated temperatures. Microalloying with boron reduces moisture-induced hydrogen embrittlement and enhances grain-boundary cohesive strength, effectively increasing the ductility at ambient temperatures. Carbides and borides are added to the alloys for additional strengthening effects. In some cases, moderate amounts of cobalt and iron are added to replace Ni, and Al and Ni, respectively, for further gains in hardness and corrosion resistance. The alloys with optimum properties usually contain 5 to 15 vol. % of the...
disordered \( \gamma \) phase, which has the beneficial effect of reducing environmental embrittlement in oxidizing atmospheres at elevated temperatures. Industrial interest in these aluminide alloys is high.

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7. REFERENCES: