CONF-901105--3

# MECHANICAL PROPERTIES, FRACTURE BEHAVIOR, AND GRAIN-BOUNDARY CHEMISTRY OF B-DOPED NiAl

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CONF-901105--3

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## ABSTRACT

This paper summarizes the results of our work aimed at overcoming the intrinsic grain-boundary weakness of NiAl by microalloying with boron. In previous work we have shown that 300 wppm boron is very effective in suppressing intergranular fracture in NiAl [1]. It does this by segregating strongly to the grain boundaries and strengthening them. Despite this dramatic effect on the fracture mode, however, boron is unable to improve ductility because it is a potent solid solution strengthener, more than doubling the yield strength relative to that of undoped NiAl. The present work attempts to decrease this deleterious hardening effect by lowering the bulk concentration of boron in NiAl. Our results show that if the boron concentration in the bulk is lowered to 30 wppm, the yield strength of boron-doped NiAl is only about 30% higher than that of undoped NiAl. In addition, there is enough boron at the grain boundaries of this alloy to suppress intergranular fracture. Under these conditions, boron-doped NiAl has a tensile ductility of 2%, which is essentially identical to that of undoped NiAl. This result, namely that the strengthening of grain boundaries by boron does not by itself improve ductility, indicates that although grain boundaries might well be the weakest links in NiAl, cleavage planes are not much stronger. In other words, even though boron additions serve to strengthen the grain boundaries and suppress intergranular fracture, ductility is not improved, because the next brittle fracture mode, namely transgranular cleavage, takes over before significant plastic deformation can occur.

## INTRODUCTION

After an early report in 1966 of limited (2%) room-temperature tensile ductility in polycrystalline NiAl [2], numerous later attempts to reproduce this ductility were unsuccessful, until Hahn and Vedula [3] 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., Ref. 1]. Perhaps some of the earlier unsuccessful attempts, especially those using the powder-metallurgy approach [4,5], were plagued by interstitial element problems. For example, our recent work [1] has shown that as little as 300 wppm each of carbon or boron can embrittle NiAl, mainly by dramatically increasing the yield strength.

Notwithstanding these recent demonstrations of tensile ductility in NiAl, the room-temperature ductility of NiAl remains relatively low (2-3%). Among the reasons commonly cited for the poor room-temperature ductility of NiAl are: (*i*) limited number of deformation modes (a consequence of <100> slip), see for example Ref. 3, and (*ii*) weak grain boundaries (because undoped NiAl fractures predominantly intergranularly [1,3]). In connection with item (*i*), considerable work has gone into promoting additional slip systems by macroalloying with suitable elements. In particular, it has been reported that additions of Cr [6], Mn [6], and V [7] to NiAl promote <111> slip, 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 this paper we are concerned mainly with item (*ii*), namely attempts to improve the grain-boundary cohesion of NiAl with microalloying additions. We will first summarize our recent work on the mechanical properties and grain-boundary chemistry of NiAl microalloyed with relatively high levels of boron, carbon and beryllium, and follow it up with results of boron-doped alloys containing relatively low levels of boron.

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## EXPERIMENTAL

All alloys used in this study were arc-melted using high-purity starting materials, and drop cast into cylindrical copper chill molds measuring 25.4 mm in diameter and 102 mm in length. After homogenizing in vacuum for 24 h at 1100°C, the ingots were canned in mild steel and extruded at 900°C at an extrusion ratio of 9:1. Buttonhead tensile specimens were ground from the extruded rods and electropolished, as described previously [1]. The specimens were then annealed in vacuum so as to produce fully recrystallized microstructures with a grain size of ~30 μm. This ensured that differences in mechanical properties were not due to differences in grain size. Tensile tests were performed in air at an engineering strain rate of 2.4 x $10^{-3}$/s.

Grain-boundary chemistry was analyzed by Auger electron spectroscopy in either a PHI 590 or PHI 660 scanning Auger microprobe. The former was operated at a beam voltage of 5 kV and beam currents of 7-8 nA, and the latter at a voltage of 10 kV and currents of 50-300 nA. Both intergranular and transgranular areas were analyzed in each sample, and atomic concentrations were calculated from the Auger peak height ratios as previously described [1]. In all the alloys (except for the boron-doped alloys), fracture is predominantly intergranular and we had no trouble finding sufficient numbers of grain boundaries for analysis. By contrast, the boron-doped alloys fracture transgranularly, and it is normally very difficult to expose grain boundaries for Auger analysis. Our previous attempts to embrittle the grain boundaries by cathodically charging hydrogen into the specimens were not very successful [1]. We have had a little more success in this study, principally because we have allowed more time for the cathodic charging (> 2 days). Nevertheless, less than 10% of the fracture surface was usually intergranular. Therefore, our Auger results for the boron-doped alloys are from the relatively weaker boundaries, which presumably contain lower levels of boron. Consequently, our calculated grain-boundary boron concentrations are likely to be lower bounds. All the boron-doped alloys were impact fractured in a liquid nitrogen cooled stage in the PHI 660; the remaining alloys were impact fractured at room temperature in the PHI 590.

## RESULTS AND DISCUSSION

The effects of various microalloying additions on the fracture mode of stoichiometric NiAl are shown in Fig. 1. In agreement with the observations of Hahn and Vedula [3], undoped NiAl fractures in a predominantly intergranular manner. Auger analysis of several grain boundaries in this alloy failed to detect any impurities [1], indicating that the grain boundaries in stoichiometric NiAl are intrinsically brittle. This intrinsic grain-boundary brittleness can be overcome by microalloying with boron and, as shown in Fig. 1, the addition of 300 wppm boron is able to very effectively suppress intergranular fracture in NiAl. Auger analysis confirmed that boron does indeed segregate to the grain boundaries in this alloy [1], indicating that boron enhances grain-boundary cohesion in stoichiometric NiAl. The average grain-boundary boron concentration in this alloy is estimated to be 5.4 ± 1.8 at.% on one half of the fractured specimen.[†]

Carbon and beryllium, by contrast, are unable to suppress intergranular fracture in NiAl (Fig. 1). Consistent with this, Auger analysis of the carbon-doped alloy showed that carbon does not segregate to the grain boundaries in NiAl [1]. Analysis of the beryllium-doped alloy is rather more difficult because of the overlap in the 104-eV Be and 102-eV Ni peaks. We were able to overcome this problem in our present study by comparing spectra from grain boundaries with those from transgranular regions. The reasoning being that since the transgranular regions do not contain any detectable beryllium, the peak should consist entirely of nickel. Therefore, if the intergranular peaks are the same size as the transgranular peaks, they also should consist entirely of nickel, and there should be no beryllium on the grain boundaries. This, in fact, was the case, and we therefore conclude that neither beryllium nor carbon segregates to the grain boundaries in NiAl. For a microalloying element to suppress grain-boundary fracture it must, at

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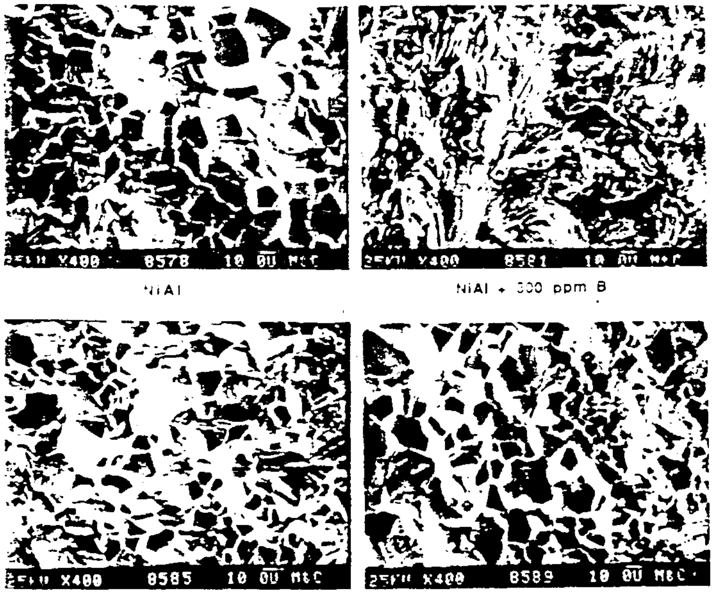
[†] In our previous study [1] we had mistakenly used the elemental sensitivity factors for a beam voltage of 5 kV, whereas the actual voltage was 10 kV. As a result, we estimated the grain-boundary boron concentration to be 2.7 ± 0.9 at.%. When the correct sensitivity factors are used, the boron concentration is calculated to be 5.4 ± 1.8 at.%, as reported above.

the very least, segregate to the grain boundaries. Thus, the reason beryllium and carbon are unable to suppress intergranular fracture is that they do not segregate to the grain boundaries.



NiAl

NiAl + 300 ppm B

NiAl + 300 ppm C

NiAl + 500 ppm Be

FIG. 1. Room-temperature fracture modes of stoichiometric NiAl.

Despite the dramatic effect of boron on the fracture mode of NiAl (Fig. 1), it is unable to improve tensile ductility. In fact, as shown in Table I, addition of 300 wppm boron results in a significant *decrease* in room-temperature tensile ductility. The same is true for carbon addition. Beryllium, on the other hand, actually improves ductility (slightly), although it does not suppress intergranular fracture. These effects can be rationalized by considering the effects of the microalloying elements on the yield strength of NiAl (Table I), which in turn can be rationalized by comparing the sizes of the available interstitial sites in NiAl with the atomic sizes of the microalloying elements [1]. Such an analysis shows that boron and carbon are likely to occupy interstitial sites, whereas beryllium, being a larger atom, is likely to occupy substitutional sites. Similar behavior is observed for these microalloying elements in $Ni_3Al$ [8]. However, because the interstitial sites in NiAl are considerably smaller than the corresponding sites in $Ni_3Al$ [1], boron and carbon should increase the yield strength of NiAl much more than that of $Ni_3Al$, in agreement with our experimental observations. By the same token, beryllium should have only a modest effect on yield strength. Therefore, even though boron is able to suppress intergranular fracture in both NiAl and $Ni_3Al$, because of its strong hardening effect in NiAl it is unable to improve ductility as it does in $Ni_3Al$.

TABLE I. Room-temperature tensile properties of NiAl microalloyed with B, C and Be [1].

| Alloy Composition (wppm) | Yield Strength (MPa) | Ultimate Strength (MPa) | Tensile Elongation (%) |
|---|---|---|---|
| NiAl | 154.4 | 229.6 | 2.2 |
| NiAl + 300 B | ‡ | 328.9 | ‡ |
| NiAl + 300 C | ‡ | 335.8 | ‡ |
| NiAl + 500 Be | 177.9 | 306.8 | 3.0 |

‡ *Fracture before macroscopic yielding.*

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Clearly, any potential benefit of boron on the grain-boundary cohesive strength of NiAl is more than offset by its strong solid solution hardening effect. In an attempt to decrease this deleterious hardening effect we studied additional boron-doped alloys containing lower levels of boron in the bulk. Our goal was to identify boron concentrations for which the yield strength is not dramatically increased. However, this was not to be achieved at the expense of grain-boundary cohesiveness. As will be shown below, we have been successful in both these efforts.

Table II shows the tensile properties of stoichiometric NiAl microalloyed with various amounts of boron. The increase in yield strength with increasing boron concentration can be clearly seen. Not surprisingly, ductility shows a concurrent decrease -- a direct consequence of the increase in yield strength. The yield strength of the alloy containing 30 wppm B is 200.6 MPa, which is only about 30% higher than the yield strength of undoped NiAl. Consistent with this, it has a tensile ductility of 2%, which is almost identical to that of undoped NiAl. With additions of as little as 100 wppm boron, the yield strength of NiAl is more than doubled, with the result that ductility decreases to 0.7%. A plot of yield strength *vs* boron concentration (up to 100 wppm B) shows an (almost) perfect linear dependance, and a least squares fit of the data gives a slope of approximately 4500 MPa / at.% B, which is more than an order of magnitude greater than the solid solution hardening effect of boron in $Ni_3Al$, 370 MPa / at.% B [9].

TABLE II. Room-temperature tensile properties of boron-doped stoichiometric NiAl.

| Boron Level (wppm) | Yield Strength (MPa) | Ultimate Strength (MPa) | Tensile Elongation (%) |
|---|---|---|---|
| 0 | 154.4 | 229.6 | 2.2 |
| 30 | 200.6 | 246.1 | 2.0 |
| 100 | 332.3 | 332.3 | 0.7 |
| 300 | ‡ | 328.9 | ‡ |

‡ *Fracture before macroscopic yielding.*

The addition of boron was able to almost completely suppress grain-boundary fracture in all three boron-doped alloys investigated in this study. Their room-temperature fracture surfaces looked essentially identical to the fractograph shown in Fig. 1 for the 300 wppm B alloy, i.e. fracture in all the boron-doped alloys took place by transgranular cleavage, including the alloy containing only 30 wppm boron. Auger analysis of the boron-doped alloys revealed that boron was present on all the grain boundaries that were examined (between 14 and 26 grain boundaries were examined in each alloy). The average grain-boundary boron concentrations are plotted in Fig. 2 as a function of the bulk boron concentration. There is a clear increase in grain-boundary boron concentration with bulk boron concentration up to about 100 wppm boron. Beyond that, it is not clear whether the curve in reality flattens out, or decreases as appears to be the case in Fig. 2. The uncertainty arises from the fact that the cathodic charging procedure used to reveal grain boundaries in boron-doped NiAl was changed slightly for this study: in our previous study [1], in which the data for the 300 wppm B alloy was obtained, we hydrogen-charged for about a day, but in this study the time was increased to > 2 days. As a result more grain boundaries were available in this study than in our previous study. When relatively few boundaries are available, they are likely to be the weakest ones, and therefore the ones with lowest levels of boron [10]. Thus, the calculated grain-boundary boron concentrations for the 300 wppm B alloy are likely to be underestimates compared to those for the 30 and 100 wppm B alloys. Of course, the calculated grain-boundary boron concentrations for *all* the boron-doped alloys are likely to be underestimates (relative to the true average boron concentration) because even at the longest times the hydrogen-charging procedure was unable to produce more than 10% intergranular fracture.

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Nevertheless, there are important conclusions to be drawn from this study. First, even in the 30 wppm B alloy, there is enough boron at the grain boundaries to suppress intergranular fracture. Second, the grain-boundary boron level in NiAl is considerably higher than that in $Ni_3Al$. For example, in the NiAl alloy containing 100 wppm B in the bulk, the grain-boundary boron concentration is ~10 at.%, whereas in $Ni_3Al$ containing 300 wppm B in the bulk, the corresponding grain-boundary boron level is less than about 3 at.% [10]. This difference is exaggerated even more when one considers that the hydrogen-charging procedure is able to produce more than 50% intergranular fracture in $Ni_3Al$, and less than 10% intergranular fracture in NiAl. The tendency for a solute to segregate to the grain boundaries generally increases as its size misfit in the solvent lattice increases [11]. And, as discussed before, the size misfit of boron in NiAl is considerably greater than its misfit in the $Ni_3Al$ lattice. Therefore, it is not surprising that boron segregates much more strongly to grain boundaries in NiAl than to boundaries in $Ni_3Al$.

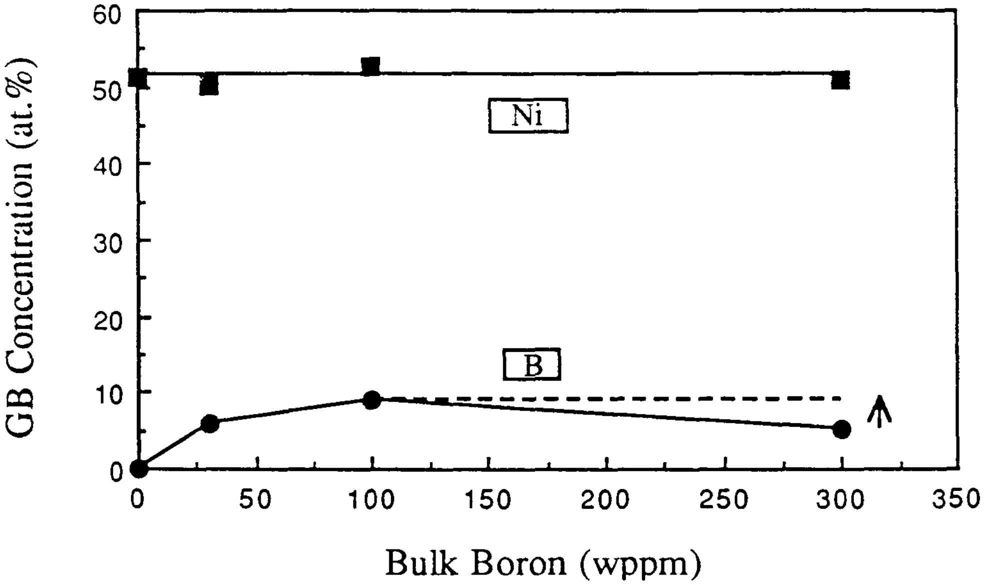

FIG. 2. Variation of grain-boundary B and Ni concentration as a function of bulk boron level in stoichiometric NiAl.

Another point of interest in Fig. 2 is the insensitivity of the grain-boundary nickel concentration to the bulk boron concentration. In particular, the grain-boundary nickel content of the undoped alloy is essentially identical to that of the boron-doped alloys, indicating that there is no tendency for B-Ni cosegregation (i.e., there is no boron-induced nickel enrichment at the grain boundaries).† This agrees well with our earlier work on boron-doped $Ni_3Al$ [12], in which also we found no evidence for B-Ni cosegregation. These results are important for the following reasons: If present, nickel enrichment is indirect evidence for the boron-induced disordering of grain boundaries. This disorder is thought to facilitate slip transfer across grain boundaries [13,14] and, thus, account for the ductilizing effect of boron in $Ni_3Al$ [15,16]. Other investigators [14,17,18] have reported strong B-Ni cosegregation in $Ni_3Al$. However, as we have pointed out before [12], these observations were made either on a very limited number of grain boundaries [14], or on materials that were not processed similarly [17,18] so that the differences between the undoped and boron-doped alloys could have been processing-related. When a large number of boundaries in identically-processed alloys is examined, as in this study of NiAl, or our previous study of $Ni_3Al$ [12], there is no clear evidence for boron-induced nickel enrichment. Of course, this does not rule out the existence of disorder at the grain boundaries

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† The grain-boundary Ni concentrations were calculated from the Ni/Al Auger peak height ratios in the intergranular regions by assuming that the transgranular regions had the true bulk composition, as described previously [1].

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

## CONCLUSIONS

Boron is very effective in overcoming the intrinsic grain-boundary brittleness of stoichiometric NiAl and suppressing intergranular fracture. It does this by segregating strongly to the grain boundaries and strengthening them. However, because boron is also a potent solid solution strengthener in NiAl, its concentration has to be carefully controlled. Otherwise, any potential benefit of improved grain-boundary cohesiveness is more than offset by the concomitant increase in yield strength, leading to brittle transgranular cleavage (instead of brittle intergranular fracture). Yield strength increases in an almost perfectly linear manner with bulk boron content, at the rate of about 4500 MPa / at.% B. As little as 100 wppm B (0.04 at.%B) more than doubles the yield strength relative to undoped NiAl. At a bulk level of 30 wppm B, the yield strength of NiAl is only about 30% higher than that of the undoped alloy. Additionally, at this low bulk level, there is enough boron at the grain boundaries to suppress intergranular fracture. Thus, we have successfully controlled the boron concentration so as to get its beneficial grain-boundary effect, without excessively increasing yield strength. However, the ductility of this alloy is still quite poor ( 2%, almost identical to that of undoped NiAl). This indicates that although grain boundaries may well be the weakest links in NiAl, cleavage planes are not much stronger, so that increasing grain-boundary cohesive strength by itself is not enough to ductilize NiAl.

## ACKNOWLEDGMENTS

Research sponsored by the Advanced Industrial Concepts Division, Office of Industrial Technologies, U.S. Department of Energy under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

## REFERENCES

1. E. P. George and C. T. Liu, J. Mater. Res. **5**, 754 (1990).
2. A. G. Rozner and R. J. Wasilewski, J. Inst. Metals, **94**, 169 (1966).
3. K. H. Hahn and K. Vedula, Scripta Metall. **23**, 7 (1989).
4. E. M. Schulson and D. R. Barker, Scripta Metall. **17**, 519 (1983).
5. K. Vedula and J. R. Stephens, in MRS Symp. Proc., vol. 81, p. 381, Mater. Res. Soc., Pittsburgh, PA (1987).
6. D. B. Miracle, S. Russell, and C. C. Law, in MRS Symp. Proc., vol. 133, p. 225, Mater. Res. Soc., Pittsburgh, PA (1989).
7. R. Darolia, D. F. Lahrman, R. D. Field, and A. J. Freeman, p. 113 in Ref. 6.
8. N. Masahashi, T. Takasugi, and O. Izumi, Acta Metall. **36**, 1815 (1988).
9. C. T. Liu, in MRS Symp. Proc., vol. 122, p. 429, Mater. Res. Soc., Pittsburgh, PA (1988).
10. A. Choudhury, C. L. White, and C. R. Brooks, Scripta Metall. **20**, 1061 (1986).
11. D. McLean, Grain Boundaries in Metals (Clarendon Press, Oxford, 1957).
12. E. P. George, C. T. Liu, and R. A. Padgett, Scripta Metall. **23**, 979 (1989).
13. A. H. King and M. H. Yoo, p. 99 in Ref. 5.
14. I. Baker, E. M. Schulson, and J. R. Michael, Philos. Mag. **B57**, 379 (1988).
15. E. M. Schulson, T. P. Weihs, D. V. Viens, and I. Baker, Acta Metall. **33**, 1587 (1985).
16. P. S. Khadkikar, K. Vedula, and B. S. Shale, Metall. Trans. **18A**, 425 (1987).
17. D. D. Sieloff, S. S. Brenner, and M. G. Burke, p. 87 in Ref. 5.
18. D. D. Sieloff, S. S. Brenner, and Hua Ming-Jian, p. 155 in Ref. 6.