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GRAIN BOUNDARY CHEMISTRY IN Ni$_3$Al AND Ni$_3$Si

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Abstract Measurements of the Ni/Al ratio at grain boundary regions in Ni$_3$Al have been performed, using x-ray microanalysis of thin foils in a scanning transmission electron microscope, as a function of both alloy stoichiometry and the addition of boron. It is shown that whilst grain boundaries of Al-rich and stoichiometric Ni$_3$Al have a composition similar to the matrix composition, boundaries in Ni-rich Ni$_3$Al can be highly Ni-enriched. The addition of B to Ni$_3$Al produces Ni enrichment in grain boundaries, the extent of which increases with increasing Ni content of the alloy. Also Auger electron spectrometry has been used to show that B segregates to the grain boundaries irrespective of the Ni:Al ratio. The chemistries of grain boundaries in Ni-rich Ni$_3$Si (Ni$_3$Si only exists on the Ni-rich side of stoichiometry), with and without B, have also been measured by AES. The results are similar to those from Ni$_3$Al, that is, the grain boundaries are enriched in Ni and the addition of B further increases this Ni-enrichment. The implications of these results on the degree of grain boundary atomic order and on the ductility of polycrystals are discussed.

INTRODUCTION

This paper presents measurements of the effects of both deviation from stoichiometry and the addition of boron on the composition of grain boundaries in the L1$_2$-structured compound Ni$_3$Al. Also presented is the chemistry of the grain boundaries in the isostructural intermetallic Ni$_3$Si, both with and without B. Ni$_3$Si only exists on the Ni-rich side of stoichiometry.

The addition of B has three effects. First, it increases the lattice resistance to slip /1-7/. Second, it reduces the contribution of grain boundaries to the yield strength of Ni-rich and stoichiometric Ni$_3$Al /2,3,6,8/. Third, it improves the ductility of stoichiometric and Ni-rich Ni$_3$Al /9-13/ and accordingly increases the extent of transgranular fracture at the expense of intergranular fracture. Data for Ni$_3$Si are less extensive but all three of these effects also occur on addition of B to this compound /14-17/.

The brittle intergranular fracture of both Ni$_3$Al and Ni$_3$Si at room temperature appears to be intrinsic to the compounds /9,12,18-20/. The salutary effect of B on ductility arises due to its segregation to the grain boundaries /5,12,19-27/; although B segregates to the grain boundaries of Al-rich Ni$_3$Al alloys /16,27/ such alloys remain brittle /12/, indicating that B segregation alone is not sufficient to improve ductility; that is, it appears that B segregation is necessary but not sufficient condition for ductility. Also, Ni enrichment of grain boundaries has also been observed in stoichiometric /28,29/ and Ni-rich /23,27/ Ni$_3$Al. The enrichment reduces the degree of long-range atomic (chemical) order, at least in Ni-rich Ni$_3$Al, as observed by lattice imaging /30/, and thus changes the properties of the material within the vicinity of the boundary. Two models, which are not mutually exclusive, have been presented for the role of B in improving the ductility of Ni$_3$Al and presumably also apply to Ni$_3$Si. First B has been suggested to improve the grain boundary cohesion /12,16,31/. Second, B has been suggested to ease slip transmittal /8,32/ across grain boundaries. The latter suggestion is consistent with theoretical analyses /33-36/ which show that localized disordering eases the accommodation of slip at grain boundaries and presumably reduces the stress concentration to below that required to nucleate cracks.
EXPERIMENTAL

Eight alloys were studied. For Ni₃Al: Ni-24A1, Ni-25A1 and Ni-26A1 (compositions are quoted throughout in atomic percent) with and without B (-0.35 at.%). For Ni₃Si: Ni-23Si with and without B (0.19 at.%). All of the alloys were prepared by hot extrusion of powders to rod. Details of the processing conditions and chemical analyses of the alloys may be found elsewhere /2,3,17,37/.

The chemistry of grain boundaries was studied using two techniques. Energy dispersive x-ray microanalysis on a high resolution field emission gun scanning transmission electron microscope, STEM (VG HB501), was used to examine grain boundaries in thin foils and the data quantified using the Cliff-Lorimer ratio method /38/. A scanning Auger electron microscope, SAM (PHI660), was used to examine the chemistry of grain boundaries and transgranular surfaces of specimens fractured in-situ (by a hammer blow at ~1×10⁻⁸Pa), some of which (B-doped stoichiometric and B-doped Ni-rich Ni₃Al) were cooled to liquid nitrogen temperature prior to fracture. In addition, the thin foils of Ni₃Al were examined, using convergent beam electron diffraction (CBED), in a transmission electron microscope, TEM, (JEOL 2000FX). Thin foil preparation is described elsewhere /27,28/.

RESULTS

Fracture surfaces (of Auger samples) of Ni₃Al showed a trend consistent with an increasingly ductile fracture with increasing Ni:Al ratio and with B additions. Al-rich Ni₃Al with and without B and B-free stoichiometric Ni₃Al fractured in a wholly intergranular manner. Specimens of both stoichiometric Ni₃Al with B and B-free Ni-rich Ni₃Al fractured in a mostly intergranular manner with some transgranular regions. Ni-rich B-doped Ni₃Al fractured mostly transgranularly with a few intergranular areas. Specimens of the latter material often required more than a single hammer blow to fracture them and were subsequently found to be bent on removal from the SAM, a feature consistent with the considerable ductility exhibited by this composition /6/. It is worth noting that selected area channelling patterns could not be obtained from the fracture surface of any of the Ni₃Al alloys, indicating at least local plasticity during fracture.

![Fig. 1. Auger electron spectra from intergranular facets of B-doped a) Ni-26Al, b) Ni-25Al, and c) Ni-24Al.](image)

AES from grain boundaries in all Ni₃Al alloys often showed the presence of oxygen, see figure 1a. Oxygen has been identified by chemical analysis at levels up to ~200 ppm (wt.) in these alloys /2,37/. A small number of particles were present on many, but not all, grain boundaries. Auger analysis indicated that these were high in
oxygen and Al indicating that they were probably Al$_2$O$_3$. Auger spectra from grain boundaries in the all B-doped alloys showed a clear B peak, see figure 1. The magnitude of the peak did not clearly vary with the composition of the alloy, in agreement with earlier results [16,27].

Line scans (128 channels, 1 nm wide at 5 seconds per channel) were performed in the STEM across grain boundaries in thin foils viewed at a magnification of $10^5$ times and x-rays corresponding to the Ni K$_\alpha$, Ni L$_\alpha$ and Al K$_\alpha$ emission peaks were collected together with the bright field intensity. In Al-rich Ni$_3$Al, both with and without B and in B-free stoichiometric Ni$_3$Al, this technique revealed no differences between the composition of the matrix and the grain boundaries, see figure 2. In B-doped stoichiometric Ni$_3$Al, line scans showed a dramatic fall in Al K$_\alpha$ counts at the grain boundary over a narrow region (~5 nm), figure 2b. In Ni-rich Ni$_3$Al with no B, some boundaries were found that were highly Ni-enriched across a large width (~20 nm), figure 2c, whilst other grain boundaries showed only a slight Ni enrichment. In B-doped Ni-rich Ni$_3$Al, all grain boundaries examined showed a large Ni enrichment over a considerable width up to 20 nm, see figure 2d. Line scans performed across a few twin boundaries in B-doped Ni-rich Ni$_3$Al showed no evidence of Ni enrichment.

![Fig. 2. Line scan across grain boundaries in a) Ni-26Al + B, b) Ni-25Al + B, c) Ni-24Al and d) Ni-24Al + B.](image)

In order to obtain both better statistics (more counts) and quantification of the above results, the stationary beam was directed at a grain boundary, and then at the adjacent matrix in one or both grains, for 100s each. At the boundary, the accumulation of x-rays was periodically interrupted in order to correct for any specimen drift. The resulting x-ray spectra were recorded and the grain boundary compositions were determined from the Ni K$_\alpha$ and Al K$_\alpha$ emission peaks. The matrix data from either side of each boundary were used as standards to obtain a thickness-corrected k-factor so that each set of measurements could be corrected for Al K$_\alpha$ x-ray absorption. The results confirmed the line scan observations, see figure 3. First, the compositions of grain boundaries in (B-free and B-doped) Al-rich and stoichiometric Ni$_3$Al are essentially the same as the matrix.
Note that the addition of B to Al-rich Ni₃Al appears to produce either slight or negligible Ni-enrichment at the grain boundaries, see figure 3b. Second, some of the boundaries in B-free, Ni-rich Ni₃Al are strongly Ni-enriched, whilst others are only slightly Ni-enriched, see figure 3b. And, third, the addition of B to stoichiometric and Ni-rich Ni₃Al leads to grain boundaries becoming Ni-enriched in the former and strongly Ni-enriched in the latter. The Ni enrichment in the B doped Ni-rich Ni₃Al (figure 3b) is greater than in the B-free Ni-rich Ni₃Al (figure 3a).

TEM examinations of thin foils of Ni-rich Ni₃Al clearly showed the presence of the boundary phase, up to ~15 nm wide, see figure 4a. The phase was continuous along grain boundaries in the B-doped Ni-rich Ni₃Al but occurred intermittently along grain boundaries in B-free Ni-rich Ni₃Al, see figure 4: the regions containing the phase were presumably the strongly Ni-enriched ones indicated in figure 3a, whereas the boundaries without a phase presumably were the lightly Ni-enriched ones in figure 3a. Note that the phase was not found on the Ni-enriched grain boundaries of B-doped stoichiometric Ni₃Al, possibly because a phase, if it exists, was too thin to be resolved. CBED patterns showed that the phase (figure 4b) had the same orientation as one of the grains (figure 4c) but that it was disordered (f.c.c.) as evidenced by the lack of superlattice reflections. The presence of a disordered region (~5nm wide) at a grain boundary in B-doped Ni-rich Ni₃Al has previously been demonstrated using lattice imaging /30/.

Turning to Ni₃Si, Auger samples, both with and without B, fractured in an almost wholly intergranular manner. A few grains were found that fractured by transgranular cleavage and some transgranularly fractured regions were found around otherwise intergranularly fractured grains. The B-doped Ni₃Si exhibited more grains which had fractured transgranularly or had a lip of transgranularly fractured material around otherwise intergranularly fractured grains. AES of transgranular fracture surfaces of both B-doped and undoped Ni₃Si revealed the presence of Ni and Si only. Ni/Si ratios from transgranular fractured areas were averaged and the result used to obtain corrected sensitivities assuming that the correct Ni/Si ratio was 77/23. AES data from seven grain boundaries in undoped Ni₃Si showed that they were Ni enriched compared with the material as a whole, with an average Ni concentration of 84.2 ± 1.7. Auger spectra from intergranular fracture surfaces of B-doped Ni₃Si showed peaks from Ni, Si and segregated B/17/. AES data from six grain boundaries (with the B counts excluded) again showed that the grain boundaries are Ni enriched compared with the matrix with an average Ni concentration of 87.3 ± 1.5. Note that the Ni enrichment is about 30% greater than for undoped Ni₃Si with an average Ni/Si ratio of 6.9 for Ni₃Si+B compared to 5.3 for Ni₃Si.

**DISCUSSION**

A summary of the fracture modes observed and the grain boundary compositions determined is shown in Table 1. The results on B-free Ni₃Al and Ni₃Si will be discussed first. These data show that the grain boundaries in Al-rich Ni₃Al and in stoichiometric Ni₃Al have essentially the same composition as the material as a whole. By
comparison, in Ni-rich Ni$_3$Al some grain boundaries are slightly Ni-enriched, and some grain boundaries were highly Ni-enriched. The highly Ni-enriched boundaries had regions of discrete disordered second phase at the boundary which had the same orientation as one of the grains. The implication is that these highly Ni-enriched regions contain so much Ni that they are no longer ordered Ni$_3$Al but are a disordered solid solution of Al in Ni. Grain boundaries in Ni-rich Ni$_3$Si are also Ni-enriched. These results are in good agreement with pair-potential-based calculations /39/ and embedded atom calculations /40,41/.

Table 1. Fracture modes and grain boundary compositions for Ni$_3$Al and Ni$_3$Si alloys.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Fracture Mode</th>
<th>G.B. Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$_3$Al</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al-rich</td>
<td>I.G.</td>
<td>Same as matrix</td>
</tr>
<tr>
<td>Al-rich+B</td>
<td>I.G.</td>
<td>B-rich but Ni:Al ratio as matrix</td>
</tr>
<tr>
<td>Stoichiometric</td>
<td>I.G.</td>
<td>Same as matrix</td>
</tr>
<tr>
<td>Stoichiometric+B</td>
<td>Mostly I.G., some T.G.</td>
<td>Ni- and B-enriched</td>
</tr>
<tr>
<td>Ni-rich</td>
<td>Mostly I.G., some T.G.</td>
<td>Some strongly, some lightly Ni-enriched, all B-enriched</td>
</tr>
<tr>
<td>Ni-rich+B</td>
<td>Mostly T.G., some I.G.</td>
<td>All very strongly Ni- and B-enriched</td>
</tr>
<tr>
<td>Ni$_3$Si</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-rich</td>
<td>Mostly I.G., very few T.G.</td>
<td>Ni-enriched</td>
</tr>
<tr>
<td>Ni-rich+B</td>
<td>Mostly I.G., some T.G.</td>
<td>Strongly Ni- and B-enriched</td>
</tr>
</tbody>
</table>

It is worth noting that a recent AES study of grain boundaries in Ni$_3$Al has indicated that grain boundaries in Ni-24Al were Ni-enriched /43/, and that the addition of B appeared to have a minor effect on the Ni segregation to grain boundaries. However, given the variability of chemistry from one grain boundary to another, as indicated in figure 3, and that the AES technique only examines the weakest boundaries /1/, it is clear that AES of in-situ fractured samples cannot provide the complete picture. In other words, the highly Ni-enriched boundaries, which we assume here are the strongest, probably will not be examined by this technique.

It is worth reconsidering the two models presented earlier for the role of B on the ductility of Ni$_3$Al and Ni$_3$Si in light of the present results. A problem with the cohesion model /12,16,31/ is its inability to explain the lack of ductility in B-doped Al-rich Ni$_3$Al even though B segregates strongly to the grain boundaries in this alloy /16,27/. The slip transmittal model /8,32/ is supported by the observations that brittle, undoped Ni$_3$Al /2/ and Ni$_3$Si /17/ yields discontinuously before breaking, which implies that plastic flow is a prerequisite to fracture. The model is also supported by the observation that plastic flow is localized beneath the fracture facets of brittle Ni$_3$Al /44/, and that dislocations pile up at grain boundaries in Ni$_3$Al /45/. Again, these observations point to the importance of microplasticity to the process of fracture. The other supporting evidence is the observation that B lowers /3/ the effectiveness with which grain boundaries impede slip in stoichiometric /3/ and in Ni-rich Ni$_3$Al /6/ and in Ni-rich Ni$_3$Si /17/ (all of which show ductility) but not in Al-rich Ni$_3$Al /6/ (which shows no ductility improvement). These last points indicate that ductility is related to the ease of slip transmittal across grain boundaries.

In the B-doped alloys of both Ni$_3$Al and Ni$_3$Si, the ductility improvement coincides with (an increase in) Ni segregation to the grain boundaries. The results of CBED and lattice imaging /30/ indicate that, at least in some alloys, this leads to the presence of a disordered second phase at the grain boundary. That disordering produces a change to a more ductile (transgranular) fracture mode has recently been shown by proton irradiation of Ni$_3$Al /46/. (The need for a disordered second phase at the grain boundary of an intermetallic compound has recently been suggested as a requirement for ductility in ordered alloys in general /47/.) That is, the measurements here support the slip transmittal model.

One problem with the suggestion that constitutional disordering of grain boundaries due to Ni segregation per se is responsible for the ease of slip transmittal and the improvement in ductility is that grain boundaries in Ni-rich Ni$_3$Al and Ni$_3$Si are already Ni-enriched. For example, in cast Ni-rich Ni$_3$Al the grain boundaries are Ni-enriched even without B but fracture still occurs in a brittle manner /48/. This problem is particularly evident when examining the data from B-free Ni-24Al and B-doped Ni-25Al in figure 3. Grain boundaries in Ni-24Al are the more Ni-enriched but this alloy is brittle. This "problem" may be resolved in two ways. The first concerns the number of boundaries examined. Whilst grain boundaries in B-free Ni-24Al have a higher Ni enrichment than B-doped Ni-25Al, it may be that there are a few boundaries in the former which are so little Ni-enriched that these initiate brittle fracture of this alloy when under tension. The second possibility is that in Ni$_3$Al and Ni$_3$Si both disordering of the grain boundary and an improvement in grain boundary cohesion by B are required for ductility.

(1) The study was complicated by the fact that the boron-doped nickel-rich Ni$_3$Al was hydrogen-charged prior to fracture.
CONCLUSIONS

Grain boundaries in Ni$_3$Al have been examined as a function of the deviation from stoichiometry and of B additions, using AES, EDS on a STEM and CBED on a TEM. It has been shown that:

1) Grain boundaries in Al-rich and stoichiometric Ni$_3$Al have the same composition as the matrix, whilst Ni-rich Ni$_3$Al has Ni-enriched grain boundaries, some of which are so strongly enriched that a second phase is present.

2) B segregates to the grain boundaries in Ni$_3$Al irrespective of the Ni:Al ratio.

3) B doping of Ni$_3$Al produces (further) Ni-enrichment of grain boundaries in Ni-rich Ni$_3$Al and stoichiometric Ni$_3$Al but has little effect on the chemistry of grain boundaries in Al-rich Ni$_3$Al.

4) The second-phase which is present on some grain boundaries in undoped Ni-rich Ni$_3$Al, which can be up to 20 nm wide, is disordered f.c.c.

An Auger spectroscopy study of in-situ fractured Ni$_3$Si with and without B has shown that:

5) Grain boundaries in Ni-rich Ni$_3$Si are enriched in Ni relative to the matrix.

6) B segregates to grain boundaries in Ni$_3$Si and further increases their Ni enrichment.

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