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Microchemical Analysis of
Intermetallic Alloys Using the
Field-Ion Microscope Atom Probe

FINAL REPORT

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MICROCHEMICAL ANALYSIS OF INTERMETALLIC ALLOYS
USING THE FIELD-ION MICROSCOPE ATOM PROBE

FINAL REPORT

In this final report we summarize the results of our studies on Ni_3Al and comment on the future use of field-ion microscopy techniques to elucidate the ductilization effect of boron.

Segregation of boron: Grain boundary segregation of boron in Ni_3Al is readily observed by atom probe microanalysis and sometimes visually by field-ion microscopy as well. The maximum measured boron concentration was usually found to be between 1 and 5 atomic percent. The true concentration must be greater since the enriched zone is most likely narrower than the diameter of the probed area (2 to 3 nm). If it is assumed that the segregated layer is 2 to 4 atoms wide the boron concentration at the boundary is then approximately between 10 and 20 at. % which agrees with results obtained by Auger spectroscopy. Nearly all of the boundaries studied were of the general high-angle type. It is difficult to be selective in choosing boundaries of certain orientations because of the shape of the field-ion microscopy specimen. The concentration of grain boundary boron varied considerably not only from boundary to boundary but also along a given boundary.

Frequently, it was observed that considerable boron was still found at distances as great as 2 or more nm from the boundary. It was not established whether this tail in the profile was due to the grain-refinement processing of the material.

Co-segregation of nickel: One of the controversies that arose between different groups working on Ni_3Al was the degree of co-segregation of nickel (or equivalently the depletion of aluminum) that occurs in Ni_3Al . The occurrence of co-segregation of nickel in Ni-rich Ni_3Al was first reported by us several years ago. More recent results of the analysis of a much larger number of boundaries showed that the evidence for co-segregation of nickel is often not as clear as the initial results indicated and, similarly to the boron segregation, varies widely not only between boundaries but also along a given boundary plane. For instance, a boundary that was analyzed at eleven consecutive points along the boundary showed that in four out of the eleven analyses the aluminum concentration in the boundary region was nearly equal to or higher than the average measured aluminum concentration. The remaining analyses showed a depletion of aluminum ranging from one to seven atomic percent. The aluminum depletion was significant in less than half of the analyses. Nevertheless, a frequency distribution of the composition of blocks of atoms taken from the matrix as well as the grain boundary region indicated that, overall, the aluminum concentration of the grain boundary regions was approximately 4 at. % less than that of the matrix. It should be pointed out that if the depleted layer is only a few atom diameters wide the true Al concentration would be still lower. It would be desirable to construct frequency plots for B-free and Al-rich alloys but they are difficult to construct because of the large number of atoms that are required.

Grain boundary decoration: The grain boundaries in B-doped Ni_3Al examined in our study showed no visible evidence of segregation when first examined. After uncontrolled field-evaporation or partial fracture of the specimen, which sometimes occurred, the boundaries were often observed to be decorated by bright spots which were identified to be due to boron

atoms. The boron concentration at decorated boundaries was sometimes found to be higher than normal but there was no evidence for the presence of a distinct three-dimensional phase. The boron atoms are brightly imaging because they are protruding from the surface. The reason this occurs and how is not clear.

Segregation of other solutes: The segregation of carbon, beryllium and hafnium to boundaries in Ni_3Al has also been studied. The segregation of beryllium is difficult to measure quantitatively because Be^+ and Al^{++} ions have the same m/e ratios. The segregation of carbon was found to be more diffuse than that of boron and may be of the non-equilibrium type. Of the solutes investigated boron was found to segregate the strongest. No strong interaction between boron and hafnium atoms was found which is somewhat surprising considering the stability of hafnium boride.

Analysis of boron in Al-rich Ni_3Al : No decisive difference in the segregation of boron to grain boundaries of Al-rich Ni_3Al was found which could explain their much lower ductility. For a given boron content the grain boundary enrichment appears to be somewhat less in the Al-rich alloy but equivalent segregation can be obtained by increasing the nominal boron content.

The formation of large numbers of small clusters of boron containing 2 to 3 atoms has been reported to occur in the Al-rich alloys but not in the Ni-rich alloys. While such clusters apparently do not appreciably affect the grain boundary concentration of boron they could be responsible for the observed increase in the flow stress of the matrix. However, we have observed comparable numbers of boron clusters in Ni-rich alloys and it is doubtful that they are the primary cause of the stoichiometric effect on ductility. It is possible that these small clusters

are actually artifacts and appear because of field-evaporation effects. Thermal treatments have little or no effect on their concentrations.

Grain boundary phases: There has been discussion in the literature on the formation of grain boundary phases in Ni_3Al . Of the 50 to 100 grain boundaries that were examined in the course of this study only 2 to 3 gave any indication for the possible formation of a three-dimensional grain boundary phase and even in those cases it appeared to be discontinuous. The observed "phase" showed a high boron content suggesting the formation of a boride similar to the precipitates we have observed occasionally in the matrix.

A large number of boundaries were analyzed in the as- received extruded material supplied by Dartmouth. We have not observed either by TEM of the specimen needles or by atom probe microanalysis the up to 20 nm wide Ni-rich layer, presumably gamma phase, reported by the Dartmouth group. Instead, the grain boundary profiles were substantially the same as those obtained from conventionally cast materials. We have observed gamma phase precipitates in the matrix of the Dartmouth material. If gamma phase forms at some of the boundaries but not at others it is possible that during the preparation of the FIM needles the etchant preferentially attacks the coated boundaries leaving only bare boundaries in the region near the tip.

Degree of atomic ordering at grain boundaries: Disorder of the grain boundary layer has been proposed to explain the improved ductility of B-doped Ni-rich Ni_3Al . Ordering of alloys can be ascertained in two ways by the FIM/atom probe. Visually, ordering manifests itself in the field-ion microscope by the presence of alternating dim and bright atom layers along the superlattice directions. The contrast is due to the difference in composition of the alternating

atomic layers, changing from pure nickel to 50Ni50Al. More quantitatively, ordering can be measured by analyzing the composition of the alternating superlattice planes. To measure the degree of ordering on both sides of a boundary, the boundary should traverse superlattice planes. The results of such analyses have convinced us that at least in random, high angle boundaries, a high degree of order persists in the matrix on both sides of the boundaries at least up to within a distance of 1nm from the boundary.

Conclusion: The FIM/atom probe results obtained thus far cannot explain the ductilization effect of boron in Ni₃Al and the strong stoichiometric effect on ductility. It now appears that neither compositional disordering of the boundary regions in Ni-rich alloys or the formation of small boron clusters in Al-rich alloys can be the primary factor in determining ductility. We conclude that the effect is either due to very subtle differences in the grain boundary chemistry of very narrow regions or is due to differences in the fine-scale arrangement of the atoms on the grain boundary plane. A theory due to Vitek and Chen proposes that in the B-doped, Ni-rich alloy boundary atoms can relax to alter the shape and size of discontinuities at which in the B-free or the Al-rich alloys cracks can nucleate. If this is the case, it is doubtful whether field-ion microscopy or atom probe microanalysis can generate any decisive information that would either confirm or disprove the proposed model. Small atomic relaxations cannot be measured readily by field-ion microscopy because of the stresses introduced by the application of the high electric fields during imaging and atom probe analysis. We suggest that the latest theoretical developments should be carefully evaluated before further FIM/atom probe work on Ni₃Al is undertaken.

Publications:

The following publication and report have resulted from recent work:

1. S. Sidney Brenner and Hua Ming-Jian "FIM/Atom probe analysis of grain boundaries in B-doped Ni_3Al ", Scripta Metallurgica et Materiala, 25, 1271 (1991).
2. S. Sidney Brenner "FIM/Atom probe study of grain boundaries in Ni_3Al " DOE/BES Workshop on "Scientific Issues on Intermetallic Compounds - Status and Forecast for Fundamental Research" September 11-14, 1991, La Jolla, California.

Reprints of these papers are attached to this report. *(removed and
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