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AN ATOM PROBE FIELD ION MICROSCOPE INVESTIGATION OF THE ROLE OF BORON IN PRECIPITATES AND AT GRAIN BOUNDARIES IN NiAl

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ABSTRACT

The high resolution analytical technique of Atom Probe Field Ion Microscopy (APFIM) has been used to characterize grain boundaries and the matrix of a stoichiometric NiAl alloy doped with 0.04 (100 wppm) and 0.12 at. % (300 wppm) boron. Field ion images revealed boron segregation to the grain boundaries. Atom probe elemental analysis of the grain boundaries measured a boron coverage of up to 30% of a monolayer. Extensive atom probe analyses also revealed a fine dispersion of nanoscale boride precipitates in the matrix. The boron segregation to the grain boundaries was found to correlate with the observed suppression of intergranular fracture. However, the decrease in ductility of boron-doped NiAl is attributed in part to the precipitation hardening effect of the boride phases.

INTRODUCTION

Nickel aluminides and other intermetallics have been the focus of intense study in recent years because of their potential applications in aggressive high temperature environments. Although these alloys typically have high strength and corrosion resistance at elevated temperatures, their brittleness at low temperature severely restricts their technological applications. It has been shown that stoichiometrically pure NiAl [1] and Ni_3Al [2,3] fracture intergranularly at room temperature. Efforts to ductilize these alloys have been made by adding suitable microalloying elements and correlating the resultant grain boundary chemistry with the type of fracture mode. In Ni_3Al, the addition of boron in excess of 200 wppm results in a dramatic improvement in ductility and it has been experimentally demonstrated that the boron segregates to the grain boundaries where it suppresses intergranular fracture [3]. However, no improvement in ductility is observed with similar boron additions to NiAl even though intergranular fracture is suppressed [4].

Atom probe field ion microscopy is a powerful technique for characterizing the microstructure and microchemistry of interfaces since it combines near atomic resolution imaging and single atom detection capability in the same instrument [5]. The suitability of this technique to the study of grain boundaries in Ni_3Al and other materials has been clearly demonstrated in many previous investigations [6,7]. In this paper, the results of an atom probe field ion microscopy study of grain boundary and matrix chemistry of boron-doped NiAl are presented.

EXPERIMENTAL PROCEDURE

The alloys were prepared by arc melting high-purity elemental materials with a Ni-B master alloy to obtain stoichiometric NiAl materials with bulk concentrations of 0.04 at. % B (100 wppm) and 0.12 at. % B (300 wppm) [14]. The alloys were homogenized for 24 h at 1100°C. The ingots

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were canned in mild steel and extruded at 900°C. The 0.12 at. % B alloy was then subjected to two subsequent heat treatments; 1) 1 h at 500°C and 2) 1 h at 1100°C, and the 0.04 at. % B alloy was heat treated for 1 h at 900°C.

Field ion specimens were prepared from these samples by standard techniques [7]. Since the needle-shaped field ion specimen typically has an end radius of approximately 50 nm, there is a low probability of randomly producing a specimen with a grain boundary in the analyzable volume of the specimen in this relatively large grain size material. Therefore, some additional steps were performed to obtain suitable specimens. The field ion specimens were first examined in a Phillips CM 30 transmission electron microscope operated at 300 kV in order to pre-select those specimens which contained a grain boundary in the electron-transparent region of the specimen. If the grain boundary was not in the apex region of the needle, these specimens were then ion-milled in a GATAN 645 Precision Ion Milling System (PIMS) and examined further in the electron microscope [8]. This process was repeated until a grain boundary was positioned within the analyzable volume of the apex. A transmission electron micrograph of a field ion specimen (0.04 at. % B) with three grain boundaries in the electron transparent region is shown in Fig. 1.

Specimens containing grain boundaries in the analyzable region were then transferred to the Oak Ridge National Laboratory energy-compensated atom probe for analysis [9]. The field ion micrographs were obtained with neon as the imaging gas at a specimen temperature of 50 K. The orientation relationships between the grains was determined from the field-ion micrograph by the method described in Bowkett and Smith [10] and based on the reasonable assumption that the field ion image resembles a stereographic projection. All compositions quoted in this paper are in atomic percent.

RESULTS AND DISCUSSION

A field ion micrograph of the specimen shown in Fig. 1 is shown in Fig. 2. From the orientation relationship of the two visible grains (A and B), the boundary was determined to be a $\Sigma 3$ twin boundary. The grain boundary is characterized by brightly-imaging spots which were identified by atom probe analysis as boron atoms. This imaging behavior is similar to that previously observed in boron-doped Ni_3Al [6]. A field ion image of the same specimen that was taken after field evaporation to expose the third grain (C) is shown in Fig. 3. The third grain is evident in two separate regions of the field ion micrograph because of the hemispherical nature of the field ion specimen. All 5 segments of 3 grain boundaries shown in this micrograph exhibit the brightly-imaging spots due to boron segregation. This brightly-imaging behavior was present on all boundaries examined in the field ion microscope. These observations, taken in conjunction with previous Auger measurements [14], seem to indicate that boron segregates to most, if not all, boundaries.

Atom probe analysis of the matrix adjacent to the boundary revealed that the boron segregation was limited to within approximately 1 nm of the boundary. It is possible that the boron is confined to a narrower region than this value, however, experimental considerations, such as accurately maintaining the position of the probe aperture during the atom probe analysis, small trajectory aberrations of the ions from the boundary [11], and small local perturbations in position of the boundary, limit the spatial resolution of this type of analysis. Assuming that the boron is confined to the boundary plane, the coverage was estimated to be between 10% to 30% of a monolayer. This estimate is consistent with Auger measurements which place the lower bound for boron concentration at grain boundaries at 10% [14]. The amount of boron segregated to grain boundaries in this relatively large grained material was estimated to be less than 5% of the available boron. No consistent trend was observed in the nickel composition at the boundary and hence it is not possible to comment on the question of nickel cosegregation and the related issue of grain boundary disorder.

Extensive atom probe analyses of the matrix revealed that the boron concentration in the 0.12% alloy was 0.003 ± 0.0007% in the material that was annealed for 1 h at 500°C and 0.023 ± 0.003% in the material that was annealed for 1 h at 1100°C and in the 0.04% B alloy was 0.026 ± 0.003%. All these measurements indicate that the matrix is substantially depleted from the nominal compositions of the alloys and indicates that the solubility of boron in the B2-ordered matrix is extremely low at low annealing temperatures. This behavior is distinctly different from the $L1_2$-ordered Ni_3Al material where the majority of the boron remains in solid solution in the matrix [12].

The fracture behavior of boron-doped NiAl clearly indicates that boron segregation to grain boundaries is successful in suppressing intergranular fracture [4]. In contrast to the behavior of boron-doped Ni_3Al, the suppression of intergranular fracture in NiAl is not accompanied by an improved ductility. The addition of 0.12% of boron to NiAl increases the tensile yield stress from 154 MPa for the undoped material to >328.9 MPa with specimen failure occurring before macroscopic deformation [4]. The beneficial effect of grain boundary strengthening due to boron segregation is apparently nullified by the accompanied hardening of the matrix of this material. The source of this hardening effect can be traced to the formation of nanoscale precipitates in the NiAl matrix as revealed in the field ion images and by atom probe analyses.

Small, brightly-imaging precipitates were observed in the field ion image, examples of which are shown in Fig. 4. The particles ranged in size from less than 1 nm to approximately 10 nm in radius. The composition of these precipitates was determined by atom probe analyses to be diborides consistent with $(Ti,V,Cr)B_2$. Occasionally, refractory elements such as W were also detected in the metallic part of the precipitate. These precipitates were observed in both alloys although in a lower number density in the 0.04% B alloy [13]. From the composition of the precipitates, a combined total of only 500 appm of metallic impurities would be required for the formation of these precipitates. Such quantities of metallic elements are often present as trace impurities even in high purity Ni and it would appear that the excess boron in the matrix scavenges these impurities to form the precipitate phases during the heat treatment. It should be noted that since the boron content of the matrix is extremely low and the size of these precipitates is less than 10 nm, even the addition of 0.04% boron is sufficient to produce a substantial number density of precipitates. In fact, in the 0.12 at. % B alloy that was annealed for 1 h at 500°C, the combined level of boron in the matrix and at boundaries accounts for only about 6% of the total available boron and the remainder (approximately 1110 appm) is in the precipitates.

Solid solution hardening has been previously cited as being the primary mechanism responsible for the enormous strengthening observed in boron-doped NiAl [4]. However, the boron concentration in the matrix, makes only a small contribution to the increase in yield stress whereas a significant proportion comes from precipitation hardening due to highly stable and hard TiB_2 type precipitates [13]. An estimate based on a simple Orowan-type mechanism has revealed that the increase in yield stress can be explained by these precipitates [13].

This argument is further reinforced by the results of a more recent study of the mechanical properties and grain boundary chemistry of NiAl doped with 0.012 at. % (30 wppm) boron in which intergranular fracture is suppressed by grain boundary segregation but a 2.0% tensile elongation is maintained [14]. Although atom probe studies have not been made on this material, our estimate of boron solubility at higher temperatures (0.023 at. %) would indicate that all of the available boron in this material should be in solution. Solid solution hardening would then be the sole mechanism responsible for the observed 30% increase in the yield stress since precipitation hardening was absent.

CONCLUSIONS

Atom probe measurements of boron-doped NiAl have clearly demonstrated evidence of boron segregation at grain boundaries. A significant proportion of the boron is in the form of small $(Ti,V,Cr)B_2$ precipitates. The observed loss of ductility, despite the suppression of intergranular fracture, is due to a combination of solid solution and precipitation hardening with the latter accounting for a significant portion of the increase in yield stress.

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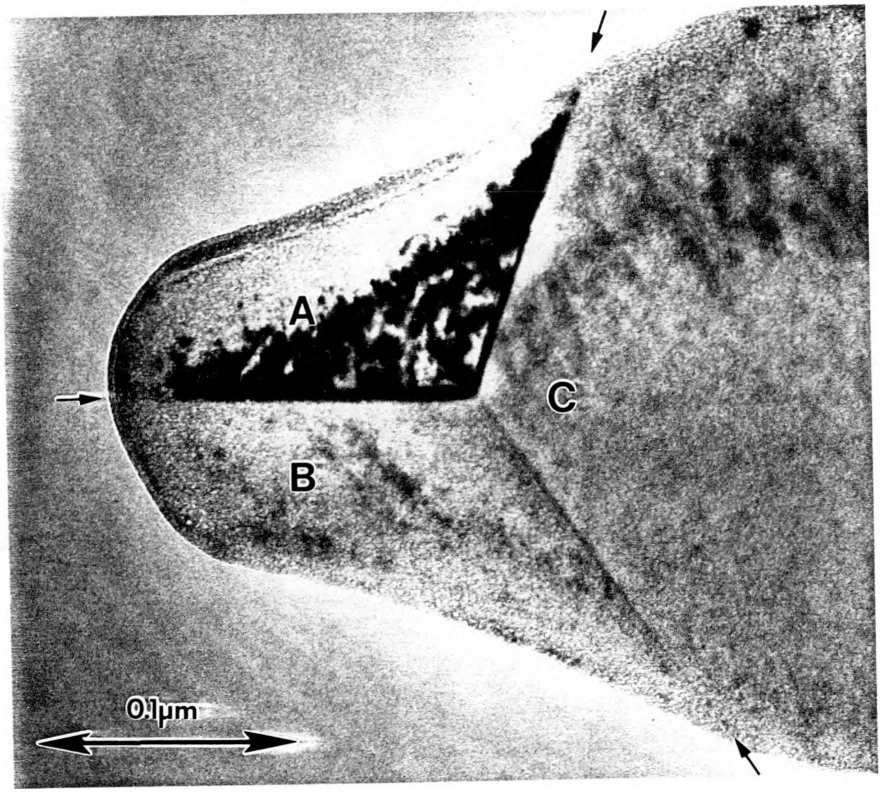

Fig. 1. Bright-field transmission electron micrograph of a 0.04 at. % boron-doped NiAl FIM specimen showing grain boundaries (arrowed) intersecting the apex region of the specimen. The grains "A", "B" and "C" are consistently labelled in Figs. 1, 2 and 3.

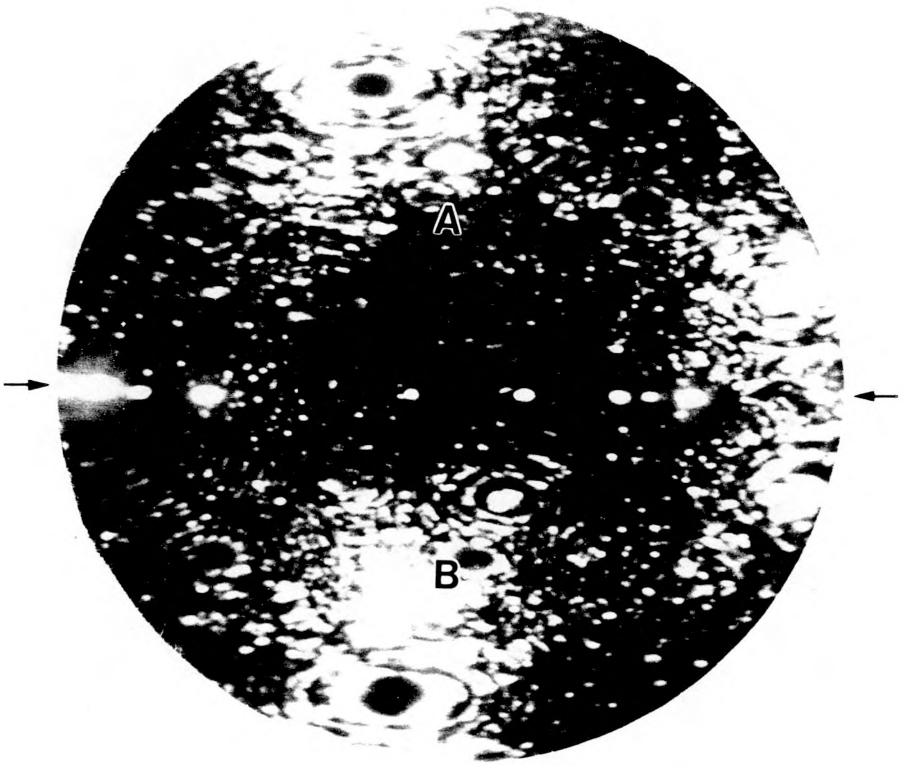

Fig. 2. Field ion micrograph of an NiAl specimen showing showing brightly -imaging boron atoms along a grain boundary (arrowed).

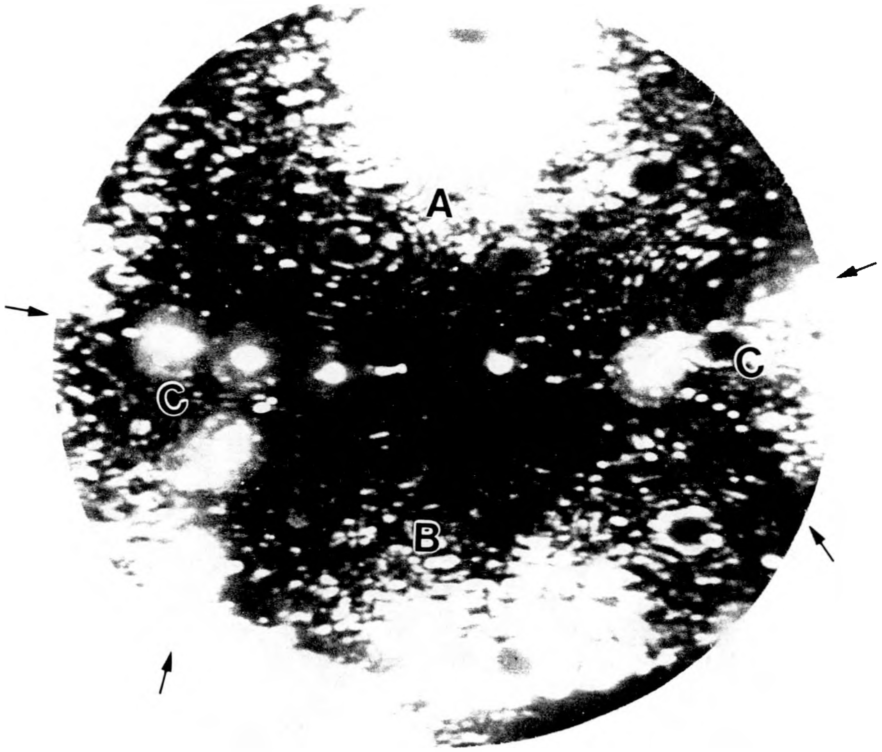

Fig. 3. Field ion micrograph of an NiAl specimen with multiple grain boundaries (arrowed) intersecting the specimen surface.

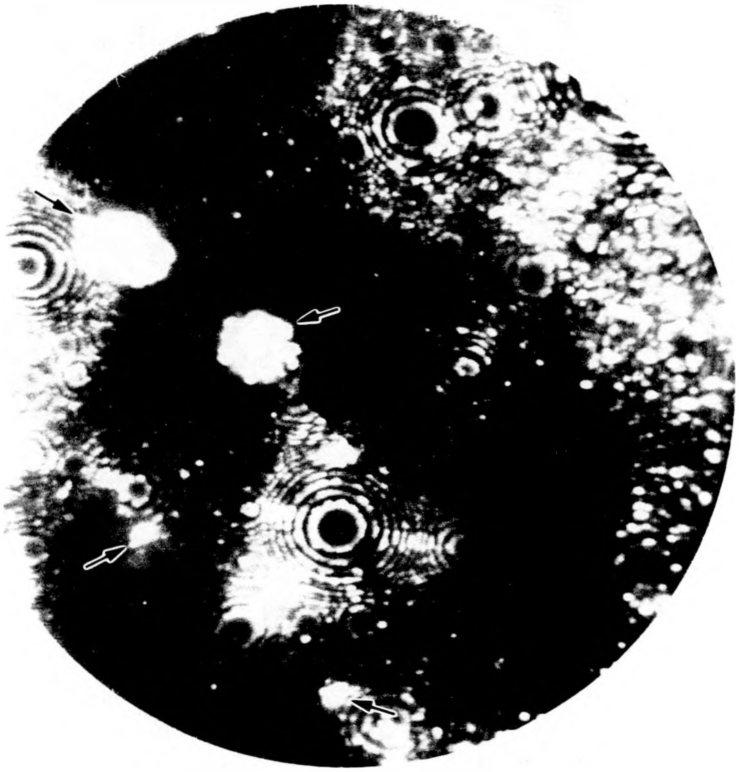

Fig. 4. Field ion micrograph of TiB_2 precipitates (arrowed) in the NiAl matrix.