INFLUENCE OF DISLOCATION-SOLUTE INTERACTIONS ON THE MECHANICAL PROPERTIES OF ZIRCONIUM-DOPED NiAl

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ABSTRACT

Atom probe field ion microscopy (APFIM) has been used to characterize NiAl microalloyed with molybdenum and zirconium. Field ion images and atom probe analyses revealed segregation of zirconium to dislocation strain fields and ribbon-like morphological features that are probably related to dislocations. These results provide direct experimental evidence in support of the suggestion that the tremendous increase in the ductile-to-brittle transition temperature (DBTT) in zirconium-doped NiAl is due to pinning of dislocations by zirconium atoms. Atom probe analyses also revealed segregation of zirconium to grain boundaries. This result is consistent with the change from an intergranular fracture mode in undoped NiAl to a mixture of intergranular and transgranular fracture mode in zirconium-doped NiAl. The NiAl matrix was severely depleted of the solutes molybdenum and zirconium. Small Mo-rich precipitates, detected in the matrix and grain boundaries, are likely to contribute to the significant increase in the room-temperature yield stress of microalloyed NiAl through a precipitation hardening mechanism.

INTRODUCTION

Mechanical properties of NiAl, such as room-temperature ductility and fracture toughness and high-temperature creep strength, need to be improved substantially if it is to find technological applications. An approach to accomplish this goal involves microalloying NiAl with suitable elements [1,2]. A significant improvement in fracture behavior was observed in zirconium-doped NiAl which exhibited a mixture of transgranular and intergranular fracture as compared to predominantly intergranular fracture of the undoped NiAl [3] . This change in the fracture mode correlated with segregation of zirconium to grain boundaries and refinement in grain size [3]. However, this beneficial effect of zirconium on the grain boundaries is offset by the enormous increase in the DBTT from ≈550 K in the undoped NiAl to ≈850 K and 1050 K in 0.05 and 0.1 at. % Zr-doped alloys, respectively [3,4]. It has been suggested that a possible mechanism for this increase in DBTT could be the segregation of zirconium to dislocations [5]. It has also been argued that zirconium atoms segregated at the grain boundaries could influence the DBTT by pinning extrinsic grain boundary dislocations [4].

In this work, atom probe field ion microscopy (APFIM) has been applied to NiAl doped with molybdenum and zirconium to investigate the influence of the microalloying elements on the increase in DBTT. Previous studies have revealed that the addition of 0.4 to 1.6 at. % Mo results in a substantial increase in the room-temperature ductility and high-temperature yield strength [6]. Significant improvements in oxidation resistance and creep life were also observed when NiAl was microalloyed with a combination of molybdenum and zirconium [6].

EXPERIMENTAL

High-purity (99.99 wt%) elemental materials were arc melted and drop cast into cylindrical

copper chill molds to obtain an alloy with the nominal ccmposition of stoichiometric NiAl + 0.7 at. % Mo + 0.4 at. % Zr. After the initial extrusion at 900° C, the NiAl ingots were given two separate annealing treatments: (1) 1 h at 1000° C and step-cooled 4 h at 800° C + 24 h at 600° C + 72 h at 400° C and subsequently furnace-cooled to room temperature, (2) 1 h at 1000° C + oil quenched to room temperature. Tensile property measurements on this alloy suggested that the DBTT was ≥ 1050 K and the room-temperature yield stress increased to 600 MPa from 154 MPa in the undoped stoichiometric NiAl [6]. Field ion microscope (FIM) specimens were prepared using standard techniques and analyzed in the Oak Ridge National Laboratory (ORNL) energy-compensated atom probe [7]. Thin foil transmission electron microscopy (TEM) specimens were examined in the Philips CM30 microscope at an operating voltage of 300 kV.

RESULTS

Field ion images of matrix dislocations in the step-cooled NiAl were characterized by bright-spot decoration, as shown in Fig. 1 [8]. Dislocations typically image as spirals in the FIM whereas concentric rings, characteristic of atomic terraces, are observed in defect-free regions of the crystal [9]. The spirals do not necessarily signify screw dislocations since it has been shown that such configurations can be generated by a stack of atomic planes with any perfect dislocation as long as neither the dislocation line direction vector nor the Burger's vector lie in the plane of the atomic terrace ($\mathbf{n.b}$, $\mathbf{n.l} \neq 0$ where $\mathbf{n}$, $\mathbf{b}$ and $\mathbf{l}$ represent the unit plane normal vector, the Burgers vector and the unit line vector, respectively) [10]. Atom probe analyses of the bright spots decorating the dislocations revealed them to be zirconium atoms. The zirconium concentration in the vicinity of the dislocations was estimated to be between 3 - 5 at. %. However, bright-spot decoration was not observed in approximately one third of all the dislocations imaged in the FIM. The absence of decoration was consistent with atom probe analyses which did not detect zirconium segregation to any significant level in these cases. The majority of the dislocations possessed the <100> Burgers vector.

Brightly-imaging zirconium-rich regions, approximately 1 to 2 nm in width and a monolayer in thickness, were also analyzed in the matrix of the step-cooled alloy. Some of these regions occurred adjacent to dislocations, as shown in Fig. 2. Atom probe analyses and field evaporation sequences revealed that these regions extended from 10 - 30 nm in length suggesting a ribbon-like morphology. The composition of the ribbon-like precipitates consisted entirely of zirconium atoms as no other solutes or impurities were detected. Some of the zirconium-rich regions, shown in Fig. 3, were not associated with spirals or other known defect structures although they were similar in morphology and composition to the ones associated with dislocations.

The microstructure of the oil-quenched NiAl differed from the step-cooled material in two respects. Approximately 80% of the dislocations in the oil-quenched alloy did not exhibit any bright-spot decoration, as shown in Fig. 4. Atom probe analyses of these dislocations did not reveal any zirconium enrichment. Further, in contrast to the step-cooled NiAl, the ribbon-like zirconium-rich regions were not observed in the matrix of the oil-quenched alloy.

Atom probe analyses of the matrix in both alloys revealed significant depletions of molybdenum and zirconium as compared to their bulk value. The matrix concentrations of zirconium were determined to be 0.007 ± 0.002 and 0.009 ± 0.004 at. % Zr in the step-cooled and oil quenched NiAl, respectively. The molybdenum concentration was nearly the same in both alloys and was estimated to be 0.002 ± 0.001 at. %.

Direct evidence of zirconium segregation to grain boundaries in both alloys was obtained from field ion images, Fig. 5, and atom probe analyses. The zirconium segregation was observed in both alloys and the width of the zirconium-enriched region was estimated to be less than 1 nm from the boundary plane. The zirconium coverage at the grain boundary was estimated to be a maximum of ≈60% of a monolayer [11,12]. Brightly-imaging precipitates approximately 10 - 25 nm in diameter, Fig. 6, were detected at the grain boundaries and in the matrix in the two alloys. These precipitates

were predominantly molybdenum-rich and the composition was determined to be 97.0 ± 0.5 at. % Mo - 3.0 ± 0.5 at. % Al.

The grain size in these alloys was uniform and was estimated by TEM to be 1.0 ± 0.3 μm. Dislocations were also observed in TEM images, Fig. 7, along with the Mo-rich precipitates. Preliminary analyses of dislocations revealed that these were of the <100> type Burger's vector. The number densities of the dislocations and the Mo-rich precipitates were estimated to be $\approx 3 \times 10^{13}$ m^{-2} and 2×10^{21} m^{-3}, respectively. Coarse precipitates, 100 - 500 nm in diameter, were also detected as stringers along grain boundaries [8]. Their number densities were not high enough to be detected in the atom probe. Energy dispersive x-ray spectrometry (EDS) measurements indicated that the metallic content of these precipitates was predominantly rich in zirconium with the remainder consisting of nickel and aluminum [8]. Previous studies of similar alloys have suggested that these precipitates may be Heusler phases [6].

DISCUSSION

The dominant deformation mode in polycrystalline NiAl at temperatures below the DBTT is the <100>/{110} slip system [13]. The enormous increase in DBTT in Zr-doped NiAl has, therefore, been attributed to the pinning of <100> dislocations by zirconium atoms [4,5]. The atom probe results in this investigation provide clear evidence of zirconium segregation to dislocations and lend support to the mechanism suggested for the DBTT increase in Zr-doped NiAl. The dislocations that are pinned by zirconium atoms are rendered immobile thereby impeding tensile elongation at lower temperatures. However, at sufficiently high temperatures the dislocations become mobile and promote ductility [4].

Although individual zirconium atoms were associated with some dislocation strain fields (Fig. 1), interpretation of the ribbon-like zirconium-rich regions that were not associated with spiral structures (Fig. 3) is less clear. It would appear that they were formed on dislocations that did not satisfy the visibility criterion for imaging in the FIM [8]. It is also conceivable that they were formed on dislocations that subsequently migrated or by homogeneous nucleation in the NiAl matrix.

As pointed out earlier, the nature of the dislocation cannot be determined from FIM images since the spiral structure can originate from either a pure edge or screw dislocation. Limited TEM analyses of dislocations in this material indicated that most of the dislocations were of the edge type. It seems plausible from physical arguments that zirconium is more likely to segregate to edge rather than screw dislocations. This is based on the notion that zirconium, being a large-sized atom, is likely to occupy a substitutional site in the NiAl lattice. Since a large substitutional solute atom tends to dilate the region around it, the strain energy will be lowered if the solute atom occupies the relatively vacant region below the edge of the extra plane of the dislocation. It has been pointed out that the spherical strain field of a substitutional atom may not interact strongly with the pure shear strain field of a screw dislocation and therefore solute atmospheres in the vicinity of screw dislocations are unlikely [14].

The change in the fracture mode from intergranular in undoped stoichiometric NiAl to a mixture of intergranular and transgranular in Zr-doped NiAl [3] correlated with the segregation of zirconium to grain boundaries. Apparently, the zirconium segregated at the grain boundaries plays a beneficial role by strengthening the boundaries. Zirconium segregation to grain boundaries is also consistent with the refinement in grain size observed in Zr-doped NiAl [3]. Atom probe results did not indicate the presence of molybdenum or trace impurities such as carbon or boron at the grain boundaries.

Atom probe analyses of the matrix composition revealed severe depletion of the solutes Zr and Mo. Although the number of dislocations exhibiting zirconium segregation were far fewer in the oil quenched NiAl, no statistically significant difference was measured in the matrix zirconium content of this material (0.009 ± 0.004 at. % Zr) compared to the step-cooled material (0.007 ± 0.002 at. % Zr) within the error bars. This can be understood from the fact that only a small fraction of the total

zirconium in the alloy (0.4 at. %) segregates to dislocations. A rough calculation, based on the TEM estimate of dislocation density and the assumption that there is one zirconium atom per interatomic distance along a dislocation in the B2 structure, leads to the conclusion that only 0.05% of the bulk concentration (i.e., 0.0002 at. % Zr) of zirconium is associated with dislocations. Similar estimates revealed that approximately 7% of the bulk zirconium concentration is at grain boundaries, assuming a grain size of 1μm diameter and 60% zirconium coverage. These estimates suggest that the majority of the zirconium atoms ≈90% are contained in the relatively large (100 - 500nm) blocky stringers along grain boundaries.

In view of the low solute concentrations, solid solution hardening is unlikely to contribute significantly to the observed increase in room-temperature yield stress from 154 MPa in the undoped stoichiometric NiAl to 600 MPa in the Zr-and Mo-doped NiAl. The small (10 - 25 nm diameter) Mo-rich precipitates and the ribbon-like Zr-rich regions are more likely to contribute to the yield stress through a precipitation hardening mechanism. The large Zr-rich stringers play a negligible role in influencing mechanical properties due to their low number density. They may even be detrimental to crack initiation and their number density could be reduced by lowering the zirconium content in the alloy.

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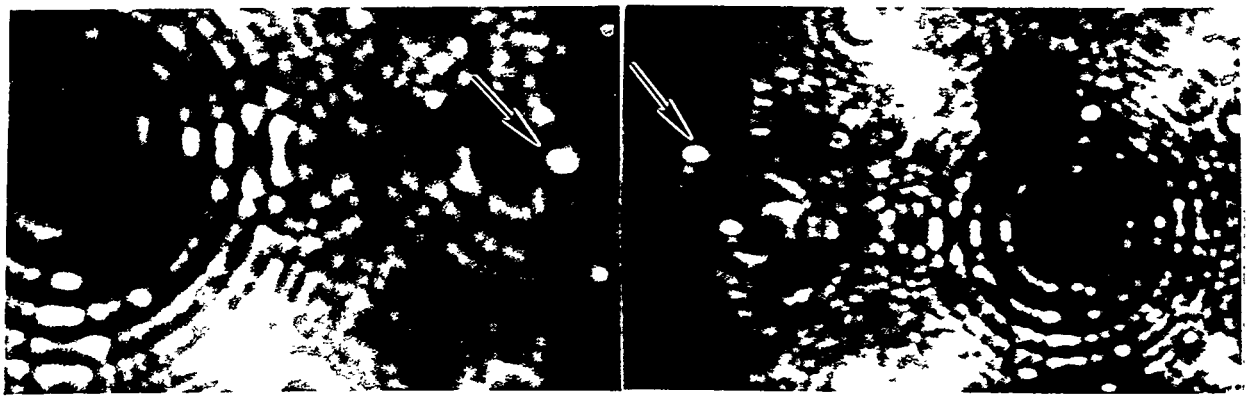

Fig. 1. Field ion micrographs showing segregation of zirconium atoms (arrowed bright spots) to dislocations in NiAl specimens of the step-cooled alloy doped with 0.7 at. % Mo and 0.4 at. % Zr.

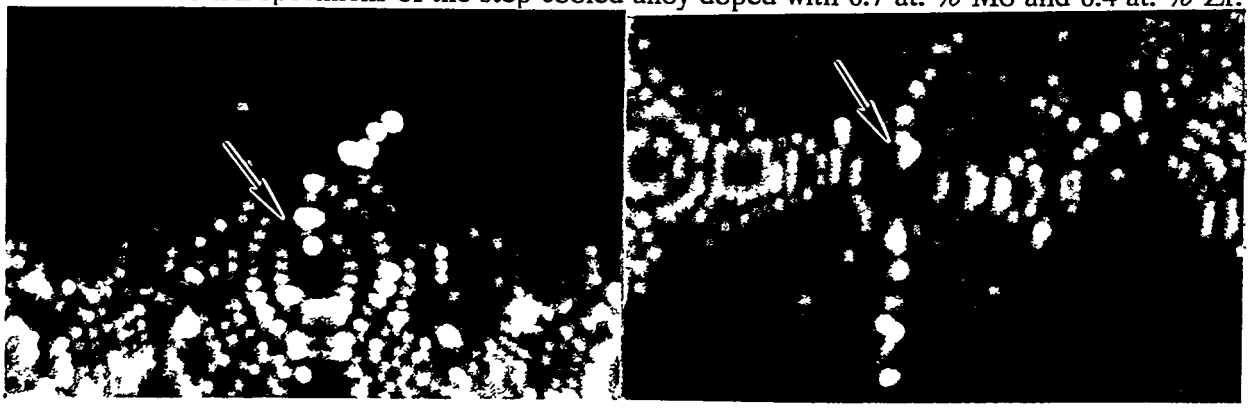

Fig. 2. Field ion micrographs of Zr-doped step-cooled NiAl specimens revealed ribbon-like Zr-rich regions (arrowed) that were associated with dislocations.

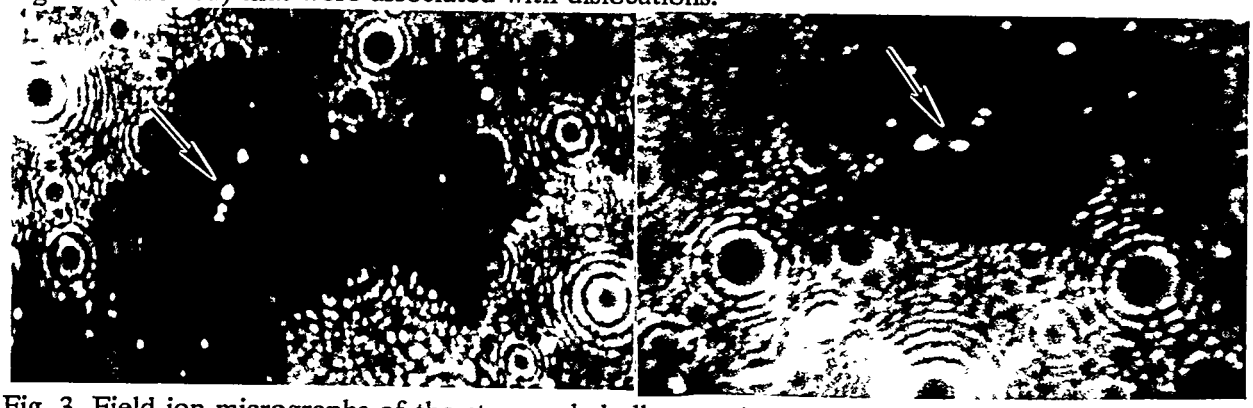

Fig. 3. Field ion micrographs of the step-cooled alloy specimens also revealed Zr-rich ribbons that did not appear to be associated with dislocations.

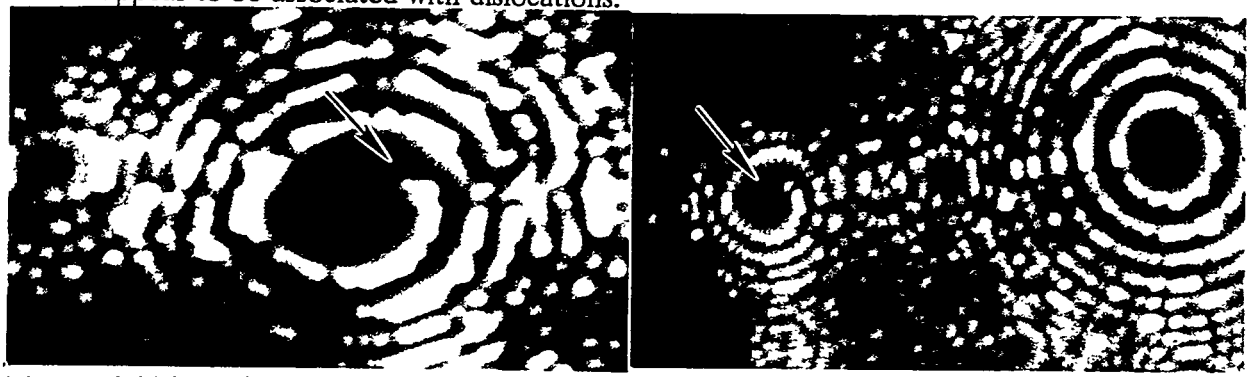

Fig. 4. Field ion micrographs of the oil-quenched NiAl specimens showed that approximately 80% of the dislocations did not exhibit any zirconium enrichment.

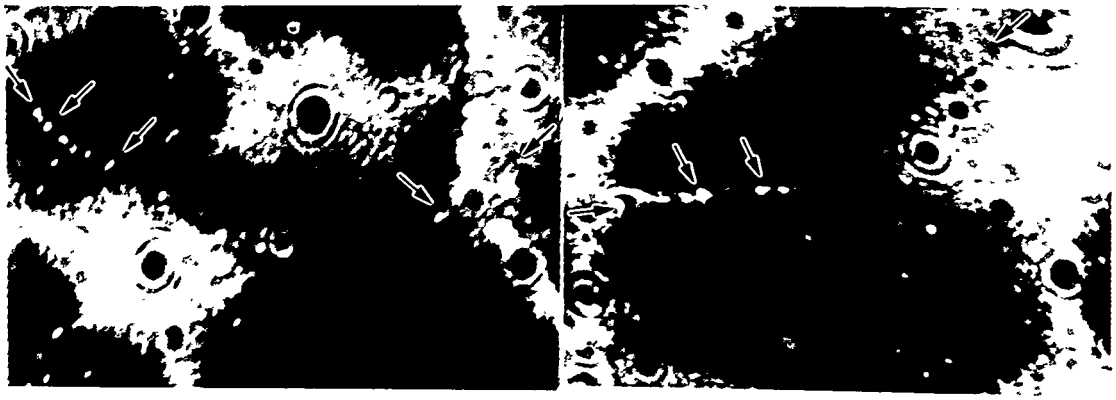

Fig. 5. Field ion micrographs of decorated grain boundaries in both alloys revealed zirconium segregation (arrowed).

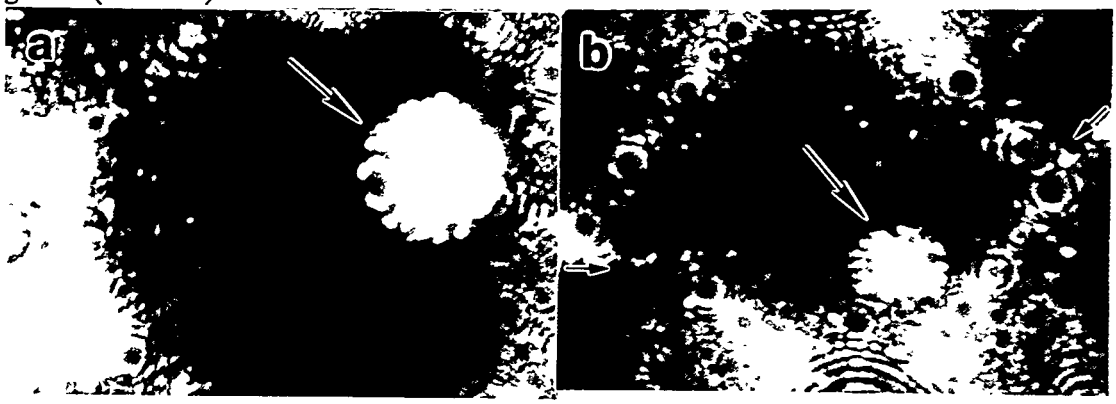

Fig. 6. Field ion micrographs of brightly-imaging Mo-rich precipitates that were detected in the matrix (Fig. 6a) and at grain boundaries (Fig. 6b) in the two alloys.

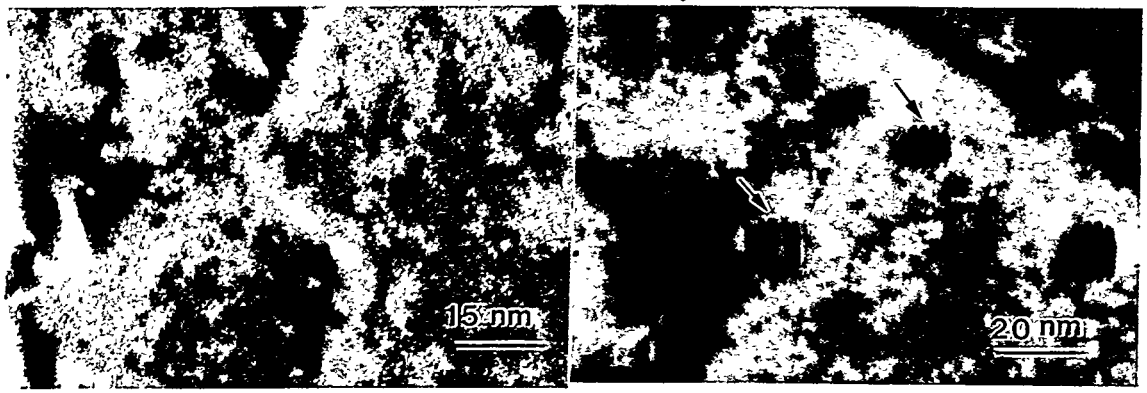

Fig. 7. TEM micrographs of step-cooled NiAl specimens indicated dislocations and Mo-rich precipitates in the matrix.

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