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CHARACTERIZATION OF SEGREGATION IN NICKEL AND TITANIUM ALUMINIDES

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Abstract

Atom probe field ion microscopy has been used to characterize the distributions of microalloying additions in the microstructure of a variety of nickel and titanium aluminides. In Ni_3Al , boron additions were found to segregate to dislocations, low angle boundaries, stacking faults, antiphase boundaries, and grain boundaries. The boron and aluminum levels at grain boundaries were found to vary both from boundary to boundary and also along an individual boundary segment. In some cases, a boron-enriched film up to ~3 nm thick was observed. In aluminum-enriched Ni_3Al , ultrafine clusters containing up to approximately 10 boron atoms were detected in the matrix.

In contrast, the majority of the boron additions in NiAl was determined to be in the form of ultrafine MB_2 -type precipitates. These precipitates offset the benefits of the boron segregation to the high angle grain boundaries. In molybdenum-doped NiAl , atom probe analyses indicated extremely low solubilities of the molybdenum and other trace impurities in the matrix and significant enrichments of molybdenum, nitrogen and silicon, boron, and iron at the grain boundaries.

In boron-doped two phase $\alpha_2+\gamma$ TiAl containing chromium, niobium, and tungsten, the boron level was found to be significantly depleted from the bulk level in both the α_2 and γ phases and a variety of coarse borides including TiB , TiB_2 and a finer chromium-enriched $(\text{Ti,Cr})_2\text{B}$ precipitate was observed. The tungsten and chromium were determined to partition preferentially to the α_2 phase and also to segregate to the $\alpha_2-\gamma$ and $\gamma-\gamma$ interfaces. These results indicate that a significant proportion of the microalloying elements are consumed by the boride precipitates.

Introduction

Nickel and titanium aluminides have attractive potential for technological applications due to their superior high temperature properties. However, the brittleness of these materials at room temperature makes fabrication difficult and therefore limits their application. One of the traditional methods of improving the properties of these types of materials is to add microalloying elements.

A variety of microalloying elements including boron and molybdenum have been used to improve the mechanical properties of both Ni_3Al and NiAl . Boron additions to the L1_2 -ordered Ni_3Al of as little as 200 parts per million produce dramatic improvements in ductility [1,2]. However, boron additions to the B2 -ordered NiAl have a significantly different effect on the microstructure and the mechanical properties [3]. Although additions of as little as 20 parts per million of boron improve the ductility, larger amounts significantly increase the yield strength. The addition of between 0.4 and 1.6% molybdenum to NiAl has been shown to significantly improve the room temperature ductility and high temperature yield strength [4].

Efforts to enhance the ductility and refine the grain size in TiAl -based materials have focused on the addition of a variety of microalloying elements such as boron, silicon, tungsten, chromium, vanadium, manganese and molybdenum [5]. Boron additions of greater than ~0.5 at. % are effective in refining the grain size in cast materials [5,6] and additions at the level of only a few hundred parts per million have been shown to refine and stabilize the lamellar structure in γ -based TiAl alloys [7-10]. Tungsten additions to TiAl enhance oxidation resistance and improve creep resistance and strength whereas chromium additions enhance the ductility. However, the exact mechanism by which these

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refinements are accomplished for these various elements is not understood [11]. In order to understand these mechanisms, one of the first requirements is to determine the distribution of these microalloying additions in the microstructure.

The atom probe field ion microscope (APFIM) is well suited to the characterization of the segregation and partitioning behavior of the microalloying elements in the microstructure due to its near atomic spatial resolution, light element sensitivity, high mass resolution, and low detection levels [12,13]. These atom probe characterizations have focused on the quantification of the solubility levels of the microalloying elements in the matrix, the estimation of the levels of segregants at grain boundaries and other interfaces, and the determination of the size and composition of precipitates. This approach is required to determine the actual distribution of the microalloying elements in the microstructure so that their effectiveness may be more thoroughly evaluated.

Experimental

Atom probe field ion microscopy analyses were performed in the Oak Ridge National Laboratory energy-compensated atom probe field ion microscope [14]. Field ion specimens of these materials were produced by standard electropolishing procedures of either material cut from bulk samples or, in the case of Ni_3Al , wires produced by rapid solidification techniques [12]. The field ion micrographs were recorded with the use of neon as the imaging gas. Due to the low probability of randomly encountering some of these microstructural features in the atom probe, some field ion specimens were initially screened in the transmission electron microscope and suitable specimens were then selected for examination in the atom probe. This pre-selection process also provided additional information as to the precise nature of the defect. The compositions of the matrix and the precipitates were determined by selected area atom probe analysis. Experimental conditions were chosen to prevent systematic errors due to preferential evaporation and retention of any solute.

In the case of grain boundary segregation, the solute coverage may be fundamentally determined with a method based on the Gibbsian interfacial excess. The Gibbsian interfacial excess [15,16] of element i , Γ_i , is defined as

$$\Gamma_i = \frac{N_{i(\text{excess})}}{A} = \frac{N_i - N_{i(\alpha)} - N_{i(\beta)}}{A}, \quad (1)$$

where $N_{i(\text{excess})}$ is the excess number of solute atoms associated with the interface, A is the interfacial area over which the interfacial excess is determined, N_i is total number of solute atoms in the volume analyzed, $N_{i(\alpha)}$ and $N_{i(\beta)}$, are the number of solute atoms in the two adjoining regions α and β either side of the dividing surface. The interfacial area A that is sampled in a typical atom probe experiment is given by $A = \pi r_a^2 / \cos \phi$, where r_a is the effective radius of the probe aperture and ϕ is the angle between the unit normal to the interface plane and the unit vector parallel to the cylinder of analysis ($\phi \neq 90^\circ$) and is determined from either the projection of the interface in the field ion micrographs or examination of the field ion specimen in the transmission electron microscope. The actual number of atoms collected must take account of the less than perfect detection efficiency of the single atom detector. The detection efficiency of the atom probe used in these investigations has been determined to be 0.62. The interfacial excess can be related to the fractional monolayer coverage of solute, Φ , by comparing it to the saturation value of the excess, $\Gamma_{i(\text{sat})}$, i.e., $\Phi = \Gamma_i / \Gamma_{i(\text{sat})}$. There are a number of interpretations of what constitutes a monolayer [17]. The method used in this paper was based on the number of atoms expected on the closest packed plane of the crystal structure. For example, in NiAl this is the (110) plane and therefore a monolayer coverage consists of 1.72×10^{19} atoms m^{-2} with a width $w = d_{110} = 0.20$ nm.

Results and Discussion

Ni_3Al

In boron-doped Ni_3Al , atom probe analysis revealed that most of the boron addition remained in solid solution in the matrix. In addition, field ion microscopy revealed that boron was found to segregate to

dislocations, Fig. 1, low angle boundaries, Fig. 2, stacking faults (SISF), Fig. 3, antiphase boundaries, Fig. 4, and grain boundaries Figs. 5 and 6 [18-21]. All the dislocations and boundaries shown in these field ion micrographs are decorated with brightly-imaging spots. The unique single atom identification capability of the atom probe was used to determine that these brightly-imaging spots are individual boron atoms. In the cases of the low angle boundary and the stacking fault, the boron decoration is more clearly revealed in field ion micrographs that were taken during field evaporation, shown in Figs. 2b and 3b, since the contrast due to the individual atomic terraces (i.e., the concentric rings) is minimized rendering the brightly-imaging boron atoms more prominent. It is evident from the narrow width of the segregation exhibited in these field ion micrographs that the boron segregation is confined to the interface plane. Boron segregation to the dislocations, low angle boundaries, stacking faults and antiphase boundaries should influence the mechanical properties through a solute drag type mechanism.

A pair of field ion micrographs of two different grain boundaries is shown in Fig. 5. It is evident from the distribution of the brightly-imaging atoms in the field ion micrographs that the boron coverage at the grain boundaries varies significantly. This variation was also observed along different regions of the same grain boundary as shown in Fig. 6. For example, in some regions the coverage was extremely low, e.g., Figs. 6a and 6d, whereas in other regions there was significantly higher coverage, e.g., Fig. 6c and 6e. Atom probe quantification of the boron level and the nickel to aluminum ratio at two grain boundaries is summarized in Table 1. In addition the local solute distribution along a single grain boundary is shown. The boron coverage along this grain boundary was found to vary from over a significant range of 9.4 to 61.9%. Similar wide variations have been observed at other grain boundaries. The $\text{Ni}:\text{Al}$ ratio was found to vary from 2.2 to 3.4. It should be noted that the $\text{Ni}:\text{Al}$ ratio of the matrix in these aluminum-depleted materials was 3.1. No simple correlation between the $\text{Ni}:\text{Al}$ ratio and the boron coverage was found.

Table 1. The Gibbs interfacial excesses of boron at grain boundaries in Ni_3Al .

Analysis	Ni:Al Ratio	Gibbs Interfacial Excess, Γ_i atoms m^{-2}	Coverage %
1a	3.40	4.5×10^{18}	26.7
1b	2.92	4.2×10^{18}	24.0
1c	2.23	4.8×10^{18}	27.0
1d	2.30	1.7×10^{18}	9.4
1e	2.81	3.6×10^{18}	20.4
1f	2.70	1.1×10^{19}	61.9
1 (avg.)	2.73	5.0×10^{18}	28.2
2 (avg.)	2.73	2.3×10^{18}	13.0

Some grain boundaries exhibited evidence of more extensive boron segregation, as shown in Fig. 7. In most cases, the boron segregation appeared as extended brightly-imaging lenticular regions at the grain boundary. The maximum thickness of these regions was estimated to be ~ 3 nm and their length was often larger than the field-of-view of the image, i.e., greater than ~ 100 nm. The composition of these regions was determined to be 26-31 at. % Al and up to 5 at. % B. Although the possibility of multilayer segregation cannot be totally excluded, it is more likely that this boron-enriched region is an ultrathin precipitate or grain boundary film. However, the measured composition does not appear to be consistent with the tau phase (nickel-aluminum-boride).

In addition to this extended morphology, some shorter (5 to 10 nm in length) boron-enriched regions were also observed, as shown in Figs. 7b and 7c. Most of the segment of the grain boundary shown in Fig. 7b exhibited low coverage with only an isolated boron atom evident. However, a small facet that exhibited significantly higher boron coverage was also observed on this grain boundary. This observation indicates that the local boundary plane can have a strong influence on the segregation behavior. These smaller boron-enriched regions were also observed to be located preferentially on one side of the grain boundary as shown in Fig. 7c. It should be noted the absence of rings in

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Fig. 1. Field ion micrograph of a boron-decorated dislocation in Ni_3Al .

Fig. 2. Field ion micrograph of a boron-decorated low angle boundary (misorientation $<1^\circ$) in Ni_3Al .

Fig. 3. Field ion micrograph of a boron-decorated stacking fault in cold worked Ni_3Al annealed for 1 h at 800°C .

Fig. 4. Field ion micrograph of a boron-decorated antiphase boundary in Ni_3Al .

Fig. 5. Field ion micrographs of boron-decorated grain boundaries in Ni_3Al .

Fig. 6. Field ion micrograph of a boron-decorated grain boundary in Ni_3Al .

Fig. 8. Field ion micrographs of boron clusters in (a) Ni_3Al and (b) $\text{Ni}_{74}\text{Al}_{26}$.

Fig. 7. Field ion micrographs of a grain boundary boron-enriched phase in Ni_3Al .

the field ion images of these boron-enriched regions does not necessarily indicate that they are amorphous regions since the imaging behavior of boride phases (see below) is such that few if any rings are normally observed in the field ion images of crystalline boride precipitates.

No ultrafine intragranular precipitates have been observed in these boron-doped Ni-24.2 at. % Al alloys. However, boron clustering has been observed in alloys with higher aluminum contents (Ni-25 at. % Al and Ni-26 at. % Al), as shown in Fig. 8 [18]. These features were found to contain up to approximately 10 boron atoms and were classified as clusters due to their small size and the absence of any other elements. The presence of these clusters suggests that there is a abrupt change in the boron matrix solubility at the stoichiometric composition.

NiAl

In boron-doped NiAl, atom probe analyses revealed that boron segregates to the grain boundaries, as shown in Fig. 9. As in the case of Ni₃Al, the variation of the brightly-imaging boron atoms indicated that the boron coverage varied along the grain boundary. Due to the favorable orientation of this grain boundary, $\phi = 90^\circ$, several analyses at different positions along its length were possible. The results are summarized in Table 2 in order of analysis position along the boundary. The boron coverage was found to vary by a factor of ~7.5 from 3.6 to 27.4% or $\Gamma_1 = 6.2$ to 46.3×10^{17} atoms m^{-2} . Most sections of the boundary exhibited nickel depletion (Ni:Al = 0.84) with one section exhibited a significant nickel enrichment (Ni:Al = 1.27). Boron enrichment was observed in both nickel depleted and nickel enriched sections. No strong correlation between the Ni:Al ratio and the coverage was apparent in these data. It should be noted that despite the extremely small radius of the cylinder of analysis used in these grain boundary analyses, $r_1 = 0.4$ to $r_2 = 0.75$ nm, a significant number of atoms from the grain interior on either side of the boundary were also collected. Although this extended radius does not affect the coverage, it influences the accuracy of the Ni:Al ratio at the exact boundary plane.

Table 2. The Gibbs interfacial excesses of boron at a $\Sigma 3$ coincident site lattice grain boundary in NiAl + 0.04 at. % B aged 1 h at 900°C.

Analysis	Ni:Al Ratio	Gibbs Interfacial Excess Γ_1 atoms m^{-2}	Coverage %
1	0.77	9.6×10^{17}	5.7
2	0.91	6.2×10^{17}	3.6
3	1.27	8.7×10^{17}	5.2
4	0.79	8.7×10^{17}	5.2
5	0.80	1.2×10^{18}	7.2
6	0.88	1.3×10^{18}	7.6
7	0.84	2.3×10^{18}	13.4
8	0.94	1.5×10^{18}	9.1
9	0.82	1.9×10^{18}	11.0
10	0.81	4.6×10^{18}	27.4
Average	0.88	1.6×10^{18}	9.5

Previous atom probe characterization of a binary Ni-49 at. % Al alloy by Camus et al. demonstrated that approximately two thirds of the analyzed grain boundaries were depleted in aluminum to $-40 \pm 1\%$ Al (Ni:Al = 1.5) at the boundary and the remaining one third did not exhibit any significant depletion [24,25].

Unlike boron-doped Ni₃Al which exhibits significant matrix boron solubility, atom probe analysis of the matrix in an NiAl + 0.15 at. % B alloy revealed that the boron solubility was extremely low (0.003 ± 0.007 at. % B after aging for 1 h at 500°C and 0.026 ± 0.003 at. % B after aging for 1 h at 1100°C) [22]. However, the boron in the matrix and at the grain boundaries does not fully account for the total boron in the material and indicates that the remaining boron must be associated with another microstructural feature.

The majority of the boron was determined to be partitioned to ultrafine precipitates ranging in size from 1 to 20 nm, as shown in Fig. 10. Atom probe analysis revealed that the precipitate composition was consistent with a MB₂ type precipitate where the metallic content M was a mixture of titanium, vanadium, chromium and tungsten. The metallic content was found to vary significantly from precipitate to precipitate suggesting that these precipitates were formed from the trace elements in the material. Some carbon was also detected in these precipitates. Similar ultrafine MC precipitates have also been observed in carbon-doped NiAl [22] and un-doped single crystal NiAl [23].

Due to their small size and relatively high number density, these precipitates produce significant precipitation hardening and are therefore detrimental to the mechanical properties. This precipitation hardening also offsets the benefits of the boron segregation to the high angle grain boundaries. It has been shown that the number density of these precipitates can be decreased by reducing the quantities of trace impurities in the alloy by zone refinement [23]. Alternatively, the number density of these precipitates can be reduced and their size increased with an appropriate heat treatment [22].

In NiAl containing 0.7 at. % Mo annealed 1 h at 1000°C and 1 h at 500°C, atom probe analysis [26] indicated extremely low solubilities of the molybdenum and other trace impurities in the matrix: Ni- 50.4 $\pm$ 1.2 at. % Al - 0.005 $\pm$ 0.001 % Mo, 0.007 $\pm$ 0.002 % Fe, 0.005 $\pm$ 0.001% Si and N and 0.0004 $\pm$ 0.0004 %V. The large error on the aluminum content indicates a significant variation from one region to another.

The majority of the molybdenum in this alloy was found to be concentrated in a low number density (~ 1 to $2 \times 10^{21} m^{-3}$) of 10- to 50-nm-diameter spherical molybdenum precipitates. The composition of these body-centered cubic precipitates was determined to be Mo- 3.3 $\pm$ 0.6 at. % Al with residual amounts of 0.06 $\pm$ 0.03% B, 0.04 $\pm$ 0.02% Ni, 0.01 $\pm$ 0.01% Fe, and 0.04 $\pm$ 0.02% V. The precipitates were observed both in the NiAl matrix, as shown in Fig. 11, and also at grain boundaries. Calculations based on an Orwin mechanism indicate that these precipitates generate a significant increase in yield stress of between 82 and 210 MPa depending on the measured minimum and maximum size of the precipitate. These values are in good agreement with the differences in the yield stresses of the molybdenum-doped (254 MPa) and undoped alloys (154 MPa) since a larger number of the smaller diameter precipitates were observed.

A field ion micrograph of a $\Sigma 3$ coincident site lattice grain boundary in NiAl containing 0.7 at. % Mo annealed 1 h at 1000°C and 1 h at 500°C is shown in Fig. 12. Due to the favorable orientation of the grain boundary plane with respect to the specimen axis, $\phi = 90^\circ$, extensive characterization of this boundary was possible. The Gibbsian interfacial excesses of the solutes along this boundary are summarized in Table 3. These coverages were significantly lower than the boron coverages observed in the boron-doped NiAl. Despite the relatively low coverages, significant enrichments of molybdenum, nitrogen and silicon, carbon, boron, and iron are evident at the grain boundary.

Table 3. The Gibbs interfacial excesses of solute at a $\Sigma 3$ coincident site lattice grain boundary in NiAl + 0.7 at. % Mo aged 1 h at 1000°C and 1 h at 500°C.

Element	Gibbs Interfacial Excess, Γ_1 atoms m^{-2}	Coverage %
Mo	9.9×10^{16}	0.58
N/Si	6.5×10^{16}	0.38
C	1.1×10^{16}	0.07
B	5.7×10^{15}	0.03
Fe	3.8×10^{15}	0.02

A 2 1/2 D reconstruction of the solute distribution along this grain boundary is shown in Fig. 13. This reconstruction was created by taking the z coordinate of each solute atom as position along the composition profile. The solutes were then assumed to be randomly distributed along the grain boundary plane to give the x coordinate ($y=0$). Since the diameter of the cylinder of analysis varied from 3.4 to 4.3 nm during this

Fig. 9. Field ion micrographs of a boron-decorated grain boundary in NiAl.

Fig. 10. Field ion micrographs of MB₂-type precipitates in NiAl.

Fig. 11. Field ion micrograph of a molybdenum precipitate in molybdenum-doped NiAl.

analysis, this randomization will only introduce a small one-dimensional uncertainty in the reconstruction. Although most of the solute was distributed uniformly along the grain boundary, there was some visual evidence of regions of higher than average local concentrations of iron, molybdenum, nitrogen and carbon. There was also some evidence of molybdenum-nitrogen enrichment. This small non-uniformity in the solute distribution may arise from small changes in the boundary plane or the presence of grain boundary dislocations which changes the local atomic environment and thereby influence the segregation behavior.

TiAl

These materials differ from the previous examples in that they contain two primary phases: an $L1_0$ -ordered γ phase and a DO_{19} -ordered α_2 phase. In addition, the compositions of these phases vary significantly depending on the heat treatment and may be far from their equilibrium or steady state values. For example, in the materials examined, the aluminum content of the γ phase was found to vary from ~40-50 at. % Al and that of the α_2 phase was typically 34-36 at. % Al. Due to these variations, the identity of phase based solely on the aluminum content alone was not reliable. Since the α_2 phase is known to scavenge oxygen and other interstitial elements [27,28], it typically has an oxygen content of one to two orders of magnitude higher than the γ phase. For example, the oxygen content of the α_2 phase in a Ti-47% Al-2% Cr-1.8% Nb-0.2% W-0.15 % B alloy was found to be ~33 times that of the γ phase. Therefore, phase identification was based on the measured aluminum content in conjunction with the measured oxygen levels as well as the appearance of the phase in the field ion image.

Field ion micrographs of the γ and brightly-imaging α_2 phases are shown in Fig. 14. The width of these α_2 laths was found to vary from less than 5 nm (Fig. 14b) to more than 20 nm (Fig. 14a) in Ti-47% Al-2% Cr-1.8% Nb-0.2% W-0.15 % B that was stress-relieved for 2 h at 900°C. No evidence for boron segregation to the γ - α_2 phase interface has been obtained from atom probe analysis of the interface.

These materials also contain a significant number of γ - γ interfaces as shown in Fig. 15. However, no evidence for boron segregation to the γ - γ phase interface has been obtained. The segregation behavior of the other microalloying elements is discussed below.

The boron levels in the γ and α_2 phases were found to be significantly depleted from the bulk alloy concentration. For example, the solubilities of boron in the γ and α_2 matrix phases were found to be 0.011 ± 0.006 at. % B and <0.003 at. % B, respectively in Ti-47% Al-2% Cr-1.8% Nb-0.2% W-0.15 % B that was stress-relieved for 2 h at 900°C.

The majority of the boron was concentrated in a variety of borides including TiB, TiB₂ and a chromium-enriched (Ti,Cr)₂B precipitate [29]. A field ion micrograph of a M₂B precipitate in a Ti-47% Al-2% Cr-1.8% Nb-0.2% W-0.15 % B alloy that was stress-relieved for 2 h at 900°C is shown in Fig. 16. With the exception of the smaller (< 50 nm thick) chromium-enriched (Ti,Cr)₂B precipitates, most of the borides were larger than the field of view of the field ion microscope, i.e., greater than ~100 nm. The compositions of some of the precipitates are summarized in Table 4. It is evident that a significant proportion of the microalloying additions is present in these boride precipitates. The partitioning of the microalloying elements to these borides may reduce their availability for other more beneficial mechanisms. Although these coarse borides may help pin the grain boundaries and retard grain growth, it is likely that improvements could be made in the effectiveness of the boron additions.

Table 4. Composition of boride precipitates as measured in the atom probe. (atomic %)

Alloy	Measured Composition	Type
Ti-47% Al-2% Cr-1.8% Nb-0.2% W-0.15 % B	(Ti _{94.3} Nb _{3.2} Cr _{1.1} W _{1.1} Al _{0.3})B _{1.7}	MB ₂
	(Ti _{92.6} Nb _{2.5} Cr _{0.6} W _{0.6} Al _{3.7}) _{0.95} B	MB
	(Ti _{89.5} Nb _{0.5} Cr _{3.0} W _{3.1} Al _{2.7}) _{0.6} B	M ₂ B

A field ion micrograph of an α_2 - γ interface in a tungsten containing Ti-47% Al-2% Cr-1.8% Nb-0.2% W-0.15 % B alloy that was stress-relieved for 2 h at 900°C is shown in Fig. 17. Several brightly-imaging atoms are apparent both at the interface and in the near boundary region in the α_2 phase. Since this alloy contains boron and several refractory elements that all exhibit similar brightly-imaging behavior, it is not possible to positively identify these brightly-imaging atoms from their appearance in the field ion image. The average tungsten content of the γ phase in this material was determined to be 0.16 ± 0.02 at. % W. The tungsten content of the α_2 phase was found to vary significantly from one region to another [30]. The measured compositions ranged from 0.17 ± 0.15 at. % W to 0.39 ± 0.08 at. % W with an average of 0.33 ± 0.06 at. % W. Part of this variation may be due to a tail in the segregation profile at the α_2 - γ interface as indicated by the width of the decoration in the field ion micrograph. These results indicate that tungsten is partitioning to the α_2 phase. The α_2 - γ interface region was found to be enriched to a level of 0.68 ± 0.45 at. % W. The tungsten interfacial segregation supports the previous observation that tungsten additions stabilize the α_2 lamellae against dissolution during thermal aging [8-10].

Tungsten segregation to the γ - γ interfaces was also observed in these materials [30]. A composition profile taken such that the axis of the cylinder of analysis was aligned almost precisely along a γ - γ interface is shown in Fig. 18. The orientation of the interface with respect to the specimen axis is shown in the transmission electron micrograph of the needle-shaped field ion specimen shown in Fig. 19. This orientation permitted the distribution of solute along the interface to be examined. It is evident from the composition profile that there was a significant and relatively uniform enrichment of tungsten at this γ - γ interface. The average coverage at this interface was determined to be 4.6% W (Gibbsian interfacial excess $\Gamma_1 = 6.4 \times 10^{17} \text{ m}^{-2}$). This coverage gives an enhancement factor of ~29 over the γ matrix level. A tungsten composition profile taken across a γ - γ interphase is shown in Fig. 20a. The average coverage at this interface was determined to be 3.7% W (Gibbsian interfacial excess $\Gamma_1 = 4.7 \times 10^{17} \text{ m}^{-2}$). This coverage gives an enhancement factor of ~23 over the γ matrix level. The chromium and niobium composition profiles taken across this γ - γ interphase are also shown in Fig. 20b. Although the chromium indicates some enrichment at this γ - γ interface, the niobium does not. The variation in chromium enrichment from interface to interface is in agreement with previous results from Yamaguchi et al. [31, 32].

The chromium and niobium additions were also found to partition between the γ and α_2 phases. In Ti-47% Al-2% Cr-1.8% Nb-0.2% W-0.15 % B that was stress-relieved for 2 h at 900°C, the average chromium content of the α_2 phase was 2.9 ± 0.2 at. % Cr and that of the γ phase was 1.6 ± 0.06 at. % Cr indicating that chromium is enriched in the α_2 phase. In the Ti-47% Al-2% Cr-1.8% Nb-0.2% W-0.15 % B alloy, the niobium was also found to have a slight preference for the γ phase (1.9 ± 0.06 at. % Nb) over the α_2 phase (1.6 ± 0.13 at. % Nb).

Atom probe analyses of the chromium and niobium levels at both the γ - γ and γ - α_2 phase interfaces revealed that some interfaces were enriched in both niobium and chromium and some interfaces exhibited no enrichments.

Conclusions

In boron-doped Ni₃Al, the boron additions were found to segregate to dislocations, low angle boundaries, stacking faults, antiphase boundaries, and grain boundaries. The boron and aluminum levels at grain boundaries were found to vary both from boundary to boundary and also along an individual boundary segment. In some cases, a boron-enriched thin film up to 3 nm thick was observed. In aluminum-enriched Ni₃Al, ultrafine clusters containing up to approximately 10 boron atoms were detected in the matrix.

In contrast, the majority of the boron in boron-doped NiAl was determined to be in the form of ultrafine MB₂-type precipitates. These precipitates are detrimental to the mechanical properties and offset the benefits of the boron segregation to the high angle grain boundaries. In molybdenum-doped NiAl, atom probe analyses indicated extremely low

Fig. 12. Field ion micrograph of a $\Sigma 3$ grain boundary in molybdenum-doped NiAl.

Fig. 13. Reconstruction of the solute segregation along a $\Sigma 3$ grain boundary in molybdenum-doped NiAl. Each symbol is an individual atom.

Fig. 14. Field ion micrograph of brightly-imaging α_2 laths in TiAl. (a) 5 nm and (b) 20 nm thick.

Fig. 15. Field ion micrograph of a γ - γ interface in TiAl.

Fig. 16. Field ion micrograph of a chromium-enriched M_2B precipitate in TiAl.

Fig. 19. Transmission electron micrograph of the field ion specimen used to produce the composition profile shown in Fig. 18

Fig. 17. Field ion micrograph of an α_2 - γ interface in TiAl.

Fig. 18. Composition profile along a γ - γ interface in TiAl.

Fig. 20. Composition profiles for tungsten, chromium and niobium across a γ - γ interface in TiAl.

solubilities of the molybdenum and other trace impurities in the matrix and significant enrichments of molybdenum, nitrogen and silicon, boron, and iron at the grain boundaries.

In boron-doped two phase α_2 - γ TiAl containing chromium, niobium, and tungsten, the boron level was found to be significantly depleted from the bulk level in both the α_2 and γ phases and a variety of coarse borides including TiB, TiB₂ and a finer chromium-enriched (Ti,Cr)₂B precipitate was observed. The tungsten and chromium were determined to partition preferentially to the α_2 phase and also to segregate to the α_2 - γ and γ - γ interfaces. These results indicate that a significant proportion of the microalloying elements are consumed by the boride precipitates.

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