

## The effect of boron on the chemistry of grain boundaries in stoichiometric Ni<sub>3</sub>Al

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### ABSTRACT

X-ray spectra have been obtained, using a 1 nm diameter electron beam, from thin foils of stoichiometric Ni<sub>3</sub>Al with and without boron (0.35 at.%). The boron addition produces nickel enrichment at grain boundaries, which implies a disordering of this region. Disordering of the grain boundary and the consequent expected increase in grain boundary dislocation mobility are suggested to be the reason for the ductility improvement of Ni<sub>3</sub>Al due to boron.

### § 1. INTRODUCTION

It is now well established that small additions of boron can improve the low-temperature ductility of polycrystalline, L1<sub>2</sub>-structured Ni<sub>3</sub>Al (Aoki and Izumi 1979, Liu and Koch 1983, Huang, Taub and Chang 1984, Taub, Huang and Chang 1984, Liu, White and Horton 1985, Weihs, Zinoviev, Viens and Schulson 1987). For example, Liu *et al.* (1985) have shown that the room-temperature elongation of nickel-rich Ni<sub>3</sub>Al can be increased from near zero to over 50% by the addition of 500 p.p.m. boron. It is known that the boron segregates to the grain boundaries (White, Padgett, Liu and Yalisgrove 1984, Liu *et al.* 1985, Choudhury, White and Brooks 1986, Miller and Horton 1986, Horton and Miller 1987) and that plastic flow precedes fracture (Schulson, Weihs, Viens and Baker 1985, Baker, Schulson and Horton 1987). A recent model suggests that the effect of this segregated boron is to ease the accommodation of slip transmittal across grain boundaries (Schulson, Weihs, Baker, Frost and Horton 1986, Schulson, Baker and Frost 1987). Consistent with this suggestion is the observation (Schulson *et al.* 1986) that boron reduces the value of the constant  $k$  (by ~40% for a 0.35 at.% addition) in the Hall-Petch-type relationship (Schulson *et al.* 1985)  $\sigma_y = \sigma_0 + kd^{-0.8}$ , where  $k$  can be associated with the difficulty of slip transmittal across grain boundaries. One reason for this easier transmittal may be that boron improves the mobility of the grain boundary dislocations (Schulson *et al.* 1986) which must, in general, be produced to accommodate the Burgers vector difference in lattice dislocations moving into and out of the boundary.

Recent modelling has indicated that, in general, slip is easier across disordered (f.c.c.) rather than ordered (L1<sub>2</sub>-structured) grain boundaries (Frost 1988, King and Yoo 1987). A possible reason, then, for the improved mobility of grain boundary

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dislocations in boron-doped Ni<sub>3</sub>Al is that the segregated boron disorders the grain boundaries (Frost 1988, King and Yoo 1987). It has been predicted that the disordering could arise because nickel is attracted to the boron-enriched boundary (Frost 1988); that is, through a process of segregation.

This paper reports the preliminary results of a study which shows that boron causes grain boundaries in stoichiometric Ni<sub>3</sub>Al to become enriched with nickel, and thus effectively to become partially disordered.

We note that nickel enrichment has previously been detected in boron-doped nickel-rich Ni<sub>3</sub>Al using time-of-flight mass spectrometry on a field ion microscope (Sieloff, Brenner and Burke 1987); no comparison was made with unalloyed Ni<sub>3</sub>Al of a similar composition. Since a recent computational study of grain boundaries in Ni<sub>3</sub>Al (Foiles 1987) has indicated that as the overall composition of Ni<sub>3</sub>Al deviates from stoichiometry the composition of the grain boundary deviates more rapidly from stoichiometry, then nickel-rich Ni<sub>3</sub>Al should have grain boundaries that are nickel-enriched. This means that no firm conclusion concerning further boron-induced nickel enrichment could be drawn from the field ion microscopy study.

## §2. EXPERIMENTAL

Discs 3 mm in diameter were cut from triple-extruded rods of stoichiometric Ni<sub>3</sub>Al with 0.35 at.% B, manufactured as described elsewhere (Schulson *et al.* 1985). Thin foils were prepared using electrochemical polishing techniques (Baker and Schulson 1984) and briefly (5 min) ion-milled before examination. For comparison, stoichiometric Ni<sub>3</sub>Al discs, both as-received and annealed for 1 h at 1273 K, were also made into thin foils.

Specimens were examined in a Vacuum Generators HB 501 FEG/STEM operated at 100 kV. Grain boundaries parallel to the electron beam were examined using a 1 nm diameter (f.w.h.m.) incident beam, and X-ray data were collected using a Link L25 Series E 13° take-off angle windowless detector and a Link AN 10000 analyser.

Two types of experiment were performed. First, the beam was directed at a grain boundary, and then at the adjacent matrix in one or both grains, for 100 s each, and either the resulting X-ray spectrum was recorded or, for quantification, the X-ray counts corresponding to the Ni K<sub>α</sub> emission peak and the Al K<sub>α</sub> emission peak were recorded. Since the composition of the matrix is 75:25 Ni:Al, the X-ray counts and composition could be used to determine the thickness of the foil using a standardless foil routine. The thickness was then used to calculate the Ni/Al ratio at the grain boundary. At the boundary, the accumulation of X-rays was periodically interrupted, and any specimen drift corrected.

Data were quantified using the Cliff-Lorimer ratio method (Cliff and Lorimer 1975), that is using

$$C_A/C_B = k_{AB}(I_A/I_B),$$

where  $C_A$  and  $C_B$  are the weight percentages of elements A and B, respectively, and  $k_{AB}$  is the constant relating the X-ray intensities  $I_A$  and  $I_B$ , for elements A and B respectively, to the chemical compositions. The calculated value of  $k_{AlNi}$  used was 0.917.

Multiple point profiles were obtained across a boundary plane. The example shown (fig. 2) consisted of 20 points, 1 min per point, spaced 5.8 nm apart. A new Link software system was used which automatically corrects for drift during the collection of the X-ray spectrum by automatically stopping X-ray acquisition followed by the acquisition

of an image of the specimen. The image is compared with the previous image using a correlation routine which determines whether there has been any drift. If there has been, then the program calculates the direction and magnitude of the drift and then returns the beam to the intended point of analysis on the specimen. For the analysis presented in this study the computer was instructed to perform the above sequence every 10 s. This system allows high-resolution compositional profiles to be obtained which are not influenced by specimen drift.

### § 3. RESULTS

Figure 1 shows X-ray spectra obtained by placing a stationary probe on a grain boundary in boron-doped stoichiometric Ni<sub>3</sub>Al (fig. 1 (a)) and on the nearby matrix (fig. 1 (b)). Comparison of the heights of the Ni L<sub>α</sub> line and Al K<sub>α</sub> line in each case indicates that the nickel concentration appears to be higher at the grain boundary. Even though the boron concentration in the grain boundary is probably around 5–6 at.% (Liu *et al.* 1985), no boron was detected.

Table 1 shows compositions for three grain boundaries (two positions per boundary) determined, as outlined above, from Ni K<sub>α</sub> and Al K<sub>α</sub> X-ray counts. These data confirm the qualitative observation shown in fig. 1 that grain boundaries in boron-doped Ni<sub>3</sub>Al are nickel-enriched. Note that this enrichment was observed when comparing Al K<sub>α</sub> lines to both Ni L<sub>α</sub> and Ni K<sub>α</sub> lines (which are respectively of shorter and longer wavelength than the Al K<sub>α</sub> line) so the enrichment is real and not a differential absorption effect, due perhaps to thickness variations. For comparison, similar data were collected from grain boundaries in unalloyed stoichiometric Ni<sub>3</sub>Al, and table 2 gives the results. The values obtained for the grain boundary composition, using the same procedure as above, were close to the stoichiometric composition and represent an evaluation of the scatter in data using this technique.

Figure 2 shows an example of compositions, obtained using the multipoint profile technique, across a grain boundary in boron-doped stoichiometric Ni<sub>3</sub>Al. Each point represents ~15 000 Ni K<sub>α</sub> counts and ~2500 Al K<sub>α</sub> counts. The boundary is clearly nickel-enriched.

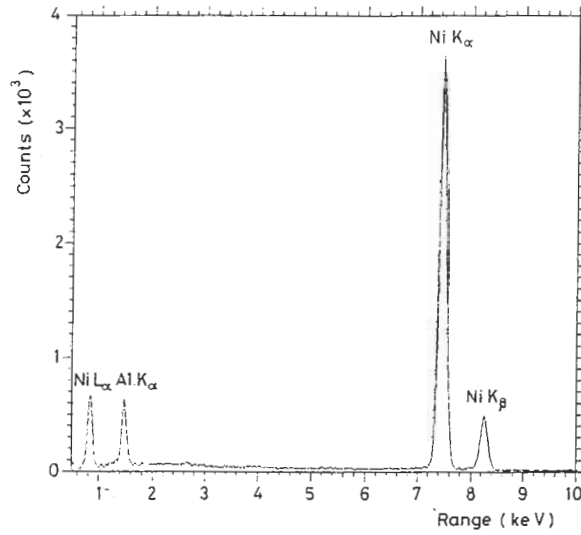
### § 4. DISCUSSION

The results show that the grain boundaries in boron-doped stoichiometric Ni<sub>3</sub>Al are nickel-enriched, as predicted by Frost (1988). This is consistent with the observation that the boride that forms at the grain boundaries in heavily boron-doped Ni<sub>3</sub>Al (i.e. doped beyond the boron solubility limit) is nickel-rich (Liu *et al.* 1985).

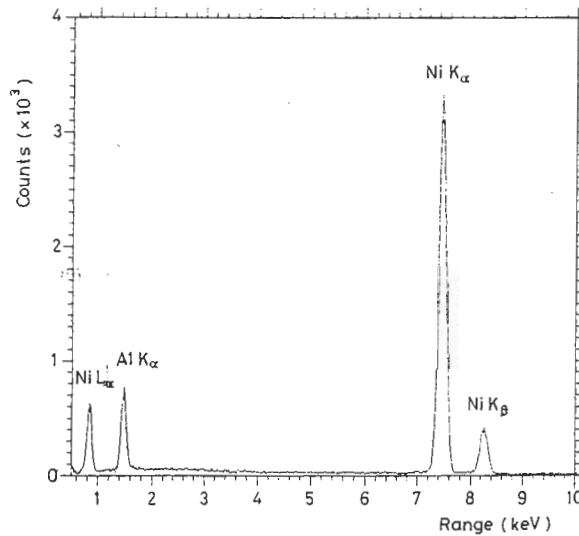
One implication of this nickel enrichment is that Auger spectrometry data used previously to determine boron concentrations at grain boundaries may need to be reassessed (White *et al.* 1984, Liu *et al.* 1985, Choudhury *et al.* 1986). The boron concentrations at intergranular fracture surfaces in these studies were obtained by comparing the boron peak with the nickel peak. Since the boron addition attracts excess nickel to the boundary, the boron concentrations at grain boundaries may be a little higher than previously suggested.

The present data indicate that the grain boundaries in boron-doped Ni<sub>3</sub>Al are nickel-enriched, but since the X-ray data were obtained from a volume greater than that occupied by the grain boundary alone, grain boundary enrichment is presumably higher than is indicated in table 1. This nickel enrichment is presumably the root of the

Fig. 1



(a)



(b)

X-ray spectra from (a) a grain boundary and (b) the nearby matrix in boron-doped stoichiometric  $\text{Ni}_3\text{Al}$ . Note that the height of the  $\text{Ni L}_\alpha$  peak is greater than that of the  $\text{Al K}_\alpha$  peak at the boundary.

disordering which was suggested (Frost 1988) to be the cause of the greater mobility of grain boundary dislocations in boron-doped  $\text{Ni}_3\text{Al}$ .

Excess nickel, then, at a grain boundary can be pictured as disordering or reducing the degree of long-range atomic order of the boundary, possibly by producing a composition at the grain boundary corresponding not to  $\text{Ni}_3\text{Al}$  but to a  $\text{Ni}(\text{Al})$  solid solution. The role of the boron is to attract excess nickel to the grain boundary; it is this

Table 1. Ni K<sub>α</sub> and Al K<sub>α</sub> X-ray counts from three grain boundaries and the adjacent matrix in stoichiometric Ni<sub>3</sub>Al containing 0.35 at.% B. The calculated grain boundary 'compositions' are given (see the text for details).

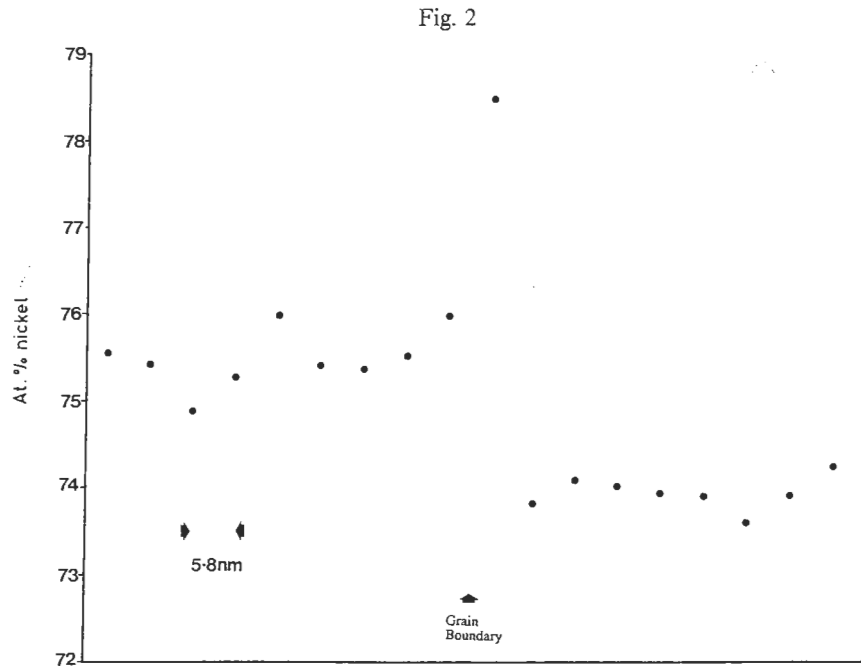
Grain boundary number	Matrix No. 1		Matrix No. 2		Grain boundary		Calculated composition at grain boundary (at.%)	
	Ni	Al	Ni	Al	Ni	Al	Ni	Al
1	44767	5528	—	—	45604	4547	78.7	21.3
	34321	4326	—	—	35444	3348	79.8	20.2
2	16188	1321	—	—	15988	692	84.5	15.5
	17436	1335	—	—	17483	539	87.4	12.6
3	31769	4055	35887	3986	34721	3179	79.0	21.0
	—	—	—	—	40101	3892	78.0	22.0

Table 2. Ni K<sub>α</sub> and Al K<sub>α</sub> X-ray counts from three grain boundaries and the adjacent matrix in stoichiometric Ni<sub>3</sub>Al annealed for 1 h at 1273 K. The calculated grain boundary 'compositions' are also given (see the text for details).

Grain boundary number	Matrix No. 1		Matrix No. 2		Grain boundary		Calculated composition at grain boundary (at.%)	
	Ni	Al	Ni	Al	Ni	Al	Ni	Al
1	75348	11311	81721	12200	72801	10510	75.7	24.3
	124565	17375	135999	18959	99275	13365	75.7	24.3
2	174419	19646	184641	20068	176127	19428	75.0	25.0
	64584	8418	102972	13010	91033	11734	75.2	24.8
3	49333	6953	56672	7846	63792	8494	75.9	24.1

excess nickel that disorders the boundary and improves the ductility (by improving the mobility of grain boundary dislocations). This effect allows us to explain the effect of boron on different compositions of Ni<sub>3</sub>Al. Nickel-rich Ni<sub>3</sub>Al, when boron-doped, should have highly nickel-enriched—and hence disordered—grain boundaries, and be very ductile. However, grain boundaries in aluminium-rich Ni<sub>3</sub>Al, which are expected to be normally aluminium-enriched, would also contain more nickel when the alloy is boron-doped, but this would make the grain boundary composition less aluminium-enriched. That is, adding boron to aluminium-rich Ni<sub>3</sub>Al 'orders' rather than 'disorders' the grain boundaries and, hence, does not improve the ductility of the material. The composition of grain boundaries of boron-doped and unalloyed Ni<sub>3</sub>Al of non-stoichiometric composition is at present being studied.

One suggestion from the present work is that ductility in strongly ordered alloys requires the grain boundaries to be (partially) disordered, although at present the concept of long-range atomic ordering at the grain boundary is somewhat vague.



Compositions obtained from a multipoint profile across a grain boundary in boron-doped stoichiometric  $\text{Ni}_3\text{Al}$  (see text for details).

### §5. CONCLUSIONS

The addition of boron to stoichiometric  $\text{Ni}_3\text{Al}$  leads to nickel enrichment at the grain boundaries and, presumably, to 'disorder' there. Nickel, in other words, co-segregates with boron. This enrichment and attendant disordering is presumably the cause of the improved mobility of grain boundary dislocations in boron-doped  $\text{Ni}_3\text{Al}$  which, it has been suggested (Schulson *et al.* 1986, Schulson *et al.* 1987), is the reason for the ductility improvement and for the decrease in the effectiveness with which grain boundaries strengthen  $\text{Ni}_3\text{Al}$ .

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