

Effects of Hafnium, Boron and Zirconium on the Ductility of $Ni_3(Al, Fe)$ Intermetallic Compounds

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Abstract Effects of hafnium, boron and zirconium on the ductility of $Ni_3(Al, Fe)$ intermetallic compounds were studied using tensile test and SIMS analysis. $Ni_3(Al, Fe)$ alloy with 0.1 at.% Hf, 0.05 at.% B and 0.1 at.% Zr additions showed maximum elongations of about 30% at 300K, 10% at 300K and 14% at 473K, respectively. The fracture mode of the alloy without the additive was the mixture of intergranular and transgranular fractures, but the addition of Hf, Zr or B changed the fracture mode to transgranular only. SIMS analysis showed that the beneficial effects of Hf, Zr or B segregation on the grain boundary strength are consistent with the grain boundary cohesion theory.

Introduction

Ni_3Al intermetallic compounds, like many other $L1_2$ ordered alloys (Cu_3Au structure), exhibit anomalous yield strength behavior with increasing temperature^{1,2)}, which is a very desirable property for high temperature applications. The adherent aluminium oxide film formed on the surface of this material preserves corrosion and oxidation. Also, advantages of low density and low cost compared with commercial superalloys make the intermetallic compounds a promising substitute for high temperature applications. However, at present, they are not put into practical use in structural applications because they are extremely brittle at room temperature. The low ductility of polycrystalline Ni_3Al has been attributed to the inherent weakness of the grain boundaries, since single crystals of the intermetallic compound have been shown to exhibit high ductilities in all crystal orientations.³⁾

While it appears that the segregation of embrittling impurities on the grain boundaries is not responsible for the inherently low cohesive strength of the grain boundaries of some

$L1_2$ intermetallic compounds, the strength of these boundaries can be improved by segregation of other impurities. Aoki and Izumi^{4,5)} have shown that boron addition in Ni_3Al alloy suppresses the tendency for intergranular fracture, resulting in high ductility at ambient temperature. Also Taub et. al.⁶⁾ obtained a further improvement of ductility up to 10% using boron addition and rapid solidification of Ni_3Al alloy. These works stimulated that the ductile Ni_3Al intermetallic compounds may be developed by the alloying or by the crystallographic modification which lowers the degree of order or compositional deviation from stoichiometry. Takasugi and Izumi⁷⁾ found that a partial replacement of aluminium with iron or manganese in Ni_3Al reduced the valency and the size differences between nickel and modified aluminium atoms, resulting in significantly improving the ductility and lowering the propensity for grain boundary fracture in Ni_3Al alloys. The segregation of chemical species, which are present as solutes at very low concentrations, at the grain boundaries has attracted a great deal of attention in recent years.

The objectives of this paper are to present a consistent approach to describe the grain boundary segregation in $Ni_3(Al, Fe)$ intermetallic compounds and to discuss the implications or behavior of the grain boundaries.

Experimental Procedure

Boron-, hafnium- or zirconium- added $Ni_3(Al, Fe)$ intermetallic compounds were prepared using a vacuum arc melting furnace in an argon atmosphere. The material was remelted several times, each time inverting the material on the hearth plate to obtain homogeneous material. Raw materials used in this study were 99.99% pure nickel, 99.9% pure aluminium, 99.9% pure iron and 99% pure boron, hafnium and zirconium. The size of ingots was about $75mm \times 20mm \times 10mm$. The compositions of the alloy are shown in Table 1.

Table 1. Alloy Composition(at.%)

Ni	Al	Fe	B	Hf	Zr
bal.	12.5	12.5	0.05	—	—
bal.	12.5	12.5	0.10	—	—
bal.	12.5	12.5	—	0.05	—
bal.	12.5	12.5	—	0.10	—
bal.	12.5	12.5	—	—	0.05
bal.	12.5	12.5	—	—	0.10

Chemical analysis of the alloy was not performed, but the weight loss during each melting was very slight. (The chemical composition reported above is based on this assumption.) The bulk crystals and a polycrystalline button were homogenized at 1273K for 48h in a vacuum of better than 10^{-4} Torr to achieve micro-homogeneity and then air-cooled to room temperature. After the heat treatment, the ingots were machined into standard specimens of 3mm gauge diameter. X-ray analysis of the polycrystalline button, carried out on a diffractometer, showed that the materials consist of mainly $L1_2$ ordered structure at room temperature.⁸⁾ Tensile tests were carried out at a strain rate of approximately $1.3 \times 10^{-3} s^{-1}$ in

an Instron testing machine at several temperatures, then sliced with a diamond saw into small specimens ($2mm \times 3mm \phi$) for SIMS analysis.

All specimens were polished to the #1500 sand paper and cleaned with the ion milling before SIMS analysis. The operating conditions were as follows : primary ion = O_2^+ , ion energy = 8KeV, ion current = 1×10^{-8} A, scanning size = $250\mu m \times 250\mu m$, and beam size = $\sim 10\mu m$. Cameca IMS-4F SIMS system was used to analyse the surfaces. To examine the distribution of boron, hafnium and zirconium in $Ni_3(Al, Fe)$, elemental mapping was employed. The X-ray diffraction studies were made using Rigaku diffractometer with crystal monochromated Cu $K\alpha$ radiation. Crystal structures were determined from the X-ray data. The operating conditions were as follows : accelerating voltage = 30KV, current = 40mA, and scanning speed = $4^\circ / min$.

Results & Discussion

The tensile elongations of $Ni_3(Al, Fe)$ intermetallic compounds with B, Hf or Zr are shown as a function of temperature in Fig. 1. The room temperature tensile elongation of a 0.1 at.% Hf (Fig. 1(a)) in the $Ni_3(Al, Fe)$ alloy was significantly higher (30%) than that of Ni-10Al-15Fe alloy (8%) prepared using a vacuum arc melting furnace by T. Takasugi et. al.⁹⁾ Also, the tensile elongations of $Ni_3(Al, Fe)$ alloy with 0.1 at.% B (FIG. 1(b)) and 0.1 at.% Zr (FIG. 1(c)) were 10% and 14%, respectively. The fracture behavior of the $Ni_3(Al, Fe)$ samples without additive, broken by tensile tests, were found to be the mixed fracture mode, whereas that of the sample with B, Hf or Zr additions was the transgranular fracture. The results of the fractography are in agreement with the previous works¹⁰⁻¹⁹⁾ which reported that the alloying with the ternary additions significantly increases the ductility and reduces the propensity for the intergranular fracture in the Ni_3Al alloy.

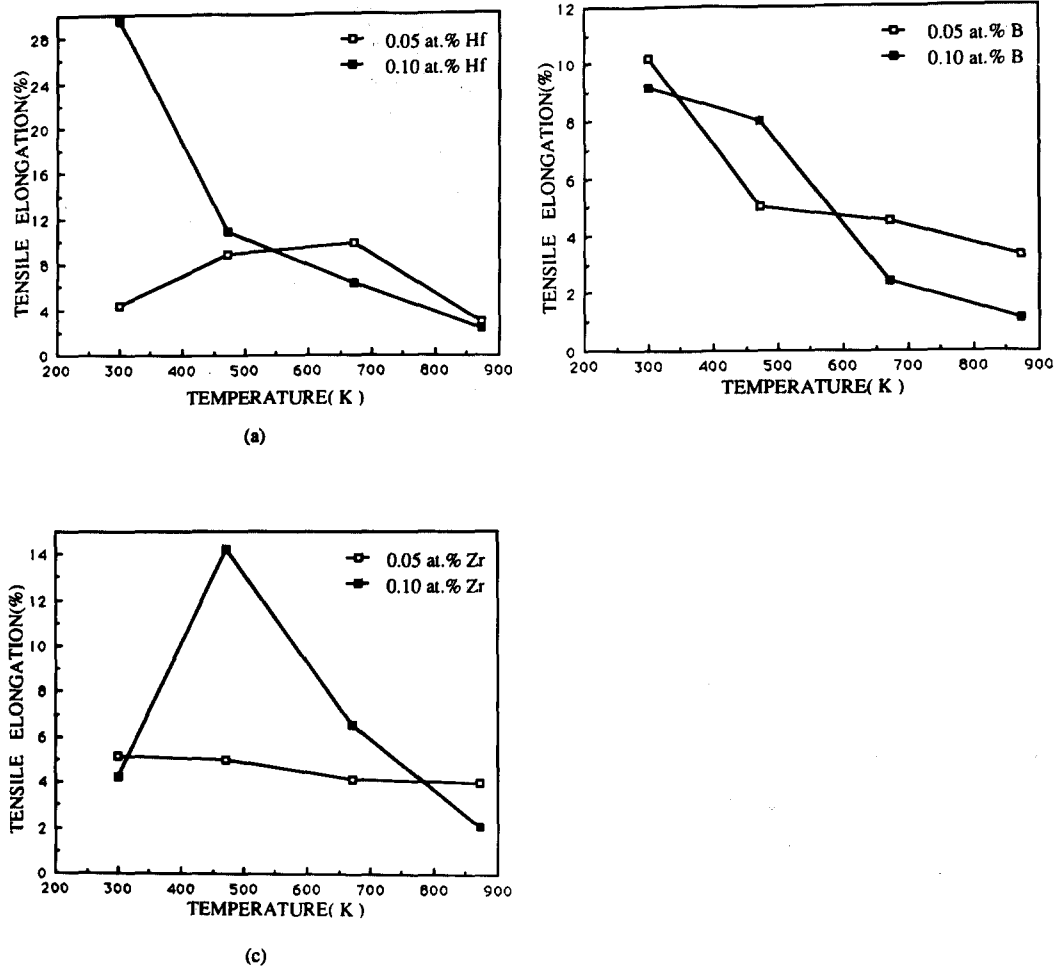


Fig. 1. Temperature dependence of tensile elongation in Ni₃(Al, Fe) intermetallic compounds with additives.

Segregation of B, Hf and Zr to grain boundaries was studied using mapping and line scanning across the grain boundaries after the heat treatment. A typical set of results obtained on heat treated Ni₃(Al, Fe) alloys is shown in Fig. 2. The experimental observations of the B, Hf and Zr segregation to grain boundaries are consistent with the Rice's segregation theory²⁰. Rice has developed a grain boundary cohesion theory that relates the relative intensity which a solute segregates at grain boundaries and free surfaces to the nature of that solute's effect on grain boundary cohesion. Rice's analysis recognizes the possibility that some elements might segregate strongly in the grain boundaries, but not in the

free surfaces. For such cases, the analysis predicts an enhancement of grain boundary cohesion (i.e. demote grain boundary failure). The experimental segregation behavior results in an effective increase in grain boundary cohesive energy that suppresses fracture along the grain boundaries. Understanding of this phenomena would prove to be most valuable in selecting the microalloying components in alloy design efforts where grain boundary fracture is the main problem. Such understanding would also provide a focal point for the future research on grain boundary segregation and fracture.

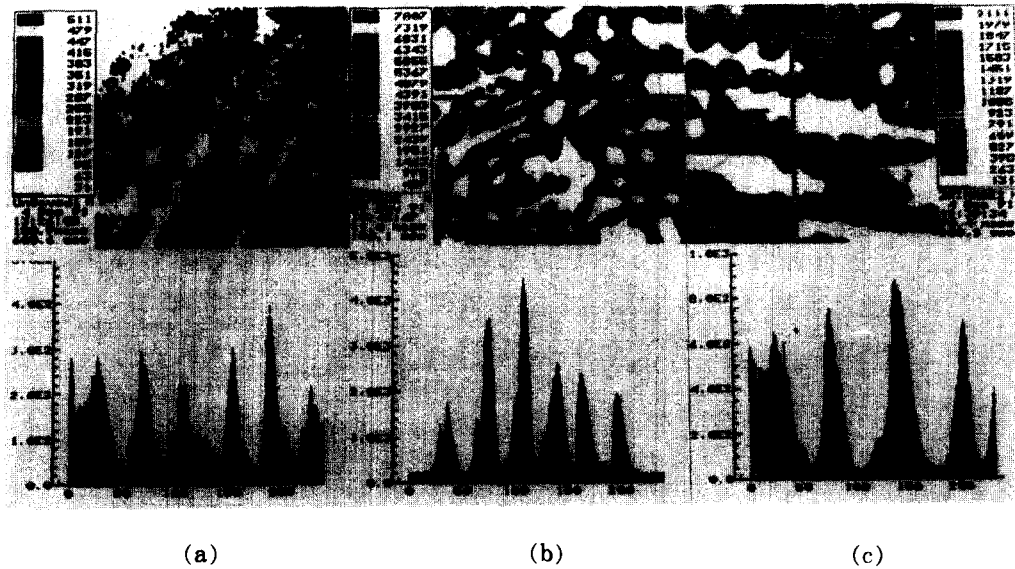


Fig. 2. SIMS mappings and line scanings of (a) hafnium, (b) boron and (c) zirconium in $Ni_3(Al, Fe)$ intermetallic compounds.

Conclusion

1. $Ni_3(Al, Fe)$ alloy with 0.1 at.% Hf addition showed a maximum elongation of about 30% at 300K, 0.05 at.% B addition showed about 10% at 300K, and 0.1 at.% Zr addition showed about 14% at 473

2. The fracture mode of $Ni_3(Al, Fe)$ alloy without additive were mixed, but the additions of Hf or Zr or B to the $Ni_3(Al, Fe)$ alloy changed the fracture completely to the transgranular fracture mode.

3. The SIMS analysis showed that the beneficial effects of Hf or Zr or B segregation on the grain boundary strength are in qualitative agreement with the grain boundary cohesion theory.

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