Title	Effects of boron doping on the grain growth behaviour of γ / γ nickel-aluminium alloy
Author(s)	Chiu, YL; Ngan, AHW
Citation	Materials Research Society Symposium: Nucleation and growth processes in materials, Boston, MA., 29 November-1 December 1999, In Materials Research Society Symposium Proceedings, 1999, v. 580, p. 189-194
Issued Date	2000
URL	http://hdl.handle.net/10722/46659
Rights	Materials Research Society Symposium Proceedings. Copyright © Materials Research Society.

EFFECTS OF BORON DOPING ON THE GRAIN GROWTH BEHAVIOUR OF γ/γ' NICKEL-ALUMINIUM ALLOY

Y.L.CHIU, A.H.W.NGAN

Department of Mechanical Engineering, The University of Hong Kong, Pokfulam Road, Hong Kong, P.R.China

ABSTRACT

Effects of 0.5 at. % boron doping on $Ni_{85}Al$ γ/γ' superalloys were investigated for the first time, yielding a number of observations not previously observed in the literature. First, the grain growth kinetics of both the doped and undoped alloys were found to disobey the simple Nielsen law $d = Ct^n$, but instead follow an equation of the type $d = C\ln(t) + C_0$. The constants C and C_0 were found to be respectively 10.2 and 23.2 for the boron-free alloy, and 6.2 and 14.2 for the boron-doped alloy, i.e., the grain growth rate was retarded significantly upon boron doping. Such a retarding effect is thought to be due to the formation of a boron-nickel cosegregated zone observed at the grain boundaries of the doped alloy; the width of the zone, in μm's, is two to three orders of magnitude larger than the boron induced disordered layer found in nickel rich Ni_3Al compounds doped with boron. Other associated effects of the cosegregated zone include a sharp increase in toughness, much better slip transmission across grains and reduced work-hardening rates. Another intriguing point is that the γ' precipitates were found to segregate to the grain boundaries in the boron-free alloy after cold rolling, but no such segregation of γ' precipitates has been observed in the boron-doped alloy. The different deformation microstructures and the retarded grain growth rates upon boron doping will be discussed.

INTRODUCTION

Effects of boron doping on the mechanical properties and microstructures of Ni_3Al alloys have been widely investigated since the observation that small amounts of boron addition could significantly ameliorate the ductility of hypo-stoichiometric Ni_3Al alloys[1,2]. This boron-induced ductilizing effect might be accounted for by several means. First, the grain boundary cohesive strength in Ni_3Al, which was believed to be intrinsically weak as demonstrated in many theoretical computations, was found to be strengthened upon boron doping in theoretical calculations[3,4]. Furthermore, the grain boundary energy of the boron doped Ni_3Al was found to be less than that of the pure binary Ni_3Al[5]. Boron doping is also very effective in hindering environment embrittlement, say in H_2O environment, but not in dry H_2, either by preventing the formation of atomic hydrogen or by retarding the diffusion of atomic hydrogen along grain boundaries[6,7]. Another proposed explanation attributed the ease of dislocation intergranular slip to the formation of a disordered grain boundary phase upon boron doping[8,9].

Although it has been well recognised that boron doping ductilizes nickel-rich Ni_3Al alloys, no general agreement has yet been reached on the effect of boron doping on the recrystallisation in Ni_3Al alloys[10,11]. The work of Yang and Baker[10] demonstrated a retarded recrystallisation kinetics in Ni_3Al upon boron doping, while the observations of Zhou et al.[11] showed no difference in the recrystallisation kinetics of Ni_3Al as boron doped up to 500 ppm. Moreover, they found that grain growth kinetics of Ni_3Al followed the equation of $d = Ct^n$ with n ranging from 0.2 to 0.4 regardless of the amount of boron addition. The grain growth behaviour should have been affected if solute atoms, say boron, had segregated to the grain

Mat. Res. Soc. Symp. Proc. Vol. 580 © 2000 Materials Research Society

boundaries. It was therefore natural to ascribe the lack of effects on grain growth behaviour to insufficient amount of boron, which might be the result of the desegregation process at high temperatures[12].

EXPERIMENT

Two alloy ingots with composition of $Ni_{85}Al$ were prepared by melting pure nickel and aluminium in a high frequency induction melter with argon protection. The ingots were remelted several times and homogenised at 1100 °C for 48 hours in vacuum to remove composition fluctuation. Boron addition with a nominal value of 0.5 at. % was added in one ingot while the other one is left boron-free. After homogenisation, the toughness of both alloys was evaluated by Charpy impact tests carried out on specimens pre-notched with a wire cutter. Compression tests were conducted at a strain rate of 10^{-3} s^{-1} to investigate the yield behaviour of both alloys. The compression specimens were of dimension 4×4×7 mm and electro-polished for *post-mortem* trace observation. Homogenised microstructure and the fractured surface were observed in scanning electron microscopes. Thin foils were prepared from the deformed alloys, electro-polished in H_2C_5OH + $HClO_4$ and observed in a transmission electron microscope. The homogenised alloys were cold rolled homogeneously to 80% reduction in thickness, then annealed at 1200°C for different duration to evaluate the grain growth behaviour of both alloys.

RESULTS

1. Homogenised microstructure

After homogenisation, both the boron-free and the boron-doped alloy have grain sizes of about 200μm. However, significant difference exists between the grain boundary structures of the two alloys. As shown in fig 1(a), the γ' precipitates are of similar sizes up to the grain boundaries in the boron-free alloy. However, a transition zone can be easily identified in the homogenised boron-doped alloy (fig. 1(b)). This grain boundary zone is of μm's in width, i.e., two to three orders of magnitude larger than the boron-induced disordered layer reported in nickel-rich Ni_3Al compounds. The γ' precipitates inside the zone are considerably smaller than that at the grain interior. Upon EDX analysis, the nickel composition in this zone was found to be higher than that at the grain interior.

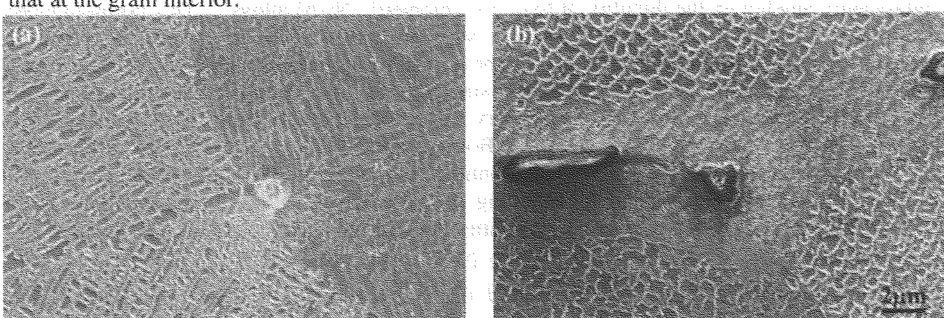

Fig.1. SEM micrographs showing the homogenized microstructure of (a) the boron-free alloy and (b) the boron-doped alloy.

2. Grain growth kinetics

As shown in fig.2, the grain growth behaviour of both alloys was found to obey an equation of the type $d = C\ln(t) + C_0$ rather than the simple Nielsen law $d = Ct^n$. Moreover, the grain growth rate of the boron-doped alloy is much larger than that of the boron free one, i.e., C and C_0 are 10.2 and 23.2 respectively for the boron-free alloy while they are only 6.2 and 14.2 for the boron-doped alloy. This retardation in grain growth kinetics upon boron doping will be explained later.

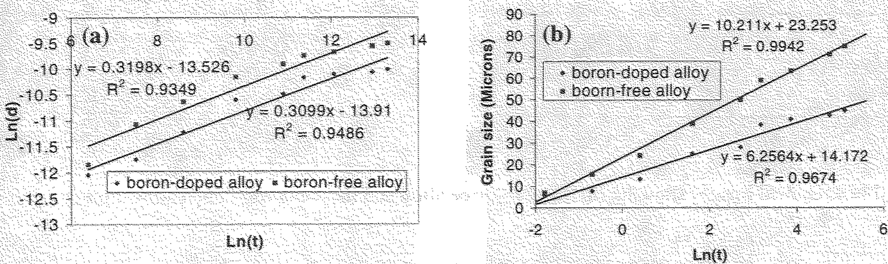

Fig.2. The grain growth behaviour plotted (a) after Nielsen law and (b) as an equation $d = C\ln(t) + C_0$ for the boron-free and boron-doped alloy. There is systematic deviation between the data points and Nielsen's law.

3. Mechanical Properties and deformation microstructure

The energy absorption per unit area in the Charpy impact tests of the superalloy was found to increase by more than 5 times from about 0.18 MN/m to 1.0 MN/m after only 0.5 at.% boron addition. As shown in fig.4, the fracture behaviour of both alloys differs significantly. The boron-doped alloy fractured in a ductile mode characterised by a dimpled appearance. The boron-free alloy, however, fractured in a completely transgranular fashion, and the fracture surface was rather smooth and free from deformation marks. Some intergranular cracks are also observable.

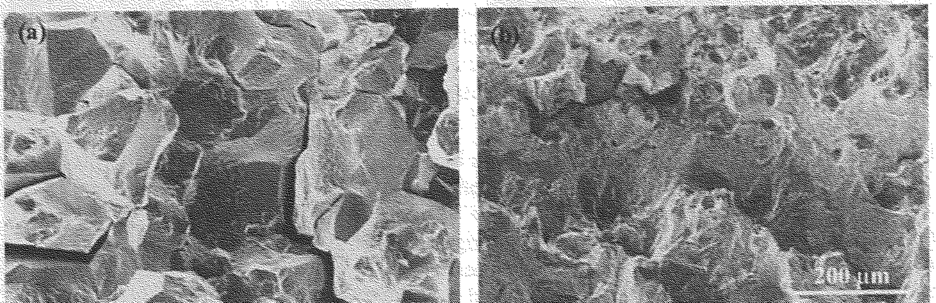

Fig.3. Fractography of (a) the boron-free alloy and (b) the boron-doped alloy obtained in impact test.

The compression yield stress of the boron-doped alloy was found to be about 410 MPa, a little larger than the 380MPa for the boron-free alloy. On the other hand, the work hardening rate was found to be decreased upon boron doping. Consistently, the hardness value of the boron-free and the boron-doped alloy are 233 HV and 212 HV respectively, i.e., being slightly lower in the boron-doped alloy than the boron free one. Fig.4 shows the slip trace on the lateral surface of the boron-doped and boron-free specimens compressed to a similar strain. The slip lines start and terminate at grain boundaries in the boron-free alloy. Moreover, grains protrude out heavily after compression. This, however, is not the case for the boron-free alloy, where slip lines span widely and no grain protrusion can be identified.

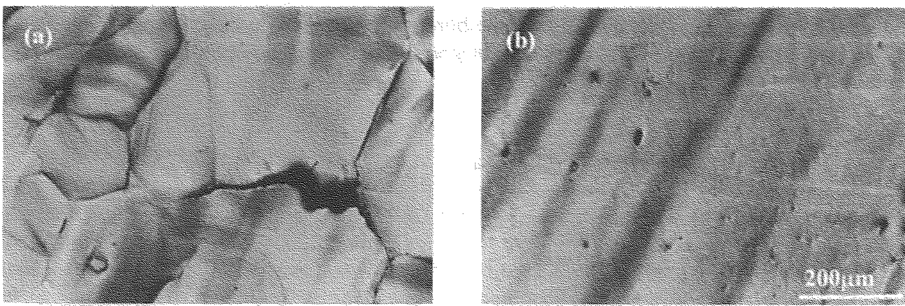

Fig.4. Optical images showing (a) the boron-free alloy and (b) the boron-doped alloy after compressed to ~7% strain

Fig. 5(a) and (b) show the grain boundary microstructures of the boron-free and boron-doped alloys after compressed to about 7% permanent strain. The dislocation density in the γ' precipitates at the vicinity of the boron-free alloy is much higher than that in the boron-doped alloy. The electron channelling contrast images of the same grain boundaries are shown in fig.5(c) and (d). A grain boundary zone can also be identified in the boron-doped alloy.

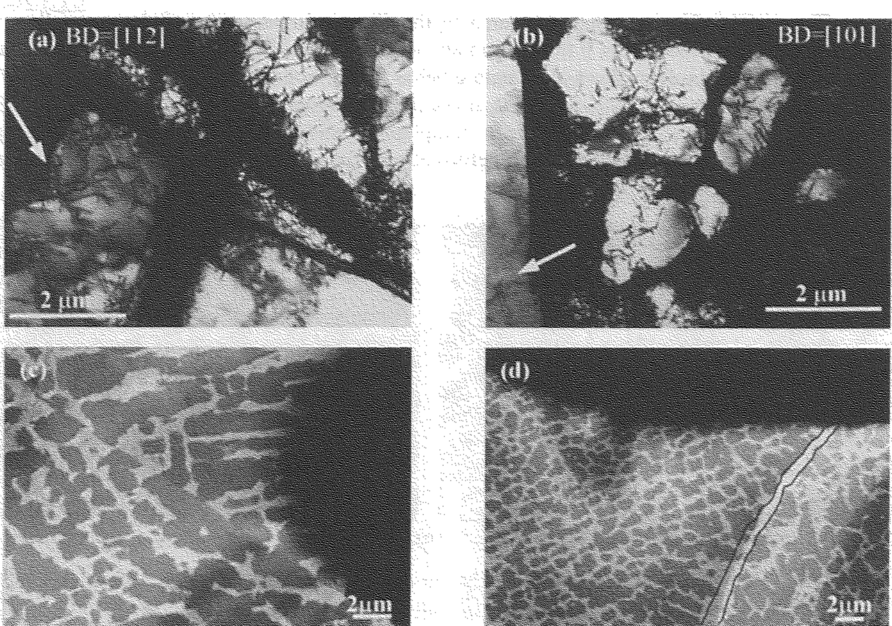

Fig.5. TEM images showing grain boundary of (a) the boron-free alloy with higher dislocation density ($g = [1\bar{1}\bar{1}]$) and (b) the boron-doped alloy with lower dislocation density (g=[020]]) after compressed to ~7% strain. The grain boundaries in (a) and (b) as viewed by electron channeling contrast are shown in (c) and (d) respectively. A grain boundary zone is seen as outlined in (d) in the boron-doped alloy.

Fig.6 shows the microstructure of the boron-free and boron-doped alloys after homogeneously cold rolled to 80% reduction in thickness. The γ' precipitates, which show dark contrast in images, segregate to grain boundaries in the boron-free alloys after cold rolling while no such segregation of γ' precipitates can be identified in the boron-doped alloy.

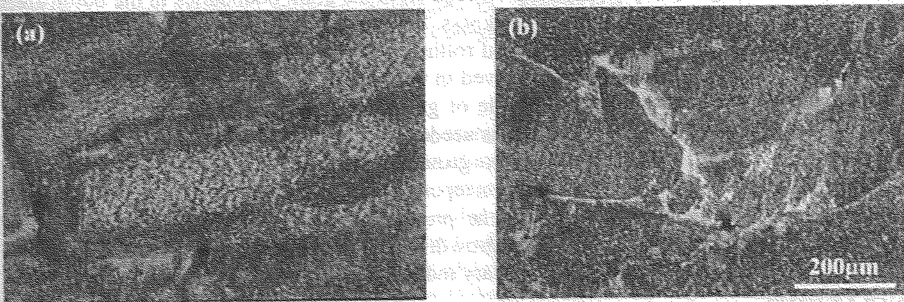

Fig.6. Optical images showing the microstructure of (a) the boron-free alloy and (b) the boron-doped alloy after cold rolled to 80% reduction in thickness.

DISCUSSION

Segregation of boron to grain boundaries of Ni_3Al alloys has been widely investigated and well documented[13,14]. One of the most pronounced evidences was obtained using AES by Liu et al[2], where boron addition was found to strongly segregate to the grain boundaries rather than to any other free surface. Accompanying this chemical segregation at grain boundaries, boron addition changes the fracture mode from completely intergranular to completely transgranular. Furthermore, Choudhury et al.[12] found that boron desegregated from grain boundaries of Ni_3Al alloys when subjected to heat-treatment at high temperatures, say 1050°C. Fracture mode of the boron-doped samples changed from transgranular for those slowly cooled to intergranular mode for those rapidly quenched. In the present investigation, a similar change in the fracture mode has also been observed after 0.5 at.% boron doping and this is associated with a significant increase in the impact toughness (the energy absorption per unit area increased by more than five times). The segregation of boron to grain boundaries, therefore, might also be responsible for the toughening incurred.

Schulson and co-workers have proposed a mechanism which ascribed the boron induced ductilizing of Ni_3Al alloy to a grain boundary chemical composition change after boron-doping[9]. Ni_3Al pertains the ordered $L1_2$ structure up to very near its' melting temperature[15]. However, Baker and Schulson[16] observed a disordered grain boundary phase of about 20nm wide with TEM after boron doping. Moreover, *in-situ* observation of dislocation intergranular slip in the boron-doped alloy was also made[9]. In addition, boron-induced reduction of the Hall-Petch slope was identified by several researchers[17]. The dislocation slip across grain boundaries in the boron-doped Ni_3Al alloys, therefore, was facilitated mainly by the disordered phase formed along grain boundaries[8].

Schulson's mechanism is highly favoured as far as the microstructural observations in the present study are concerned. Firstly, as shown in fig. 1 (b), a grain boundary nickel-rich zone has been observed in the homogenized boron doped alloy while no such zone has ever been found in the boron-free alloy. The size of such a grain boundary zone is several microns wide. The difference between the size of the grain boundary phase reported[16] in Ni_3Al alloys and the size of the grain boundary nickel-rich zone in the present study may be due to the different surplus nickel contents in the two cases. The large quantity of surplus nickel atoms in the present study may make the formation of larger sized nickel-rich zone possible while the size of the grain boundary disordered phase in Ni_3Al alloys may be mainly restricted by the limited amount of surplus nickel.

As shown in fig. 6(a), γ precipitates segregated to the grain boundaries in the boron-free alloy after cold rolled to 80% reduction in thickness. However, such a segregation of γ has never been found in the boron-doped alloy after cold rolling. The facts that only 0.5 at. % boron was added and that a well defined zone was observed in the homogenized boron-doped alloy before cold rolling strongly suggest an important role of grain boundary structure in the cold rolling process. Further investigation into this aspect is needed. In the present study, the most intriguing point concerns the significantly retarded grain growth kinetics upon 0.5 at. % boron doping. Comparing with the experimental temperature reported for boron desegregation to happen in Ni_3Al alloys, the annealing temperature in the present study, say 1200°C, is much higher. Nevertheless, the significantly retarded grain growth rate upon boron doping strongly suggest a hindering effect of boron solute in grain boundary mobility.

CONCLUSIONS

In the present study, 0.5 at. % boron doping in a γ/γ' nickel-aluminium alloy was found to retard the grain growth kinetics significantly, improve the impact toughness by about five times, and to decrease the work hardening rate. These phenomena can be related to a grain boundary nickel-rich zone observed after boron doping. This grain boundary zone may also account for the observed different microstructures after cold rolling.

ACKNOWLEDGEMENTS

This research was supported by a grant from the Research Grants Council, Hong Kong Special Administrative Region, P.R.China (Project HKU 7078/98E)

REFERENCES

1. K. Aoki, O. Izumi, J. Jap. Inst. Metals, **43**, 1190 (1979).
2. C. T. Liu, C. L. White, J. A. Horton, Acta Metall., Vol. **33**, pp.213-229 (1985).
3. O. Ito, and H. Tamaki, Acta metall. Mater., **43**, 2731 (1995).
4. F.H. Wang, C.Y. Wang, and J.L. Yang, J. Phys.: Condens. Mater., **8**, 5527 (1996).
5. S. Frank, J. Rüsing, Chr. Herzig, Intermetallics, **4**, 601-611 (1996).
6. X.J. Wan, J.H. Zhu, and K.L. Jing, Scripta Metall. Mater., **31**, 677 (1994).
7. K.H. Lee, J.T. Lukowski, and C.L. White, Scripta Mater. **35**, 1153 (1996).
8. A.H. King and M. H. Yoo, Scripta Metall., 1987, Vol. **21**, pp. 1115-1119.
9. E. M. Schulson, T. P. Weihs, I. Baker, H. J. Frost and J. A. Horton, Acta metall., Vol. **34**, No. 7, pp. 1395-1399 (1986)
10. Y. Yang, and I. Baker, Scripta Mater., **34**, 803 (1996).
11. B. Zhou, Y.T. Chou, and C.T. Liu, Intermetallics, **1**, 217 (1993).
12. A. Choudhury, D.L. White, and C.R. Brooks, Scripta Metall., **20**, 1061 (1986),
13. D. N. Sieloff, S.S. Brenner and Hua Ming-Jian, Mat. Res. Soc. Symp. Proc., Vol. **133**, pp. 155-160. (1989).
14. D.L. Lin, D. Chen and H. Lin, Acta metall. mater., Vol. **39**, No. 4, pp. 523-528 (1991).
15. R. W. Cahn, P. A. Siemers, and E. L. Hall, Acta metall., Vol.**35**, 2753 (1987)
16. I. Baker and E. M. Schulson, Scripta Metall., Vol. **23**, pp. 1883-1886 (1989).
17. P. S. Khadkikar, K. Vedula, and B. S. Shabel, Metall. Trans., Vol. **18A**, pp. 425-428 (1987).