OVERVIEW

Ductilization of L_{12} Intermetallic Compound Ni_3Al by Microalloying with Boron*

By K. Aoki**

Many intermetallic compounds have attractive high-temperature mechanical properties; however, poor ductility at room temperature severely restrict their use as high-temperature structural materials. The brittleness in an L_{12} intermetallic compound Ni_3Al , caused by the intergranular fracture, has been dramatically overcome by microalloying with boron. Ductilization of Ni_3Al has renewed a great interest in the intermetallic compounds as a new category of structural materials. Full details of the discovered ductilizing boron effect in Ni_3Al are given in this paper.

(Received January 22, 1990)

Keywords: intermetallic compounds, nickel aluminide, ductility, ductilization, intergranular fracture, grain boundary segregation, brittleness, microalloying, structural materials

I. Introduction

Recently, high temperature ordered intermetallic compounds have attracted much attention as high temperature structural materials because of their high temperature strength, excellent creep resistance, and other good mechanical properties⁽¹⁾. Until recently, it has been generally recognized that the major obstacle to the development of structural materials based on intermetallic compounds is their extreme brittleness at room temperature. The origins of this brittleness in intermetallic compounds are the high yield stress relative to the cleavage stress, insufficient numbers of active slip systems, grain boundary intrinsic weakness, and impurity segregation to grain boundaries. In 1979, Aoki and Izumi succeeded in overcoming the grain boundary brittleness of Ni_3Al by microalloying with a small amount of boron (on the order of 0.1 mass%)⁽²⁾ which has a strong tendency to segregate to the grain boundaries. Ductilization of Ni_3Al , which has stimulated much interest in mechanical properties of intermetallic compounds, was a natural consequence of a great systematic investigations with an intention of ductilizing intermetallic compounds, and of course it could not be obtained by accident. Describing the background and the process of the development of the ductile Ni_3Al are deemed useful for the further development of intermetallic compounds. This overview paper focuses on ductilization of Ni_3Al by microalloying.

II. The Background of Ductilization of Ni_3Al

In 1969, we started a study of mechanical properties of intermetallic compounds⁽³⁾⁽⁴⁾. We initially investigated the deformation behavior of beta-brass with the B2 structure. It showed interesting mechanical properties full of variety⁽³⁾⁽⁴⁾. The first interesting phenomenon was the positive temperature dependence of the yield stress showing a maximum around 500 K⁽⁴⁾. The second was room temperature ductility showing 20–30% elongation as seen in Fig. 1⁽⁴⁾. Since intermetallic compounds were generally accepted to be very brittle at room temperature, we were impressed by room temperature ductility of beta brass, which became one of the motives for the effort to ductilize intermetallic compounds.

At that time we started the research, the positive temperature dependence of the yield stress was observed just for the following intermetallic compounds; Ni_3Si ⁽⁵⁾, β -CuZn⁽⁶⁾, and Ni_3Al ⁽⁷⁾. Since then, this anomalous be-

Fig. 1. Temperature dependence of the elongation of beta brass.

* The 1989 Meritorious Honor Award Lecture of the Japan Institute of Metals.

** Institute for Materials Research, Tohoku University, Sendai 980, Japan.

havior has been found in many intermetallic compounds, such as $\text{Co}_3\text{Ti}^{(8)}$, $\text{Ni}_3\text{Ga}^{(9)}$, $\text{Ni}_3\text{Ge}^{(10)}$, $\text{Zr}_3\text{Al}^{(11)}$, Pt_3Ti , Pt_3Cr and so on⁽¹²⁾, and $\text{TiAl}^{(13)}$. The positive temperature dependence of the yield stress was interesting, but the peak temperature of the yield stress in beta brass was too low as a practical high-temperature material. Then, we turned our attention to other intermetallic compounds which are of much practical usage.

III. Mechanical Properties of the Intermetallic Compound Ni_3Al

1. Ni_3Al as a high temperature material

There exists many intermetallic compounds with high melting points. Among them, we chose Ni_3Al and investigated mechanical properties of it for the following reasons. Ni_3Al is a major strengthening constituent of the commercial nickel-base superalloys and is responsible for their high temperature strength and creep resistance. Its yield stress shows the positive temperature dependence over a wide temperature range⁽⁷⁾. In spite of excellent high temperature mechanical properties, the practical use of it suffers from the severe problem of poor ductility at room temperature. The overcoming of the brittleness is essential for high temperature structural applications. Since the single crystal Ni_3Al showed some ductility⁽¹⁴⁾, suggesting intrinsic ductility, we expected that ductilization of Ni_3Al would be realized.

2. Compressive deformation of polycrystals of Ni_3Al —stoichiometry effects

Ni_3Al has a composition range extending approximately 2 mol% on each side of stoichiometry⁽¹⁵⁾. Constitutional vacancies in the Al-rich side were known to have a prominent influence on mechanical properties of NiAl with the B2 structure. With the objective of making clear the relation between mechanical properties and defect structures in Ni_3Al , the nature of the defect structure arising from the deviation from stoichiometry was determined from the variation of the lattice parameter and density. We were unable to detect the constitutional vacancy on either side of stoichiometry⁽¹⁶⁾. Furthermore, the long-range order parameter S showed the maximum ordering at every composition, suggesting the formation of antisite defects (aluminum atoms on nickel sites, and vice versa)⁽¹⁶⁾. Thus, the constitutional vacancy was absent, and the substitution occurred monotonously with the deviation from stoichiometry in Ni_3Al .

On the contrary, the mechanical properties were very sensitive to alloy compositions and test temperatures⁽¹⁷⁾⁽¹⁸⁾. Polycrystals of Ni_3Al were broken intergranularly as seen in Fig. 2, and did not show any elongation. On the contrary, the compressive deformation was possible as seen in Fig. 3⁽¹⁷⁾. A remarkable point in this figure was that both the yield stress and the work hardening rate were sensitive to alloy compositions. For example, the yield stress of the stoichiometric Ni_3Al was 130 MPa, while that of the Ni_3Al with 27 mol%Al was 400 MPa. The

Fig. 2. A scanning electron micrograph showing intergranular fracture of the polycrystalline Ni_3Al .

Fig. 3. Compressive stress-strain curves of polycrystalline specimens of Ni_3Al with different Al contents.

Fig. 4. Temperature dependence of the yield stress of Ni_3Al .

positive temperature dependence of the yield stress depended strongly on alloy composition below about 900 K as seen in Fig. 4⁽¹⁷⁾⁽¹⁸⁾. We kept these composition sensitive mechanical properties in mind, which later gave a decisive hint for the development of the ductile Ni_3Al .

Fig. 5. Temperature dependence of the elongation of the single crystal Ni_3Al (22.4 mol% Al).

Fig. 6. Tensile stress-strain curves of the recrystallized Ni_3Al polycrystals.

3. Tensile deformation of the recrystallized Ni_3Al

We investigated the deformation and fracture behavior of $Ni_3Al(22.4 \text{ mol\% Al})^{(19)}$, $Ni_3(Al \cdot Ti)^{(20)(21)}$ and Ni_3Ge using single crystal samples⁽²²⁾⁽²³⁾ and discussed the mechanism of the positive temperature dependence of the yield stress and the work hardening rate. These single crystals showed some elongation; especially the single crystal Ni_3Al was fully ductile showing more than 100% elongation at low temperatures as seen in Fig. 5⁽²⁴⁾, and fractured transgranularly. These results indicated that Ni_3Al itself is fully ductile, but broken down because of weakness of the grain boundaries. Noticing the ductility of single crystals of Ni_3Al , we cold rolled it and subsequently recrystallized by annealing at 1273 K. The resultant polycrystalline samples showed more than 10% elongations as seen in Fig. 6⁽²⁴⁾. This demonstrated that ductilization of Ni_3Al had been realized and suggested the possibility of ductilization of Ni_3Al by the usual

metallurgical processings. Based on this idea, we tackled the overcoming of the brittleness of Ni_3Al by microalloying.

IV. The Challenge to Ductilization of Ni_3Al

1. Scavenging effects and grain refinement by ternary trace element additions

Generally, the intergranular fracture in intermetallic compounds is caused by insufficient active slip systems, intrinsic grain boundary weakness and grain boundary impurities. The active slip systems of Ni_3Al were $\{111\}\langle 101 \rangle$, which satisfied the von Mises criterion. Then, the number of active slip systems was not the cause of the brittleness in Ni_3Al . With the objective of reducing grain boundary impurities (possibly O or S), we prepared Ni_3Al using purified Al and Ni, but they remained brittle. Another major factor controlling ductility is generally the grain size effect. Since grain refinement was impossible by the usual processing methods, we prepared Ca, Mg, Si, Mn, Ti, and rare-earth elements-doped Ni_3Al in an attempt to refine grain size and/or to scavenge impurities. However, no grain refinement was observed, and the samples remained brittle⁽²⁾. These observations indicated that the elimination of impurity segregation and the grain refinement by ternary element additions are not effective to ductilization of Ni_3Al . According to the later AES studies⁽²⁵⁾⁽²⁶⁾, no impurity element was detected on the grain boundaries, suggesting intrinsic grain boundary weakness. Then, we turned our attention and challenged to ductilize Ni_3Al by an alternative method, i.e., by microalloying with beneficial elements which suppress the intergranular fracture.

2. The grain boundary strengthening by the ternary trace element additions

We made an assumption that the intergranular fracture of Ni_3Al is overcome by microalloying with trace elements which play beneficial roles for grain boundaries of conventional alloys. A literature survey was carried out on the data concerning the effects of trace elements on mechanical properties of Ni base alloys. As a result, we knew that boron, zirconium, and hafnium were effective for the enhancement of the creep fracture life and high temperature ductility of the commercial Ni-base superalloys⁽²⁷⁾. Although the mechanism of their improvements was uncertain, these elements were considered to stabilize microstructures near the grain boundaries⁽²⁸⁾. Furthermore, there are many examples where the addition of small amounts of B has a large influence on mechanical properties. For example, a small amount of B improved drastically the tempering characteristics of alloy steels. Based on the knowledge, we tried to ductilize Ni_3Al by microalloying with B, Zr, and Hf. It was difficult to select concentrations of these elements, particularly interstitial elements such as boron. We prepared Ni_3Al microalloyed with 0.5 and 1.0 mass% of Zr or Hf, and 0.05 and 0.1 mass% of B. In addition, we expected

Fig. 7. A view of bend-tested specimens showing the effect of the boron addition on room temperature ductility of Ni_3Al .

Fig. 8. A tensile stress-strain curve of the B-doped polycrystalline Ni_3Al .

that the ductilization effect of the ternary elements depend on matrix compositions, because the mechanical properties of Ni_3Al were very sensitive to the deviation from stoichiometry. We prepared Ni_3Al in consideration of the deviation from stoichiometry, i.e. containing 23–27 mol%Al.

Ductility of samples was evaluated by means of bending and tensile tests, and cold rolling. As a very simple and handy bending test, the arc melted samples were gripped with a vice and were bent by a hammer. The Hf-doped samples were brittle, but B and Zr-doped Ni_3Al containing 24 and 23 mol%Al were easily bent as seen in Fig. 7⁽²⁾. The 0.1 mass% B-doped Ni_3Al showed 35% elongation⁽²⁾ as seen in Fig. 8, while the 0.5–1.0 mass% Zr doped Ni_3Al showed 5–20% elongations⁽²⁹⁾ as seen in Fig. 9. The B-doped samples could be cold rolled more than 90% without intermediate annealing as seen in Fig. 10⁽²⁾. The ductilized Ni_3Al exhibited essentially the transgranular fracture as seen in Fig. 11⁽²⁾. The mechanical tests and SEM observations have shown that Ni_3Al has been ductilized by suppression of the intergranular fracture. A similar ductilizing B effect has recently been observed in other L_{12} compounds⁽³⁰⁾. We attempted to see if

Fig. 9. Tensile stress-strain curves of Zr-doped polycrystalline specimens of Ni_3Al .

Fig. 10. A view of the cold rolled specimens, showing the effect of boron addition on room temperature ductility of Ni_3Al .

B was segregated to the grain boundaries, but could not find any evidence using SIMS at that time⁽²⁾. Grain boundary segregation of B has been confirmed by AES analysis⁽³¹⁾ and FIM observation⁽³²⁾.

In order to evaluate the effects of both the amounts of boron and the deviation from stoichiometry on ductility, we further prepared 0.1 and 0.5 mass% B-doped Ni_3Al alloys containing 74, 75, and 76 mol%Ni. Tensile stress-strain curves of these samples are shown in Fig. 12⁽²⁹⁾. The figure demonstrates that ductility of Ni_3Al was very sensitive to both the deviation from stoichiometry and

Fig. 11. Scanning electron micrographs of the fracture surface of 0.1 mass% B doped polycrystalline Ni_3Al , showing transgranular fracture.

Fig. 12. Tensile stress strain curves of 0.1 and 0.5 mass% B doped Ni_3Al .

the amount of B, i.e. the Ni-rich samples showed 15–35% elongations, but the Al-rich ones did not show such a substantial ductility. Can we observe such drastic change in the mechanical properties depending on the composition in solid solution alloys? We think that composition-sensitive mechanical properties are specific characteristics of ordered intermetallic compounds.

We would like to emphasize that the key factors for ductilization of Ni_3Al are (i) the beneficial boron effect and the amount of it and (ii) the matrix composition. We initially prepared 0.05 and 0.1 mass% B doped Ni_3Al . Our later experimental results showed that these amounts were just within optimum conditions for ductilization, which was confirmed by Liu *et al.*⁽³¹⁾ We knew that mechanical properties of Ni_3Al depend strongly on the deviation from stoichiometry and prepared Ni_3Al alloys in consideration of the stoichiometry effects. If we prepared only stoichiometric Ni_3Al , we would not have found out the ductilizing boron effect.

Since the discovery of the ductilizing boron effect in Ni_3Al , ten years have passed. During the recent five years, many theoretical and experimental investigations have been made to clarify the role of boron for the ductilization of Ni_3Al and to develop practical high-temperature alloys. However, the mechanism by which boron improves ductility has not yet been defined conclusively. The detail reviews on them are beyond the scope of the present paper. However, the essence of the mechanism is that the ductilization is associated either with an increase in the intergranular cohesive strength or with an increase in efficiency with which the plastic deformation is transmitted across the grain boundaries. Clarification of the mechanism of the ductilizing boron effect in the $L1_2$ intermetallic compounds including Ni_3Al is the subject for the future study.

Grain boundary segregants are most often associated with grain boundary embrittlement. Unlike most segregants, boron strengthens the grain boundaries in Ni_3Al and its ductilizing effect is extremely prominent. We have not known such a beneficial element which suppresses dramatically intergranular fracture so far. The ductilizing boron effect in Ni_3Al has posed serious questions in the field of grain boundary structures and physical and mechanical properties in intermetallic compounds.

V. Concluding Remarks

With the intention of ductilizing intermetallic compounds, we investigated the mechanical properties of Ni_3Al using single- and polycrystalline samples. The experimental results showed that the brittleness of Ni_3Al resulted from the intergranular fracture and there is a possibility of ductilization, because the polycrystalline Ni_3Al obtained by the recrystallization of the cold rolled single crystal showed some elongation. In addition, the mechanical properties of Ni_3Al were very sensitive to the deviation from stoichiometry, which gave a decisive hint for the alloy design of the ductile Ni_3Al by microalloying with ternary elements. We expected that overcoming of

intergranular fracture would be relatively easy in comparison with that of cleavage fracture. In fact, we discovered that intergranular fracture could be suppressed by the addition of a small amount of boron. We believe that the intermetallic compounds including Ni_3Al will be used practically as high temperature structural materials in the near future.

Acknowledgment

The author expresses his thanks to Dr. M. H. Yoo (ORNL) for reading the manuscript and providing constructive criticism.

REFERENCES

- (1) N. S. Stoloff: Intern. Mater. Rev., **34** (1989), 153.
- (2) K. Aoki and O. Izumi: J. Japan Inst. Metals, **43** (1979), 1190.
- (3) K. Aoki and O. Izumi: J. Japan Inst. Metals, **36** (1972), 212.
- (4) K. Aoki and O. Izumi: J. Japan Inst. Metals, **36** (1972), 113.
- (5) R. Lowrie: Trans. Met. Soc. AIME, **194** (1952), 1093.
- (6) G. W. Ardley and A. H. Cottrell: Proc. Roy. Soc., **219** (1953), 328.
- (7) J. H. Westbrook: J. Electrochem. Soc., **103** (1956), 54.
- (8) P. H. Thornton and R. G. Davies: Metall. Trans., **1** (1970), 549.
- (9) S. Takeuchi and E. Kuramoto: J. Phys. Soc. Japan, **31** (1971), 1282.
- (10) H.-R. Pak, T. Saburi, and S. Nennno: Trans. Japan Inst. Metals, **18** (1977), 617.
- (11) E. M. Schulson and J. A. Roy: Acta Metall., **26** (1978), 29.
- (12) D. M. Wee, O. Noguchi, Y. Oya and T. Suzuki: Trans. Japan Inst. Metals, **21** (1980), 237.
- (13) T. Kawabata, T. Kanai and O. Izumi: Acta Metall., **33** (1985), 1355.
- (14) S. M. Copley and B. H. Kear: Trans. Met. Soc. AIME, **239** (1967), 977.
- (15) M. Hansen: *Constitution of Binary Alloys*, McGraw-Hill Publ. Co., New York, (1958), p. 119.
- (16) K. Aoki and O. Izumi: Phys. Status Solidi, **a-32** (1975), 657.
- (17) K. Aoki and O. Izumi: J. Japan Inst. Metals, **39** (1975), 1282.
- (18) K. Aoki and O. Izumi: Phys. Status Solidi, **a-38** (1976), 587.
- (19) K. Aoki and O. Izumi: Trans. Japan Inst. Metals, **19** (1978), 145.
- (20) K. Aoki and O. Izumi: Acta Metall., **26** (1978), 1257.
- (21) K. Aoki and O. Izumi: J. Mater. Sci., **14** (1979), 1800.
- (22) K. Aoki and O. Izumi: J. Mater. Sci., **13** (1978), 2313.
- (23) K. Aoki and O. Izumi: Acta Metall., **27** (1979), 807.
- (24) K. Aoki and O. Izumi: Trans. Japan Inst. Metals, **19** (1978), 203.
- (25) T. Ogura, S. Hanada, T. Masumoto, and O. Izumi: Metall. Trans., **A-16** (1985), 441.
- (26) T. Takasugi, E.P. George, D. P. Pope, and O. Izumi: Scr. Metall., **19** (1985), 551.
- (27) R. T. Holt and W. Wallace: Intern. Metals Rev., **21** (1976), 1.
- (28) R. F. Decker and J. W. Freeman: Trans. Met. Soc. AIME, **218** (1960), 277.
- (29) K. Aoki, H. Yamagata, and O. Izumi: Collected Abstracts of the Annual Meeting of Japan Inst. Metals, Nagoya, (1979), p. 165.
- (30) A. I. Taub, C. L. Briant, S. C. Huang, K. -M. Chang, and M. R. Jackson; Scr. Metall., **20** (1986), 129.
- (31) C. T. Liu, C. L. White, and J. A. Horton: Acta Metall., **33** (1985), 213.
- (32) J. A. Horton and M. K. Miller: Acta Metall., **35** (1987), 133.