Mechanical Properties of Nb₃Al-Base Intermetallics Prepared by a Ceramic Mold-HIP Process

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The Nb₃Al-type intermetallic is expected as a candidate for high-temperature structural materials because of its high melting point and relatively lower density, though poor in plastic workability at room temperature. Here the Ceramic Mold-HIP process was employed to fabricate the NNS compacts of brittle Nb₃Al intermetallic and Nb₃Al-base composites. Complex-shape compacts such as blades and pyramids were fabricated without any cracks by adjusting the chemical composition of the Nb₃Al-base alloy to have high compressive fracture strength at room temperature. High-temperature strength in the range of 1873 to 2073 K was evaluated by compressive and tensile tests. The maximum compressive strength at 2073 K was 151.4 MPa for Nb-20 at%Al-26 at%Mo alloy, while the corresponding maximum tensile strength was only 12.9 MPa for the Nb-19.3 at%Al-44.8 at%Mo alloy. The strain rate sensitivity of compressive stress at high temperatures was also evaluated using the strain rate conversion method. Further, the 5.7% tensile elongation at room temperature was achieved by Nb-25 at%-35 at%Mo plus Nb foil composite, even though the Nb₃Al-base alloy itself is brittle at room temperature.

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I. Introduction

Strong demands for aircraft capable of higher speed and with improved fuel efficiency have led to increasingly severe environment for its engine parts. Development of next-generation aircraft engines has intended for use of the aerospace propulsion system exceeding the high-temperature performance of superalloys and refractory alloys. Accordingly, material research has been focused on intermetallic compounds, ceramics, C/C composite, etc.

Some intermetallic compounds have high melting point and low density and hence, can be expected⁽¹⁾⁽²⁾ to offer ductility superior to that of ceramic as a candidate for high-temperature structural materials. In particular, Nb₃Al intermetallic⁽³⁾ has the high melting point (2233 K) and relatively low density (7.3 Mg/m³), while its poor ductility and machinability at room temperature mandate urgent development of NNS (Near Net Shape) parts production technology. The authors have already proceeded with R&D study⁽⁴⁾ on the specific technique for the production of NNS parts of Nb₃Al using powder metallurgical method. This technique is called the Ceramic Mold-HIP process⁽⁵⁾, consisting of the lost wax process to fabricate a ceramic mold into which Nb₃Al powder is packed and the HIP process to consolidate the ceramic mold (filled up by Nb₃Al powder) through the secondary-pressure ceramic media.

In the present paper, the authors deal mainly with the

mechanical properties and their relationships with process parameters of Nb₃Al intermetallics and Nb₃Al-base composites.

II. Experimental Procedure

Nb₃Al-base alloy powder used was mostly spherical with a particle size under 60 mesh produced by the Plasma Melting-Gas Atomization (PMGA) method⁽⁶⁾. In some cases, commercial NbAl₃, Mo, W, Nb and the other bcc metal powder and further, Y₂O₃, NbC and the other ceramic fines were added to the Nb₃Al-base powder and then were mixed for 1.8 ks in a V-type mixer. The Nb₃Al is chemically active and so, Y₂O₃ powder highly stable thermodynamically⁽⁴⁾ was used to suppress oxide contamination during HIP process as the inner layer of the ceramic mold directly contacting the Nb₃Al powder and also, as the secondary-pressure media. On the other hand, a high-purity Al₂O₃ granular powder was used as the outer layer of the ceramic mold.

Figure 1 is a schematic diagram of the Ceramic Mold-HIP process⁽⁴⁾. The ceramic mold with the Y₂O₃ inner layer and Al₂O₃ outer one was produced by the Lost Wax Process⁽⁷⁾. The Nb₃Al-base powder was packed into this ceramic mold and put in a stainless steel can (114 dia. × 210 mm) and finally surrounded by the Y₂O₃ powder for the secondary-pressure media. The metal can was sealed under vacuum and treated by HIP (Hot Isostatical Pressing) system in Japan Ultra-high Temperature

Fig. 1 Schematic diagram of the Ceramic Mold-HIP process.

Materials Research Center (JUTEM). The HIP conditions were 1573 K–10.8 ks/196 MPa, where the cooling rate was controlled to 4.6 K/s in the range of 773 to 1573 K to suppress cracking due to residual stress during cooling. The NNS compacts were obtained after machining and sand-blasting to remove metal and ceramics respectively.

The mechanical properties were evaluated through compressive and tensile testing at room and elevated temperatures. Test specimens were prepared from the compacts fabricated by the Ceramic Mold-HIP process described above and also, by HIPing a Ti can directly filled up by the Nb_3Al -base powder at 1773 K/196 MPa for 10.8 ks. Some specimens were heat-treated in Ar at 1873 and 2073 K for 10.8 to 14.4 ks to improve the strength⁽⁷⁾⁽⁸⁾ of the as-HIPed compact. Compressive and tensile test specimens were cut out to the form of cylindrical one of 4 dia. $\times$ 7 mm and of sheet-like one of 3 mm $\times$ 3 mm with a gauge length of 10 mm, respectively. All the test specimens were prepared by an electrospark-wire cutting machine. Compressive and tensile tests were carried out in Ar at the strain rate of $3 \times 10^{-4} \text{ s}^{-1}$ using the Ultra-high Temperature Universal Testing System in JUTEM. Specimens were examined, clamped in both ends by tungsten disks (10 dia. $\times$ 5 mm) for high-temperature compressive tests.

Tensile tests at room temperature were also carried out for Nb_3Al -base composites with Nb foil (0.17 mm thick) which was loosely wound up and inserted into a Ti HIP can (60 dia. $\times$ 110 mm). After Nb_3Al -base powder was filled up in the gaps (2–3 mm) between Nb foil, a Ti can was sealed and then HIPed at 1773 K/196 MPa for 10.8 ks.

The strain rate dependance of the high-temperature compressive stress was evaluated using the strain rate conversion method⁽⁹⁾.

III. Results and Discussion

1. HIP-NNS molding into complex shapes

Figure 2 shows the relationship between relative density and HIP temperature for Nb–22.8 at%Al powder compacts. HIPing at 1473 K/196 MPa for 7.2 ks or more resulted in a specimen with relative density of more than 97% theoretical. Since the mechanical strength is generally improved by the high-temperature heat-treatment⁽⁴⁾⁽⁷⁾, the HIP condition was fixed to 1573 K–10.8 ks/196 MPa, in consideration of the heat resistance of HIP metal can.

Figure 3 shows the effect of Al content and the amount of Mo, W, Nb in NbAl-base compacts on the room-temperature compressive strength (strain rate $\sim 10^{-3} \text{ s}^{-1}$). All the test specimens had brittle fracture but fairly high strength was obtained for the Al content less than 20 at% or the Al content more than 20 at% plus amount of bcc metal over 20 vol%. As seen of Fig. 3(b), the addition of bcc metal powder to Nb_3Al -base one had almost no effect on room-temperature compressive strength for the Al content less than 20 at% but had a large effect for the Al content more than 20 at%. In the latter, it is inferred from Fig. 3(a) that the addition of Mo, W, Nb over 20 vol% possibly strengthened the matrix alloys because they were originally poor in ductility for the Al content more than 20 at%.

Based on the results above, a series of experiments were carried out on NNS molding of complex blade and pyramid shapes using various kinds of Nb_3Al -base PMGA powders⁽⁸⁾, with commercial NbAl₃ as well as Mo, W and other powders. Test conditions and their results are summarized in Table 1 (HIPed at 1573 K/196 MPa for 10.8 ks), where the external views of wax mold and NNS compact are shown in Fig. 4. Except for some cracks in the blade shape from the MPGA powder (Nb–18.6 at%Al–23.8 at%Mo), the NNS compacts were obtained with no cracks in the region of high-strength Al contents described above. Roughness in the NNS com-

Fig. 2 Change in relative density with HIP temperature.

Fig. 3 Effect of Al content (a) and amount of additives (b) in NbAl-base (powder) compacts on room-temperature compressive strength.

Table 1 Results of HIP-NNS trials.

Composition (at%)	Powder used	Crack of shape	
		Blade	Pyramid
Nb-18.1Al	Alloy (PMGA powder)	1*	0
Nb-18.3Al	NbAl ₃ + 78 vol%Nb powder	0	0
Nb-19.4Al	Alloy (PMGA powder)	0	—
Nb-18.6Al-23.8Mo	Alloy (PMGA powder)	many	0
Nb-20.0Al-25.0Mo	PMGA powder + 23 vol%Mo powder	0	0
Nb-20.0Al-25.0Mo	PMGA powder + 28 vol% (Nb + Mo) powder	0	—
Nb-24.5Al-29.9Mo	Alloy (PGMA powder)	many	0

* Cracked by a drop during sand-blasting.

pacts is mainly due to the transfer of the inner wall surface of the ceramic mold. Subsequently, the dimensions of blade and pyramid shapes were measured at several points in vertical and horizontal directions (Fig. 4) and their shrinkage ratios to wax mold were calculated.

Figure 5 shows the relationship between the mean

Wax model

Compact

Upper; Blade

Nb-20Al-25Mo(at%)

Lower; Pyramid

Nb-18.1Al(at%)

Fig. 4 Shapes of the blade and pyramid model.

shrinkage and the relative packing density, where the data for other ceramic mold was also referred⁽¹⁰⁾. The shrinkage obtained was somewhat lower than the theoretical one, though roughly in good agreement.

Figure 6 shows the standard deviation for the mean shrinkage. The smaller the shrinkage, the smaller is the standard deviation. Accordingly, it is recommended to use the Nb₃Al-base powder with the high packing density and the small standard deviation to improve the dimensional accuracy.

2. Mechanical properties of NNS compact

Table 2 compares the room and high temperature tensile strength of specimens HIPed by using the Ceramic Mold and Ti can (directly filled up by Nb₃Al-base powder), and then heat-treated at 2073 K for 14.4 ks. There is little difference of the tensile strength between the both methods described above. Hence in subsequent experi-

ments, the latter was employed as a method convenient for fabrication of numerous specimens.

Figure 7 exemplified compressive stress-strain curves at 2073 K of some specimens, where all the specimens were heat-treated at 2073 K before compressive test. The highest compressive strength of 151 MPa was obtained for Nb-20 at%Al-26 at%Mo alloy (bearing 97 mass% of PGMA powder) in comparison with for Nb-21.5 at%Al-7.8 at%W alloy with Y_2O_3 and NbC ceramic fines.

As previously reported⁽⁴⁾⁽⁷⁾, it therefore proved that enhancement of the high-temperature strength speculates at first to raise the melting point of the matrix alloy by

Fig. 5 Relationship between shrinkage and packing density.

Fig. 6 Standard deviation of shrinkage.

Mo, W and other bcc metals, secondly to make composite structure by addition of Y_2O_3 , NbC and other stable ceramics, and finally to induce crystal grain-coarsening⁽⁴⁾ by optimum heat-treatment such as above 2073 K.

Figure 8 shows the relationship between the logarithmic tensile strength and the logarithmic fracture strain at high temperatures, where the specimens fractured at maximum stress only for the data inside a circle.

Fig. 7 Typical compressive stress-strain curves.

Fig. 8 Relationship between tensile strength and fracture strain.

Table 2 Tensile strength of specimens by two different processes.

Composition (at%)	Consolidation process	HIP/H.T. temp. (K)	Tensile strength (MPa)			
			R.T.	1873 K	1973 K	2073 K
Nb-20.0Al-25.0Mo mixed	Ti capsule-HIP	1773/2073	81.9*	88.2	24.0	9.2
Nb-20.0Al-25.0Mo mixed	Ceramic Mold	1573/2073	115.6*	—	24.3	11.2
Nb-18.7Al-23.1Mo alloy	Ti capsule-HIP	1773/2073	182.4*	98.3	23.5	10.8
Nb-18.7Al-23.8Mo alloy	Ceramic Mold	1573/2073	157.3*	69.9	17.5	8.4

* Brittle H.T.: Heat-treated R.T.: Room-temperature.

The tensile strength is plotted on a straight line of slope 0.5 for the as-HIPed specimen as well as the one heat-treated at 1873 K, but plotted on higher level for those heat-treated at 2073 K. Such behavior can be understood from the relationship between heat-treatment temperature and microstructure, although the physical meaning of slope=0.5 was not clarified in here. Whereas the microstructure is fairly fine in both the as-HIPed specimen and the one heat-treated at 1873 K, the specimen heat-treated at 2073 K exhibited marked coarsening of crystal grains⁽⁴⁾, presumably leading to enhancement of the high-temperature strength.

Figure 9 shows the effect of Al content on tensile strength (a) and fracture strain (b) at high temperatures for the specimens heat-treated at 2073 K. As for the testing temperature, the tensile strength rises with increasing Al content at 1973 K and, on the other hand, is roughly constant irrespective of Al content at 1873 K and 2073 K. The fracture strain was less than 2% with brittle fracture at 1873 K for Al $\geq$ 21 at% and at 1973 K for Al $\geq$ 25 at%. The fracture strain at 2073 K was about 30% even for the Al content of 25 at%, while the corresponding tensile strength was not improved, as shown in Fig. 9(b). These phenomena will be attributed to segregation of the σ phase (Nb₂Al)⁽¹¹⁾ at Al-rich compositions. The σ phase is brittle at 1873 K enough to reduce the fracture strain of matrix but strengthens the matrix at 1973 K though depending on Al content. This precipitate-strengthening due to the σ phase disappears at 2073 K near the melting

point (2213 K)⁽¹²⁾. In practice, Nb-22.8 at%Al-10 mass% ZrN or TiB₂ specimens melted down during heat-treatment at 2073 K. Thus, 2073 K seems to be an extremely severe condition for Nb₃Al-base alloy.

The maximum compressive and tensile strengths, along with strength ratios, are compared in **Table 3**. The strength ratios are from 0.6 to 0.7 at 1873 and 1973 K and fall below 0.1 at 2073 K due to a sharp drop of the tensile strength. This can be related to the fact that Nb-20 at%Al-26 at%Mo plus NbC specimens (A2 alloy), with the large compressive strength at high temperature, were so brittle that it was difficult to machine out the tensile test specimen, indicating a vital problem to be overcome for the practical application of the Nb₃Al-base alloys.

Figure 10 shows the microstructures of the specimens having high compressive and tensile strength. X-ray diffraction patterns indicate that the matrix in all the specimens was A15 phase (Nb₃Al) with some σ phase (Nb₂Al) present. According to EPMA analyses, there were a mixture of Nb-Al-W and carbide (Nb₂C, NbC) phases for 90 mass% (Nb-21.5Al-7.8W) plus 10 mass%NbC and Y₂O₃ remaining along prior particle boundary (PPB)⁽¹³⁾ for Nb-25.2 at%Al-31.4 at%Mo plus 3.5 mass%Y₂O₃. On the other hand, fine Nb grains, presumably arising from NbAl₃ (2.8 mass%) added for Al adjustment, were detected for Nb-20 at%Al-26 at%Mo, although Nb and Al ingredients were homogeneously distributed. Mo grain (undiffused) was also detected for Nb-19.3 at%Al-44.8 at%Mo (added by Mo powder, 25 mass%). Trace amounts of Al₂O₃ and Nb carbides were found in all the specimens, suggesting of oxygen and carbon contamination of compacts during the process from the sample fabrication to the high-temperature mechanical testing.

Figure 11 shows the strain rate dependance of the high-temperature compressive strength which was evaluated in terms of the strain rate sensitivity m ($\sigma \propto \dot{\epsilon}^m$)⁽⁹⁾. In the figure, the m value ($\blacktriangle$) calculated from the ratios of peak strength at the strain rates of 2×10^{-3} and 10^{-2} s⁻¹ are also shown for reference. It is evident that the m values are larger for Nb-Al binary alloys than Nb-Al-Mo ternary alloys and are larger for low Al content/high temperatures from Fig. 11(b). The m values calculated

Fig. 9 Effect of Al content on tensile strength (a) and Fracture strain (b).

Table 3 Comparison between maximum tensile and compressive strength.

Test temp. (K)	Tensile strength (MPa) composition (at%) ①	Compressive strength (MPa) composition (at%) ②	Ratio ①/②
R.T.	263.4*	1575*	0.17
1873	Nb-19.4Al-23.2Mo 140.2	Nb-19.4Al-23.2Mo 237.2	0.59
1973	Nb-19.3Al-44.8Mo 114.5*	A2 alloy** 161.6	0.71
2073	Nb-25.2Al-31.4Mo-3.5 mass%Y ₂ O ₃ 12.9	A2 alloy** 151.4	0.09
	Nb-19.3Al-44.8Mo	Nb-20.0Al26.0Mo	

* Brittle.

** A2 alloy: 90 mass% (Nb-21.5Al-7.8W) + 10 mass%NbC.

Fig. 10 Some microstructures of specimens heat-treated at 2073 K.

from the ratio of tensile strength at the strain rates of $3 \times 10^{-4}/3 \times 10^{-3} \text{ s}^{-1}$ at 1873 K, using the as-HIP specimen (1773 K) of Nb-20 at%Al-25 at%Mo, were 0.47 in

Fig. 11 Dependence of strain rate sensitivity (m) on test temperature (a) and Al content (b).

good agreement with the one extrapolated from Fig. 11(a), where fracture strains were only 15.3 and 5.5%, respectively. Consequently, no superplastic elongation was observed in spite of the high m values. This suggests that plastic deformation of the Nb₃Al-base alloys is mainly due to the deformation not by superplasticity but by dynamic recrystallization⁽¹⁴⁾.

In both room-temperature compressive and tensile tests in the present work, all the specimens underwent brittle fracture within the proportional limit of stress-strain curve and whatsoever, no plastic elongation was observed.

Figure 12 shows the relationship between fracture strain and Al content in the room-temperature tensile test. In this case, fracture strain represents elastic plus plastic strain (corrected logarithmically), differently from (plastic) elongation. The lower the Al content, the larger the fracture strain tended to be, requiring the further reduction of Al content for improving room-temperature ductility. According to other report⁽¹⁵⁾, Nb solid-solution phase needs more than 40 vol% in the Nb₃Al plus Nb duplex phase region in order to achieve room-tem-

Fig. 12 Relationship between fracture strain and Al content.

Fig. 13 Typical tensile stress-strain curve of the Nb₃Al-base composite.

perature ductility. It is also reported⁽¹⁶⁾ that the sintered specimen (composite) of Nb₃Al-base alloy powder plus Nb foil has no drop-off of the Nb₃Al layer up to cracks of 5 to 6 mm. Then, a composite of Nb₃Al-base powder and Nb foil (0.17 mm thick) was fabricated by HIP at 1773 K and examined under the similar conditions to tensile test, as a study of the room-temperature ductility.

Figure 13 exemplified the tensile stress-strain curve for a composite of Nb-25 at%Al-35 at%Mo plus Nb foil. After brittle fracture of Nb₃Al-base alloy layer, a tensile elongation of 5.7% due to Nb foil was observed. This suggests that the room-temperature ductility of the brittle Nb₃Al-base alloy may possibly be improved through composite structure materialization.

IV. Conclusions

The Nb₃Al-base compacts and composites were fabricated mainly by the Ceramic Mold-HIP process and mechanically examined and evaluated as follows:

(1) The chemical compositions of the Nb₃Al-base alloys insensitive to cracking were elucidated and allowed the fabrication of complex-shaped parts free of cracks, using the HIP-NNS powder metallurgical technique as

stated earlier.

(2) It was found that the effective means for improving the high-temperature strength are at first to raise the melting point of matrix alloy by Mo, W and other bcc metal (ingredient) and secondly to make composite structure by addition of Y₂O₃, NbC and other stable ceramics, and finally to induce crystal grain-coarsening by optimum heat-treatment such as at 2073 K.

(3) The highest compressive and tensile strength at 2073 K were 151.4 MPa for the Nb-20 at%Al-26 at%Mo alloy and 12.9 MPa for Nb-19.3 at%Al-44.8 at%Mo one (strength ratio ≤ 0.1), respectively.

(4) All the Nb₃Al-base alloys were brittle at room temperature, while the composite materials consisting of Nb₃Al-base alloy plus Nb foil showed room-temperature tensile elongation of 5.7%.

In the near future, Nb₃Al and other intermetallics are expected to make a remarkable progress in terms of alloys and composite material, with the new NNS shape-making process and the many data base for alloy design.

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