Ceramic Mold-HIP Processing of Nb-Al Intermetallic Powder

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The Nb₃Al is one of the futuristic high temperature structural materials, but is poor in plastic workability. Therefore, the Ceramic Mold-HIP process is noteworthy toward powder metallurgical process for shape-making, and is as follows: The Nb₃Al powders are filled up in a ceramic mold prepared by lost wax process, which is set in secondary pressing media enclosed with a metal can, and HIPed under high temperature/pressure. Y₂O₃ ceramic and Y₂O₃/CaO mixture were mainly used as less reactive ceramic mold for the Nb₃Al powders during HIPing, and as the secondary pressing media, respectively. The Nb-25.2at%Al powders in the ceramic mold were consolidated into the tentative forms of cone, blade and tube under the HIP condition of 1573K/196MPa. The Nb-22.8/25.2at%Al powder compacts obtained showed lower compressive strength in as-HIPed state. However, when held above 1873K to remove prior particle boundary (PPB) by grain growth, they had almost 3 times compressive strength compared to as-HIPed one (ex. over 100 MPa at 1773K). Furthermore, the Nb₃Al-base composites with 10 wt% of ceramic fines such as Y₂O₃ and ZrO₂ were elucidated to have a potential for the improvement of high temperature strength.

Keywords: powder metallurgy, shape-making, lost wax process, Y₂O₃, ZrO₂, CaO, HIP, NNS compact, compressive strength

I. Introduction

In general, intermetallic compounds such as aluminide and silicide have high specific strength, some of which are expected as high temperature structural materials⁽¹⁾⁽²⁾ in the near future. Especially, Nb-aluminides have been currently considered as one⁽³⁾ of advanced structural materials for aerospace propulsion system etc. The Nb₃Al intermetallic⁽⁴⁾ (A15-Type) has higher melting point (2233K) and lower density (7.3Mg/m³) than Ni-base superalloys as usual, but is very difficult to hot-work as a drawback⁽⁵⁾ common to high temperature intermetallic compounds. So, new 3-dimensional (3D) shape-making process⁽⁶⁾ has been recently required and carried out to put Nb₃Al to practical use. This type of intermetallic compounds may possibly be processed to near net shape (NNS) products by means of precision casting or powder metallurgical(P/M) technology.

The objective of this work is to fabricate a Nb₃Al NNS compact directly from its powder by Ceramic Mold-HIP (Hot Isostatic Pressing) process⁽⁶⁾, one of P/M technologies combined with lost wax process⁽⁷⁾. This process is as follows: The Nb₃Al powders are filled up in a ceramic mold which is prepared by lost

wax process, are set into ceramic granules in a metal can, and are HIPed after the metal can being sealed. Here, the ceramic granules act as pressing media giving pseudo-isostatical pressure to the ceramic mold in the metal can(hereafter referred to as HIP can). The compact taken out is heat-treated and then, machined to net shape if necessary.

Authors investigated the P/M route conditions for NNS shape-making, especially the mold materials to active Nb₃Al under high temperature/pressure and the relationships between compressive strength and microstructure of the compact obtained and further, elucidated the possibility of strength improvement by adding some ceramics to Nb₃Al.

II. Experimental procedure

The Nb₃Al powders were produced using a gas atomization equipment with the special melting furnace/tundish⁽⁸⁾ in Mitsubishi Materials Corporation. These powders are Nb-22.8/25.2at%Al with particle size under 60mesh. Besides them, pure Nb powder was used for comparison (provided by H. C. Stark). Reagent-grade ceramic fines (~a few microns) also were blended as additives to prepare Nb₃Al plus ceramic composites.

Figure 1 is a schematic diagram of the Ceramic

Mold-HIP process. Here, lost wax process (omitted in the figure) consists of the following: A wax model is made by the injection molding of wax into a given metal mold. The wax model obtained is dipped in

III. Results and discussion

1. Materials of ceramic mold

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

the slurry of ceramic fine (filler)/binder solution and further, coated with ceramic powders (stucco) and dried in air. After a series of this procedure being repeated several times, the green mold is dewaxed in an autoclave and fired at 1173-1773K for 3.6ks. The Nb₃Al powder and others are filled up in a ceramic mold⁽⁹⁾ and HIPed at 1573K/196MPa for 7.2ks as in the figure, where Y₂O₃-70vol%CaO granules are used as secondary pressing media. The CaO-mixed granules after consolidated are volumetrically expanded and easily resolved by means of immersing in water. The residual ceramic also is carefully taken off using a hand grinder with diamond-whetting stones.

The compacts were evaluated about appearance, density etc. from the shape-making point of view. For mechanical properties and others, 20dia. x 40mm ceramic mold was used for convenience. The specimens obtained were, in part, held at 1673-2073K for 3.6ks in Ar and provided for compression test, optical-and SEM-observation, and EPMA- and X-ray diffraction-analysis. The compression test specimen was cut out into 4dia. x 7 mm by an electrosark-wire cutting and examined using an ultra-high temperature universal testing system in Japan Ultra-high Temperature Materials Research Center, at a strain rate of 3×10^{-4} /s.

An attention first needs to be focused on the material choice of ceramics in this P/M route. Especially, the ceramic mold contacts Nb₃Al under high temperature/pressure, at which some chemical compounds form containing Nb and/or Al. Here, the following items will be mainly requisite for ceramic mold materials:

- not melted-down during HIPing
- not reactive to Nb₃Al readily
- stable chemically at high temperature

Figure 2 shows the standard molar free energies of formation⁽¹⁰⁾ (ΔG^0) of ceramics. The ceramics which have ΔG^0 smaller than those of Nb- and Al-chemical compounds and the melting point above 2273K⁽¹¹⁾ are MgO, CaO, ZrO₂, Y₂O₃ for oxide, TiC, ZrC for carbide, TiN, ZrN for nitride and TiB₂, ZrB₂ for boride. These ceramics are suggestive of being non-reactive to Nb and Al element only on thermodynamical consideration. Consequently, MgO, CaO, ZrO₂, Y₂O₃, TiN, ZrN, TiB₂ and ZrB₂ together with Al₂O₃ were tested as non or less reactive ones to Nb₃Al, except for unobtainable ones. The Nb-22.0at%Al ingot melted by a Cold Crucible/Levitation Furnace was set in ceramic fines (under 20microns) charged in a Nb can (40dia. x 60mm) and its Nb can was sealed and HIPed at 1873K/100MPa for 3.6ks.

Fig. 2 Standard molar free energies of formation at 2000K for high temperature ceramics.

Figure 3 exemplifies a SEM-image and EPMA element maps in the cross-section of $\text{Nb}_3\text{Al}/\text{MgO}$ interface. There are many dark spots in the vicinity of the interface in Fig. 3(a). The dark spots were confirmed to be rich in Al as in (b) with trace of oxygen, indicative of Al-oxide. As shown in (c), the light spots of Mg were detected only in the surface layer. Such morphology in the vicinity of the interface, in which the layer of the dark spots on SEM image is considerably thicker than that of the light spots of a metallic element in ceramic on EPMA map, was observed for the other combinations of $\text{Nb}_3\text{Al}/$ ceramics. It is therefore inferred that such a ceramic (mold) was partly decomposed into its constituent elements, a metallic one and other, at high temperature, which diffused into Nb_3Al matrix, individually.

Figure 4 shows the correlation in thickness be-

Fig. 4 Correlation in thickness between two kinds of diffusion layers in the particular region (Nb_3Al site).

tween these two kinds of diffusion layers in the particular region (Nb_3Al site). In the figure, Y_2O_3 , ZrO_2 , ZrN and ZrB_2 prove to be less reactive to Nb_3Al and Y_2O_3 was selected as a mold material from the practical point of view. Both Y_2O_3 powder and fine are easily obtainable, albeit costly to our regret. So, the Y_2O_3 ceramic was used for inner layers directly contacting the Nb_3Al itself, while Al_2O_3 ceramic for outer layers in a ceramic mold as shown in Table 1.

Figure 5 shows the results of rupture test on Y_2O_3 and Al_2O_3 powder compacts after fired at various temperatures for 3.6ks. It is evident from the figure that the rupture strength increases non-linearly

Fig. 3 SEM-image and EPMA-elemental maps in the vicinity of $\text{Nb}_3\text{Al}/\text{MgO}$ interface after HIPed at 1873K/100MPa.

Table 1 Combination of mold ceramics used.

Inner layers (Y_2O_3)			Outer layers (Al_2O_3)		
Binder	Filler	Stucco	Binder	Filler	Stucco
CMC	Y_2O_3	Y_2O_3	Al_2O_3	Al_2O_3	Al_2O_3
solution	-350#	-100#	solution	-350#	-36#

CMC: Carboxy Methyl Cellulose

with increasing firing temperature and reaches more than 2MPa requested usually for lost wax operation, when fired above 1573K.

Fig. 5 Change of rupture strength of mold ceramics (Y_2O_3 , Al_2O_3) with firing temperature.

2. Fabrication and evaluation of Nb₃Al compacts

Wax model was represented by the three followings:

- Cone simply designed
- Blade in asymmetry
- Tube requiring a core

Figure 6 exemplifies the appearance/relative density of Nb-25.2at%Al and Nb NNS compacts (blades) which were fabricated under a HIP condition at 1573K/196MPa for 7.2ks using the specific ceramic mold (Table 1). For tube fabrication, a mild steel bar was used as a core material of ceramic mold and finally, dissolved away in conc. HCl/H₂O₂ solution. A simple Nb₃Al cone was easily taken out of mold ceramics in almost a perfect shape. Both the Nb₃Al blade and tube, being relatively complicated, were slightly cracked alike. However, no crack was observed in the region of asymmetrically curved surface, and no remarkable diffusion zone near the interface of Nb₃Al/ceramic mold was detected as in Fig. 7.

On the other hand, the oxygen content in Nb₃Al and Nb blades were 2.0 and 0.7wt%, respectively, and may possibly promote crack initiation to not

Fig. 6 Appearances of Nb-25.2at%Al and Nb compacts.
(): Relative density

only Nb₃Al compact, but also Nb one being fairly ductile by nature. It is therefore affirmed that 3D-shaped Nb₃Al compacts can be fabricated without any cracks under more suitable process-parameters. In reality, a faultless Nb₃Al blade has been fabricated by use of a HIP can larger enough compared to ceramic mold under lower oxygen level. Both the Nb₃Al blade and tube above have lower relative density of 96.6 and 80.6% [theoretical density : 7.28 Mg/m³], respectively.

In sequence, the Nb₃Al specimens (4dia. x 7mm) obtained in the same way were examined on mechanical properties, microstructures etc. Figure 8 shows the results of compression test in the temperature range of 1673-1873K for Nb-22.8/25.2 at%Al specimens. Experimental values of Nb₃Al powder compacts and castings (Nb-18-26at%Al) reported elsewhere⁽¹²⁾⁻⁽¹⁷⁾ were plotted together in the figure, of the order of strain rate: 10⁻⁴/s. The compressive strength (peak stress) of as-HIPed specimens (◆ marked) are fairly lower than a solid line.

Figure 9(a) exemplifies the microstructure of Nb-25.2at%Al specimen in as-HIPed state. The as-HIPed specimen is fine in crystal grain and also, has PPBs originating in Nb₃Al powders. These specimens were heat-treated at various tempera-

Fig. 7 EPMA-line analysis in the vicinity of $\text{Nb}_3\text{Al}/\text{Y}_2\text{O}_3$ ceramic interface. (HIPed at 1623K/196MPa)

Fig. 8 Compressive strength of Nb_3Al specimens.

tures for 3.6ks. As the results, the PPBs almost disappeared due to grain growth at 1873K as in Fig. 9(b). As expected from this microstructural change, each compressive strength of the specimens heat-treated at 1873K (● marked) is plotted almost on a

Fig. 9 Microstructures of Nb-25.2at%Al compacts, (a)as-HIPed at 1573K/196MPa and (b)HIPed and heat-treated at 1873K.

solid line in Fig. 8.

Figure 10 shows the relationships between compressive strength⁽¹³⁾⁽¹⁴⁾⁽¹⁸⁾ at 1773K and heat-treating temperature in Nb_3Al specimens, where its melting point (2233K) was employed as the heat-treating temperature of castings for convenience. Consequently, the high temperature strength of the compact tends to be improved with being heat-treated at higher temperature, although not neces-

Fig. 10 Relationships between compressive strength at 1773K and heat-treating temperature in Nb_3Al specimens.

sarily fixed to the same process/test conditions in both the graphs above.

3. Nb₃Al composite with ceramic powders

In Figure 8, the compressive strength of Nb₃Al decreases as a whole with increasing test temperature. Incidentally, the high temperature strengthening of Nb₃Al may be expected in the form of composite⁽¹⁹⁾ with ceramic powders by means of powder metallurgy. This cermet-type Nb₃Al was fabricated using some ceramic fines, Y₂O₃, ZrO₂, TiC, ZrC, TiN, ZrB₂ as less reactive ones to Nb and Al thermodynamically (see Fig. 2). The Nb-22.8at%Al powder mixed with 10wt% of ceramic fine was filled up in a ceramic mold and HIPed at 1573K/196MPa for 7.2ks. The Nb₃Al/ceramic composite obtained was heat-treated at 2073K for 3.6ks in Ar.

Figure 11 shows the results of compression test for these Nb₃Al/ceramic composites, together with the plots on a solid line for the compacts heat-treated in Fig. 8, for comparison. All the compressive strengths of Nb₃Al/ceramic composites are roughly on higher level than a solid line at 1873K and decrease abruptly with increasing test temperature. Especially, the compressive strength of Nb₃Al/Y₂O₃ composite is kept relatively high even on higher temperature side.

Fig. 11 Compressive strength of Nb-22.8at%Al/ceramic composites heat-treated at 2073K.

Figure 12 is the microstructures of Nb₃Al/ceramic composites heat-treated above. Ceramic fines exist in the configuration filling the gap of Nb₃Al particles constituting powder compacts. As for Nb₃Al/Y₂O₃ and ZrO₂ composites [Fig. 12(a) and (b)], there were dark areas around the light particles, and some precipitations in the particles were observed. The dark areas were Y₂O₃ and ZrO₂, respectively, and the light particles were constituted by

Nb₃Al and Nb₂Al as described below, although the pre-cipitations were not identified. On the other hand, as for the other composites such as (c) and (d), there were not any dark areas around the particles, and the microstructures were a little different from those of (a) and (b).

Table 2 shows some chemical compounds in Nb₃Al/ceramic composites detected by X-ray diffraction analysis. The original ceramic was detected only for Nb₃Al/Y₂O₃ and ZrO₂ composites. As for the other composites, some chemical compounds which will be produced by the reaction between Nb₃Al and ceramics such as TiC and ZrB₂ were detected. It is consequently assumed that Y₂O₃ and ZrO₂ ceramic fines remain nearly undissolved in the Nb₃Al matrix (through heat-treating), while the others react with the Nb₃Al matrix and disappear partially.

As the results above, it is considered that the Nb₃Al composite with ceramic fines less reactive to Nb and Al turned out to have the possibility of improving its high temperature strength.

Table 2 Chemical compounds detected by X-ray diffraction of Nb-22.8at%Al/ceramic composites after heat-treated at 2073K for 3.6ks.

Y ₂ O ₃	ZrO ₂	TiC	ZrC	TiN	ZrB ₂
Nb ₃ Al	Nb ₃ Al	Nb ₃ Al	Nb ₃ Al	Nb ₃ Al	Nb ₃ Al
Nb ₂ Al	ZrO ₂	Nb ₂ Al	Nb ₂ Al	Nb ₂ Al	Nb ₂ Al
Y ₂ O ₃	Al ₂ O ₃	Nb ₂ C (NbC) (Ti ₃ Al)	Nb ₂ C	Nb ₂ N (Ti ₃ Al)	(Nb ₅ B ₆)

III. Conclusions

The Nb₃Al-type intermetallics were fabricated by P/M process and evaluated as follows:

(1) The 3D-shaped Nb₃Al compacts (ex. gas turbine blade) were substantiated to be fabricated by Ceramic Mold-HIP process. Here, Y₂O₃ ceramic was finally selected as less reactive one to Nb₃Al under high temperature/pressure (HIP) and hence, the ceramic molds were prepared in the configuration: Y₂O₃ ceramic for inner layers and Al₂O₃ one for outer layers by using lost wax method.

(2) As for compression test, the Nb₃Al powder compacts obtained have almost 3 times high temperature strength (ex. over 100MPa at 1773K) compared to as-HIPed one, when isothermally held above 1873K, presumably due to the disappearance of PPBs by grain growth.

(3) The high temperature strength may possibly be fairly improved for (cermet-type) Nb₃Al composites with 10wt% of ceramic fines such as Y₂O₃, ZrO₂. Especially, the Nb₃Al/Y₂O₃ composite showed the higher compressive strength of 83MPa even at 1973K.

In the near future, Nb₃Al is expected to make a

Fig. 12 Microstructures of Nb-22.8at%Al + 10wt% ceramic composites HIPed at 1573K/196MPa and heat-treated at 2073K.

techniques by P/M process, albeit such problems as brittleness, oxidation resistance remain yet to be solved for Nb_3Al as well as Ti-Al P/M one⁽²⁰⁾, or precision casting one⁽²¹⁾ partly in a trial use.

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