Microstructures and Mechanical Properties of Nb/Nb-Silicide *in-situ* Composites Synthesized by Reactive Hot Pressing of Ball Milled Powders

C. L. Ma¹, A. Kasama¹, H. Tanaka¹, Y. Tan¹, R. Tanaka¹, Y. Mishima² and S. Hanada³

¹Japan Ultra-high Temperature Materials Research Institute, Ube 755-0001, Japan

²Department of Materials Science and Engineering, Tokyo Institute of Technology, Yokohama 226-8502, Japan

³Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

To develop advanced structural materials at very high temperatures, ball milling followed by reactive hot pressing was employed to fabricate binary Nb/Nb-silicide *in-situ* composites with 3.5 to 16 mol% silicon content. Changes in morphology during milling of niobium and silicon elemental powders were studied, and microstructures and mechanical properties of reactively hot pressed composites were evaluated by OM, SEM, XRD, DTA and EPMA. No detectable niobium silicide was formed during milling. Reactive hot pressing of the milled powders yields two kinds of silicides, Nb₃Si and Nb₅Si₃, through *in-situ* reaction between heavily deformed niobium particles and fragmented silicon particles. DTA revealed that silicide formation occurs at 940 K for Nb₃Si and 1050 K for Nb₅Si₃. Fully dense Nb/Nb-silicide *in-situ* composites with equiaxed grain microstructures are produced by the reactive hot pressing of milled powders. All of the composites exhibit considerable compressive ductility without cracking even at room temperature. Annealing at high temperature results in growth of equiaxed grains of niobium and silicide, thereby increasing high temperature strength.

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1. Introduction

In-situ composites based on Nb-Si binary alloys are potential candidates for high-temperature structural applications and have been extensively studied in recent years.¹⁻¹³⁾ In this two-phase composite system, the ductile metal phase of a Nb solid solution (Nb_{ss}) provides room-temperature toughness and the intermetallic of Nb₅Si₃ provides high-temperature strength. According to the Nb-Si binary equilibrium phase diagram,¹⁴⁾ Nb_{ss} and Nb₅Si₃ coexist in a wide range of temperature (room temperature~2043 K) and silicon content (0.5~37.5 mol%). These features of the phase diagram enable to fabricate an *in-situ* two-phase composite with a high degree of thermodynamical and microstructural stability at high temperature, which is a prerequisite for high temperature structural materials. Several different processes for producing this *in-situ* composite have been developed using arc-melting, rapid solidification, directional solidification, and powder processing.⁵⁻⁸⁾ Different characteristic microstructures were evolved depending on processes, which strongly affected the balance of high-temperature strength and low-temperature damage tolerance. When Nb-Si binary alloys with silicon contents from 10 to 16 mol% are cast and heat treated, the equilibrium microstructure is composed of large primary Nb_{ss} particles and fine eutectoid of Nb_{ss} and silicide.^{5,6)} These alloys, which are referred to as ductile-brittle *in-situ* composites,^{2,9)} have a low fracture toughness value at room-temperature in the range of 6 to 9.6 MPa·m^{1/2}.⁶⁾ When the cast alloys are extruded so that the primary Nb_{ss} particles are elongated along the extrusion direction, fracture toughness increases to ~21 MPa·m^{1/2} without degrading high temperature strength.⁶⁾ This result suggests that microstructural control through fabrication processing is one of crucial issues to develop high performance Nb_{ss}/Nb silicide *in-situ* composites.

Powder processing via reactive sintering, hot isostatic pressing, vacuum hot pressing, extrusion, or plasma spraying *et al.*, is known to provide a means of controlling microstructure in a high productivity setting. In addition, the powder processing can avoid the limitations imposed by the solidification path. However, few data for Nb_{ss}/Nb silicide *in-situ* composites prepared by powder processing are available at present. In a pioneer research work,¹³⁾ niobium and Nb₅Si₃ powders were mechanically blended and hot pressed to synthesize Nb_{ss}/Nb silicide *in-situ* composites. In this case, structural inhomogeneities caused by interface reaction were observed. On the other hand, in hot pressing of pre-alloyed powders, the control of homogeneity and porosity as well as the consolidation was very difficult because of high strength of silicide at high temperature.

The objective of this study is to fabricate Nb_{ss}/Nb silicide *in-situ* composites by reactive hot pressing of ball milled powders and to evaluate their microstructures and mechanical properties. In this study, the ball milling process was employed as a pre-treatment to enhance subsequent reactive sintering. It is generally accepted that ball milling conditions greatly affect particle size, purity and particle structure, thereby changing the chemistry and microstructure of subsequently sintered materials.¹⁵⁻¹⁷⁾ Therefore, the characteristics of ball milled powders of niobium and silicon were investigated, especially for the powders milled for 30 h which were selected for reactive hot pressing. Heat treatment was given to reactively hot-pressed materials for homogenization.

2. Experimental Procedure

2.1 Ball milling

Elemental niobium powder (<325 mesh) with 99.9 mass% in purity was blended with semiconductor grade silicon (<300 mesh) at compositions of Nb-3.5 mol%Si, Nb-

Table 1 The contamination of Nb-16Si powder with milling time (in mass%).

Milling time	Fe	C	Ni	Cr	Si	Nb
30 h	0.21	0.004	0.018	0.028	4.85	balance
60 h	1.94	0.004	0.032	0.054	4.87	balance
110 h	3.36	0.006	0.046	0.083	4.37	balance

6 mol%Si, Nb-10 mol%Si and Nb-16 mol%Si (these alloys will be abbreviated here after as Nb-3.5Si, Nb-6Si, Nb-10Si, and Nb-16Si, respectively, otherwise unstated).

Ball milling was performed in a planetary ball mill. About 200 g of blended elemental powders was filled in a cylindrical stainless steel (SUS304) vial. Stainless steel (SUS304) balls of 10 mm in diameter were used and the ball-to-powder ratio in weight was about 4 : 1. Four steel vials were fixed on the rotation disk of the planetary ball mill. The diameter of the rotation disk is about 400 mm. Before milling, the vials were evacuated and then backfilled with high purity argon gas to avoid the contamination due to oxygen and nitrogen during milling. The mill was operated at the rotation speed of about 150 rpm, and milling was interrupted at a certain time (1, 3, 14, 30, 60, and 110 h) and a part of powders was withdrawn from the vial for structural analysis.

The morphology and structure of ball milled powders were evaluated by optical microscopy (OM), scanning electron microscopy (SEM), electron probe microanalysis (EPMA) and X-ray diffraction (XRD). Thermal analysis of the milled products was carried out by differential thermal analysis (DTA).

Iron contamination has been claimed to be a serious problem if steel balls and vials are used.¹⁶⁾ Therefore, the contamination due to iron, nickel, chromium and carbon, which are primary components of SUS304 stainless steel, was analyzed in milled powders. The results obtained from Nb-16Si powder are summarized in Table 1. Note that the silicon content is also included in Table 1.

2.2 Reactive hot pressing and subsequent thermal treatment

The powders milled for 30 h were selected for hot pressing, mainly because these powders are of relatively lower contamination due to impurities (see Table 1) and a uniform microstructure is obtained (which will be described in a latter section). The milled powders were sintered in vacuum by hot pressing in a graphite die at 1773 K for 3 h under 40 MPa. A part of the hot pressed compacts was annealed for 24 h at selected temperatures to check changes in microstructure and mechanical property.

2.3 Mechanical properties

The deformation behavior of the reactively hot-pressed alloys was examined by compression test at room temperature to 1773 K. Compression specimens with a dimension of approximately $3 \times 3 \times 6 \text{ mm}^3$ were electro-discharge machined (EDM) from the alloys so as to have a compression axis perpendicular to the hot-pressing direction. Surfaces of the specimens were abraded on sufficiently fine SiC paper. Compression tests were carried out at a strain rate of $3 \times 10^{-4} \text{ s}^{-1}$

in an argon atmosphere, using an Instron-type machine, and were stopped when a plastic strain exceeded 16%.

3. Results

3.1 Characterization of ball milled powders

3.1.1 Microstructure of as-milled powders

Similar microstructural evolution was observed during ball milling for the mixture powders with silicon contents from 3.5 to 16 mol%. As an example, the microstructural changes of ball milled powders with a composition of Nb-16Si during ball milling are demonstrated in Fig. 1. In the initial stage of milling, hard brittle silicon particles were fractured into fine particles and embedded on the surface of Nb particles, while ductile Nb particles were flattened by compressive force in ball milling and colligated together to form large composite particles through cold welding. Fine silicon particles trapped at boundaries between welded niobium particles can be clearly seen in Fig. 1(a), where a cross section of a particle is observed by OM. As milling proceeds, the composite particles are repeatedly deformed and a lamellar-like structure is formed. As illustrated in Fig. 1(b), the lamellar structure consists of elongated niobium plates and fine silicon particles dispersed at the boundaries of elongated niobium particles. The observation revealed that the composite particles at this stage are not uniform in structure and chemistry. At longer milling times, the composite particles are further refined, the lamellar spacings decrease (see Fig. 1(c) after 30 h), and the

Fig. 1 Optical morphology of a cross section of Nb-16Si powders milled for (a) 3 h, (b) 14 h, (c) 30 h and (d) 60 h.

Fig. 2 X-ray diffraction patterns of (a) Nb-10Si and (b) Nb-16Si element powders milled for various milling times.

lamellae become convoluted (see Fig. 1(d) after 60 h). It is noted that silicon particles are finely dispersed after milling for longer than 30 h. At the same time, it is also noted that, as shown in Table 1, the iron contamination of powders milled for longer than 30 h is much more significant than that of powders milled for 30 h.

The changes in XRD patterns of Nb-10Si and Nb-16Si powders are shown in Figs. 2(a) and (b) as a function of milling time. With increasing milling time, Bragg reflection intensity from silicon becomes weak quickly and disappears when the milling time is longer than 30 h for Nb-10Si. While, for Nb-16Si, a Si(111) peak is still detectable even the milling time longer than 60 h. Bragg reflection intensity from niobium decreases very quickly and the peak becomes broad at the early stage of milling. The peak broadening may be caused by grain size refinement and/or by internal stress in niobium. When milling time is prolonged to 110 h, Bragg reflections (110), (200), and (211) from niobium are still visible, although reflection peaks become broader. The XRD result clearly indicates that no discernible peak other than the niobium and silicon peaks can be observed after milling for 110 h. This observation is in agreement with the result obtained by Kumar and Manna.¹⁸⁾ According to them, the mechanical alloying behavior of Nb-Si binary alloys exhibited composition dependence; no silicide was formed when milling powders had a silicon content less than 10 mass%

(~26.8 mol%), while an amorphous product was obtained at a silicon content higher than 10 mass%.

3.1.2 Phase formation by heating

Figure 3 illustrates the DTA curve of Nb-16Si powder milled for 30 h, where the measurement was carried out at the heating rate of 20 K/min to a maximum temperature of 1773 K in a flowing argon atmosphere. On the DTA curve, three exothermic peaks can be seen at 930, 1030, and 1220 K. In order to explain reactions at these peaks, the formation of phases corresponding to the peaks was examined by XRD. The XRD profiles are shown in Fig. 4, where the result of as-milled powder is included for comparison. As can be seen, no detectable change on the XRD profile occurs on heating to 800 K, below the first peak temperature. On heating to 950 K, slightly higher than the first exothermic peak temperature (930 K), some peaks are identified as Nb₃Si with A15 structure. This fact indicates that the exothermic peak at 930 K corresponds to the formation of Nb₃Si. It is also noted that a Si peak is still visible, though its intensity is very weak. On heating to 1050 K, slightly higher than the second peak temperature (1020 K), peaks of Nb₅Si₃ with D8₁ structure appear. That is, the second exothermic peak at 1020 K is due to the formation of Nb₅Si₃. On heating to 1240 K, slightly higher than the third peak temperature (1220 K), and on heating to 1400 K, no new peak corresponding to another compound is observed, although diffraction intensities of Nb₅Si₃ and Nb₃Si increase. The reaction corresponding to the third exothermic peak is not clear at present, but one possible explanation is that the third peak is caused by recrystallization of deformed niobium particles, because heavily deformed niobium is known to exhibit a higher recrystallization temperature than 1273 K.¹⁹⁾

3.2 Characterization of reactively sintered alloys

3.2.1 Microstructure of as-hot pressed alloys

Optical micrographs of as-hot pressed compacts with various compositions are presented in Fig. 5. We can see irregularly arranged, very fine particles, where the bright area is Nb_{ss} and dark fine particles are mainly Nb₅Si₃ (XRD and EPMA results indicated the existence of a small amount of Nb₃Si). It is obvious from Figs. 5(a)–(d) that the volume fraction of silicide increases with increasing silicon content in the

Fig. 3 DTA curve for Nb-16Si element powders milled for 30 h at a heat rate of 20 K/min in a flowing argon atmosphere.

Fig. 4 X-ray diffraction patterns of ball milled Nb-16Si powder after heating to various temperatures.

Fig. 5 Optical micrographs of Nb-Si powders hot pressed at 1773 K for 3 h under 40 MPa. (a) Nb-3.5Si, (b) Nb-6Si, (c) Nb-10Si, and (d) Nb-16Si.

compacts, and the silicide particles are distributed along a certain direction in a group manner. As mentioned above, very fine silicon particles are distributed along elongated bound-

Fig. 6 Back scattered electron image of as-hot pressed Nb-10Si at high magnification. Dark particles (silicide) are distributed in the light matrix (Nb_{ss}).

Fig. 7 Densities of hot-pressed Nb-Si binary alloys as a function of silicon content. Notice the calculated densities are included for comparison.

aries between deformed niobium particles in milled composite particles (see Fig. 1). From comparison of the microstructures of the hot pressed alloys with those of as-milled powders, it is found that the microstructural features of milled powders are maintained after sintering. This observation suggests that reactive sintering to form silicide takes place between niobium and silicon. These features were also observed by SEM in a backscattered electron image (BEI). BEI micrographs evidencing the reactive sintering in Nb-10Si are shown in Fig. 6. Another important observation is that few pores were seen in the compacts, suggesting that almost fully dense compacts were obtained through this process. This was also confirmed by density analysis. The densities of as-hot pressed compacts with various nominal compositions are plotted in Fig. 7, together with theoretical densities calculated from the Nb-Si binary phase diagram.¹⁴⁾ It can be seen that the densities of as-hot pressed compacts are very close to the theoretical densities. This result also indicates that the compacts have an average composition close to the nominal composition.

3.2.2 Mechanical properties of reactively hot pressed alloys

Vickers hardness and the volume fraction of silicide are plotted in Fig. 8 as a function of Si content. Evidently, Vickers hardness linearly increases with increasing silicon (sili-

Fig. 8 Vickers hardness and silicide volume fraction of hot-pressed Nb-Si alloys as a function of silicon content.

Fig. 9 Compressive stress-strain behaviors of as-hot pressed Nb-Si alloys at room temperature.

Fig. 10 Temperature dependence of compressive yield stress for as-hot pressed Nb-Si alloys.

cide) content. Compression tests of hot pressed compacts were carried out at room temperature, 1273, and 1773 K. The compressive stress-strain behavior of hot pressed compacts at room temperature is shown in Fig. 9. The compressive yield strength of these compacts is plotted in Fig. 10 as a function of test temperature. All of the hot pressed compacts exhibit high

compressive yield strength, considerable compressive ductility and work hardening at room temperature without cracking. The high compressive ductility may be related to the fine microstructures. Grain size refinement has been proposed as a means of ductility enhancement in metallic materials. With increasing test temperature, the yield strength rapidly decreases and reaches a value of 20 ~ 30 MPa at 1773 K which is slightly higher than that of pure niobium. This result may be explained by considering grain boundary sliding at high temperatures and/or low strength of the niobium phase at elevated temperatures.

3.3 Annealing of reactively sintered alloys

3.3.1 Microstructures of hot pressed and annealed alloys

To complete the reactive sintering, homogenize the hot pressed compacts and stabilize the microstructures, heat treatments were performed on the hot pressed Nb-10Si and Nb-16Si compacts at 1773, 1873, 1973 and 2073 K for 24 h. XRD profiles of the hot pressed and annealed Nb-16Si are presented in Fig. 11 as a function of annealing temperature, where XRD profile of as-hot pressed Nb-16Si is also included for comparison. As described above, the as-hot pressed alloys consist of Nb_{ss}, Nb₅Si₃, and a small amount of Nb₃Si. Nb₃Si is still detectable after annealing at 1773 K for 24 h, while it disappears after annealing at 1873 K for 24 h, implying that Nb₃Si decomposes completely into Nb_{ss} and Nb₅Si₃ through the eutectoid reaction. After annealing at 1973 and 2073 K, only Nb_{ss} and Nb₅Si₃ exist. It should be noted that the annealing temperature of 2073 K is slightly higher than the eutectoid temperature (2043 K) according to the Nb-Si binary phase diagram.¹⁴⁾ That is, Nb₃Si is a stable phase at 2073 K. No Nb₃Si was observed, however, in XRD and EPMA analyses. The reason is uncertain, but some impurities may affect the phase transformation, or Nb₃Si formation may be very sluggish.

Microstructural changes by the heat treatments after hot pressing were also observed by SEM. Figure 12 shows the

Fig. 11 X-ray diffraction patterns of Nb-16Si compact at various annealing temperatures.

Fig. 12 SEM micrographs of Nb-16Si compacts annealed at various temperatures.

Table 2 Grain sizes of the constituent phases at various annealing temperatures.

Annealing temperature	As-hot pressed	1773 K	1873 K	1973 K	2073 K
Size Nb _{ss}	<1.0	~2.0	~4.0	~4.5	~5.5
(μm) Silicide	<1.0	~1.5	~3.0	~4.0	~5.0

Fig. 13 Annealing temperature dependence of compressive yield stress at (a) 1773 K and (b) 300 K for Nb-10Si and Nb-16Si.

SEM micrographs of Nb-16Si annealed at various temperatures. The SEM observation has revealed that equiaxed dual phase alloys are formed, and their microstructures are quite different from those of alloys prepared by ingot metallurgy. Furthermore, grain coarsening during annealing is not so significant. The sizes of the constituent phases measured from SEM micrographs are given in Table 2. It is noted from Table 2 that the average particle sizes are smaller than 6 μm in spite of high temperature annealing for a long time (2073 K, 24 h). As far as creep strength is concerned, this type of fine grain structure will be unfavorable. Another comment to be noted is the formation of round shaped pores with diameters less than 1 μm at grain boundaries. Some pores may originate from interfaces of particles which are not consolidated completely during hot processing. And some pores may be formed in a polishing process by chipping. The presence

of these pores will degrade the mechanical properties of the alloys.

3.3.2 Mechanical properties of hot pressed and annealed alloys

Figure 13 shows the annealing temperature dependence of compressive yield strength in Nb–10Si and Nb–16Si at room temperature (a) and 1773 K (b). At 1773 K, the compressive yield strength rapidly increases with increasing temperature from 20 MPa to about 100 MPa for Nb–16Si. For Nb–10Si, slightly lower yield strength is obtained compared with Nb–16Si. In contrast, at room temperature, the yield strength of Nb–16Si decreases with increasing annealing temperature. These dependences can be explained in terms of grain size effect for strength at room temperature and of grain boundary sliding for strength at 1773 K. That is, Hall-Petch equation expressing the grain size dependence of yield strength predicts higher strength for finer-grained materials annealed at lower temperature. On the other hand, the grain boundary sliding occurs more frequently for finer-grained materials, thereby decreasing high temperature strength. As shown in Table 2, the grain size increases with increasing annealing temperature.

4. Discussion

The present results indicate that the Nb_{ss}/Nb silicide *in-situ* composites fabricated by reactive hot pressing of ball milled powders are of characteristic microstructures, which are very different from those of composites prepared by ingot metallurgy.^{5,6} As mentioned in the previous section, the cast and heat treated Nb–Si alloys with silicon contents from 10 to 16 mol% have the equilibrium microstructures consisting of large dendritically formed Nb_{ss} particles and eutectic of Nb_{ss} and Nb₅Si₃.^{5,6} These composites exhibit a high brittle-to-ductile transition temperature of about 1473 K and low fracture toughness at room-temperature in the range of 6 to 9.6 MPa·m^{1/2}.⁶ On the contrary, Nb–Si alloys with the same compositions as above, which were prepared by powder metallurgy, have the microstructures consisting of fine equiaxed grains (see Figs. 6, 7, and 12). These composites exhibit high compressive ductility at room temperature (see Fig. 9), implying low ductile-to-brittle transition temperature and improved fracture toughness. Further studies are needed to evaluate the high temperature strength and the low temperature fracture toughness for Nb_{ss}/Nb silicide *in-situ* composites prepared by powder metallurgy.

This work also reveals that the reactive hot pressing of milled powders is a viable process to produce fully dense Nb_{ss}/Nb silicide *in-situ* composites. The fabrication of Nb_{ss}/Nb silicide *in-situ* composites with Si contents higher than 10 mol% has been said to be difficult because of extremely high melting temperature if a conventional ingot metallurgy process is employed. Moreover, it is rather difficult to obtain thermodynamically stable microstructures in cast Nb–Si alloys, as compared with alloys prepared by powder metallurgy processing. Long time heat treatment is necessary to get a thermodynamically equilibrated microstructure. It is evident, however, that the present process allows us to produce crack-free *in-situ* composites with high silicon contents.

The grain growth of the alloys prepared by powder metallurgy processing is found to be very sluggish in this study even on annealing at high temperature. Although fine-grained alloys exhibit good compressive ductility at room temperature, their creep strength will be inferior. A study to control microstructure is required to realize a better balance between fracture toughness at room temperature and strength at elevated temperature.

5. Conclusions

In the present work, the reactive hot pressing of ball milled elementary powders was employed to fabricate Nb_{ss}/Nb silicide *in-situ* composites based on Nb–Si binary alloys. The ball milled powders and reactively hot-pressed compacts were evaluated by OM, SEM, DTA, XRD and EPMA. The mechanical properties of hot-pressed materials were examined by compression test. The obtained results are summarized as follows:

- (1) During ball milling niobium particles are heavily deformed and elongated, while silicon particles are fragmented and distributed along at boundaries of niobium particles.
- (2) Niobium silicide is not formed during ball milling.
- (3) Reactive hot pressing of the milled powders at 1773 K yields Nb₃Si and Nb₅Si₃ through *in-situ* reaction between niobium and silicon.
- (4) On heating of ball milled powders silicide formation occurs at 940 K for Nb₃Si and 1050 K for Nb₅Si₃.
- (5) Almost fully dense Nb_{ss}/Nb silicide *in-situ* composites with equiaxed grain microstructures are produced by the reactive hot pressing of milled powders.
- (6) All of the composites exhibit considerable compressive ductility without cracking even at room temperature.
- (7) Annealing of the hot pressed composites at high temperature results in growth of equiaxed grains of niobium and silicide, thereby increasing high temperature strength.

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