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Simultaneous synthesis and densification of niobium silicide/niobium composites

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Introduction

Refractory metal silicides, particularly those of niobium, have received considerable attention in recent years for their potential application as a high-temperature structural materials [1]. However, their brittleness at room temperature is a serious drawback. There are three silicides of niobium: Nb₃Si, which is only stable between 1765°C and 1975°C; NbSi₂ and Nb₅Si₃, with the highest melting point in the Nb–Si system, 2515°C. Nb₅Si₃ has a very limited range of solubility with niobium and NbSi₂. It has two tetragonal equilibrium phases with a transition at 1940°C, and a hexagonal carbon-stabilized phase. The high melting point and essentially line-compound behavior of Nb₅Si₃ make it ideal for forming composites with niobium, molybdenum, and other refractory metals, because it is thermodynamically stable with these materials.

One approach to improving toughness in this brittle intermetallic is to make a composite with a more ductile phase, for instance metallic niobium. This is known as ductile phase toughening. The fracture toughness of Nb₅Si₃ is 1–2 MPa√m [2], but it has been shown that including niobium particles in the Nb₅Si₃ matrix will bridge cracks and thus improve these values. Extensive work with Nb₅Si₃/Nb laminates [2,3] and with arc-cast composites [4–6] has been done to investigate the phenomenon of ductile phase

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toughening in this system. The work of Lewandowski's group on arc-melted composites used niobium with 10–16 at.% silicon added as reactants: they reported fracture toughness improvements up to 21 MPa \sqrt{m} [5]. 10–16 at.% silicon in the reactants is equivalent to 4–8 mol% Nb₅Si₃ and 96–92 mol% Nb in the final product. In terms of volume, this distribution is equivalent to 25–39 vol% Nb₅Si₃. The materials described in the present paper range from 100 to 10 mol% Nb₅Si₃, which is equivalent to 100 to 44 vol% Nb₅Si₃.

Several techniques to manufacture Nb₅Si₃/Nb composites besides arc-casting include directional solidification [7], CVD [8], sputter deposition with or without subsequent self-propagating high-temperature synthesis (SHS) [9–11], and mechanical alloying and combustion synthesis under pressure [2,12]. SHS from powders has produced Nb₅Si₃ when energy is added, such as via pre-heating [13] or by the application of an electric field. Field-activated combustion synthesis, or FACS, has been utilized to make Nb₅Si₃ both alone and as a composite with Nb [14].

In two projects most closely related to this work, Kajuch et al. [2,12] reacted and consolidated Nb₅Si₃ and 70 vol% Nb₅Si₃/30 vol% Nb from the elements in a vacuum hot press. Ma et al. mechanically milled and then hot-pressed several mixtures of Nb and Si, ranging from 3.5 to 16 mol% Si (13–44 vol% Nb₅Si₃) [15]. They also formed 44 vol% Nb₅Si₃ composites from mechanically milled mixtures using “reactive spark plasma sintering”, or field-activated pressure-assisted combustion synthesis [16].

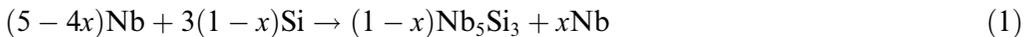
In this paper, we report our success in forming dense Nb₅Si₃ and Nb₅Si₃/Nb composites via field-activated pressure-assisted combustion synthesis. This method utilizes the simultaneous application of pressure and electric current to a graphite die containing Nb and Si powders in the appropriate proportions to make Nb₅Si₃ with or without excess niobium. The use of this method to simultaneously synthesize and densify monolithic materials, including nanometric phases, has been previously demonstrated [16–19]. We have made composites in compositions from 100 to 10 mol% Nb₅Si₃ with densities close to 100% of the theoretical density. The wide range of compositions available is of great advantage in tailoring the material properties to a specific purpose and in the formation of functionally graded Nb/Nb₅Si₃ composites.

Experimental procedure

The apparatus utilized in this research is the spark plasma sinterer (SPS) manufactured by Sumitomo Coal Mining Company, Inc. of Japan [20]. This machine consists of a uniaxial 100 kN press combined with a 15 V, 5000 A pulsed DC power supply, to simultaneously provide current and pressure to a conductive die and sample. The pulse cycle utilized in this work was 12 ms on and 2 ms off. Joule heating of the die and the sample results in the combustion of the sample, and the applied pressure densifies the sample at the same time. A similar apparatus built in our laboratory was used for experiments with smaller samples: the field-activated pressure-assisted synthesis apparatus (FAPASA) also consists of a 100 kN press and a current source, but the current is 60 Hz AC, and the maximum current is 1750 A at 10 V. The SPS may be controlled via

a temperature controller or manually by current, while the FAPASA has only manual current control. In both machines, temperature is measured on the surface of the die by means of a pyrometer. The SPS also has computer data collection of the voltage, current, load applied, temperature, displacement (shrinkage) and displacement rate. The FAPASA displays voltage, current, and temperature, but has no recording capability. In this case measurements are recorded manually every 30 s.

Elemental powders of niobium and silicon were used in this work. The niobium (Atlantic Equipment Engineers, Bergenfield, NJ) was 1–5 μm and 99.8% pure. The silicon (Alfa Aesar) was –325 mesh (less than 45 μm) and 99.5% pure. Powders were mixed in stoichiometric proportions according to the following equation:



so that concentrations of Nb could be expressed as a fraction of the total products. The powders were dry mixed in a Turbula® mixer for 1 h using 7 mm diameter zirconia-stabilized tetragonal alumina balls (ball to powder ratio 1:1 by weight). To form a sample, the appropriate quantity of mixed powder was weighed out and poured into a graphite die lined with graphite foil, shown schematically in Fig. 1, and cold pressed at 8.9 kN (31.4 MPa for the small dies). Two sizes of samples were produced: in the more powerful SPS, disks 45 mm in diameter and 5 or more mm tall were produced, while in the FAPASA, smaller disks 19 mm in diameter and 5 mm tall were produced. The volume of an SPS disk is approximately five times the volume of a FAPASA disk.

After packing, the samples were reacted either in the SPS or the FAPASA, under a load that varied with the sample size and the machine. Samples reacted in the FAPASA were subjected to a pressure of 78.6 MPa (22.3 kN), while the larger samples reacted in

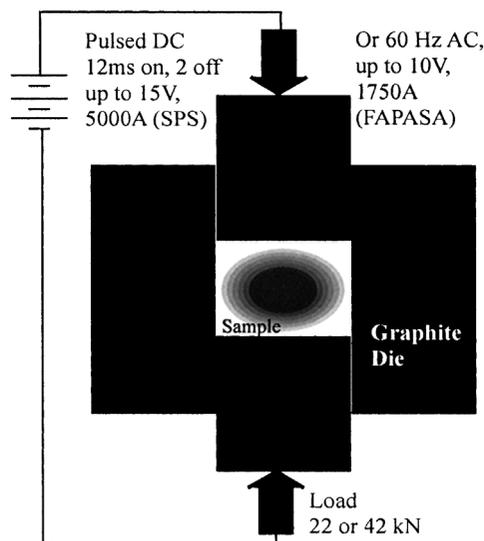


Fig. 1. Sample and die assembly schematic.

the SPS were subjected to a pressure of 26.4 MPa (42 kN). The decrease in pressure for the larger samples was necessary to prevent breakage of the larger die due to increased hoop stress in the die wall. The large samples were heated to 1400°C in 55 min (approximately 25°C/min), then held for 20 min, until the compaction rate had decreased to nearly zero, then allowed to cool naturally in the machine. The small samples with compositions 100–60 mol% Nb₅Si₃ were heated at 100 A/min to 1700 A, then held for a total of 25 min, before natural cooling. Samples with 50 mol% Nb₅Si₃ or less were heated at 50 A/min to 1500 A, then at 100 A/min to 1700 A, for a total of 25 min before natural cooling. The slower heating rate was necessary to prevent catastrophic reaction, as discussed below.

After the reactions, the samples were removed from the dies and lightly ground to remove the graphite foil. Specimens for X-ray diffraction (XRD) and microscopy were chipped off the as-pressed discs using a hammer and chisel. This material is very difficult to cut with a diamond saw, although electro-discharge machining (EDM) is quite effective. Samples were powdered for XRD and chips were mounted in epoxy and polished on SiC paper and diamond or alumina for microscopic examination. For grain size measurements, samples were polished with 0.3 and 0.03 μm alumina then etched with a solution of 70 ml distilled water, 20 ml nitric acid, and 10 ml hydrofluoric acid for 30–60 s.

The resulting samples were characterized by XRD using CuKα radiation for bulk phase identification. Mounted and polished samples were examined using optical microscopy and electron microprobe analysis (EPMA) for phase distribution and chemical species distribution. Using EPMA, back-scattered electron images and X-ray dot maps for NbLα and SiKα wavelengths were collected at magnifications of 500× and 1000×. A 1 μm spot size at 20 kV and 10 nA was used for WDS analysis of the phases present. Density was measured via both geometric and Archimedes' (submersion in methanol) methods. Microhardness was also measured on the epoxy-mounted and etched samples using a Vickers (square pyramid) indenter and loads from 2.94 to 11.76 N with a dwell time of 12 s. Grain size was measured for a 100% Nb₅Si₃ sample and a 60% Nb₅Si₃ sample, using the Heyn lineal intercept method with circular intercept lines (after ASTM E112). The sampled area was slightly smaller than recommended.

Results and discussion

XRD from powdered samples demonstrates that the reaction has gone to completion at 1400°C. Fig. 2 reveals that for 100% Nb₅Si₃ (synthesized at 1400°C), phases present are α-Nb₅Si₃ and traces of Nb₅Si₃:C. The sample with 40% Nb₅Si₃ contains Nb but no Nb₅Si₃:C. The 100% Nb₅Si₃ sample synthesized at 1000°C also contains NbSi₂, as explained below. The carbon-stabilized form of Nb₅Si₃, Nb₅Si₃:C, appears to form near the sample surface. Backscattered electron micrographs also show the presence of NbO and SiO₂ in all samples. These phases are assumed to be a result of oxides initially present on the reactant silicon, as the reactions were conducted either in argon or in a vacuum of less than 13 mPa. Fig. 3 shows backscattered electron micrographs taken at

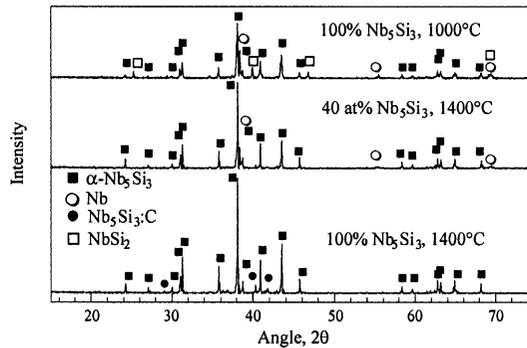


Fig. 2. XRD patterns for (a) 100 mol% Nb_5Si_3 , (b) 40 mol% Nb_5Si_3 /60 mol% Nb and (c) 100 mol% Nb_5Si_3 , heated to only 1000°C.

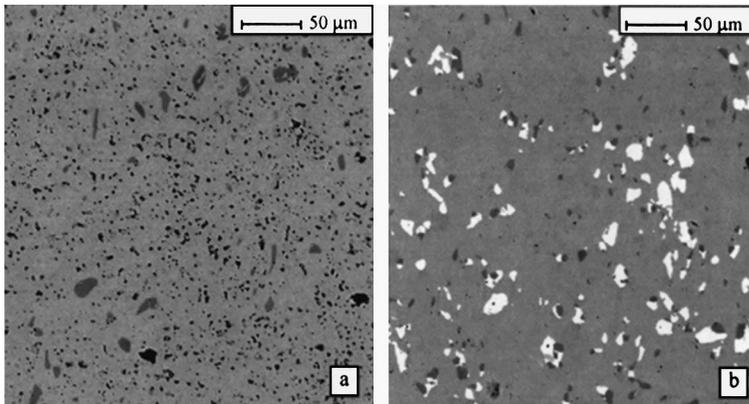


Fig. 3. Backscatter electron images of (a) 100 mol% Nb_5Si_3 and (b) 60 mol% Nb_5Si_3 /40 mol% Nb.

low magnification. The first (a) is 100% Nb_5Si_3 and the second (b) is 60 mol% Nb_5Si_3 , showing the typical structure of the samples. The black spots are primarily SiO_2 , the dark gray spots are NbO, and the bright spots are Nb. Some of the black spots in Fig. 3(a) and most of those in Fig. 3(b) are pores. The matrix is Nb_5Si_3 .

The nominal grain diameter for the 100% Nb_5Si_3 sample is 1.1–2.3 μm . For the 60% Nb_5Si_3 sample, the grain diameter for Nb_5Si_3 is 4–5.6 μm , as shown in Fig. 4. There are regions where much smaller grains are evident, and scattered smaller grains are evident throughout the microstructure. In secondary electron images such as Fig. 4, it was not possible to identify Nb grains in the 60% Nb_5Si_3 sample. A large, pure Nb_5Si_3 sample had a Vickers hardness of between 570 and 970 kgf/mm^2 and K_{Ic} of 2.3–5.5 $\text{MPa}\sqrt{\text{m}}$, for a range of loads between 2.94 and 11.76 N. Others have reported K_{Ic} of 1–2 $\text{MPa}\sqrt{\text{m}}$ on similarly synthesized samples in tests done according to ASTM E 399-83 [2].

The densities of the large 100% Nb_5Si_3 samples were between 94% and 97% of theoretical, while the smaller composite samples were denser: all small samples were above

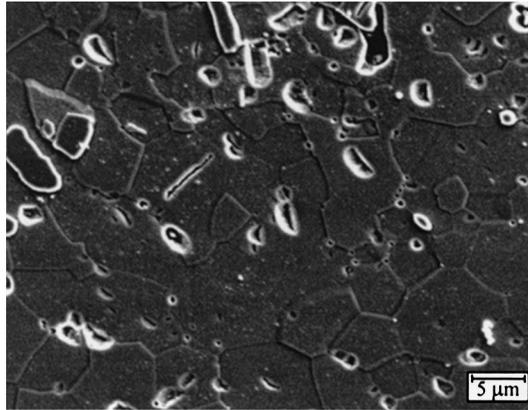


Fig. 4. Etched sample: 60 mol% Nb_5Si_3 , showing grain size and morphology.

99% of theoretical. When samples were heated slowly, full reaction and full density were obtained at 1400°C (measured on the die surface). When a mixture without excess Nb was heated too quickly, a sudden reaction took place, accompanied by a large compaction, at a surface temperature of about 1000°C . Samples cooled immediately after this event contained only Nb_5Si_3 and traces of Nb and oxides. This phenomenon has also been observed in MoSi_2 synthesis [19,21]. When this occurred in a large Nb–Si sample, the sample usually cracked in a radial pattern. This is believed to be due to the sudden change in volume, although Ma et al. did not observe this phenomenon in milled samples [16]. If the sample continued under pressure and current, the current arced across the crack surfaces, causing the appearance of arc-melted regions on the crack surfaces. With slower heating rates (50–100 A/min), compaction occurred slowly and the reaction went to completion without cracking, but full density was reached only at an external temperature of 1400°C . More excess Nb required a slower heating rate to prevent sudden compaction.

The difference in reaction rate is believed to be due to the behavior of the silicon. When the heating rate is rapid, the internal temperature rises above the eutectic temperature of 1400°C between Si and Nb_5Si_2 . As a result, large-scale melting of the silicon occurs, which ignites the reaction to form Nb_5Si_3 . The reaction occurs immediately, with instantaneous shrinkage. When the heating rate is slower, the silicon diffuses into the niobium either in solid state or with minor melting at the contact points between particles and forms NbSi_2 . Once all the silicon has been consumed, the temperature may be raised without catastrophic melting. In fact, the temperature must be raised to drive the further reaction between NbSi_2 and Nb to form Nb_5Si_3 and achieve near-theoretical density. Fig. 5 is a backscattered electron image of a sample that was heated slowly to 1000°C and then quenched, showing the typical structure of Nb_5Si_3 surrounding pure Nb, with many pores. NbSi_2 is present in the darker regions at the edges of pores. XRD reveals the presence of significant amounts of NbSi_2 , but no remaining silicon, as shown in Fig. 2.

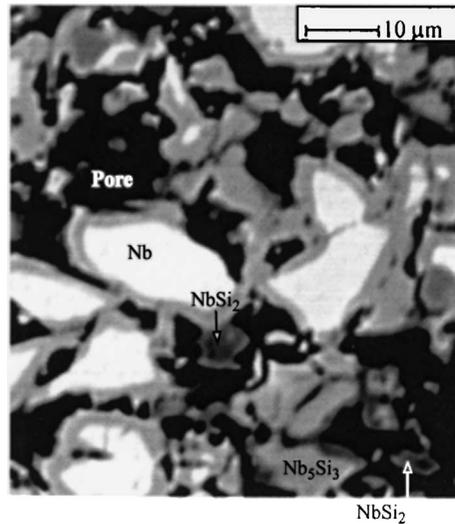


Fig. 5. Backscatter electron image of 100 mol% Nb₅Si₃, heated to 1000°C, showing black pores, white Nb, gray Nb₅Si₃ and dark NbSi₂.

Conclusions

Dense niobium silicide (Nb₅Si₃) and composites up to 90 mol% niobium have been made via the novel technique of field-activated, pressure-assisted combustion synthesis. A complete reaction with full densification was obtained after just 25 min and densities as high as 99.9% were achieved. It is necessary to raise the green compact to a temperature just below the eutectic of NbSi₂ and Nb to enable diffusion of the silicon without initiating catastrophic shrinkage which causes cracking during the reaction, then raise the temperature to drive formation of Nb₅Si₃. The grain size is fine and roughly equiaxed, and the Nb is well distributed. Some SiO₂ and some NbO remain due to initial oxygen on the surfaces of the powders. The wide range of Nb₅Si₃/Nb compositions available allows the tailoring of the material properties to specific purposes and also allows the formation of ductile/brittle functionally graded materials. These topics are currently under investigation.

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