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High-Frequency Induction-Heated Combustion Synthesis and Consolidation of Nanostructured $NbSi_2$ from Mechanically Activated Powders

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Abstract Dense nanostructured $NbSi_2$ was synthesized by high-frequency induction-heated combustion synthesis (HFIHCS) method within 1 minute in one step from mechanically activated Nb and Si powders. Highly dense $NbSi_2$ with relative density of up to 99% was simultaneously synthesized and consolidated under the combined effects of an induced current and mechanical pressure of 60 MPa. The average grain size and mechanical properties (hardness and fracture toughness) of the compound were investigated.

Keywords : High-frequency induction heated combustion, Intermetallic, Sintering, Nanophase, Mechanical properties, $NbSi_2$

1. Introduction

Transition metal silicides such as $NbSi_2$ are of great interest as high-temperature structural material, mainly due to its high melting point, low density, high oxidation resistance in air, and good mechanical strength at high temperature [1]. In addition, the disilicide ($NbSi_2$, WSi_2, $MoSi_2$, $TiSi_2$) has found wide applications as thin film in microelectronics, as a result of its high electrical conductivity, high-temperature stability, corrosion resistance, and the ability to form good contacts with silicon [2, 3]. However, as in the case of many intermetallic compounds, the current concern about these materials focuses on their low fracture toughness below the ductile-brittle transition temperature [4-6]. To improve on ductility combined with enhanced strength is expected to be achieved in nanostructured materials [7, 8].

Four decades ago, high energy ball milling and mechanical alloying of powder mixtures, were reported to be efficient techniques for the preparation of nano-crystalline metals and alloys. However, in such a case, it is necessary to add a consolidation step to obtain a fully dense material.

A few years ago, the simultaneous effect of an applied pressure during the combustion from mechani-

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cally activated powder mixture is demonstrated as a means to simultaneously synthesize and consolidate nanostructured compounds [9]. Especially, in a recent paper [10], the method of pulsed current activated and pressure-assisted combustion synthesis has been successfully employed to synthesize and densify nanostructured material from the mechanically activated powders in one step within 1 minute. This material, which is generally characterized by low adiabatic combustion temperature, cannot be synthesized directly by the self-propagating high-temperature synthesis (SHS) method.

More recently, a new approach has been developed in which synthesis and densification can be effected simultaneously. This new process, referred to as the high-frequency induction heated combustion synthesis (HFIHCS), has been successfully used to synthesize and densify materials in one step in a relatively short period of time (1 min) [11-13].

The objective of this study is to investigate the preparation of dense nanophase $NbSi_2$ by the HFIHCS method starting from a mixture of mechanically activated Nb and Si powders.

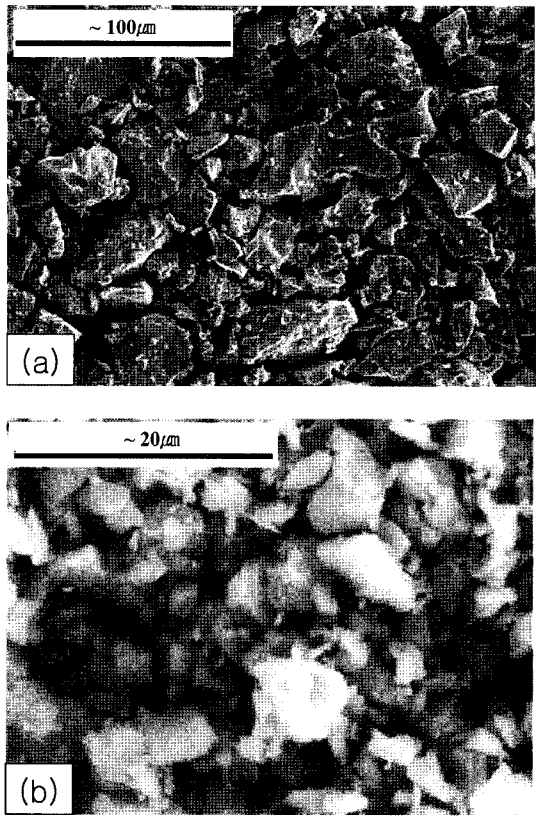

Fig. 1. Scanning election microscope images of raw materials : (a) niobium and (b) silicon.

2. Experimental Procedure

Powders of 99.8% pure niobium (-325 mesh, Alfa Products) and 99% pure silicon (-325 mesh, Aldrich Products) were used as starting materials. Fig. 1 shows the SEM images of the raw materials. Powder mixtures of Nb and Si in the molar proportion of 1:2 were first milled in a high-energy ball mill (Pulverisette-5, planetary mill) at 250 rpm for 10 h. Tungsten carbide balls (5 mm in diameter) were used in a sealed cylindrical stainless steel vial under argon atmosphere. The weight ratio of ball-to-powder was 30:1. Milling resulted in a significant reduction of grain size. The grain size and the internal strain were calculated by C. Suryanarayana and M. Grant Norton's formula [14],

$$B_r (B_{crystalline}+B_{strain}) \cos\theta = k\lambda/L + \eta\sin\theta \qquad (2)$$

where B_r is the full width at half-maximum (FWHM) of the diffraction peak after instrument correction; $B_{crystalline}$ and B_{strain} are FWHM caused by small grain size and internal stress, respectively; k is constant (with a value of 0.9); λ is wavelength of the X-ray radiation; L and η are grain size and internal strain, respectively; and θ is the Bragg angle. The parameters B and B_r follow Cauchy's form with the relationship: $B = B_r + B_s$, where B and B_s are FWHM of the broadened Bragg peaks and the standard sample's Bragg peaks, respectively.

Fig. 2 shows XRD patterns of the raw powders and the milled Nb + 2Si powder mixture. The FWHM of the milled powder is greater than that of the raw powders due to internal strain and grain size reduction. In the milled powder mixture, $NbSi_2$ phase reacted from Nb and Si during the milling is detected.

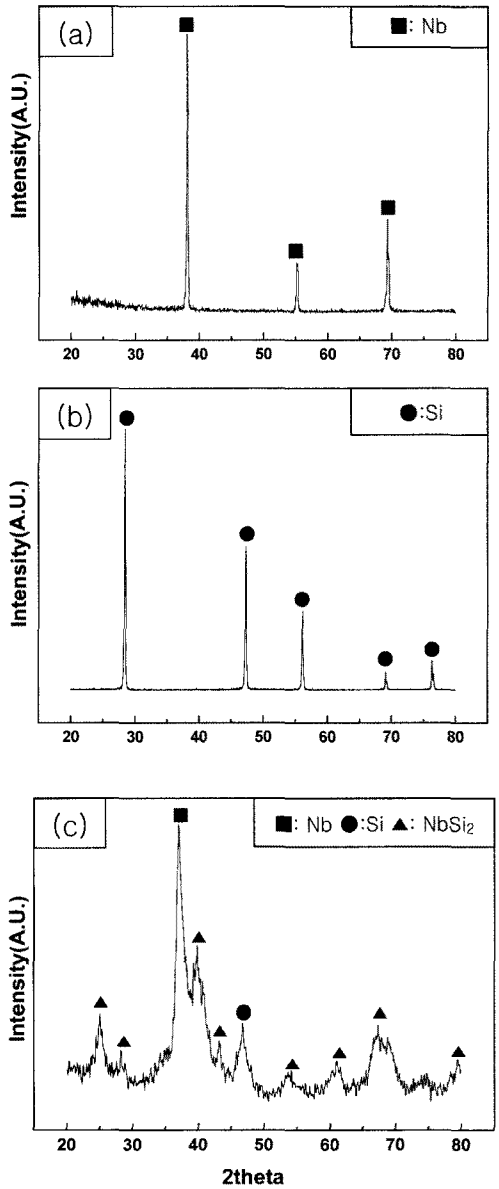

Fig. 2. XRD patterns of raw materials: (a) Nb, (b) Si and (c) milled Nb+2Si.

After milling, the mixed powders were placed in a graphite die (outside diameter, 45 mm; inside diameter, 20 mm; height, 40 mm) and then introduced into the high-frequency induction-heated combustion system, shown schematically in Fig. 3. Following the introduction of the die into the apparatus, the system was evacuated and a uniaxial pressure of 60 MPa

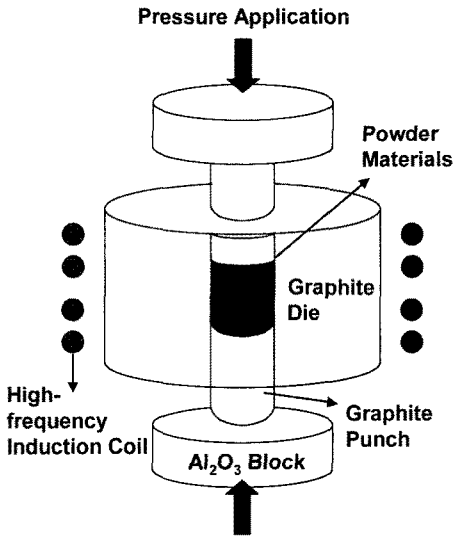

Fig. 3. Schematic diagram of the high-frequency induction heated combustion apparatus.

was applied. An induced current (frequency of about 50 kHz) was then activated and maintained until densification was attained as indicated by a linear gauge measuring the shrinkage of the sample. Temperature was measured by a pyrometer focused on the surface of the graphite die. At the end of the process, the sample was cooled to room temperature. The process was carried out under a vacuum of 40 $\times 10^{-3}$ torr.

The relative densities of the synthesized sample were measured by the Archimedes method. Microstructural characterization was made on product samples which had been polished and etched using a solution of HF (10 vol.%), HNO_3 (20 vol.%) and H_2O (70 vol.%) for 2 min at room temperature. Compositional and microstructural analyses of the products were made through X-ray diffraction (XRD) and scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDAX). Vickers hardness was measured by performing indentations at a load of 15 kg and a dwell time of 15 seconds.

3. Results and Discussion

The interaction between these phases, i.e.,

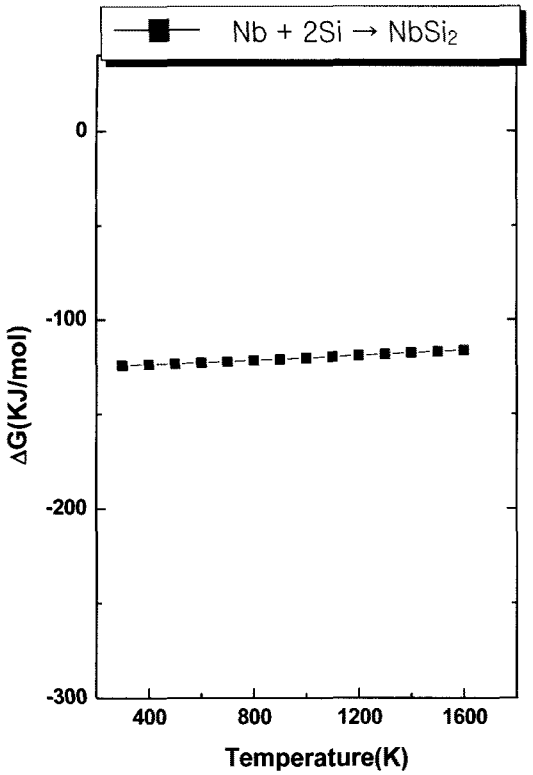

Fig. 4. Temperature dependence of the Gibbs free energy for the interaction between niobium and silicon.

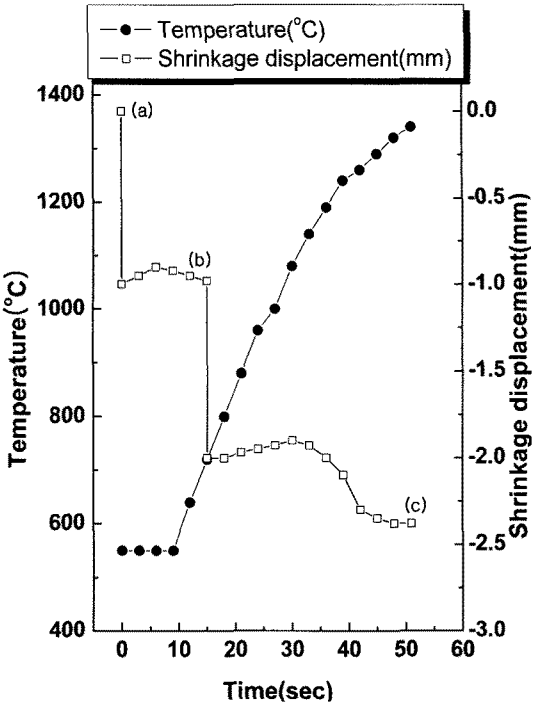

Fig. 5. Variations of temperature and shrinkage displacement with heating time during high-frequency induction heated combustion synthesis and densification of $NbSi_2$ (under 60MPa, 90% output of total power capacity).

$$Nb + 2Si \rightarrow NbSi_2 \quad (1)$$

is thermodynamically feasible, as can be seen from Fig. 4.

The variations in shrinkage displacement and temperature with heating time during the processing of Nb + 2Si system are shown Fig. 5. As the induced current was applied the specimen showed initially a small (thermal) expansion and the shrinkage displacement increased gradually with temperature up to about 600°C, but then abruptly increased at about 700°C. When the mixture of Nb + 2Si was heated under 60 MPa pressure to 600°C, no reaction took place and no significant shrinkage displacement as judged by subsequent XRD and SEM analyses. Figs. 6 (a), (b), and (c) show the SEM (secondary electron) images of (a) powder after milling, (b) sample heated to 600°C and (c) sample heated to 1350°C, respectively. Figs. 6(a) and (b) show the presence of the reactants as separate phases. X-ray diffraction results, shown in Fig. 7(a) and Fig. 7(b) exhibit peaks pertaining to the reactants (Nb, Si) and mechanically alloyed $NbSi_2$. However, when the temperature was raised to 1350°C, the starting powders reacted producing highly dense products. SEM image of an etched surface of the samples heated to 1350°C under a pressure of 60 MPa is shown in Fig. 6(c). A complete reaction between Nb and Si took place under these conditions. X-ray diffraction analyses of this sample showed peaks of $NbSi_2$, as indicated in Fig. 7(c). And minor phase (Nb_5Si_3) observed by X-ray diffraction analyses, as show in Fig. 7(c). The presence of Nb_5Si_3 of the sample suggests a deficiency of Si. It is considered that this observation is related to entrapped oxygen in the pores of the interior portion of the sample during pressing or maybe due to a little oxidation of Si during the heating.

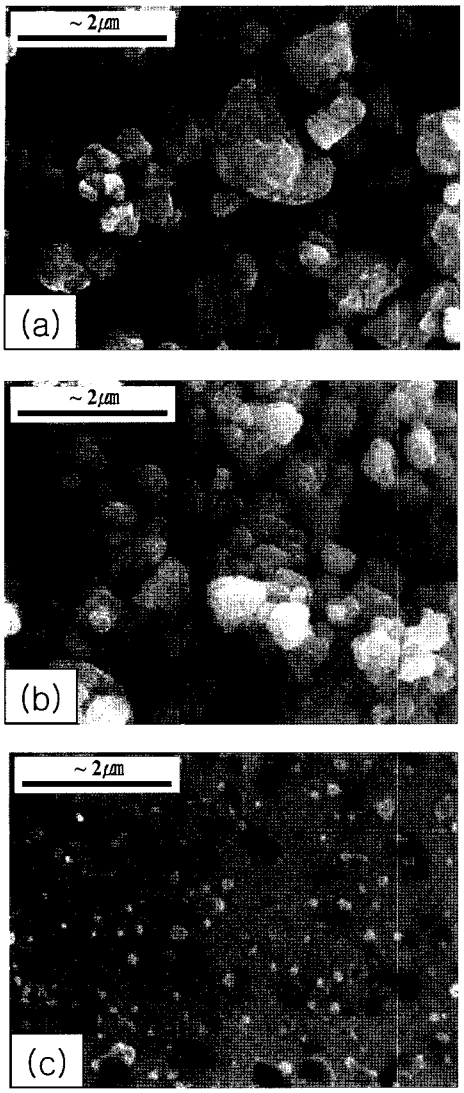

Fig. 6. Scanning electron microscope images of Nb+2Si system: (a) after milling, (b) before combustion synthesis and (c) after combustion synthesis.

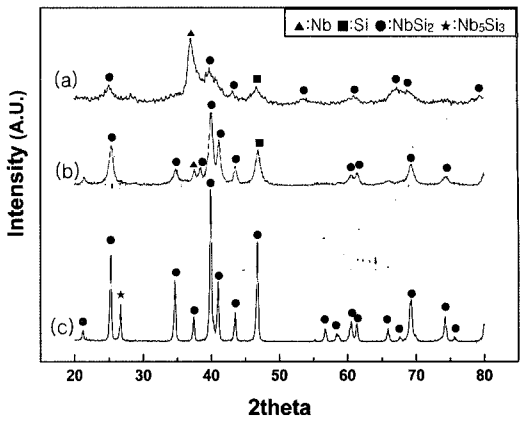

Fig. 7. XRD patterns of the Nb+2Si system: (a) after milling, (b) before combustion synthesis and (c) after combustion synthesis.

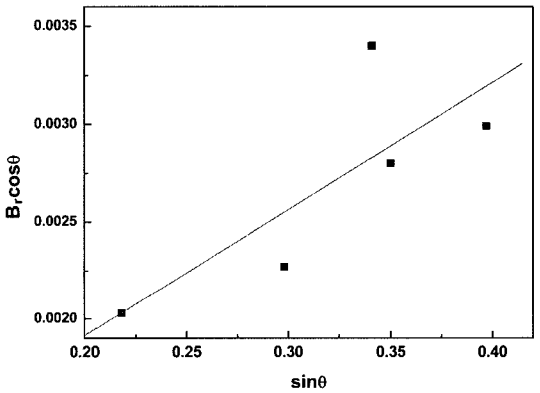

Fig. 8. Plot B_r cosθ against sinθ, indicating that the intercept ($k\lambda/L$) and slop (η) can be used to calculate the crystallite size (L) and lattice strain (η) of $NbSi_2$.

The abrupt increase in the shrinkage displacement at the ignition temperature (about 700°C) is due to the increase in density as a result of molar volume change associated with the formation of $NbSi_2$ from the reactants (Nb and Si) and the consolidation of the product. This temperature is lower than that of metal silicide reported as about 1200°C [15]. It is considered that mechanically activated reactant powders from high energy ball milling can reacted rapidly. Fig. 8 shows the plot of C. Suryanarayana and M. Grant Norton's formula [14]. The average grain sizes of $NbSi_2$ calculated from intercept (k λ/ L= 0.0006157), was about 220 nm.

Vickers hardness measurements were made on polished sections of the $NbSi_2$ using a 15 kg load and 15 s dwell time. The calculated hardness value, based on an average of five measurements, of the $NbSi_2$ is 906 kg/mm^2. Indentations with large enough loads produced median cracks around the indent. The length of these cracks permits an estimation of the fracture toughness of the materials by means of the expression [16]:

$$K_{IC} = 0.204(c / a)^{-3/2} \cdot H_v \cdot a^{1/2}$$

where c is the trace length of the crack measured from the center of the indentation, a is the half of average length of two indent diagonals, and H_v is the hardness. Typically, one to three additional cracks were observed to propagate from the indentation corner. The calculated fracture toughness value for the $NbSi_2$ is about 3.0 MPa·$m^{1/2}$. As in the case of the hardness value, the toughness value is the average of measurements on five measurements. The absence of reported values for hardness and toughness on $NbSi_2$ precludes making direct comparison to the results obtained in this work to show the influence of grain size.

4. Summary

Using the high-frequency induction-heated combustion method, the simultaneous synthesis and densification of nanostructured $NbSi_2$ was accomplished using powders of Nb and Si. Complete synthesis and densification can be achieved in one step within 1 min. The relative density of the composite was 99% under an applied pressure of 60 MPa and the induced current. The average grain sizes of $NbSi_2$ phases was about 220 nm, respectively. The average hardness and fracture toughness values obtained were 906 kg/mm^2 and 3.0 MPa·$m^{1/2}$, respectively.

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