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Simultaneous Synthesis and Densification of Ti_5Si_3 and Ti_5Si_3-20 vol%Nb Composite by Field-Activated and Pressure-Assisted Combustion

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A method to simultaneously synthesize and consolidate Ti_5Si_3 and Ti_5Si_3-20 vol%Nb composite from powders of Ti, Si and Nb was investigated. Combustion synthesis was carried out under the combined effect of an electric field and mechanical pressure. Highly dense Ti_5Si_3 and Ti_5Si_3-20 vol%Nb with relative densities up to 98% was produced from powders of Ti, Si and Nb under the application of 60 MPa pressure and 3000A current on the reactant.

Key words : Ti_5Si_3, Ti_5Si_3-Nb composite, Combustion synthesis SHS, Field-activated combustion synthesis

I. Introduction

Silicides have recently been investigated as potential materials for high temperature structural applications and for applications in the electronics industry. Among the former, the compound Ti_5Si_3 has been the focus of considerable attention as an attractive material for high temperature temperature (2403 K), good strength at high temperature, good creep resistance, low density (4.32 g/cc), and high oxidation resistance.[1-3] However, as in the case of many intermetallic compounds, the current concern about this material is focused on its low fracture toughness (2.5 $MPa \cdot m^{1/2}$) below the ductile-brittle transition temperature.[4] To improve its mechanical properties, a second phase is typically added to form Ti_5Si_3 composites. The addition of Nb is an example. Niobium has a high ductility and a high melting temperature (2745 K). The main toughening mechanism in the Ti_5Si_3-Nb system is assumed to be plastic dissipation in the ductile reinforcements that bridge the crack face.[5] Thus, the mechanical properties of Ti_5Si_3 can be improved by forming composites with appropriate reinforcements of Nb. As in the case of many similar high-temperature compounds, dense Ti_5Si_3 is usually prepared in multistep process.[6] The process begins from synthesizing Ti_5Si_3 by reacting mixed stoichiometric cmposition of Ti and Si powder at high temperature. The second step involves the crushing and milling of the hard product to produce fine powders. Finally, the powders are sintered at high temperatures under a pressure to obtain dense Ti_5Si_3.

A new process, Field-Activated Combustion Synthesis (FACS), has recently been developed. This method has been used to synthesize a variety of ceramics and composites, including $MoSi_2$-SiC, SiC and others.[7-12] Such materials are characterized by low adiabatic combustion temperature and thus cannot be synthesized directly by Self-propagating High-temperature Synthesis (SHS). In this work, we combine field-activated combustion synthesis with the application of mechanical pressure to produce dense Ti_5Si_3 and Ti_5Si_3-20 vol%Nb composite.

II. Experimental Procedure

Powders of 99.5% pure Titanium (-400 mesh, Cerac Inc.), 99.5% pure Silicon powder (Alfa products, Inc.) and 99% pure Niobium powder (Alfa Products, Inc.) were used. The last two powders had a sieve classification of -325($\leq$44 μm). Two different compositions were investigated. Composition 1 was a mixture of 5Ti and 3Si to give composition of Ti_5Si_3. Composition 2 was mixtures of Titanium, Silicon and Niobium to give composition of Ti_5Si^3+20 vol%Nb. A schematic diagram of the experimental setup of the field-activated and pressure-assisted (FAPA) combustion is shown in Fig. 1, and the four major stages in the synthesis are depicted in Fig. 2. The mixed powders were placed in a graphite die (outer diameter : 45 mm; inner diameter : 20 mm; height : 40 mm) and the system was evacuated (stage 1). This was followed by the application of pressure up to 10, 30 or 60 MPa (stage 2). The powder mixture was then Joule-heated by DC current until densification was attained as indicated by a linear gauge measuring the sample (stage 3). Temperature were 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 at a given rate of 600°C/min (stage 4). Typical parameters for FAPA combustion under 2×10^{-2} torr vacuum are presented in Table 1.

The densities of the synthesized samples were measured using the Archimedes method. To reduce the thermal stress of the products, each sample was heat-treated at 1100°C for 1h and then cooled down to room temper-

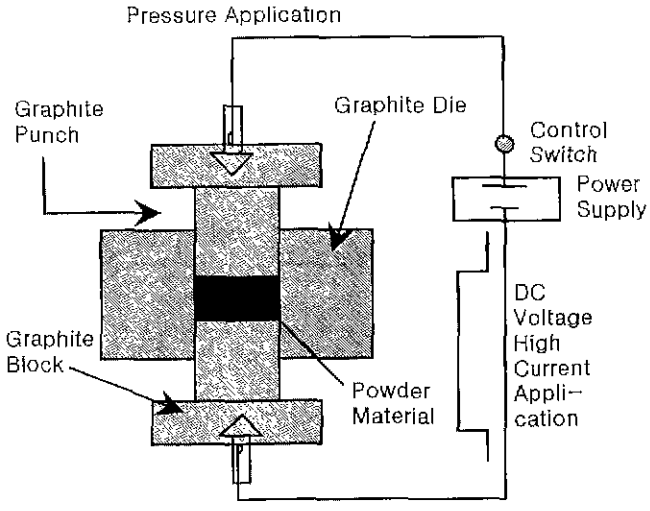

Fig. 1. Schematic diagram of field-activated and pressure-assisted combustion synthesis and densification.

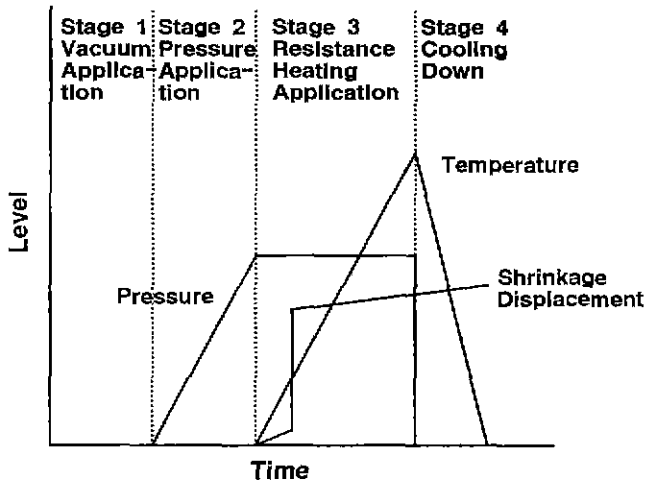

Fig. 2. Schematic representation of the temperature profile, pressure and shrinkage displacement during field-activated and pressure-assisted combustion synthesis and densification.

ature at a rate of 10°C/min. To obtain microstructural information, the product samples were polished and etched using a solution of HF (2 vol%), H_2O_2 (6 vol%), and H_2O (92 vol%). Compositional and microstructural analysis of the products was made through X-ray diffraction (XRD) and and Scanning Electron Microscopy (SEM) with EDX. Vickers microhardness measurements and microhardness indentation fracture toughness measurements (under 10 kg force) were made on the synthesized Ti_5Si_3 and Ti_5Si_3-20 vol%Nb samples.

III Results and Discussion

The shrinkage and temperature with time during the processing of 5Ti+3Si are shown in Fig. 3. Shrinkage displacement increased gradually with temperature just below about 940°C. Sharp rise in displacement occured

Table 1. Processing Parameters for Field-activated and Pressure-assisted Combustion Synthesis of Ti_5Si_3 and Ti_5Si_3-20 vol% Nb Composites

Parameter	Applied value
Vacuum level	2×10^{-2} torr
Applied pressure	10, 30, 60 MPa
Resistance heating	
Voltage	18V
Current	3000A
Duration	1 min
Heating rate	1200°C/min
Maximum temperature	1000°C
Cooling rate	600°C/min

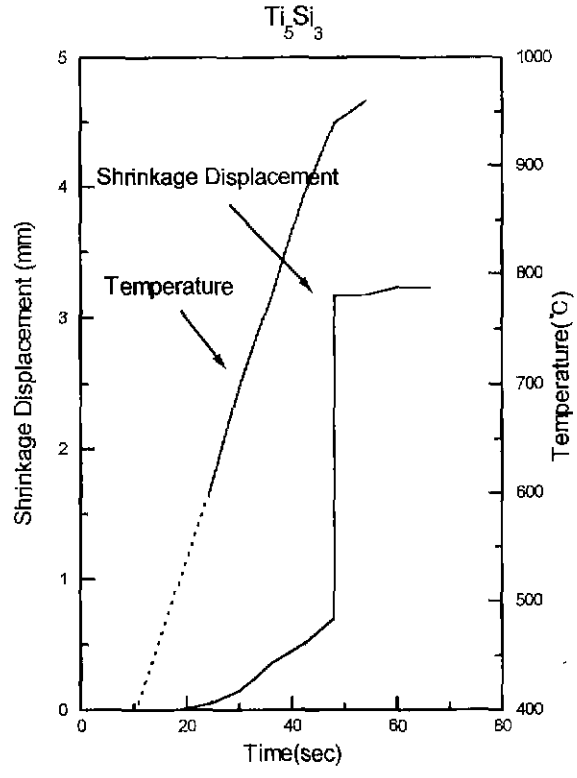

Fig. 3. Variation of shrinkage displacement with heating temperature during field-activated and 60 MPa pressure-assisted combustion synthesis and densification of Ti_5Si_3.

at about 940°C, but then abruptly increased at about this temperature. When a stoichiometric 5Ti/3Si mixture was heated to 900°C under 60 MPa pressure, no reaction took place as confirmed by subsequent XRD analysis. Secondary electron images and X-ray mapping of the sample heated to 900°C under 60 MPa are shown in Fig. 4. As can be seen from the X-ray mapping diagrams, Fig. 4(b) and (c) for Ti and Si, respectively, that a reaction between Ti and Si did not take place under these conditions. This is supported by the X-ray diffraction pattern shown in Fig. 5(a) where only peaks of the reactants are present. However when the temperature was raised to 950°C, the starting powder reacted producing a highly dense product. Secondary electron images and X-ray mapping of a sample heated to 950°C under 60 MPa

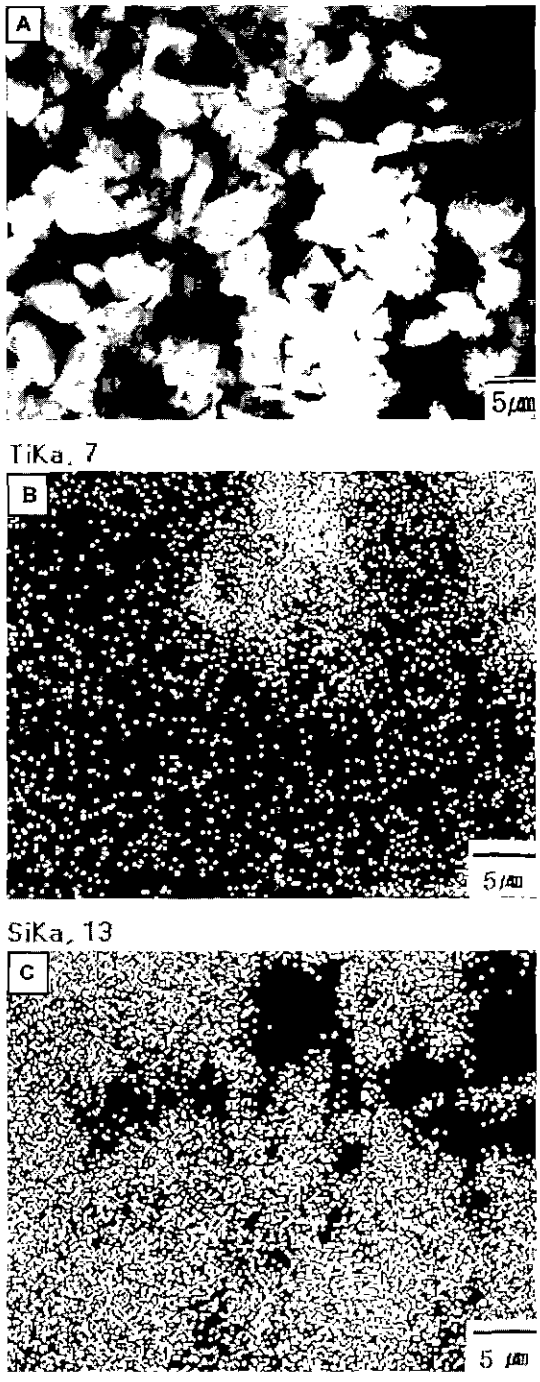

Fig. 4. SEM image and X-ray mapping of 5Ti+3Si compact heated to 900°C: (a) SEM image of product, (b) X-ray mapping: Ti and (c) X-ray mapping: Si.

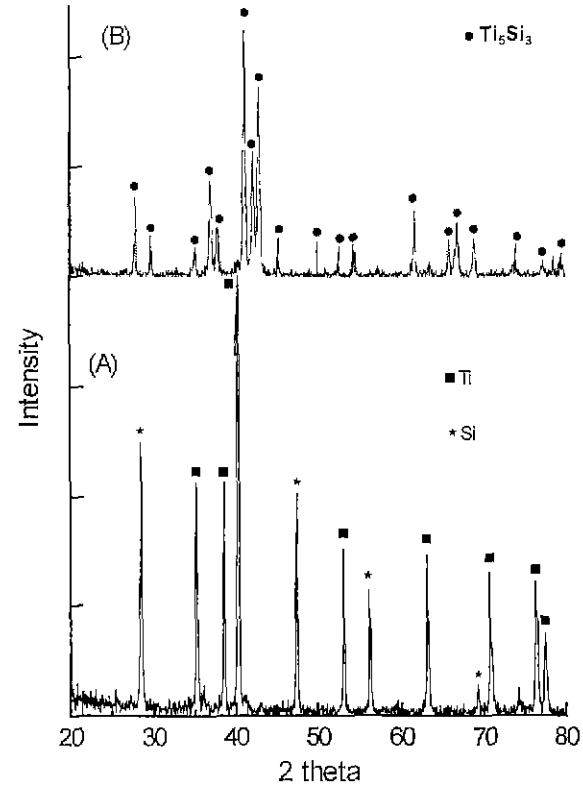

Fig. 5. XRD patterns of the system 5Ti+3Si heated to 900°C (a) and heated to 950°C (b).

are shown in Fig. 6. It can be seen from the maps for Ti and Si, Fig. 6(b) and (c), respectively, that a complete reaction between these elements has taken place under these conditions. X-ray analysis of such samples shows the formation of the desired product, as indicated Fig. 5(b). The abrupt increase in the shrinkage displacement at the ignition temperature (see Fig. 3) is due to the increase in density as a result of molar volume change associated with the formation of Ti_5Si_3 and the further consolidation of the product. It should be recalled that the measured temperatures are those of the surface of the die and are, therefore, likely to be lower than the values in the middle of the sample. Thus the onset of the reaction to form the silicide (and the concomitant rapid shrinkage) may be at a higher temperature than the observed value of 950°C. Since the adiabatic combustion temperature for Ti_5Si_3 is high (2275°C), it is expected that Si and Ti would melt during the reaction. This is most likely the reason for the significant increase in shrinkage beyond the value dictated by the molar volume change. The relative density obtained in this work (98%) is higher than the reported values (72%) for samples made by conventional hot isostatic pressing of Ti_5Si_3 powder.[6] It is believed that the higher density obtained in this work is due to the presence of a liquid phase during the synthesis process. Table 2 shows the densities, sample volumes and volume changes at different stages in the synthesis and densification process of Ti_5Si_3. These results show that 22% of the total volume shrinkage occurred prior to ignition and 78% occurred during the synthesis stage.

The variation of the shrinkage displacement and the temperature with heating time during the processing of 5Ti+3Si+20 vol%Nb are shown in Fig. 7. The shrinkage displacement increased gradually with heating temperature up to about 1080°C and then abruptly increased at this temperature. As in the case for the synthesis of the

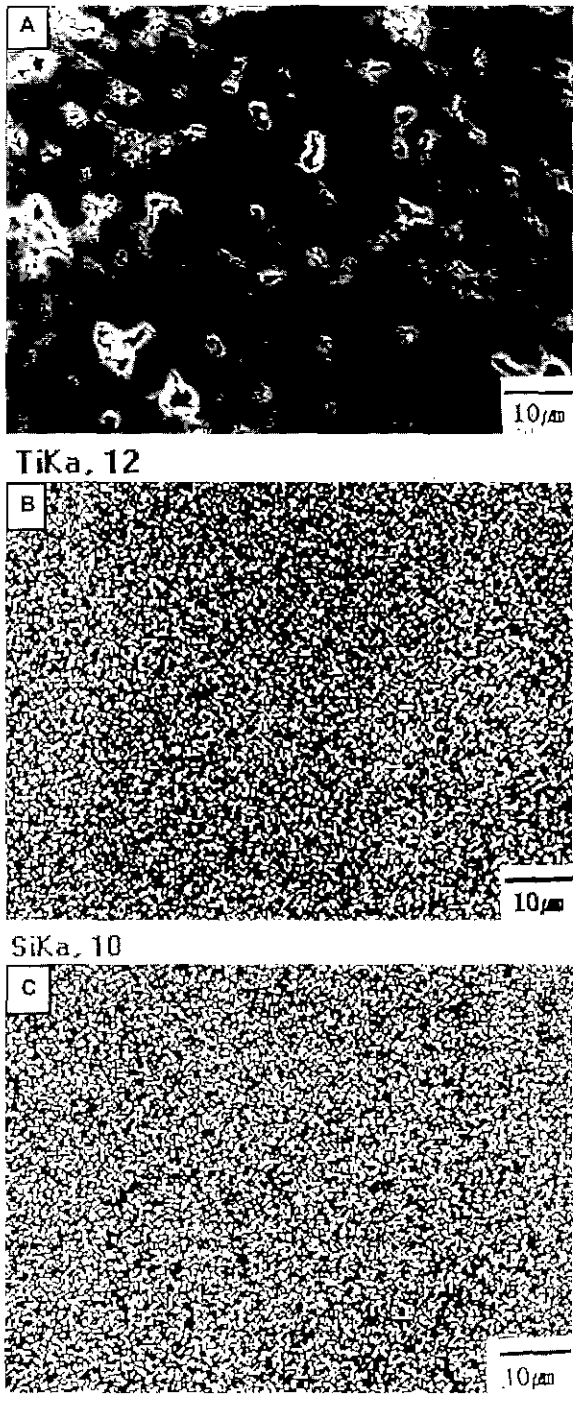

Fig. 6. SEM image and X-ray mapping of combustion synthesized Ti_5Si_3: (A) SEM image, (B) X-ray mapping: Ti and (C) X-ray mapping: Si.

single phase silicide, no reaction took place when the 5Ti+3Si+20 vol%Nb mixture was heated to 1050°C. Secondary electron images and X-ray mapping of a sample heated to 1050°C (under 60 MPa) are shown in Fig. 8. The distribution of Ti and Si, Fig. 8(b) and (c), is not uniform indicating the absence of a significant reaction. X-ray analysis confirmed this conclusion, as seen in Fig. 9(a) where only peaks of the reactants are present.

Table 2. Density, Volume and Volume Change During Field Activated and Pressure-assisted Combustion Synthesis of Ti_5Si_3

	Initial sample	Before ignition	Reactant (theo.)	Product	
				Expt.	Theo.
Density (g/cm^3)	2.77	2.99	3.24	4.23	4.32
Sample volume (cm^3)	2.89	2.67	2.47	1.89	1.85
Pore volume (cm^3)	0.42	0.2	0.0	0.04	0.0
Volume change (%)	0.0	7.61	14.53	34.60	35.98
Incremental volume change (%)	0.0	7.61	6.92	20.07	1.83

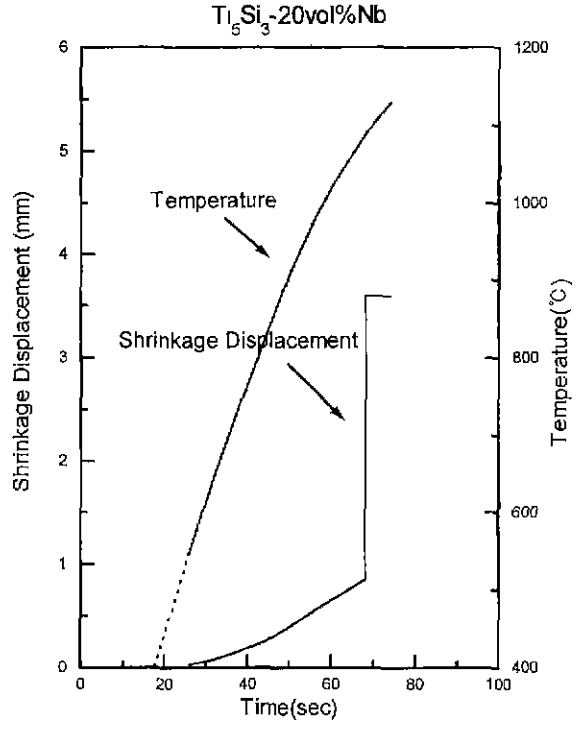

Fig. 7. Variation of shrinkage displacement with heating time during field-activated and 60 MPa pressure-assisted combustion synthesis and densification of Ti_5Si_3-20 vol%Nb.

However, when the reaction temperature was raised to 1100°C, the powders reacted, producing the desired product in a dense form. Secondary electron images and X-ray mapping of such a sample are shown in Fig. 10. The secondary electron image shows a two-phase microstructure and the Ti and Si elemental distributions indicate a homogeneous distribution, indicative of the formation of titanium silicide. X-ray diffraction results, Fig. 9(b), confirm this conclusion. Table 3 shows the densities, sample volumes and volume changes at different stages in the synthesis and densification process of the Ti_5Si_3-20 vol% Nb composite. The results show that 22% of the total volume shrinkage occurred prior to the initiation of the reaction with the remaining 78% occurring during and subsequent to synthesis. As indicated in the experimental section, the applied pressure was varied from 10 to 60 MPa. The effect of the applied pressure on the

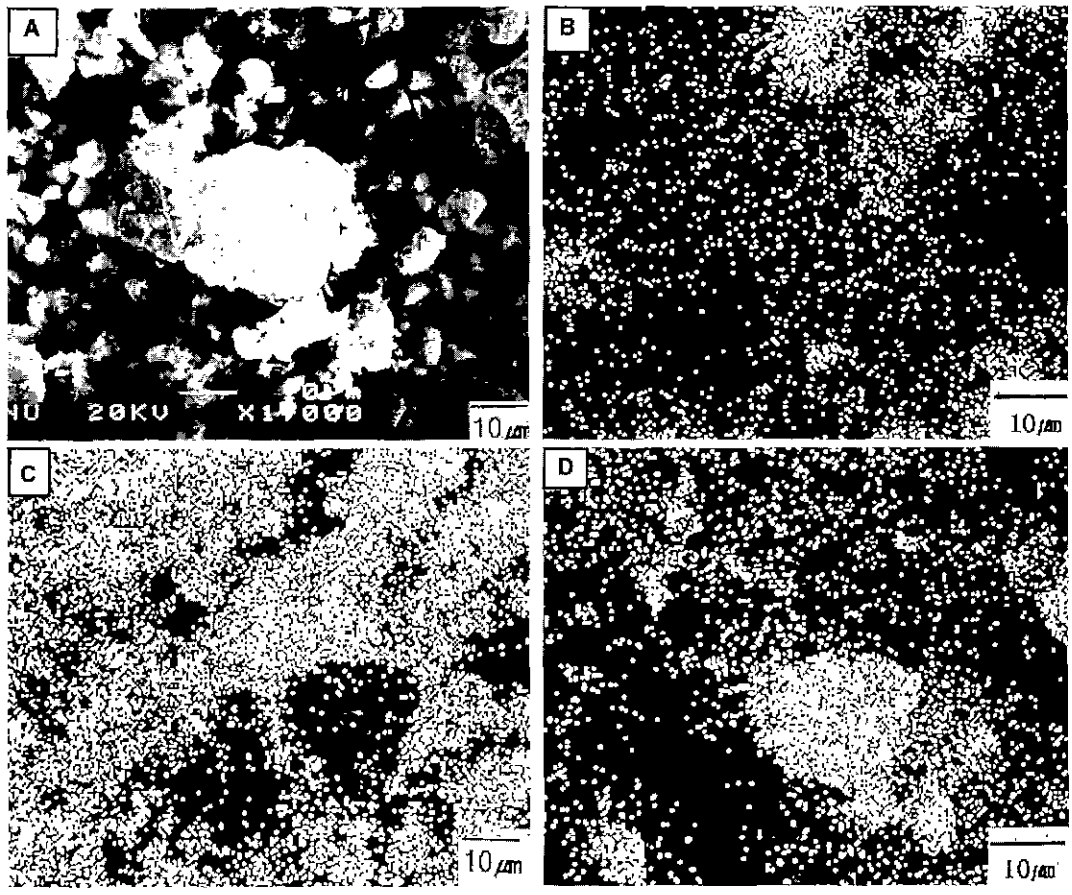

Fig. 8. SEM image and X-ray mapping of 5Ti+3Si+20 vol%Nb compact heated to 1050°C: (A) SEM image of product, (B) X-ray mapping: Ti, (C) X-ray mapping: Si and (D) X-ray mapping: Nb.

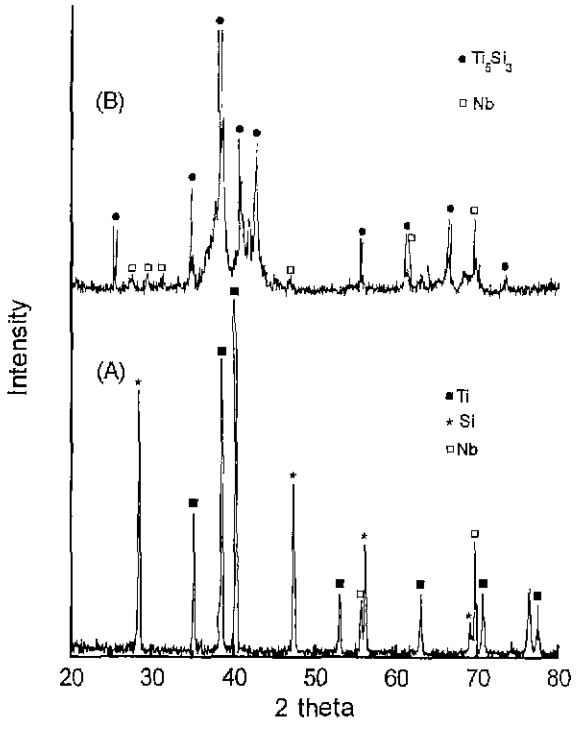

Fig. 9. XRD patterns of the system 5Ti+3Si+20 vol%Nb (a) heated to 1050°C and (b) heated to 1100°C.

final relative density of Ti_5Si_3 and Ti_5Si_3-20 vol%Nb is shown in Fig. 11. The relative density of the composite material increased nearly linearly from 83 to 98% as the pressure was changed over this range. The corresponding change for Ti_5Si_3 is from 89 to 98%.

The micro-indentations were performed on polished sections of the 20 vol%Nb-Ti_5Si_3 matrix composite, and also on pure Ti_5Si_3 using a 10 kg load(P) under a Vickers indenter. The calculated hardness(H) of Ti_5Si_3 and Ti_5Si_3-20 vol%Nb composite was found to be about 8.5 GPa and about 6 GPa respectively. Indentation fracture toughness (K_c) for these samples were found using the following expression.[11]

$$K_c = 0.016\left(\frac{E}{H}\right)^{1/2}\left(\frac{P}{c^{3/2}}\right)$$

where c is the average crack length. Young's modulus E was estimated from the 20 volume fraction of Nb and the 80 volume fraction of Ti_5Si_3 by the rule of mixture, with E(Nb)=202 Gpa[12] and E(Ti_5Si_3)=225 Gpa.[13] The calculated fracture toughness of Ti_5Si_3 and Ti^5Si_3-20 vol%Nb composite was found to be about 3 MPa·$m^{1/2}$ and about 9 MPa·$m^{1/2}$, respectively. The 20 vol%Nb-Ti_5Si_3 matrix composite exhibited an indentation fracture toughness value 3 times greater than that of pure Ti_5Si_3.

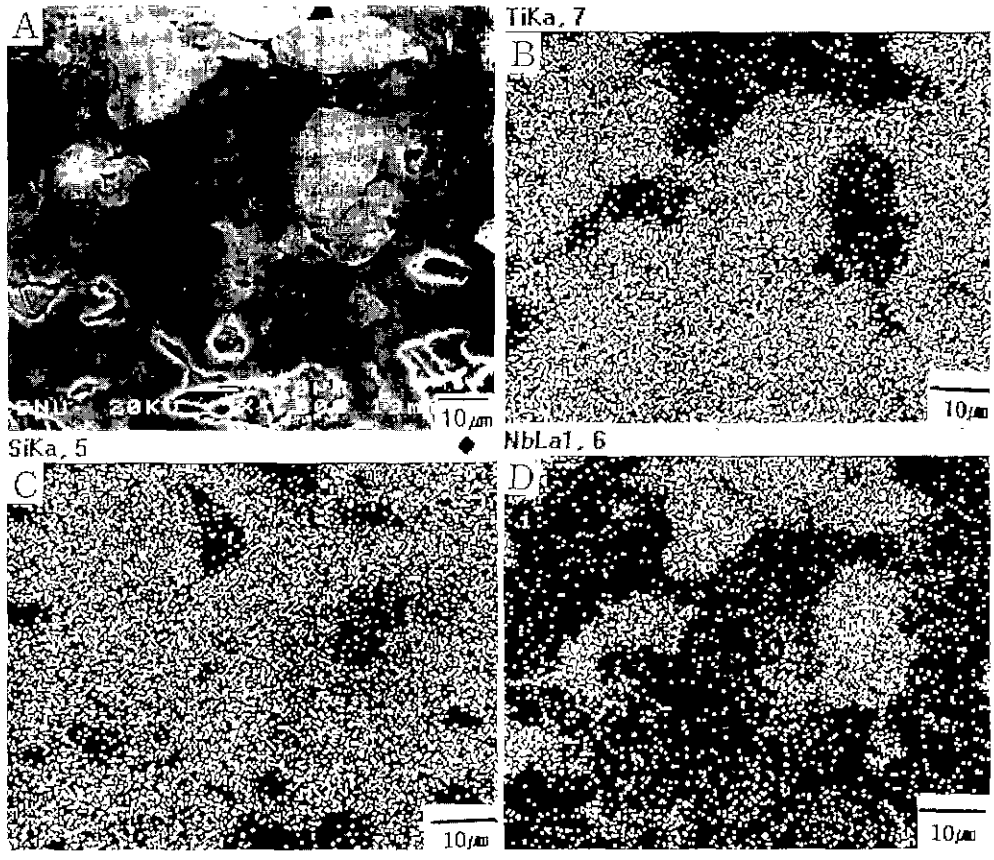

Fig. 10. SEM image and X-ray mapping of the combustion synthesized Ti_5Si_3-20 vol%Nb: (A) SEM image, (B) X-ray mapping: Ti, (C) X-ray mapping: Si and (D) X-ray mapping: Nb.

Table 3. Density, Volume and Volume Change During Field Activated and Pressure-assisted Combustion Synthesis of Ti_5Si_3-20 vol%Nb

	Initial sample	Before ignition	Reactant (theo.)	Product	
				Expt.	Theo.
Density (g/cm^3)	2.92	3.21	3.84	5.06	5.17
Sample Volume (cm^3)	2.74	2.49	1.79	1.58	1.55
Pore volume (cm^3)	0.95	0.70	0.0	0.03	0.0
Volume Change (%)	0.0	9.12	34.67	42.34	43.43
Incremental Volume Change (%)	0.0	9.12	25.55	7.67	1.09

IV. Summary

The simultaneous synthesis and densification of Ti_5Si_3 and Ti_5Si_3-20 vol%Nb composites were accomplished by rapid Joule heating of elemental reactants (with Nb for the case of the composite) under an applied uniaxial pressure. Complete synthesis and densification can be achieved in one step within about 1 min resulting in materials with relative densities of up to 98%. Shrinkage displacement during the processing of 5Ti+3Si and 5Ti+3Si+20 vol%Nb gradually increased with heating temperature just below ignition temperature and then abruptly increased at the ignition temperature due to the increase in density as a result of molar volume change associated with the formation of Ti_5Si_3 and the consolidation of the

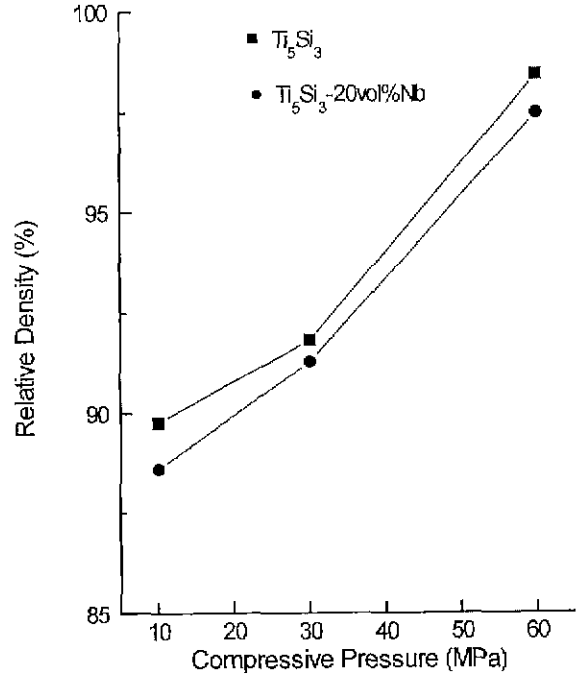

Fig. 11. Variation of relative density of Ti_5Si_3 and Ti_5Si_3-20 vol%Nb composite with compressive pressure.

product. The final density of the silicide and silicide-matrix composite increased with the increase in applied pressure. Under the application of 60 MPa pressure and 3000A current on the reactant, the relative densities of Ti_5Si_3 and Ti_5Si_3-20 vol%Nb composite were about 98%.

Acknowledgments

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