Electric field-activated combustion synthesis of Ti_5Si_3–Nb and Ti_5Si_3–ZrO_2 composites

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The field-activated combustion synthesis of the composites $Ti_5Si_3 - x$ Nb ($0 \leqslant x \leqslant 0.35$) and $Ti_5Si_3 - y\,ZrO_2$ ($0 \leqslant y \leqslant 0.3$) has been investigated. Composites with $x \geqslant 0.35$ and $y \geqslant 0.2$ can only be synthesized in the presence of an electric field. Although in the absence of a field the systems with $x = 0.35$, $y = 0.2$ and $y = 0.3$ can sustain a non-steady combustion wave, the reaction is not complete. An unstable wave propagates to the middle of the sample and then becomes extinguished. The wave velocity of the Ti_5Si_3–Nb and Ti_5Si_3–ZrO_2 composites increased slightly with the application of a field.

1. Introduction

Recent interest in titanium silicide, Ti_5Si_3, has focused on its potential for high temperature applications. Its high melting temperature (2403 K), good strength at high temperature, good creep resistance, low density ($4.32\ g\,cm^{-3}$), and high oxidation resistance are attractive features for such applications [1–3]. However, as in the case of many similar compounds, its low fracture toughness below the ductile–brittle transition temperature ($2.5\ MPa\,m^{1/2}$) is a significant limitation for its use [4]. To alleviate this problem a second phase is typically added to form Ti_5Si_3 composites. Niobium and zirconia are examples of the added phases.

Niobium is attractive as an additive because of a high melting temperature (2745 K) and a thermal expansion coefficient ($7.3 \times 10^{-6}\ K^{-1}$) nearly equal to that of Ti_5Si_3 ($7.1 \times 10^{-6}\ K^{-1}$) [5]. The principle toughening mechanism in composites reinforced with Nb is assumed to be plastic dissipation in the ductile reinforcements bridging the crack face [6]. In the case of composites reinforced with zirconia, the martensitic transformation from metastable tetragonal zirconia particles to monoclinic zirconia either spontaneously on cooling or in the vicinity of crack-tip stress fields provides the improvement in the mechanical properties [7].

The silicide Ti_5Si_3 can be successfully prepared by self-propagating high-temperature synthesis. However, depending on the amount of the added phase the direct synthesis of Ti_5Si_3 composites may not be possible by this method. To synthesize similar composites, a new method was recently developed [10]. It utilizes electric fields to activate the self-propagating high-temperature synthesis (SHS) process. With the imposition of an external electric field across the sample, ignition results in the initiation and propagation of a combustion wave in reactant systems which normally cannot sustain such a wave. This method, referred to as the field-activated combustion synthesis, FACS, has been used to synthesize a variety of materials including $MoSi_2$–Nb, $MoSi_2$–ZrO_2 composites [11], $MoSi_2$–SiC composites [12], SiC [13] and others [10]. In this paper we report on the field-activated synthesis of Ti_5Si_3–xNb and Ti_5Si_3–$y$$ZrO_2$ composites.

2. Experimental procedures

The materials used in this work were 99.7% pure titanium powder, 99.5% pure silicon powder, 99.8% pure niobium powder, and 99% pure zirconia powder. The first was obtained from the Atlantic Equipment Engineers (Bergen Field, NJ) and the last three were obtained from Alfa Products, (Ward Hill, MA). The powders had a sieve classification of -325 ($<44\ \mu m$). Two different sets of experiments using elemental powders of Ti, Si, and the additives were carried out for this study. The first set focused on the synthesis of $Ti_5Si_3 + x$ vol % Nb with $x = 0$, 10, 20, 30, 35. In the second set, the synthesis of $Ti_5Si_3 + y$ vol % ZrO_2 with $y = 10$, 20, 30 was the objective. Tetragonally-shaped reactant pellets with dimensions of $10 \times 15 \times 13$ mm were made in a two-plunger steel die by uniaxial pressing. Typical pelleting pressure and sample weight values were about 150 MPa and 5 g, respectively. The relative green density of the pellets was maintained at about 55% for all samples in both sets of experiments. The pellets were combusted inside a stainless steel combustion chamber under 1 atm (1.013×10^5 Pa) pressure of Ar gas. The chamber has two quartz windows to allow for the simultaneous

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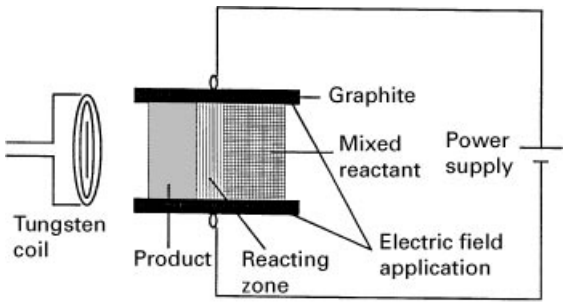


Figure 1 Schematic of the field-activated combustion apparatus.

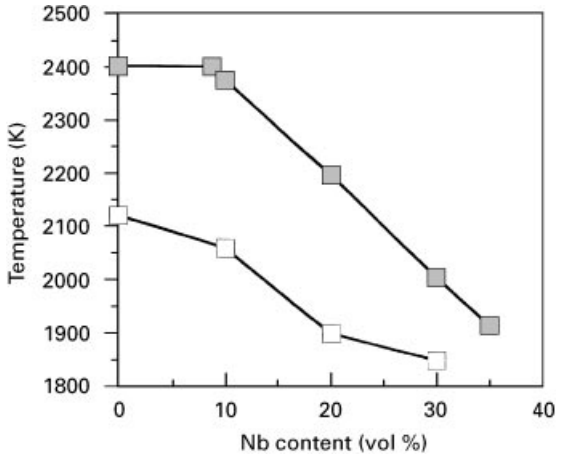


Figure 2 The variation of the combustion temperature of the Ti_5Si_3–Nb composites with the concentration of Nb. Key: (□) experimental data and (■) calculated values.

recording of the combustion wave velocity and the combustion temperature, T_c. Temperatures were also determined from the output of a W–5% Re/W–26% Re thermocouple placed inside a small hole drilled in the side of the specimen. The combustion wave velocity was determined by timing the period of the propagation from one side of the specimen to the other using a video camera with a time-code generator. The electric field was applied in a perpendicular direction to the wave propagation using two graphite electrodes, as shown schematically in Fig. 1. The distance between electrodes is 13 mm and thus field values can be calculated by dividing the voltages by this quantity. Current and voltage measurements were made simultaneously during wave propagation. Analysis of the products was made through X-ray diffraction, and microstructural and chemical analyses were made by scanning electron microscopy equipped with an energy dispersive spectrometer (EDX).

3. Results and discussion

Calculations of the adiabatic combustion temperature and its dependence on the Nb and ZrO_2 content were made using the thermodynamic data presented in Table I. Comparisons between the measured and calculated adiabatic combustion temperatures are shown in Figs 2 and 3 for the Ti_5Si_3–Nb and Ti_5Si_3–ZrO_2 systems, respectively. Because of heat loss in real experiments, the measured values are considerably lower than the calculated ones. Without Nb or ZrO_2 additives, the combustion synthesis solely produced the Ti_5Si_3 phase, as can be seen from the X-ray diffraction peaks in Fig. 4a. Fig. 4b is a back-scattered electron image of this product, showing its porous nature. The effect of the field and the addition of Nb on the combustion wave velocity is shown in Fig. 5 for the Ti_5Si_3–Nb system. The wave velocity with an applied voltage of 10 V is only slightly higher than that in the absence of a field for all Nb concentrations. Also, as expected, the wave velocity decreased with increasing Nb concentration, consistent with the decrease in the combustion temperature. The line representing the field-free combustion ends at 30 vol % Nb. Samples with higher amounts of Nb cannot produce a self-sustaining wave in the absence of a field. Under an applied voltage of 10 V, SHS reactions can be extended to a composition of 35 vol % Nb. To understand the role of the field in combustion synthesis, we examined the current and voltage profiles during the synthesis of Ti_5Si_3 35 vol % Nb with an applied voltage of 10 V. Without ignition, Fig. 6a, the voltage and current remain constant with time, the latter

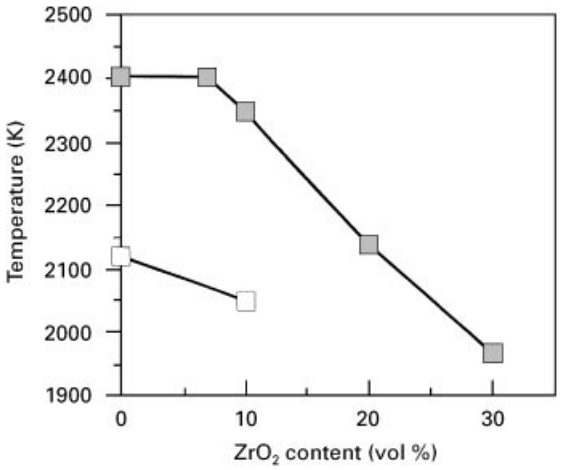
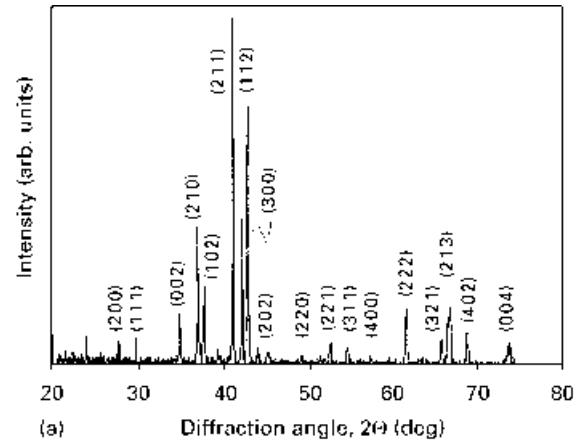


Figure 3 The variation of the combustion temperature of Ti_5Si_3–ZrO_2 composites with the concentration of ZrO_2. Key: (□) experimental data and (■) calculated values.

TABLE I Thermodynamic data for Ti_5Si_3, Nb, and ZrO_2

Material	Heat capacity of solid (J mol^{-1}K^{-1}) $C_p = A + B10^{-3}T + C10^{6}T^{-2} + D10^{-6}T^{2}$				C_p of liquid (J mol^{-1} K^{-1})	$\alpha \rightarrow \beta$ transition temperature (K)	Enthalpy ΔH $\alpha \rightarrow \beta$ transition (J mol^{-1})	Melting point (K)	Latent heat, ΔH_m (KJ mol^{-1})	Formation enthalpy at 298 H (KJ mol^{-1})
	A	B	C	D						
Ti_5Si_3	196.439	44.769	− 2.008	0				2403	178.99	579.484
Nb	27.782	− 3.837	− 0.255	3.602	41.781			2745	26.368	0
ZrO_2, α	70.120	7.021	− 1.423	0		1478	6861	2950	87.03	1101.0
β	78.601									



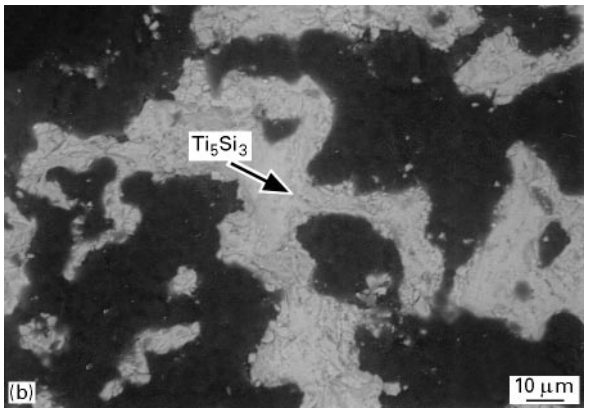


Figure 4 (a) X-ray diffraction pattern and (b) back-scattered electron image of the single-phase Ti_5Si_3 product.

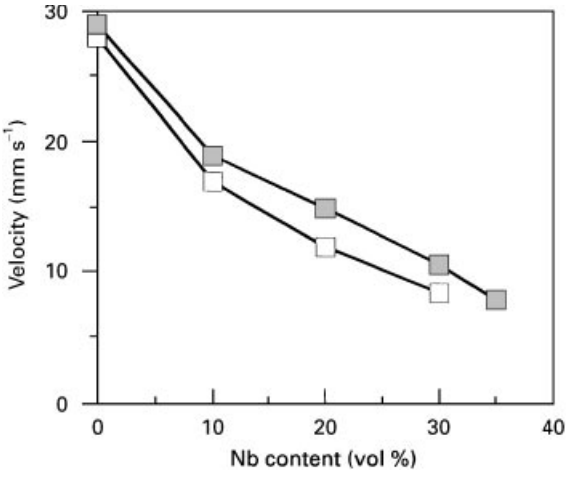


Figure 5 The variation of wave velocity of Ti_5Si_3–Nb composites with the concentration of Nb. Key: (□) 0 V and (■) 10 V.

being at an extremely low level. When an ignition source is used, however, the voltage decreased and the current increased during wave propagation, as shown in Fig. 6b. Thus the application of the field alone does not cause heating of the sample. As was proposed in a previous experimental and modelling study on SiC [13–15], the role of the field is believed to be confined to the combustion zone. The presence of a molten phase, here Si and Ti, enhances conductivity in this zone, leading to higher current densities and hence localized Joule heating. Thus, the Fourier equation for

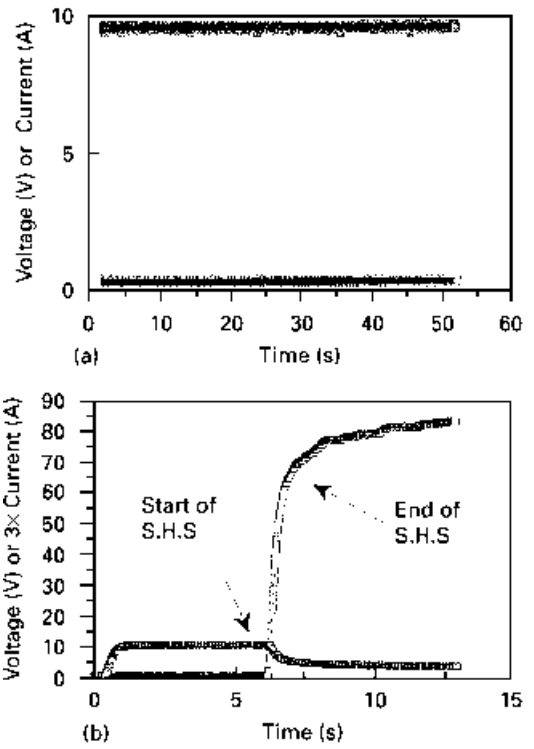


Figure 6 (■) Voltage and (□) current profiles during the synthesis of Ti_5Si_3–35 vol % Nb; (a) field application (10 V) without ignition and (b) field application (10 V) with ignition.

heat balance is modified to reflect this, i.e.,

$$\rho C_p(\partial T/\partial t) = \partial/\partial x(\kappa \partial T/\partial x) + \rho Q(\partial \eta/\partial t) + \sigma E^2 \quad (1)$$

where, C_p is the heat capacity of the product (J g^{-1} K^{-1}), ρ is the density of the product (g cm^{-3}), κ is the thermal conductivity of the product (J cm^{-1} K^{-1} s^{-1}), Q is the heat of reaction (J g^{-1}), T is the absolute temperature (K), t is the time (s), x is the dimension along which the wave is propagating (cm), η is the degree of conversion, σ is the electrical conductivity (ohm^{-1} cm^{-1}) and E is the electric field (V cm^{-1}). The heat generation terms (J cm^{-3} s^{-1}) in the combustion zone are, therefore, chemical ($\rho Q \partial\eta/\partial t$) and electrical ($\sigma E^2$). It should be recalled that E is calculated on the basis of a 1.3 cm separation between the electrodes.

As indicated above, in the absence of a field a stable self-propagating wave cannot be initiated in samples with a composition corresponding to Ti_5Si_3–35 vol % Nb. Without the field an unstable wave propagated through a small portion of the sample and then stopped. Analysis of this portion of the sample showed incomplete conversion. Fig. 7(a–c) shows the diffraction peaks for the reactants (Fig. 7a), the product of combustion without the field (Fig. 7b), and, for comparison, the product when a field is applied (Fig. 7c). In Fig. 7b, peaks for Ti_5Si_3 as well as Si, Ti, and Nb are present. In contrast, when a field is applied, the product is Ti_5Si_3 and Nb. Back scattered electron images of the products synthesized from 5Ti + 3Si with 35 vol % Nb without the electric field and with an applied voltage of 10 V are shown in Fig. 8 (a and b). Fig. 8a shows the boundary between the partially reacted and unreacted zones. In the partially reacted

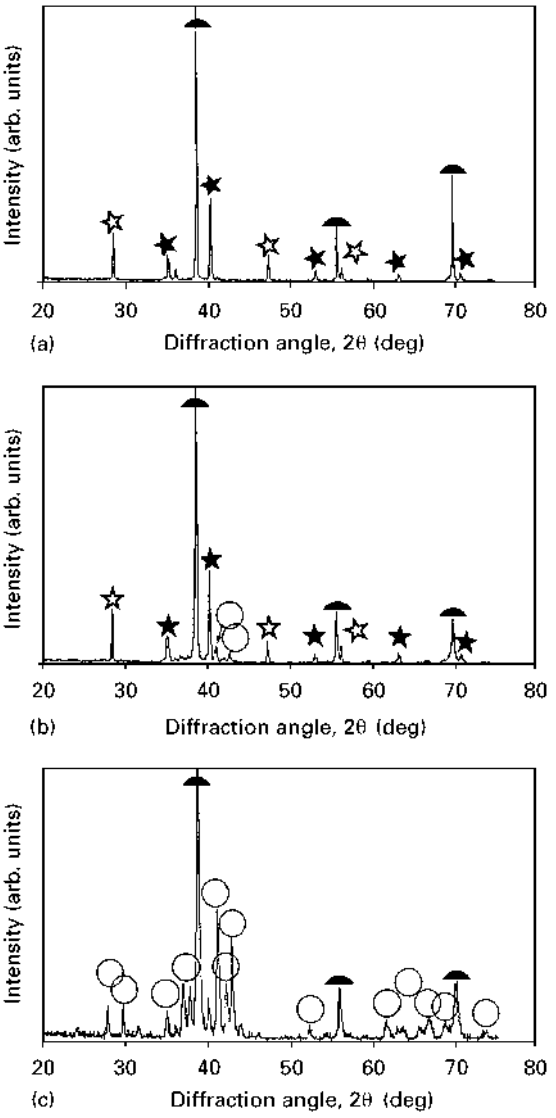


Figure 7 X-ray diffraction patterns of the synthesis 5Ti + 3Si + 35 vol % Nb; (a) reactant mixture, (b) combusted without field and (c) combusted with a 10 V field. Key: (★) Ti, (☆) Si, (◓) Nb and (○) Ti_5Si_3.

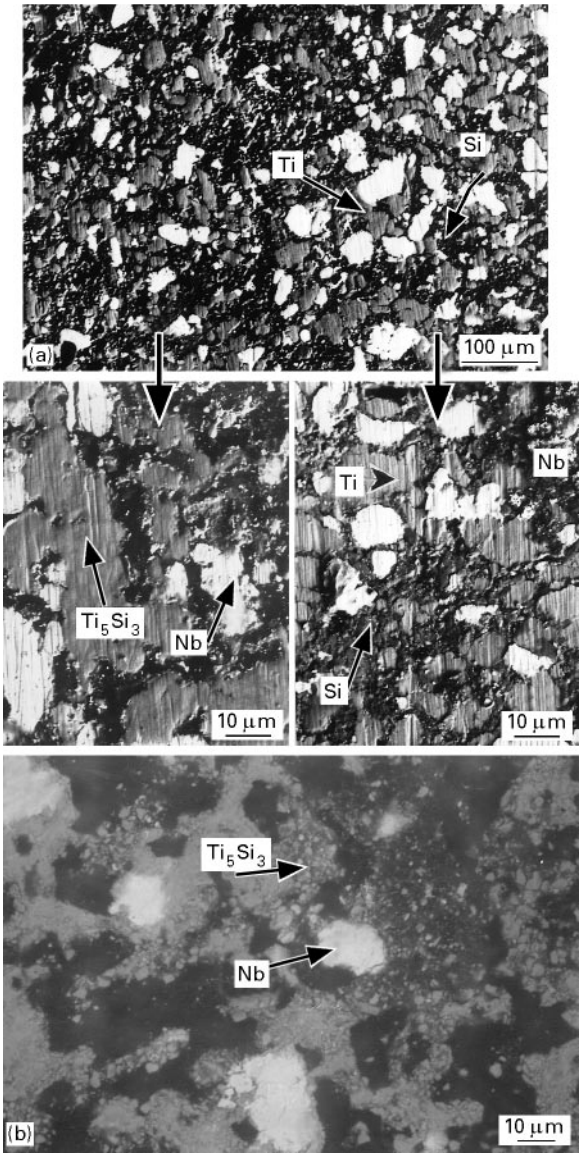


Figure 8 Back-scattered electron images of products of the 5Ti + 3Si + 35 vol % Nb, reaction; (a) synthesized without a field and (b) synthesized with a 10 V field.

zone, coarse particles of Ti_5Si_3 and relatively large regions of Nb are evident. Fig. 8b shows the microstructure of the composite prepared under the influence of a field.

Similar to the case of the Ti_5Si_3–Nb system, the initiation of a combustion wave and its velocity depended on the applied voltage and the concentration of ZrO_2 in the Ti_5Si_3–ZrO_2 samples. Fig. 9 shows that at any given ZrO_2 concentration (vol %) the effect of the voltage is relatively small. The voltage, however, dictated the extent of the ZrO_2 additive that can be added to the Ti and Si reactants and still sustain a self-sustaining reaction. Without any applied voltage, only 10 vol % ZrO_2 can be added. Higher limits (20 and 30 vol % ZrO_2) can only be achieved when higher voltages (10 and 15 V) are applied. As before, in the absence of a field (above these limits) a non-steady state wave propagates partially through the sample. Fig. 10(a–c) shows X-ray diffraction results for the synthesis of Ti_5Si_3–30 vol % ZrO_2. Diffraction pattern for an unreacted mixture are shown in Fig. 10a. For the product synthesized without an applied voltage, Fig. 10b, the identified phases are Ti_5Si_3,

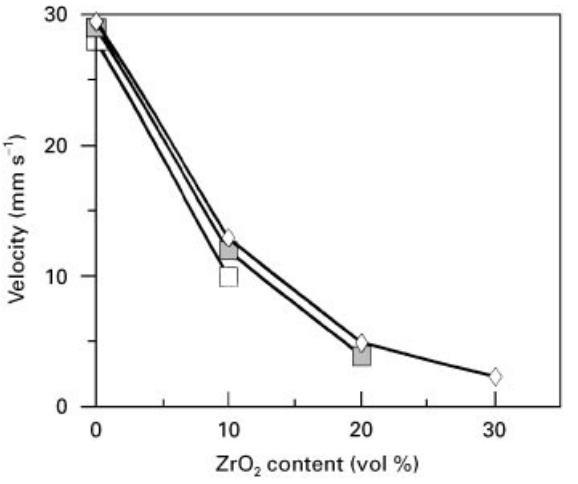


Figure 9 The variation of wave velocity of Ti_5Si_3–ZrO_2 composites with the concentration of ZrO_2. Key: (□) 0 V, (■) 10 V and (◇) 15 V.

ZrO_2 and unreacted Ti and Si. The diffraction pattern for a sample synthesized with the 15 V (Fig. 10c), solely contains peaks for Ti_5Si_3 and ZrO_2. Fig. 11 (a and b) shows the back-scattered electron images of

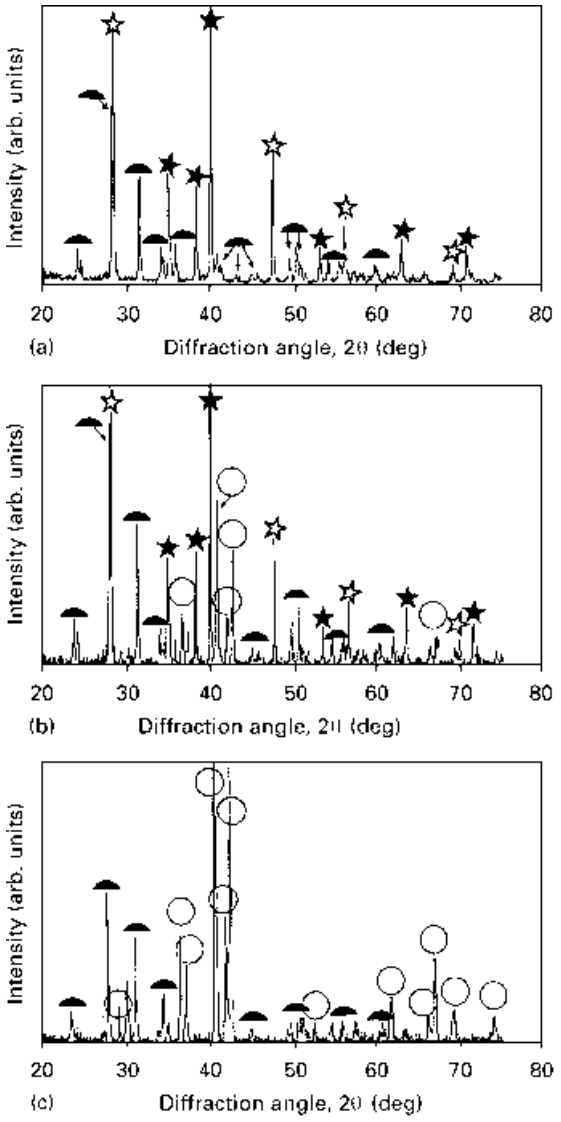


Figure 10 X-ray diffraction patterns of the synthesis 5Ti + 3Si + 30 vol % ZrO_2; (a) reactant mixture, (b) combusted without field and (c) combusted with 15 V. Key: (★) Ti, (☆) Si, (◓) ZrO_2 and (○) Ti_5Si_3.

products from 5Ti + 3Si with 30 vol % ZrO_2 reacted with and without an applied voltage of 15 V. Fig. 11a shows the boundary between the reacted and unreacted zones for the field-free case and Fig. 11b shows the microstructure of the field-assisted case. Thus, as in the case of Ti_5Si_3 35 vol % Nb, the synthesis of Ti_5Si_3 30 vol % ZrO_2 is only partially complete when a field is not present and complete conversion to the silicide phase can only be achieved when a field is present during SHS.

4. Summary

The role of an electric field in the combustion synthesis of Ti_5Si_3–xNb and Ti_5Si_3–$y$$ZrO_2$ composites has been investigated. Composites with $x \geqslant 0.35$ and $y \geqslant 0.2$ cannot be completely formed by the self-propagating combustion method without the application of an external field. For composites with Nb and ZrO_2 concentrations ranging up to these limits, the imposition of field slightly increased the velocity of the combustion wave and hence the rate of conversion to the product.

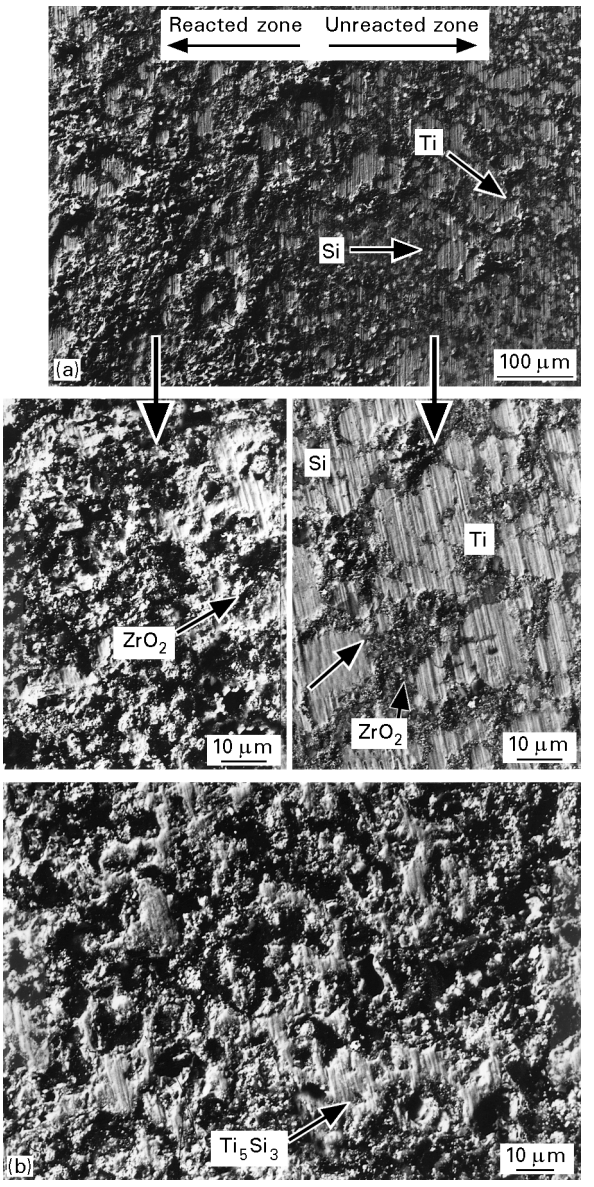


Figure 11 Back-scattered electron images of products of the 5Ti + 3Si + 30 vol % ZrO_2 reaction; (a) synthesized without a field and (b) synthesized with a 15 V field.

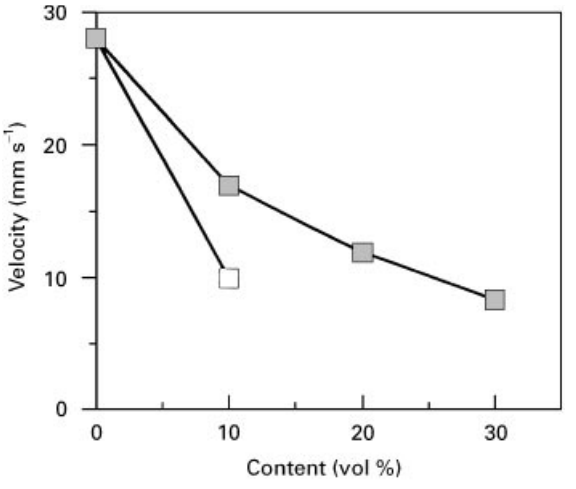


Figure 12 Comparison of the wave velocity between (▩) Ti_5Si_3–Nb and (□) Ti_5Si_3–ZrO_2 composites during the synthesis.

Acknowledgements

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