Synthesis of dense Ti_3SiC_2-based ceramics by thermal explosion under pressure

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Abstract

Self-propagating high-temperature synthesis (SHS) of Ti_3SiC_2 from the elemental powders employing different SHS modes: wave propagation and pressureless or pressure-assisted thermal explosion, has been studied. SHS reaction was ignited in the solid state below the melting point of either constituent, and started with the formation of Ti_5Si_3 and Ti-rich TiC_{1-x}. The formation of Ti_3SiC_2 took place at the later stage by crystallization from the liquid concurrent with precipitation of the stoichiometric TiC. In neither approach, a single-phase Ti_3SiC_2 material was obtained, the combustion products containing appreciable amounts of TiC. An additional 'phase' with the approximate composition of 35Ti–52Si–14C (at.%), supposedly the Ti_3SiC_2–$TiSi_2$–SiC eutectic mixture, was detected in all types of samples. A short 1 min application of a moderate 80 MPa pressure during thermal explosion (reactive forging) yielded $\geqslant 95\%$ dense samples containing ~ 45 vol.% Ti_3SiC_2. As the samples do not contain open porosity, they can be further used for HIPing without encapsulation at around 1500 °C to produce fully dense single-phase Ti_3SiC_2. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Self-propagating high-temperature synthesis; Microstructure-final; Ti_3SiC_2; Porosity; SHS

1. Introduction

The titanium-silicon ternary carbide, Ti_3SiC_2 belongs to a remarkable group of materials known as layered ternary compounds or "machinable ceramics". In general, these compounds are described by chemical formulae M_2BX, M_3BX_2 or M_4BX_3, where M is a transition metal (e.g. Ti), B is typically an element of IIIB or IVB group (e.g. Al, Si), and X is either C or N.[1] The crystal structure of these compounds is composed of carbide/nitride layers interleaved with layers of element B atoms; interlayer bonds are of the metallic type. The Ti_3SiC_2 ternary carbide, like other layered ceramics, is thermally and electrically conductive, relatively soft and readily machinable, it is relatively tough ($K_{1c} \approx 6$ MPa$\sqrt{m}$) and not susceptible to thermal shock, and behaves plastically at elevated temperatures.[2,3] At the same time, the carbide is very refractory, oxidation resistant and maintains its strength to temperatures that render the best superalloys available today unusable.[2,3]

This unique combination of properties makes Ti_3SiC_2 a likely candidate for structural applications at elevated temperatures, such as turbine blades and stators, heavy-duty electric contacts, bearings, etc.

In condensed form, Ti_3SiC_2 was first obtained as a thin film by CVD,[4–6] and later on as a bulk specimen, by arc-melting of the elemental powders[7] or by sintering Ti_3SiC_2 powder.[8] Recently, successful synthesis of dense single-phase Ti_3SiC_2 from the Ti–SiC–C powder blend by reactive hot pressing (RHP) or by reactive hot isostatic pressing (RHIP) at 1600 °C, 40 MPa, 4 h has been reported.[2,9] The product was coarse-grained (10–200 μm) and relatively soft ($H_v \approx 4$ GPa), and exhibited plastic behavior even at room temperature. The obvious disadvantage of both RHP and RHIP routes of Ti_3SiC_2 processing is the need for high temperature furnaces, long processing times (several hours) and the expensive encapsulation procedure (for HIP).

Self-propagating high-temperature synthesis (SHS) is an energetically efficient means of in situ materials processing.[10,11] The method is based on a self-sustained reaction that propagates in a starting reagent blend (combustion wave), or occurs simultaneously in the sample volume (thermal explosion, TE). The rationale

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for SHS processing is short processing time/high pro-ductivity due to the very high reaction rates and elim-ination of the need for high temperature furnaces used in conventional material fabrication due to the self gen-eration of heat required for the process.

SHS synthesis of Ti_3SiC_2 from the elemental powder blends was attempted by several researchers.[12–15] In all the reported experiments, Ti–C and Ti–Si binary phases were present in the combustion product, the content of the Ti_3SiC_2 ternary being 60% at best. Based on these results it has been suggested that the high temperatures achieved in the course of combustion synthesis do not favor the formation of the ternary carbide, and that a post-SHS annealing step at ~1500 °C is required to obtain a near-single-phase Ti_3SiC_2.[13–15]

An additional problem of SHS synthesis in general is the excessive porosity of combustion products. SHS of titanium-silicon ternary carbide is no exception, and the combustion products of Refs. 12–14 had to be ground to powder and sintered/HIPed to produce a dense Ti_3SiC_2. It has been suggested that the application of external pressure during or shortly after SHS can be effective in overcoming this limitation.[16–18] Such an approach was partially realized in Ref. 15 where Ti_3SiC_2-based material was synthesized from the ele-mental powder blend by field-activated combustion reaction under 34.4 MPa. Still, an additional hot press-ing step in vacuum (1525 °C, 34.4 MPa, 2 h) was required to produce a dense near-single-phase Ti_3SiC_2.

In the present paper, SHS synthesis of bulk Ti_3SiC_2 via SHS in its thermal explosion mode, performed in a furnace (pressureless) or under a uniaxial pressure between the press rams (reactive forging, RF) is repor-ted. Earlier, reactive forging was successfully used for the fabrication of a wide range of dense ceramic matrix composites (TiC/TiB_2, TiC/Ti_5Si_3, $Al_2O_3/TiAl$, etc.).[19,20]

2. Experimental procedure

Elemental powders of Ti (~20 μm, 99.7% purity), Si (1–5 μm, 99.9%), and C (graphite, ⩽10 μm) were used as starting materials. A homogeneous powder blend with the composition corresponding to 3Ti–Si–2C stoi-chiometry (73.4 wt.% Ti, 14.3 wt.% Si, 12.3 wt.% C) was prepared employing high-energy attrition milling in ethanol under flowing argon. The milling time was 3 h, and the balls-to-powder ratio (2.5:1) was relatively low in order to avoid chemical reactions and mechanical alloying of powders during milling operation.[21] Indeed, no peaks other than those of the starting elements (Ti, Si and graphite) were observed in the XRD pattern of the attrition milled blend.

For the SHS wave experiments, a slightly compacted Ti–Si–C blend was inserted into a vertically placed INC 718 superalloy cylinder (18 mm dia×30 mm height).

Several grams of an easily ignitable TiO_2–Al–Mg pow-der blend were placed on top and ignited with a match in order to initiate a combustion wave.

The remaining Ti–Si–C blend was compacted to ~80% density under pressure of 400 MPa. Rectangular (16×16×14 mm) and cylindrical (18 mm dia×14 mm height) compacts were prepared. In order to ignite thermal explosion, powder compacts were placed either in a furnace (close-to-the-adiabatic conditions) or reac-tively forged between the press rams under a low pres-sure (~0.4 MPa), as shown schematically in Fig. 2. The furnace and the rams were preheated to 950–1100 °C. Rectangular compacts were enveloped in a stainless steel foil (containing about 26% Cr) in order to protect them from the atmosphere. The temperature of the samples was measured by W-3Re/W-25Re thermo-couples (d = 0.2 mm) placed into drill holes reaching the sample center. For samples placed between the press rams, two thermocouples were used: one in the middle of the sample and the other at a distance of 2.5 mm from its upper edge. A computer card (National, Ltd.) provided accurate temperature monitoring (±2.5 °C) with a time resolution of 0.001 s.

When the preheating temperature (furnace or ram) was sufficiently high, thermal explosion took place. Compacts placed between the press rams were reactively forged under a moderate uni-axial pressure of up to 80 MPa applied immediately after thermal explosion. (According to our observations, no TE took place when pressure was applied from the beginning of the reactive forging experiment.) The sample was held under pres-sure for 1 min and then unloaded. Plastic flow of the SHS reaction products under pressure at the high com-bustion temperature resulted in effective densification of the sample. In order to limit the outward flow of the reaction product at the high combustion temperature and thereby prevent excessive flattening of the sample, cylindrical samples were confined within hollow cylin-ders of a larger diameter (made of the Inconel 718 superalloy). The inner surface of the cylinder was
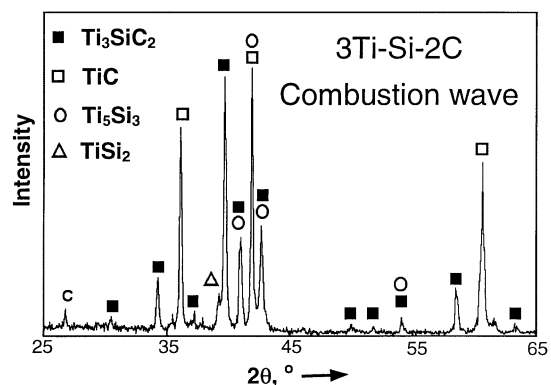

Fig. 1. XRD patterns of a 3Ti–Si–2C blend after SHS wave propaga-tion.

sprayed with a Y_2O_3/BN insulating layer to avoid reaction of the cylinder walls with the sample. The whole reactive forging procedure was performed in open air. Due to the ease of RF processing and short exposure to pressure + temperature, up to 10 samples could be fabricated in 30 min.

After processing, the phase composition of the synthesized products were characterized employing X-ray diffraction (XRD) and scanning electron microscopy (SEM) with energy dispersive analysis (EDS). Quantitative determination of porosity and different phases content was performed using a computer-aided SEM image analysis system. Microhardness of dense reactively forged samples was measured under a load of 500 gf using a Vickers diamond indenter.

3. Results and discussion

3.1. Combustion wave propagation

The ignition of a slightly compacted 3Ti–Si–2C powder blend on one end resulted in a stable combustion wave propagation. The maximum measured combustion temperature was ~1800 °C, a value comparable to $T_{comb} = 1800$–2000 °C reported in Ref. 14, however significantly lower than the estimated adiabatic temperature of Ti_3SiC_2 formation from the elemental powders, $T_{ad} = 2735$ K.[15] The SHS wave product was a partially sintered porous sponge, containing, according to XRD, (Fig. 1), the Ti_3SiC_2 ternary carbide as well as the binary phases—TiC, Ti_5Si_3 and $TiSi_2$. As can be seen in the SEM representative micrograph of a dense region, Fig. 3, the product was not uniform, some regions rich in the ternary Ti_3SiC_2 phase, and some being a two-phase mixture of Ti_5Si_3(C) and TiC. No $TiSi_2$ silicide was detected by EDS analysis. Instead, a Si-rich phase containing 52 ± 4 at.% Si, 35 ± 4 at.% Ti and 14 ± 5 at.% C was observed between the elongated grains of Ti_3SiC_2.
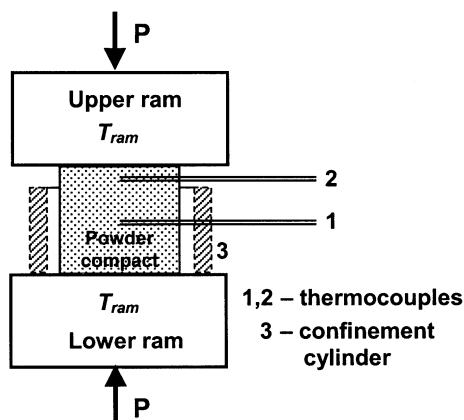
The multi-phase composition of the combustion product suggests that the formation of the Ti_3SiC_2 ternary compound in the course of SHS is a complex two- (or more-) stage process starting with the formation of binary Ti-silicides and carbides.

3.2. Thermal explosion in a furnace

In Fig. 4, the heating curves of 3Ti–Si–2C compacts placed in a furnace preheated to different temperatures are shown. Furnace heating resulted in thermal explosion (TE) when the furnace temperature T_f was 1000 °C and higher. The onset of TE was recorded at 1200–1250 °C, i.e. 100–200 °C above the furnace temperature. At $T_f = 1000$ °C, it took the sample ~1 min to reach ignition after the furnace temperature had been reached. Such delayed TE suggests the presence of interfacial barriers that are, most probably, formed in the course of diffusion-controlled precombustion reaction. Given the absence of a liquid phase in the system prior to
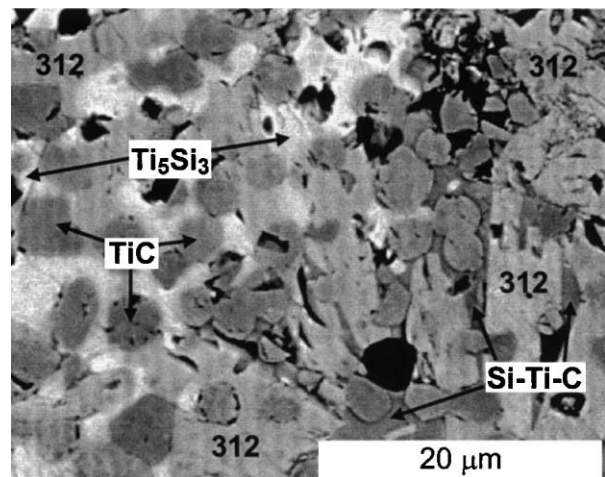
Fig. 3. A representative SEM image (in backscattered electrons, BSE) of dense region of the porous sponge obtained after SHS wave propagation in a 3Ti–Si–2C compact. '312' Denotes Ti_3SiC_2.

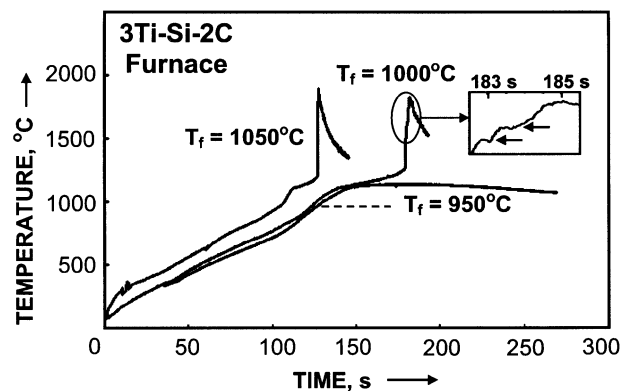Fig. 2. A schematic of reactive forging—thermal explosion under pressure between preheated press rams.

Fig. 4. Temperature evolution curves of 3Ti–Si–2C compacts placed in the furnace at three different furnace temperatures, T_f. Arrows in the inset indicate endothermic reactions.

ignition, these reaction products must be located at the initial powder particle interfaces and act as diffusion barriers.

The product of TE was very porous, Fig. 5(a), and its shape indicated the occurrence of gas evolution and melting. Indeed, two endothermic reactions apparently associated with the melting of unreacted Si and Ti (or Ti–Si liquid) can be detected in one of the heating curves (Fig. 4, insert). The maximum combustion temperature (T_{comb}) of ∼1800 °C was measured, which is lower than might be expected based on the results of the SHS wave propagation experiment. The low measured T_{comb} could possibly be explained by the lack of contact between the thermocouple and the sample during TE due to extensive pore formation. XRD pattern of the combustion product, Fig. 6(a), reveals the presence of Ti_3SiC_2, TiC and possibly some $TiSi_2$. A representative SEM image of a dense region, Fig. 5(b), shows a composite structure containing ∼65% (by volume) of

Ti_3SiC_2 in the form of elongated plate-like grains (up to 20 μm long and 5 μm wide), ∼25% of round-shaped TiC particles (a few microns in diameter), and ∼10% of the '52Si–35Ti–14C phase' previously observed in the combustion wave product.

No TE occurred at the furnace temperatures of 950 °C and less. The heating curve at T_f = 950 °C clearly indicates that an exothermic reaction did occur, resulting in sample overheating ∼200 °C above the furnace temperature. According to the XRD analysis, Fig. 6(b), the products of the precombustion reaction are TiC_{1-x} and Ti_5Si_3.

The above results indicate that two solid state reactions occur during the heating of the 3Ti–Si–2C powder blend: $5Ti + 3Si \rightarrow Ti_5Si_3$, and $Ti + C \rightarrow TiC$. Both reactions are highly exothermic (enthalpies of formation are −1.8 kJ/g and −3.0 kJ/g at 1000 °C, respectively[22])
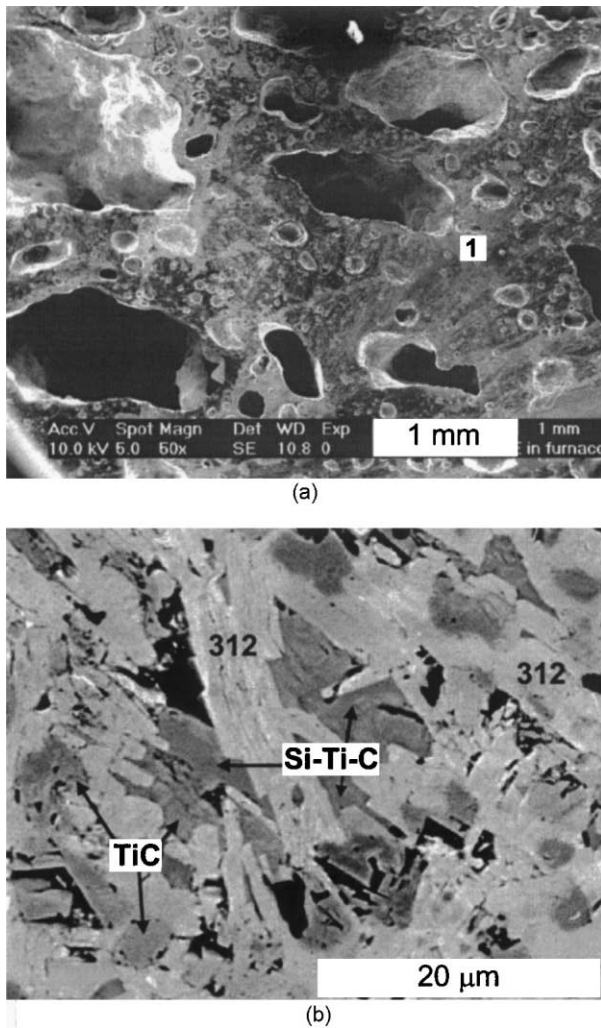

Fig. 5. SEM micrographs of a 3Ti–Si–2C sample after TE in the furnace: (a) general view (SE image), (b) a high magnification of region "1" in 'a' (BSE image). '312' Denotes Ti_3SiC_2.
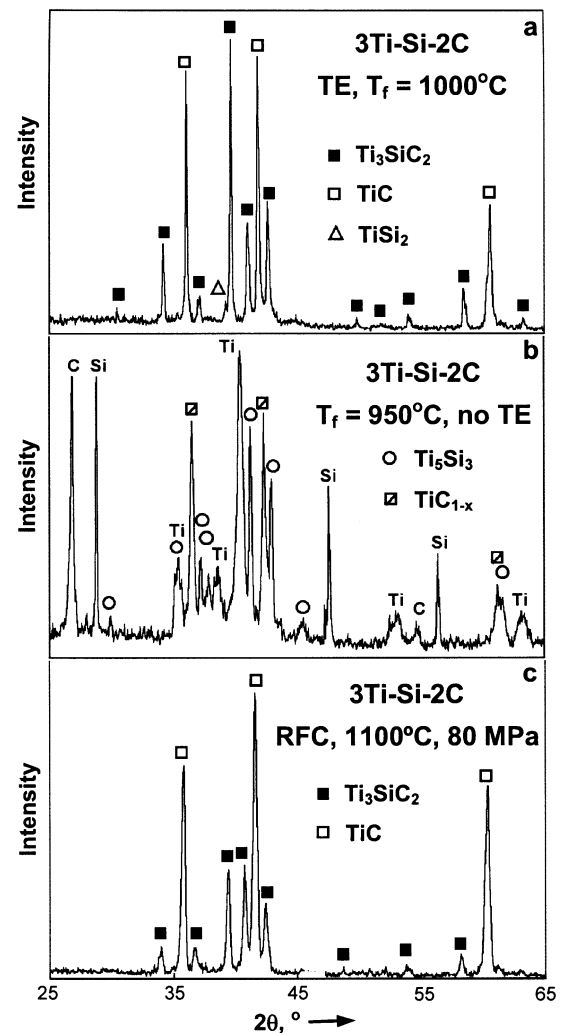

Fig. 6. XRD patterns of 3Ti–Si–2C combustion products: (a) after TE in the furnace at T_f = 1000 °C; (b) after furnace heating at T_f = 950 °C (no TE); (c) after reactive forging with confinement at T_{ram} = 1100 °C, P = 80 MPa. XRD patterns similar to 'a' were obtained from reactively forged samples without confinement.

and may become self-sustained. In our experiments with the binary blends, TE in the 1Ti–1C composition was ignited at $\sim$1250 °C, whereas a much lower TE ignition temperature, in the range of 750–950 °C, was measured for the 5Ti–3Si composition. Evidently both reactions contribute to the self-heating of the ternary 3Ti–Si–2C samples, the formation of TiC probably becoming rate-controlling at the later stages.

3.3. Thermal explosion between press rams—reactive forging (RF)

Representative heating curves obtained from samples heated between the press rams at different ram temperatures (T_{ram}) are presented in Fig. 7. At $T_{ram} = $ 1050 °C and higher, thermal explosion took place, the combustion temperature reaching $\sim$2300 °C. Similarly to TE in the furnace, the onset of an abrupt self-heating was recorded $\sim$100 °C above the ram temperature (T_{ram}). At the same time, the comparison of temperature evolution in the sample center to that close to the ram suggests that under the conditions of RF experiment, the precombustion reaction starts at temperatures as low as 900–950 °C. At this point, the curve corresponding to the sample center starts to approach and eventually intersects the curve of the close-to-the-ram edge, apparently due to the release of the reaction heat. A similar, albeit less pronounced effect was observed at $T_{ram} < 1050$ °C (e.g. 1020 °C, Fig. 7) when no thermal explosion took place.

The phase composition of the samples obtained after low-pressure reactive forging was similar to that of the thermally exploded free-standing compacts, Fig. 6(a). In neither case, a single-phase Ti_3SiC_2 structure was obtained, and the samples contained appreciable amounts of TiC. It is not yet clear whether the TiC carbide observed in the final product was formed by a diffusion-controlled reaction between Ti and C, or by the
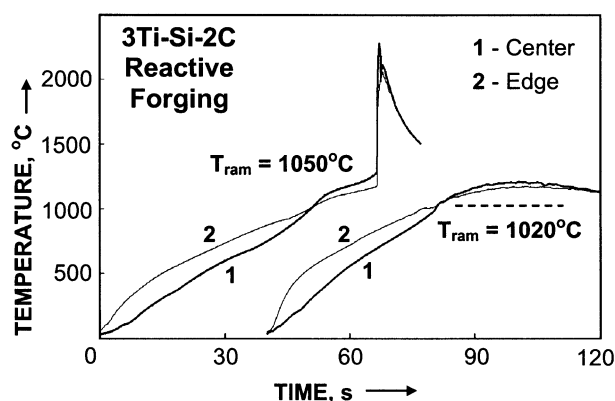

Fig. 7. Temperature evolution curves of 3Ti–Si–2C compacts placed between the press rams preheated to two different temperatures. Thick lines correspond to the sample center (thermocouple 1), thin lines correspond to the sample edge (thermocouple 2).

dissolution-reprecipitation mechanism. In contrast to the combustion wave product, no Ti_5Si_3 was present in the final TE/RF product. Most probably, the melting of Ti_5Si_3 (formed at the early reaction stages) accompanied by the dissolution of carbon occurred during combustion (assuming T_{comb}(furnace)$\approx T_{comb}$(reactive forging) = 2300 °C $> T_m^{Ti_5Si_3} = 2130$ °C) resulting in the formation of a Ti–Si–C liquid. Due to the presence of a solid/precipitated TiC, the liquid contained excess Si (compared to the 3:1:2 Ti-to-Si-to-C stoichiometry of the ternary phase), and solidified as Ti_3SiC_2 leaving behind the '52Si–35Ti–14C phase' observed in Figs. 3 and 5(b). Since the composition of this "phase" does not correspond to any known Ti–Si–C compound, it is assumed to be some kind of ternary eutectic. One possibility is a Ti_3SiC_2–$TiSi_2$–SiC eutectic reportedly formed in the Ti–Si–C system at 1473 °C,[23] hence the presence of the weak $TiSi_2$ peak in the XRD patterns, Figs. 1 and 6(a).

The product of thermal explosion between the press rams was less porous than the sample thermally exploded in the furnace, but it still contained much porosity at the edges. The application of higher pressures improved the density, but resulted in product's flattening. In order to obtain a dense near-net-shape product, reactive forging was performed within a confinement cylinder (RFC).

3.4. Reactive forging with confinement (RFC)

When a moderate pressure of 80 MPa was applied to 3Ti–Si–2C compacts during reactive forging in the confinement cylinder at 1100 °C, dense near-net-shape samples were obtained. According to XRD, Fig. 6(c), the RFC combustion product contained Ti_3SiC_2 and TiC, the peaks of Ti_3SiC_2 being noticeably weaker than for the corresponding TE/RF samples, Fig. 6(a). The EDS and image analyses of the SEM images [see, for example, Fig. 8(a)] indicate that the RFC product contains up to 40 vol.% TiC and only 45 vol.% Ti_3SiC_2 (versus 25TiC–65Ti_3SiC_2 in the TE/RF samples). Apparently, pressure application and/or enhanced heat transfer to the confinement cylinder favored the formation of TiC at the expense of Ti_3SiC_2. The '52Si–35Ti–14C phase' previously observed in the TE/RF samples constituted the remaining 15 vol.% of the RFC combustion product. According to the image analysis, RFC samples' porosity did not exceed 5%. The microhardness of the material obtained was 5.8$\pm$0.7 GPa. This is significantly higher than the 4 GPa value reported for pure Ti_3SiC_2, apparently due to the presence of a much harder ($H_v \approx 30$ GPa) TiC phase. Following the suggestion that annealing at $\sim$1500 °C favors the formation of Ti_3SiC_2 in the 3Ti–Si–2C system,[13–15] a RFC sample was vacuum annealed at 1450 °C for 5 h. According to SEM image analysis of the sample after such treatment,
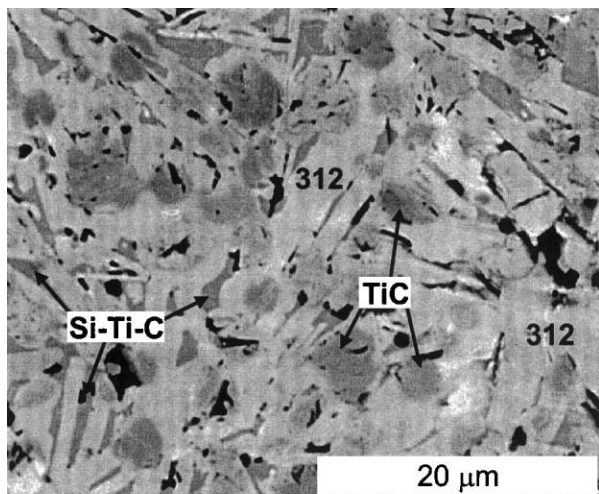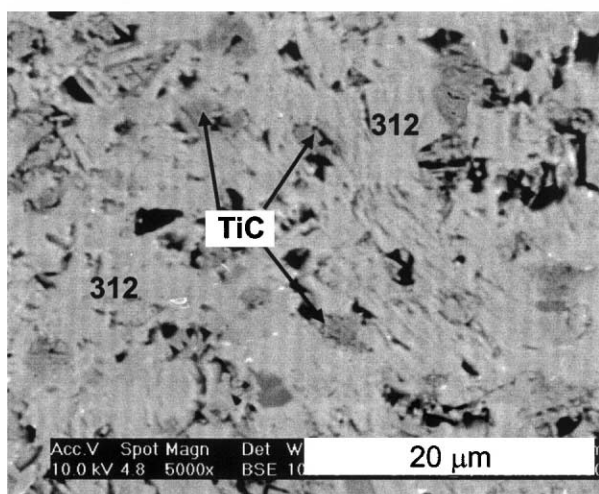
Fig. 8. SEM images (BSE) of a 3Ti–Si–2C sample reactively forged with confinement at 1100 °C, 80 MPa: (a) as-received after RFC; (b) after RFC + 5 h anneal at 1450 °C. '312' Denotes Ti_3SiC_2.

Fig. 8(b), the Ti_3SiC_2 fraction increased to $\sim$80 vol.%. Microhardness of the annealed sample dropped to 4.6 ± 0.6 GPa— a value approaching the hardness of a pure Ti_3SiC_2. The results of annealing lead one to expect that HIPing the RFC samples at $\sim$1500 °C will yield a fully dense material containing a high volume fraction of Ti_3SiC_2. Since RFC samples don't contain open porosity (the overall porosity being less than 5%), HIP in this case can be performed without the expensive encapsulation procedure.

4. Conclusions

The main thrust of the present work was the fabrication of a dense Ti_3SiC_2 ceramic material from the elemental powder blend employing different modes of self-propagating high-temperature synthesis (SHS):

combustion wave propagation, pressureless thermal explosion in a furnace and thermal explosion between the press rams (reactive forging).

In all the SHS experiments, full conversion of the reagents was achieved, with no starting blend constituents (Ti, Si or C) detected in the final product. In neither approach, however, a single-phase Ti_3SiC_2 material was obtained, the combustion products containing appreciable amounts of TiC and, in the case of the SHS wave product, Ti_5Si_3. An additional 'phase' with the approximate composition of 35Ti–52Si–14C (at.%) was detected in all types of samples and is assumed to be the Ti_3SiC_2–$TiSi_2$–SiC eutectic mixture.

Thermal explosion in the 3Ti–Si–2C blend was ignited in the solid state, below the melting point of either constituent, and started with the formation of the binary TiC_{1-x} and Ti_5Si_3 compounds. The formation of the Ti_3SiC_2 ternary is believed to have taken place at the later stage by crystallization from the liquid formed at the high combustion temperature. The concurrent process of TiC precipitation lead to the formation of Ti_3SiC_2/TiC-based multi-phase combustion product. This is in agreement with the earlier reports on combustion synthesis of Ti_3SiC_2 suggesting that the high temperatures and short reaction times of SHS process do not favor the formation of a single-phase Ti_3SiC_2 product.[13,15]

The application of a moderate pressure ($\sim$80 MPa) for 1 min shortly after thermal explosion between press rams preheated to 1100 °C (reactive forging) in a confinement cylinder (RFC) yielded dense (95%) near-net-shape Ti_3SiC_2/TiC-based samples. The whole RFC procedure was performed in open air at a relatively low ram temperature of 1100 °C and took no more than a few minutes. Although the ternary carbide in the final product constitutes no more than 45 vol.% by volume, post-RFC HIPing at $\sim$1500 °C without encapsulation (unnecessary due to the low ($\leqslant$5%) porosity of RFC samples) could allow the fabrication of near-net-shape fully dense single-phase Ti_3SiC_2 parts.

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