Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 39 (2013) 3663–3667

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Fabrication of Ti_3SiC_2-based ceramic matrix composites by a powder-free SHS technique

P. Istomin, A. Nadutkin, V. Grass*

Laboratory for Ceramic Materials, Institute of Chemistry, Komi Science Center, Ural Branch of the Russian Academy of Sciences, Pervomaiskaya str. 48, Syktyvkar 167982, Russian Federation

Received 9 August 2012; received in revised form 11 October 2012; accepted 12 October 2012
Available online 23 October 2012

Abstract

A powder-free technique for fabrication of Ti_3SiC_2-based composite ceramics via self-propagating high-temperature synthesis (SHS) is developed. The essence of the method is that the SHS-compaction of a multilayer stack comprised alternating layers of titanium foils and polymer films filled with either microsized silicon carbide particles or microsized silicon carbide particles mixed with charcoal particles. It is shown that SHS-compaction of non-powder materials can be used to synthesize dense particulate-reinforced ceramic matrix composites of Ti_3SiC_2–$TiSi_2$–SiC_p. Effects of the initial reactant composition and the synthesis conditions on the microstructure of the prepared materials are discussed.

Keywords: B. Composites; Ti_3SiC_2; D. SiC; Combustion synthesis

1. Introduction

Titanium silicon carbide, Ti_3SiC_2, is a representative member of the MAX phase family, a group of layered ternary compounds that uniquely endow materials based on them with properties of both structural ceramics and metals. Therefore, Ti_3SiC_2-based composite ceramics are desirable for use in a wide range of applications, and the development of innovative fabrication techniques is of current interest [1–3]. Indeed, the number of investigations of Ti_3SiC_2-based composite ceramics is steadily rising, but there still are some important points that are not covered when synthesis procedures are designed. In fact, a number of published works are focused on determining which reactant compositions are preferred for which synthesis conditions. Starting materials are usually in the form of fine powders, as is typical of traditional ceramic sintering techniques. However, there are specific cases when the use of non-powder forms of reactants may be more suitable. At least one advantage of non-powders, such as films, foils, wires, and tubes, is that they can act as a sort of load-bearing elements in green bodies, providing them with considerable mechanical strength and reducing the risk of damage before sintering. This advantage is especially important for industrial manufacturing of large ceramic items, such as large sheets, long rods or tubes. We believe that the use of non-powder reactants can open up new possibilities for the synthesis of Ti_3SiC_2-based ceramics. The research we present herein is focused on the fabrication of ceramic matrix composites of Ti_3SiC_2–$TiSi_2$–SiC_p via pressure-assisted self-propagating high-temperature synthesis, also known as SHS-compaction [4], using titanium foils and polymer films highly filled with microsized SiC or with microsized SiC mixed with charcoal particles.

2. Experimental

2.1. Materials

Titanium foils (Grade 2) of thicknesses of 55 μm and 100 μm and polymer films filled with either 70 wt% SiC particles (20 μm in size) or 70 wt% SiC particles (20 μm in size) and 3.5 wt% activated charcoal particles (90 μm in

---

*Corresponding author. Tel.: +7 8212 219921; fax: +7 8212 218477.
E-mail addresses: grass-ve@chemi.komisc.ru, vegrass@mail.ru (V. Grass).

0272-8842/$ - see front matter © 2012 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2012.10.196

size) were used as the starting materials. The SiC-filled films, with average thicknesses of 130, 165, 190, 200 and 305 μm, were tape-cast in a doctor blade process using a slurry containing polyvinyl alcohol (PVA) aqueous solution as the binder and glycerin as the plasticizer.

2.2. Sample preparation

Titanium foils and SiC-filled PVA films were cut into 24 mm × 24 mm square sheets and then stacked in alternating layers to create piles approximately 1 cm in height, as is shown in Fig. 1a. These multilayer stacks were subsequently compacted uniaxially at 1340 °C for 15 min using vacuum hot pressing without a die, as shown in Fig. 1b. The compaction pressure ranged from 0.2 to 3.5 MPa. The heating schedule was as follows. For the temperatures below 500 °C, the heating rate was kept low at 250 °C/h to favor pyrolysis of the PVA. Further heating up to 1340 °C was performed at a rate of 2000 °C/h. The samples preparation details are given in Table 1, along with the characteristics of the prepared materials.

2.3. Materials characterization

All of the prepared samples were analyzed using scanning electron microscopy (SEM) and powder X-ray

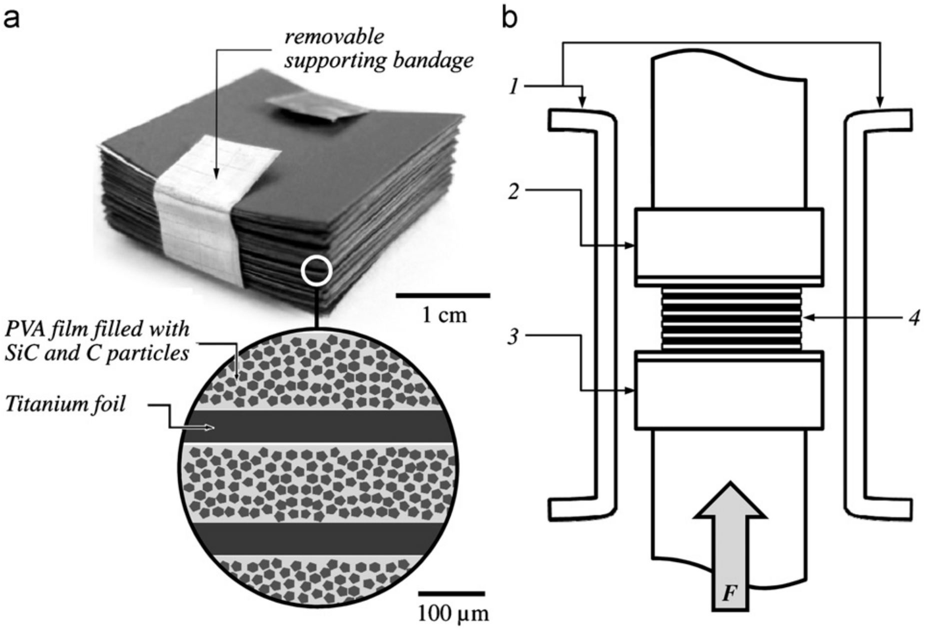

Fig. 1. General view of a reactant stack and schematic of the pre-treatment structure (a); schematic of the SHS-compaction fixture (b): 1—tungsten heaters; 2—upper graphite punch (fixed); 3—lower graphite punch (movable); 4—sample.

Table 1
Initial reactant compositions, synthesis conditions and characteristics of the prepared materials.

Sample	1	2	3	4	5	6
Thickness of the reactant materials:						
- Ti foil (μm)	55	55	55	100	100	100
- SiC-filled PVA film (μm)	130	165	130	190	305	200
Mole ratio of the reactants:						
Ti/SiC/C	$3.5/2.5/0_{+\delta}$	$3.5/3.3/0_{+\delta}$	$3.5/2.5/0_{+\delta}$	$3.5/2.2/0_{+\delta}$	$3.5/3.1/0_{+\delta}$	$3.3/2.0/0.4_{+\delta}$[a]
Value of compacting pressure:						
F (MPa)	0.2	1.0	2.0	3.5	3.5	3.5
Expected phase volume ratio in the final products according to reaction (1)*:*						
$Ti_3SiC_2/TiSi_2/SiC$	20/5/4	20/5/8	20/5/4	20/5/2	20/5/7	20/3/2
Density:						
- theoretical (g/cm^3)	4.28	4.13	4.27	4.35	4.17	4.35
- measured (g/cm^3)	3.36	3.05	3.81	3.85	3.92	3.84
- relative (%)	79	74	89	88	94	88

[a] The symbol "$+\delta$" is used herein to indicate the presence of small amounts of carbon due to PVA pyrolysis.

diffraction (XRD). The cross-sectional SEM images of polished samples without any conductive coating were recorded using a TESCAN scanning electron microscope (VEGA3 SBU; TESCAN, a.s.; Czech Republic) operating at an acceleration voltage of 10 kV. The XRD data were recorded with a Shimadzu diffractometer (XRD-6000, Shimadzu Corp., Japan) using Ni-filtered CuK$_\alpha$ radiation and operating at 30 kV and 30 mA.

The bulk density was measured using Archimedes' principle. Theoretical density was calculated from the phase compositions expected from the overall reaction between Ti and SiC, as shown in Eq. (1). The relative density was estimated as the percent ratio of measured to theoretical density.

3. Results and discussion

3.1. SHS-compaction

During heat treatments of the samples, we always detected a strong self-heating effect, i.e., SHS, which was observed through the special sight window. We found that combustion is initiated at approximately 1330 °C and spreads throughout the entire sample in less than 1 s, rendering it glowing white. According to digital temperature monitoring inside the reactant stack at a sampling rate of one measurement per 0.7 s, the value of the temperature jump is approximately 580 °C at the moment of SHS.

During the combustion period, the sample height decreases dramatically by almost half, even under low compaction pressure. It is known that similar combustion synthesis can take place during heating of powder mixtures containing Ti–SiC. In that case, SHS ignition at a temperature of approximately 1330 °C is attributed to the formation of the Ti–Ti_5Si_3 eutectic melt, as shown in [5,6]. We propose that the initiation of SHS in our samples is a result of the same process and that the strong compaction effect may be accounted by sample softening due to the presence of a large liquid phase.

3.2. Phase formation

During heat treatment of the samples, the primary mode of phase formation is pyrolysis of the PVA films filled with SiC. As shown in [7], degradation of PVA occurs in a temperature range of 200–500 °C and is accompanied by a generation of volatile products, namely hydrocarbons, aromatic hydrocarbons and water, that completely exhaust all oxygen and hydrogen. The solid carbonaceous residue present after pyrolysis is approximately 5 wt%. Thus, small amounts of free carbon will, in fact, be involved in phase formation at higher temperature.

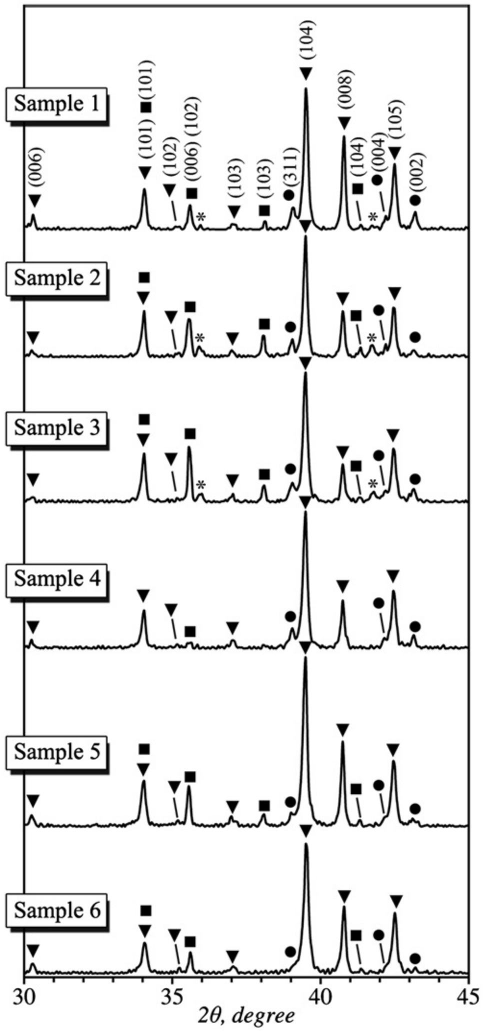

Fig. 2. XRD patterns of synthesized materials. ▼—Ti_3SiC_2; ■—SiC; ●—$TiSi_2$; ∗—TiC.

The XRD patterns given in Fig. 2 shows that the synthesized materials consist of Ti_3SiC_2, $TiSi_2$, SiC, and, occasionally, traces of TiC. It is appropriate to note here that the elemental compositions of our samples fall within the Ti_3SiC_2–$TiSi_2$–SiC equilibrium region, which exists in the Ti–Si–C system up to at least 1400 °C [8]. Therefore, we suggest that for all the samples, the phase formation was near completion, and the overall reaction can be written as:

$$(3+x)\mathrm{Ti}+(1+2x+y)\mathrm{SiC}+(1-2x)\mathrm{C}=\mathrm{Ti_3SiC_2}+x\mathrm{TiSi_2}+y\mathrm{SiC} \tag{1}$$

We propose that, for our case, the overall reaction involves the same stages as those described elsewhere [5,6] for Ti–SiC–C powder mixtures. Briefly, it can be summarized as follows. Interaction between the initial reactants gives rise to the formation of TiC and $Ti_5Si_3C_x$. The titanium silicide coexists with unreacted elemental titanium until a Ti-rich eutectic melt forms at a temperature of approximately 1330 °C. This molten phase acts as a reaction promoter and assists in switching the process into SHS mode, which is followed by more intense melting and a significant increase in the amount of the liquids. During SHS, the Ti-rich melt becomes saturated with silicon and carbon due to dissolution of the carbide phases. As this melt cools down, it crystallizes into Ti_3SiC_2 and $TiSi_2$.

It is clear from reaction (1) that the amounts of SiC and $TiSi_2$ in the products can be controlled independently by introducing an excess of SiC and carbon additives, respectively. If excess SiC is introduced, the SiC content is higher in the products; if more carbon is added, less $TiSi_2$ is formed. This explanation is in a good agreement with the observed XRD patterns, as shown in Fig. 2.

It also should be noted that the materials obtained under lower compaction pressures (Samples 1–3) contain a small amount of TiC, which is believed to be formed during the primary stages of the interaction, and then is partially retained in an undissolved state during further treatment. This behavior is most likely because some deviations from the average elemental composition can be present locally in the melt when the compaction pressure is insufficient to ensure good contact between the reactant layers.

3.3. Microstructure

SEM micrographs of the synthesized materials are shown in Fig. 3. The images taken in backscattered electron (BSE) mode show that Ti_3SiC_2 and $TiSi_2$ are distinguished from each other as ‘‘silver gray’’ and ‘‘light gray’’, respectively. The plate-like grains of Ti_3SiC_2 along with $TiSi_2$ form a chemically inhomogeneous but substantially continuous monolithic structure, which can be interpreted as a type of two-phase matrix. The reinforcing constituent of the composites is the SiC particles, which are embedded uniformly in the matrix and appear to have good adhesion with it.

The relative densities of the prepared samples vary from 74% to 94%, depending on the fabrication conditions, as shown in Table 1. The samples prepared under lower compaction pressures are characterized by the presence of large slit-shaped pores (Fig. 3a,b), whose topology is

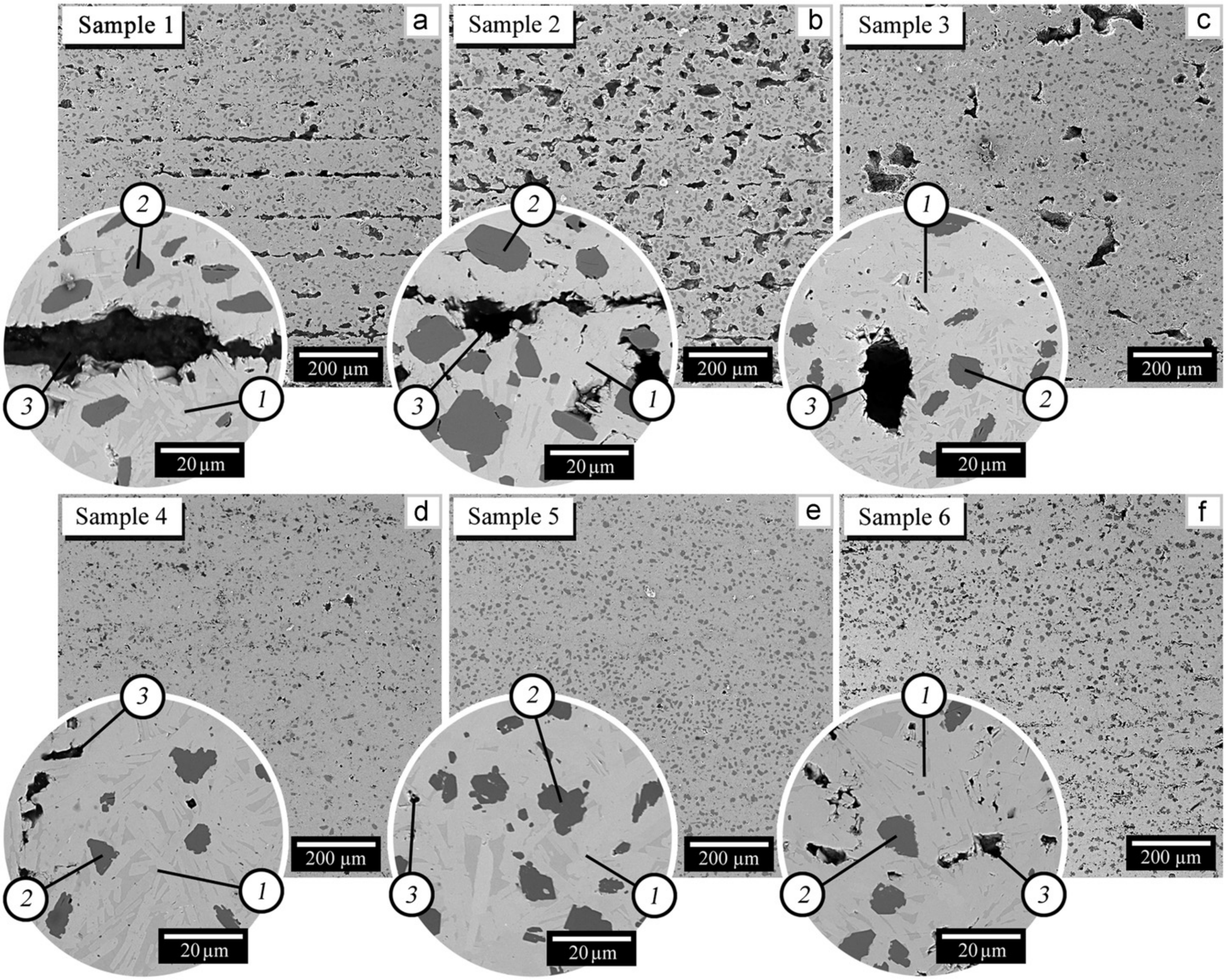

Fig. 3. Cross-sectional SEM micrographs of the synthesized materials. The circled insets are magnified BSE mode images. 1—Ti_3SiC_2–$TiSi_2$ matrix; 2—reinforcing SiC particles; 3—pores.

inherited from the layered structure of the starting reactants. In contrast, the samples prepared under higher compaction pressures contain only isolated pores, which are distributed randomly throughout the matrix (Fig. 3c–f).

We propose that such a microstructure originates from the SHS process. The Ti-rich melt that is formed during the combustion stage infiltrates the layers of SiC and almost completely fills the voids between SiC particles, leading to the formation of a particulate-reinforced matrix when the melt solidifies. Because the titanium migrates outward to the SiC layers, large slit-shaped voids are expected to occur in place of the titanium foils. However, this undesirable effect can be easily eliminated by applying a mechanical pressure of a few megapascals, which is enough to collapse the pores immediately after the SHS stage while the sample is still hot and softened.

4. Conclusion

We have shown that particulate-reinforced ceramic matrix composites of Ti_3SiC_2–$TiSi_2$–SiC_p can be fabricated using the SHS-compaction of a multilayer stack comprised of alternating layers of titanium foils and polymer matrix films highly filled with either microsized silicon carbide or microsized silicon carbide mixed with charcoal particles. The introduction of carbon additives into SiC-filled films diminishes the $TiSi_2$ content in the matrix. By varying the thickness ratios of the Ti and SiC reactant layers, it is possible to control the amount of reinforcing SiC particles embedded in the matrix. The synthesis procedure involves heating the reactant stacks above 1330 °C to initiate SHS and compacting them under the mechanical pressure of a few megapascals to suppress the formation of large slit-shaped pores, which arise in place of the titanium foils. The ceramic matrix composites obtained under these conditions are well densified and have no signs of anisotropy from the layered structure of the reactant stacks. Thus, the proposed powder-free technique for the synthesis of Ti_3SiC_2-based materials looks to be an attractive and efficient alternative to the known methods.

Acknowledgments

This study was financially supported by the Russian Foundation for Basic Research (Project no. 11-03-00529-a).

References

[1] M.W. Barsoum, The $M_{N+1}AX_N$ phases: a new class of solids: thermodynamically stable nanolaminates, Progress in Solid State Chemistry 28 (2000) 201–281.

[2] H.B. Zhang, Y.W. Bao, Y.C. Zhou, Current status in layered ternary carbide Ti_3SiC_2, a review, Journal of Materials Science AND Technology 25 (2009) 1–38.

[3] Z.M. Sun, Progress in research and development on MAX phases: a family of layered ternary compounds, International Materials Reviews 56 (2011) 143–166.

[4] A.G. Merzhanov, The chemistry of self-propagating high-temperature synthesis, Journal of Materials Chemistry 14 (2004) 1779–1786.

[5] Y. Zou, Z.M. Sun, H. Hashimoto, L. Cheng, Reaction mechanism in Ti–SiC–C powder mixture during pulse discharge sintering, Ceramics International 36 (2010) 1027–1031.

[6] P.V. Istomin, A.V. Nadutkin, V.E. Grass, Effect of heating schedule on fabrication of Ti_3SiC_2-based composites from Ti–SiC powder mixture, International Journal of Applied Ceramic Technology 9 (2012) 991–997.

[7] J.W. Gilman, D.L. VanderHart, T. Kashiwagi, Thermal decomposition chemistry of poly(vinyl alcohol), in: G.L. Nelson (Ed.), Fire and Polymers II: Materials and Tests for Hazard Prevention, American Chemical Society, Washington, DC, 1995, pp. 161–185.

[8] Y. Du, J.C. Schuster, H.J. Seifert, F. Aldinger, Experimental investigation and thermodynamic calculation of the titanium–silicon–carbon system, Journal of the American Ceramic Society 83 (2000) 197–203.