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Ceramics International 36 (2010) 375–379
CERAMICS INTERNATIONAL
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Short communication

Effect of the amounts of silicon on the in situ synthesis of Ti_3SiC_2 based composites made from TiC/Si powder mixtures

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Received 12 February 2009; received in revised form 29 June 2009; accepted 24 July 2009

Abstract

This paper describes how variations in silicon content and heat treatment influence the phase composition of TiC/Si powder mixtures during heat treatment. The sintering procedure is investigated with respect to the phases produced with a particular emphasis on maximisation of the Ti_3SiC_2 content. The heat treated products have been analysed using scanning electron microscopy, energy dispersive spectroscopy and X-ray diffractometry. In the heat treated products Ti_3SiC_2 and TiC are the dominant phases and SiC and $TiSi_2$ are found in smaller (0–30 vol.%) amounts. The composition was found to depend on both Si content and heat treatment temperature and time. The silicon content can be optimised with respect to maximum Ti_3SiC_2 production, but its value changes with different temperature programs. The highest amount (56 vol.%) of Ti_3SiC_2 is achieved by heat treating powder mixtures of initial composition 3TiC/2.2Si at 1350° for 1 h. Heat treatment at lower temperatures (1250–1300 °C) results in an incomplete reaction and production of $TiSi_2$.

Keywords: A. Powders: solid state reaction; A. Sintering; B. Composites; D. Carbides

1. Introduction

Titanium silicon carbide, Ti_3SiC_2, is a ceramic material that has received increased attention over the past three decades because of its attractive combination of properties. It belongs to a group of ternary layered nitrides and carbides known as the MAX phases; with general formula of $M_{n+1}AX_n$, where M is an early transition metal, A is an element from groups 12 to 16 in the periodic table of the elements, X is either nitrogen or carbon and n is an integer: 1–3. Ti_3SiC_2 is the most well known of the MAX phases and it possesses some of the most appreciated qualities of ceramics e.g. it is refractory, light weight and stiff but it is also damage tolerant, machinable with conventional tools, and not susceptible to thermal shock [1].

Production of monolithic Ti_3SiC_2 has been reported by many authors [2–6] but in some cases secondary phases such as titanium carbides, silicon carbide and/or titanium silicides are found in the final products [7–11]. These phases are not necessarily detrimental to the material properties; some studies have shown that by controlling the amount of the different phases in the samples it is possible to adjust the properties of the material. The binary carbides TiC and SiC have been shown to reinforce the Ti_3SiC_2, producing composites with interesting properties and enhanced oxidation resistance [5,12]. Both TiC- and SiC–Ti_3SiC_2 composites have been reported to possess damage tolerance, fracture toughness and thermal shock resistance comparable or even superior to monolithic Ti_3SiC_2 samples [13–16].

Ti_3SiC_2 can be synthesised by powder metallurgical methods from a variety of starting powders, most of which include Ti metal powder, such as Ti/Si/C [9,17,18] Ti/C/SiC [3,11,19] and Ti/Si/TiC [2,4,20]. Ti metal is very reactive and in the form of a finely dispersed powder it is even explosive in air, which is a great disadvantage for up scaled industrial production [21]. It has been shown that Ti_3SiC_2 can be synthesised in acceptable quantities without the use of the hazardous Ti powder, from a TiC/Si powder mixture [8,9,22,23]. Previous work indicated that the amount of Si in the starting powder appears to be crucial to the phase composition of the final products.

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doi:10.1016/j.ceramint.2009.07.029

Excess silicon in the synthesis using Ti/Si/C and Ti/Si/TiC powders has been found to compensate for Si loss by evaporation, thereby counteracting the decomposition reaction [18,20]. Some authors have found, however, that large amounts of Si promote $TiSi_2$ formation in preference to Ti_3SiC_2 [2]. In TiC/Si starting powders, the optimum amount of Si with respect to the purity of the Ti_3SiC_2 is yet to be established.

The purpose of this study is to examine the influence of Si content in the starting powders on the phase reactions during sintering. In situ synthesised Ti_3SiC_2 based composites were produced by reactive sintering of TiC/Si powder mixtures. The phase compositions were evaluated by X-ray diffraction (XRD).

2. Experimental

The starting powders were TiC (Aldrich, <44 μm) and Si (Aldrich, <44 μm); they were mixed in six different molar ratios summarized in Table 1. The sample compositions were varied with TiC/Si ratios ranging from 3:1 to 3:2.8. Relative to the stoichiometry of reaction (1) sample B is deficient in Si while samples D–G contain excess Si; the TiC/Si ratio 3:2 of sample C corresponds to the stoichiometry of reaction (1). Included in Table 1 are the expected phase compositions according to the equilibrium phase diagram:

$$3TiC + 2Si \rightarrow Ti_3SiC_2 + SiC \tag{1}$$

The powders were milled in a ball mill for 24 h, using propanol and spherical zirconia media to a mean particle diameter of approximately 5 μm. The powder to media ratio was approximately 0.4, the media diameter was 10 mm and the media weight was approximately 350 g. The powder was dried and compacted by uniaxial pressing to 10 MPa, and then cold isostatically pressed to 300 MPa. The sample weight was approximately 1 g. The heat treatments were performed in alumina (Al_2O_3) boats under flowing argon gas in an Al_2O_3 tube furnace with a tube inner diameter of 25 mm. The gas flow in the tube was approximately 85 ml/min. The temperatures, heating rates and holding times of the heat treatments are presented in Table 2. Heat treated samples were polished and analysed by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). Heat treated products were also crushed into a powder and analysed by X-ray diffractometry (XRD) using Cu radiation and a proportional detector. A total of 36 samples were analysed in this study. The phase fractions were estimated using the direct comparison method [24], where the integrated intensity for a minimum of three diffraction lines of each phase were summed and the volume fractions of the individual phases were calculated using Eq. (2):

$$V_i = \frac{A_i}{A_\alpha + A_\beta + A_\gamma + \cdots} \quad \text{Where } A_j = \sum_{j=1}^{n} \frac{I_j}{R_j} \tag{2}$$

where n is the number of $h\,k\,l$ peaks for a given phase, V is the volume fraction, I is the integrated intensity, and R is the calculated theoretical intensity. Greek letters denotes the phases present in the material. The validity of this procedure has been demonstrated for two-phase steels by Dickson [25].

Table 1
Starting powder compositions.

Sample name	TiC/Si ratio	Expected phases
B	3:1	TiC, Ti_3SiC_2 and SiC
C	3:2	$TiSi_2$, Ti_3SiC_2 and SiC
D	3:2.2	$TiSi_2$, Ti_3SiC_2 and SiC
E	3:2.4	$TiSi_2$, Ti_3SiC_2 and SiC
F	3:2.6	$TiSi_2$, Ti_3SiC_2 and SiC
G	3:2.8	$TiSi_2$, Ti_3SiC_2 and SiC

Table 2
Heat treatment temperature program.

Temperature (°C)	Holding time (h)	Mean heating rate at $T > 1000$ °C (°C/min)
1250	2.5	1.6
1300	2	1.5
1350	1	1.3

3. Results and discussion

Fig. 1 shows the X-ray diffractograms of all samples sintered at 1250 °C, 1300 °C and 1350 °C for 2.5, 2 and 1 h(s), respectively. Ti_3SiC_2 denoted TSC, is seen to form in all samples in varying amounts.

Fig. 1a and b shows that TiC is the dominant phase in powders B–D sintered at 1250 °C and 1300 °C; whereas in samples E–G, Ti_3SiC_2 is the main phase with SiC and $TiSi_2$ also present at these temperatures.

Fig. 1c shows that all samples sintered at 1350 °C for 1 h contain more Ti_3SiC_2 than those sintered at lower temperatures. Here, Ti_3SiC_2 is the main phase in all samples with the exception of sample B. At 1350 °C, sample D contained the largest amounts of Ti_3SiC_2 produced in this study; approximately 56 vol.%. Fig. 2 shows how the Si content of the starting powder affected the phase fractions in the samples sintered at 1350 °C for 1 h. It is worth noting that although samples C–E contained comparable amounts of Ti_3SiC_2 (51–56 vol.%) they differed considerably in their overall phase composition. Sample C contained 15 vol.% SiC and 23 vol.% TiC while sample E contained 30 vol.% SiC and 10 vol.% TiC.

Fig. 3 shows how the Ti_3SiC_2 volume fraction in the heat treated products depends on the Si content of the starting powders, for three different heat treatments. The Ti_3SiC_2 phase fraction may be maximised by adjusting the Si content in the starting powder. A high temperature promotes Ti_3SiC_2 formation and shifts the optimised Si content of the starting powder towards lower values. As can be seen from Fig. 2, the TiC content decreased with increasing Si content from samples B to E. In samples F and G, the volume fraction of TiC increased again. This is likely to be a result of the high Si content in these samples. As $TiSi_2$ production is also highest for

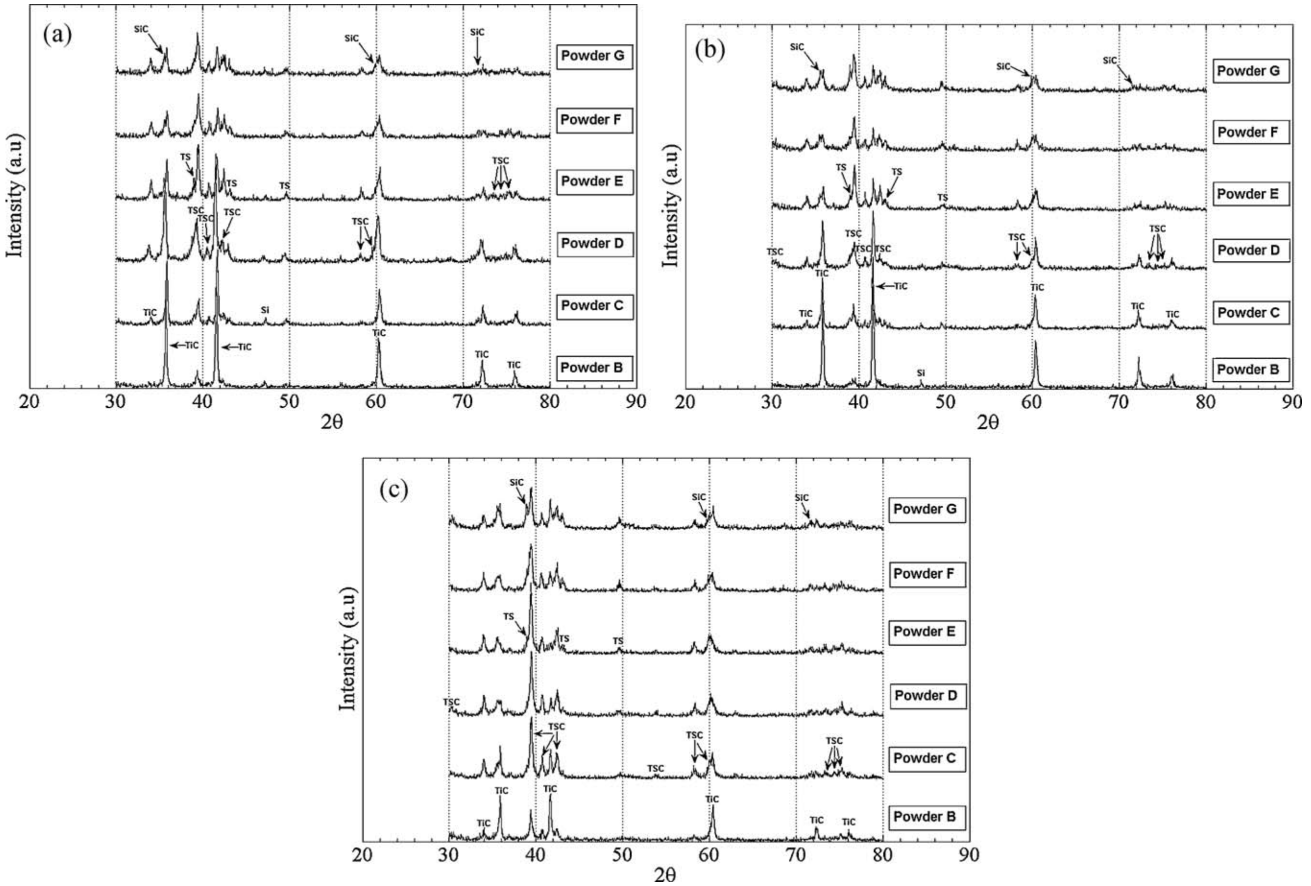

Fig. 1. X-ray diffractograms of samples B–G sintered at (a) 1250 °C for 2.5 h; (b) 1300 °C for 2 h; and (c) 1350 °C for 1 h. Ti_3SiC_2 and $TiSi_2$ peaks are denoted TSC and TS, respectively.

these samples a competing reaction to Eq. (1) is assumed to occur:

$$TiC + 3Si \rightarrow TiSi_2 + SiC \qquad (3)$$

Fig. 4 shows scanning electron micrographs of sample D. The micrograph in Fig. 4a shows the microstructure in backscattered electron mode and Fig. 4b–d shows EDS mappings of the same sample area as displayed in (a). The samples were not perfectly homogeneous and the figure shows an inhomogeneous area. The powder inhomogeneity most likely originates from some particle sedimentation in the drying step of the powder preparation.

EDS analysis of the area revealed different chemical compositions within different, well defined parts of the sample. Some parts are clearly richer in silicon and poorer in titanium and vice versa. However, no such variations in carbon

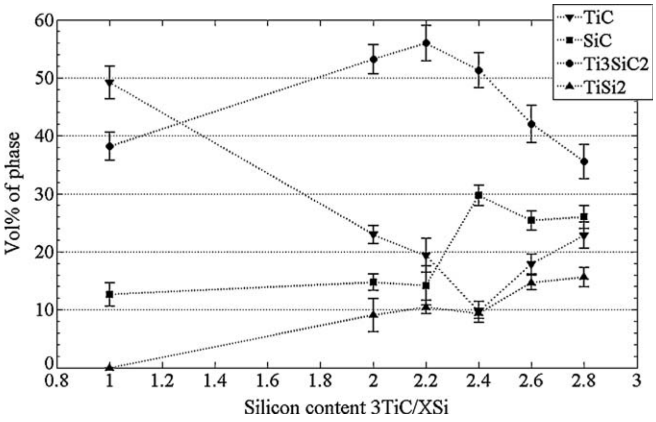

Fig. 2. Phase contents of the final products sintered at 1350 °C for 1 h. Note that the values on the *x*-axis correspond to the molar ratio 3TiC/*X*Si of the starting powder and not the composition of the final product.

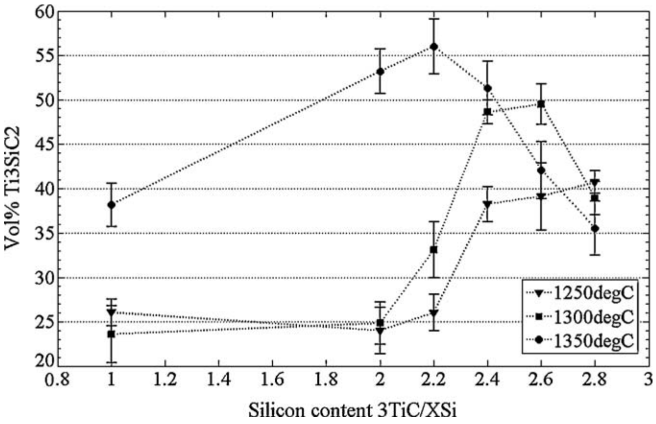

Fig. 3. Ti_3SiC_2 contents of the heat treated products evaluated with respect to silicon content of the starting powder for various heat treatments.

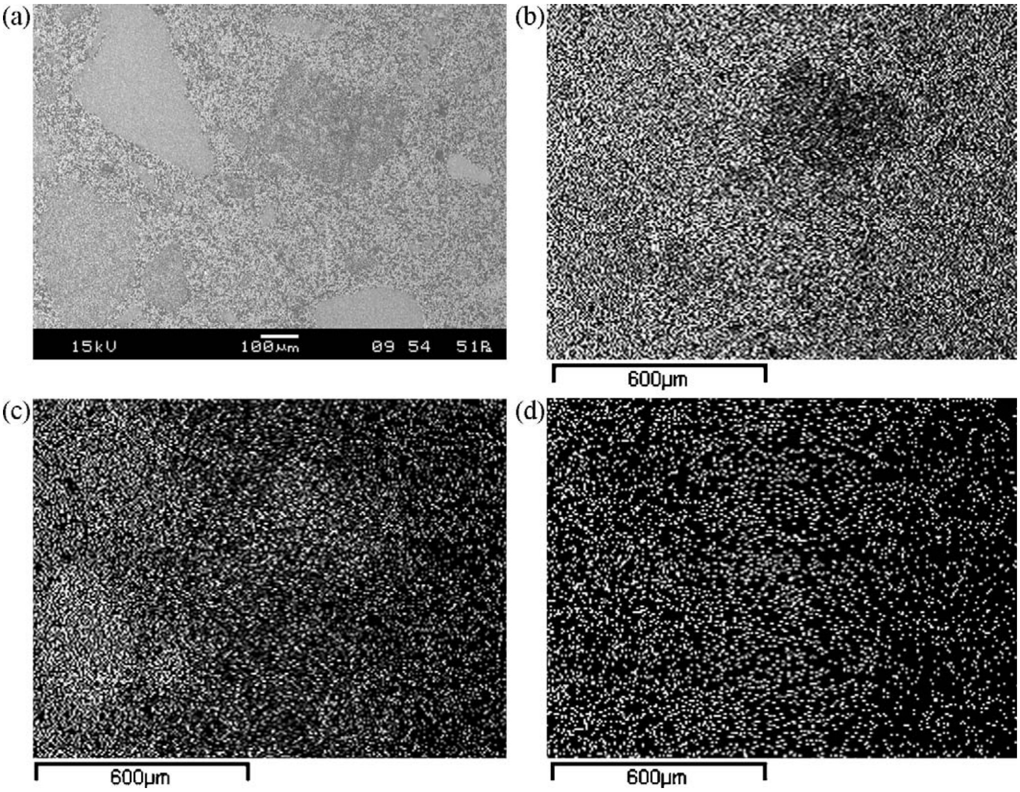

Fig. 4. SEM micrographs of sample D sintered at 1250 °C in a graphite furnace; (a) backscattered electron mode; (b) EDS mapping of titanium. Shows dark areas poor in Ti; (c) EDS mapping of silicon. Shows bright areas rich in Si; (d) EDS mapping of carbon. Shows a relatively uniform distribution of C.

distribution were detected because of the low number of electrons in the carbon atom. From the phase diagram in Fig. 5 it is clear that the carbon content should not vary greatly with varying phase composition.

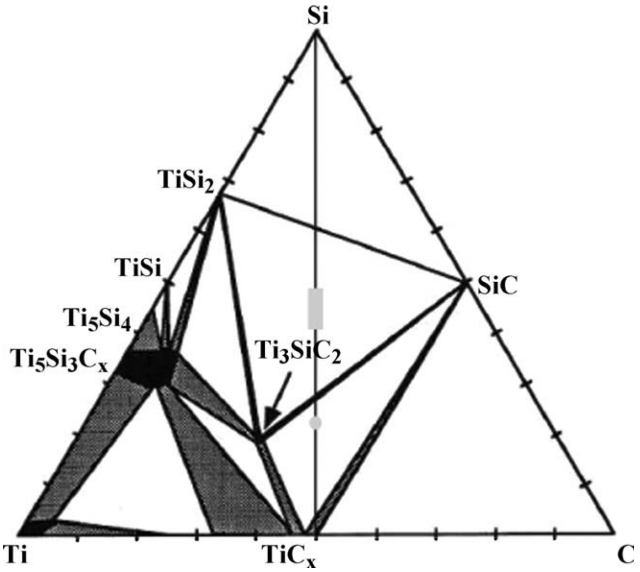

Fig. 5. 1200 °C isothermal section of the ternary phase equilibrium diagram of the Ti–Si–C system. Illustration by Arunajatesan and Carim [26], original after Ratliff and Powell [27]. The starting powder compositions used in this study are situated along the marked line; sample B at the marked circle and samples C–G within the marked rectangle.

In Fig. 2 samples C (3TiC/2Si), D (3TiC/2.2Si) and E (3TiC/2.4Si) are seen to contain comparable amounts of Ti_3SiC_2, which is linked to the inhomogeneity of the samples and it is likely that a more homogeneous and finely dispersed powder in combination with close control of Si content should result in higher Ti_3SiC_2 production. As there are local variations within the samples it may be assumed that within the E samples, some regions are closer to the composition of sample D and some are closer to that of F. The composition of sample F being rich in Si, may be compared with Si-rich areas seen in Fig. 4c, and the result is locally increased production of SiC and $TiSi_2$. As can be seen from Fig. 4b and c, the areas rich in Si are also poor in Ti, indicating that SiC is likely to be locally dominant. By using the same logic, regions rich in Ti and poor in Si are dominated by TiC and are comparable with areas within samples D of compositions closer to sample C.

The 1200 °C isothermal section of the ternary phase equilibrium diagram of the Ti–Si–C system is shown in Fig. 5. The composition of the B samples is represented in the figure by a circle and the compositions of the other samples are found within the marked rectangle. The B samples had an initial composition within the Ti_3SiC_2–SiC–TiC three-phase area. Some of the B samples however, also contained small amounts of $TiSi_2$, resulting from the inhomogeneity discussed. The evaporation of silicon is commonly reported in the literature which may explain the very low amounts of Ti_3SiC_2 and SiC obtained in sample B. If silicon is lost by evaporation, the compositions of the samples shift along the marked line in the figure towards the Ti–C base line of the diagram. This shift will move the composition towards the TiC phase area and thereby deplete the samples of the other two phases.

The initial composition of samples C–G is situated within the $TiSi_2$–SiC–Ti_3SiC_2 three-phase area. These three phases were indeed observed in the samples, together with TiC, which is assumed to be residual, unreacted starting powder. Evaporation of silicon from these samples appears to shift the phase composition along the Si–TiC line, towards the Ti_3SiC_2–SiC line of the diagram; if this line is traversed, TiC will form by an equilibrium phase reaction.

Silicon also influences the kinetics of the phase reactions by providing a means for the removal of any thin oxide layers that may have formed on particle surfaces. Si may react with oxygen to from SiO(g) which can then be flushed out with the flowing argon. By this mechanism, the system is depleted in Si but the reactivity of the silicon particles that remain is greatly increased. The size of the sample and the gas flow rate can therefore influence the final composition.

4. Conclusions

The amount of Ti_3SiC_2 produced was highly dependent on the Si content of the starting powder. The most Ti_3SiC_2 was produced in the 3TiC/2.2Si (D) powder when sintered at 1350 °C for 1 h, these products contained 56 vol.% Ti_3SiC_2.

By varying the Si content of the starting powder, the phase composition of the final products may be controlled. The C–E samples sintered at 1350 °C for 1 h produced comparable amounts of Ti_3SiC_2 (51–56 vol.%) but the C sample contained 15 vol.% SiC and 23 vol.% TiC while the amounts in the E sample were 30 vol.% and 10 vol.%, respectively.

Heat treatment temperature influences the phase composition. It is particularly decisive in the formation of the $TiSi_2$ and Ti_3SiC_2 phases. Low temperatures promote $TiSi_2$, the largest volume fraction of which (approximately 20 vol.%) was achieved in the 3TiC/2.6Si (F) sample sintered at 1250 °C. A high temperature and a short holding time (1350 °C; 1 h), a homogeneous powder mixture with a 3TiC/XSi ratio of X between 2 and 2.4 promote the formation of Ti_3SiC_2 and SiC.

Acknowledgements

I. Kero gratefully acknowledges financial support from the Swedish National Graduate School of Space Technology.

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