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Phase reactions in a hot pressed TiC/Si powder mixture

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Abstract

This work investigated the possibility of producing dense Ti_3SiC_2 by hot pressing TiC/Si powders. A hot press with graphite heating elements was used for densification and the phase reactions of some hot pressed samples were further evaluated by pressureless heating in a dilatometer. The density and phase composition of the heat treated samples were evaluated using Archimedes principle and by X-ray diffractometry, respectively. Hot pressing resulted in a low Ti_3SiC_2 yield; the main phases were TiC and $TiSi_2$ regardless of starting powder composition, temperature, holding time or pressure. A second heating without pressure resulted in Ti_3SiC_2 formation, but only in samples initially hot pressed at 1300 °C or lower. At higher hot pressing temperatures, thin oxide layers on particle surfaces were locked into the structure. Acting as diffusion barriers, they prevented the Ti_3SiC_2 forming reaction. In hot pressed samples the density was significantly higher than in samples sintered without pressure.
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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 scale-up to 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].

We have in previous studies shown the feasibility of Ti_3SiC_2 production by pressureless sintering. The results were composite materials with dominant phases of Ti_3SiC_2 and TiC [24–28]. The drawback with pressureless sintering is the relatively low density; therefore our interest is turned into pressurized sintering. Hashimoto et al. [29,30] investigated the influence of pressure on the formation of Ti_3SiC_2 and found that

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the final products consisted of Ti_3SiC_2 and TiC when the pressure was over 14 MPa. For pressure below 14 MPa, the samples also contained Ti_5Si_3 and $TiSi_2$ [29]. The same authors found that the reactivity of the starting powder affected which of the two silicides would form and act as intermediate phases [30].

El-Raghy and Barsoum produced single phase, fully dense Ti_3SiC_2 samples through reactive hot isostatic pressing with starting powders of Ti, SiC and graphite [3]. The same authors produced in an earlier study almost pure Ti_3SiC_2, with less than 2 vol% of SiC and TiC_x in the final product, by hot pressing at 1600 °C and 40 MPa [31]. Gao et al. [20,32] produced high purity Ti_3SiC_2 by hot isostatically pressing Ti/Si/TiC and Ti/SiC/C powders. Li et al. [33] managed to get highly pure Ti_3SiC_2 by hot isostatic pressing of Ti/Si/C. Lo et al. [37] fabricated TiC/Ti_3SiC_2 composites from a starting powder of TiC/Ti/Si by hot pressing under 25 MPa in Ar at a temperature of 1500 °C.

Zhu et al. [34] reported difficulties to synthesise single phase Ti_3SiC_2 by hot pressing when using TiC/Ti/Si powders. They sintered in a hot press with a pressure of 30 MPa and different temperatures (1200, 1300 and 1400 °C). They got significant amount of TiC in all samples. Zhou et al. [17,35] hot pressed elemental powders and produced Ti_3SiC_2 with small amounts of TiC and Ti_5Si_3C.

Reports on hot pressing of Ti_3SiC_2 with starting powders including TiC as the only titanium source are rare. However, Li et al. [8] fabricated SiC reinforced Ti_3SiC_2 composites by hot pressing TiC and Si powders. The hot pressing was performed at 1350 °C with a pressure of 30 MPa and directly followed by sintering in vacuum at 1500 °C. This resulted in a product of Ti_3SiC_2/SiC composite with some amount of residual TiC. Radhakrishnan used a similar procedure but received residual $TiSi_2$ instead of TiC [36].

The aim of this work was to investigate the phase reactions/high temperature chemistry of a TiC/Si powder mixture sintered under pressure in order to increase the final density of the products. In our previous studies on pressureless sintering of a TiC/Si powder mixture we received Ti_3SiC_2 samples with relatively low density [24–28].

2. Materials and methods

The starting powders were TiC (Aldrich, <44 μm, 98% purity) and Si (Aldrich, <44 μm, 99% purity). The powders were mixed with a TiC/Si ratio of 3:2. The powders were wet milled in a tumbling ball mill using propanol, Hypermer KD2 dispersant and zirconia spheres. The media diameter was 10 mm, the powder to media ratio was approximately 0.4 and the powder to propanol ratio was approximately 1.5. After milling, the powder was stir dried using a polytetrafluoroethylene (PTFE) coated stirring bar and a heated magnetic stirring plate. The plate temperature was set to 50 °C.

The powder samples of approximately 3 g were compacted by uniaxial pressing (33 MPa) into green bodies with cylindrical geometry (15 mm diameter and approximately 15 mm length). The green bodies were embedded in boron nitride (BN), inserted in a graphite pressing die and hot pressed (HP) (Thermal Technology Inc., HP 20) at 20 MPa under flowing argon gas. One sample was heated in the hot press following the same temperature program but no pressure was applied, this sample was denoted NP. It should be noted that the sample was heat treated in exactly the same surrounding; the only difference was that there was no pressure applied. The HP furnace had graphite heating elements and was heated at a rate of approximately 20 K/min. Table 1 shows the hot press parameters.

Table 1
Hot press temperatures, holding times and pressures.

Sample	Firing temp (°C)	Firing pressure (MPa)	Holding time (h)
HP1150	1150	20	1
HP1250	1250	20	1
HP1300	1300	20	1
NP1300	1300	Atm[a]	1
HP1380	1380	20	1
HP1400	1400	20	1
HP1430	1430	20	1

[a] Fired under dynamic argon atmosphere, no overpressure was used.

The density and open porosity of the samples were determined using Archimedes principle, after infiltrating the samples during 1 h in vacuum with distilled water. The phase compositions of these hot pressed samples were determined by X-ray diffractometry (XRD) (Philips 1130) using Cu Kα radiation and a proportional detector.

Some of the hot pressed samples were cut into smaller samples to fit a dilatometer (Netzsch, 402C). The dilatometer furnace had a protective tube and sample holder assembly of alumina. It operated under flowing argon gas and was heated at a rate of 10 K/min to temperatures of 1450 and 1500 °C, respectively and cooled at a rate of 20 K/min. Table 2 shows the samples heated in the dilatometer and the dilatometer end temperatures. For reference, samples of approximately 0.6 g powder were formed by cold uniaxial pressing, into cylinders of 10 mm diameter. Then, they were cold isostatically pressed (CIP) at 200 MPa. These cold pressed samples were only heat treated in the dilatometer.

The phase compositions of the samples heated in the dilatometer were determined by XRD (Siemens D 5000) using Cu Kα radiation and a proportional detector. The phase fractions were determined using the direct comparison method, which has been described elsewhere [27,38].

Table 2
Samples heated in the dilatometer and the end temperatures.

Sample	Dilatometer end temp (°C)
HP1150	1450
HP1150	1500
HP1300	1450
HP1300	1500
HP1400	1450
HP1400	1500
REF1450	1450
REF1500	1500

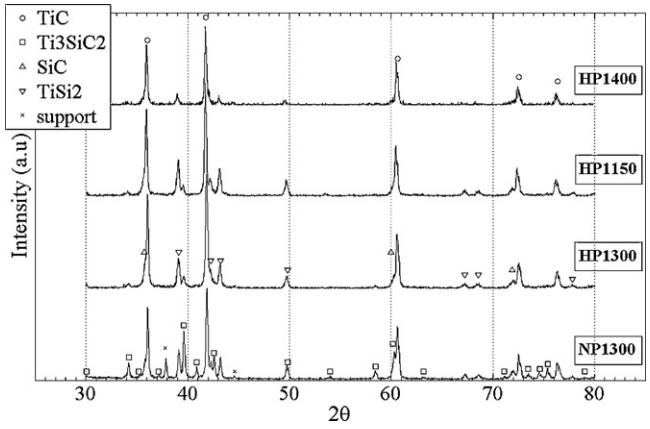

Fig. 1. X-ray diffractograms of samples heated to 1150, 1300 and 1400 °C in the hot press and held for 1 h and 20 MPa. One sample, NP1300, was also heated in the hot press furnace but without any pressure applied. *Note*: the two peaks marked with an *x* originate from the *x*rd sample support.

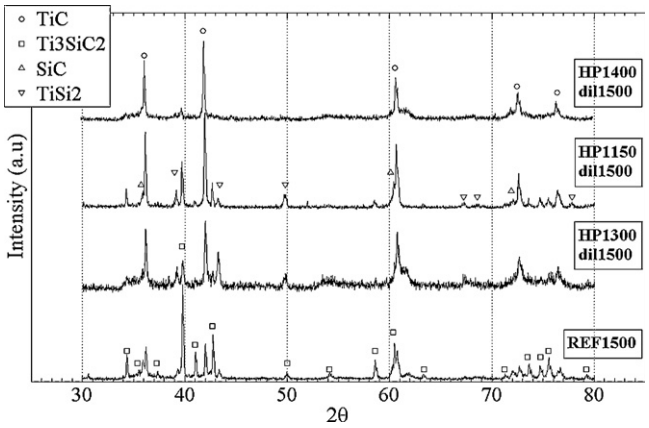

Fig. 2. X-ray diffractograms of samples HP1150, HP1300 and HP1400 °C after dilatometer runs up to 1500 °C. The sample REF1500 was only cold isostatically pressed before the dilatometer run.

3. Results and discussion

Fig. 1 shows the X-ray diffractograms of samples heated in the hot press. Small amounts of Ti_3SiC_2 were formed in the hot pressed samples fired at low temperatures. At temperatures above 1300 °C no Ti_3SiC_2 was formed. One sample was fired in the hot press furnace without pressure (NP1300), i.e., embedded in BN, inserted in the graphite die, but without any mechanical pressure applied. This sample produced a significantly higher amount of Ti_3SiC_2 (37 vol%), than the samples sintered with pressure applied, see Fig. 1.

The sample initially fired at 1250 °C was reheated in the hot press to 1420 °C, 20 MPa and held for 1 h. After reheating, no Ti_3SiC_2 remained in the sample. As seen in Fig. 1, in samples hot pressed at 1150–1300 °C there are only trace amounts of Ti_3SiC_2; the major phase is TiC and there is also a significant amount of $TiSi_2$. Samples hot pressed at temperatures above 1300 °C show no Ti_3SiC_2, but contain primarily TiC and $TiSi_2$. There may also be some SiC in the samples; however that is difficult to state, because the peaks of SiC overlap the peaks of TiC.

Fig. 2 shows the X-ray diffractograms of samples heated in the dilatometer. After reheating the samples in a dilatometer, i.e., in a pressureless surrounding, the sample HP1150 transformed into Ti_3SiC_2 (37 vol%) and TiC, with minor amounts of $TiSi_2$, see Fig. 2. HP1400 did not show any phase reaction at all during the run in the dilatometer. HP1300 exhibited intermediate behaviour, with some Ti_3SiC_2 formation (28 vol%). Ti_3SiC_2 is the dominant phase in the CIP:ed reference sample (49 vol%).

The lack of Ti_3SiC_2 in the hot pressed samples may be explained by the fact that there are thin layers of oxides on the surfaces of the powder particles before sintering, arising from the milling and handling processes. Earlier experiments with pressureless thermal synthesis of these powders have shown that the oxides will be reduced and given off as carbon monoxide gas [28]. These experiments have been discussed elsewhere and will not be given in detail here. The powder pressed in cold isostatic pressing is still an open system, i.e., there are open channels for the gases to evaporate. However, in the hot press, the samples are under pressure in a closed system and these open channels are compressed. The oxides on the particle surfaces act as diffusion barriers and the reactions are hindered. When reheating the sample first hot pressed at 1150 °C without pressure, the channels are still sufficiently open to let the oxide gases out, leaving clean powder particle surfaces which give a more reactive system. Only a small degree of sintering has occurred at 1150 °C, and the formation of Ti_3SiC_2 can take place. In contrast, the sample hot pressed at 1400 °C has sintered to a significant degree and the porosity is reduced, see Table 3. This means that the oxides on the particle surfaces cannot escape; they are locked in the structure, acting as diffusion barriers and hinder the formation of Ti_3SiC_2 over the entire temperature range. The sample hot pressed at 1300 °C falls in between those hot pressed

Table 3
Densities and open porosity before and after heating in the dilatometer.

Sample	Dil. end temp (°C)	Density before dil. (g/cm^3)	Density after dil. (g/cm^3)	Open porosity before dil. (%)	Open porosity after dil. (%)
HP1150	1450	2.7	2.5	37	42
HP1150	1500	2.7	2.4	37	45
HP1300	1450	3.4	3.3	21	22
HP1300	1500	3.4	3.2	21	27
HP1400	1450	3.7	3.6	11	12
HP1400	1500	3.7	3.6	11	16
REF1500	1500	–	1.7	–	59

at 1150 and 1400 °C and shows a corresponding intermediate amount of Ti_3SiC_2. In this sample the densification begins to occur but the diffusion is slow. Therefore enough porosity remains to allow some gases to escape in the dilatometer. The following reactions are suggested to describe the formation of Ti_3SiC_2 when oxides in the form of TiO_2 and SiO_2 are present, leading to CO(g) formation:

$$7TiC + TiSi_2 + SiC + TiO_2 \leftrightarrow 3Ti_3SiC_2 + 2CO(g) \quad (1)$$

$$8TiC + TiSi_2 + SiO_2 \leftrightarrow 3Ti_3SiC_2 + 2CO(g) \quad (2)$$

An overpressure of CO(g) may form in a closed system and when the material is sintered under pressure, reactions (1) and (2) may be driven to the left. If carbon and CO(g) are present in the furnace atmosphere, the gas may act as a means of carbon transport to the powder surfaces. Such carbon may react with the Ti_3SiC_2 to produce TiC and Si(g) according to the carburisation reaction proposed by Racault et al. [39] and Tang et al. [40] also found that carbon and silicon gases influenced the high temperature phase reactions during hot pressing. However, they suggested that hot pressing would increase the Ti_3SiC_2 content by slowing down in-diffusion of carbon and out-diffusion of silicon. Thereby the decomposition reaction would be avoided. Emmerlich et al. [41] reported that the decomposition of Ti_3SiC_2 would be accelerated by the presence of oxygen through the formation of SiO gas.

Table 3 shows the density and open porosity for the samples heated in the dilatometer. The density of the sample HP1400 is, as expected, the highest (3.7 g/cm^3) and the density increases with increasing hot pressing temperature. The density decreases slightly after heating in the dilatometer and the higher dilatometer end temperature gave a somewhat lower density. This is contradictory to the production routes employed by Radhakrishnan [36] and Li [8] who added a second annealing step after hot pressing in order to increase densification. The open porosity varies significantly depending on the hot pressing temperature, from 37% for HP1150 to 11% for HP1400 and is also highest for the highest dilatometer end temperature. When grains of the new phase grow in between the particles they may be pushed apart, leading to a slight expansion and a corresponding decrease in density. The density of the sample hot pressed at

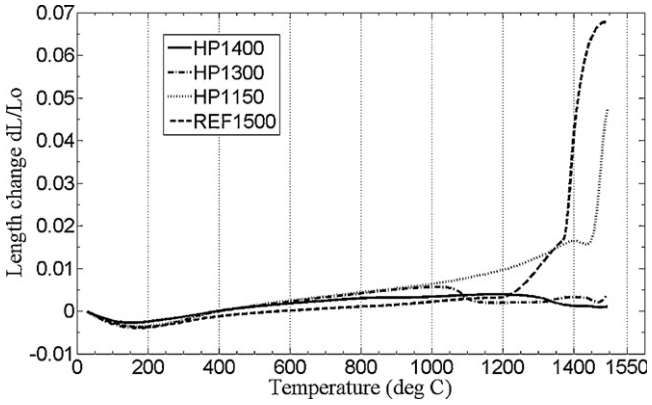

Fig. 3. Dilatometer curves of samples hot pressed at 1150, 1300 and 1400 °C and the reference sample.

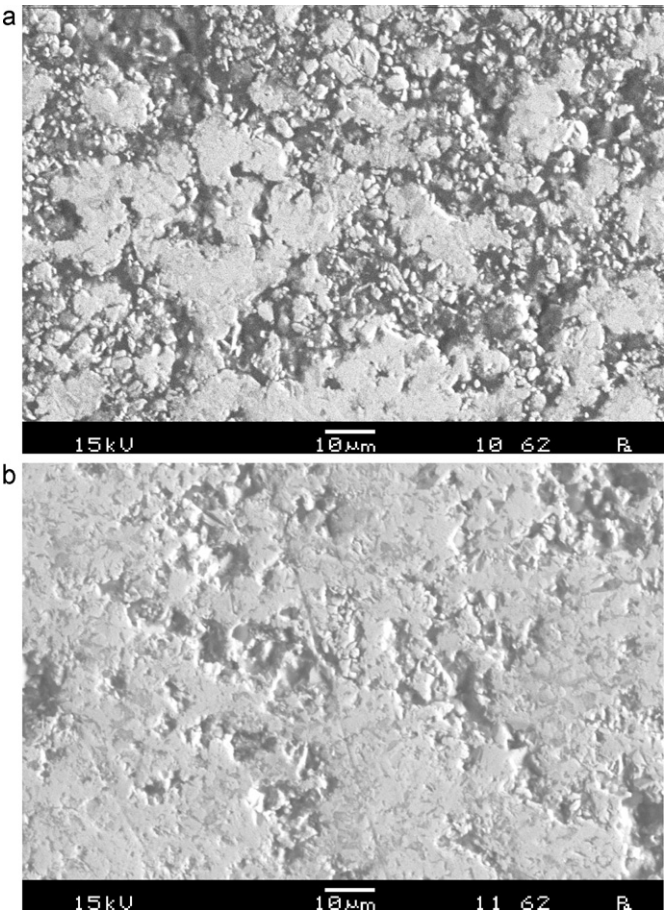

Fig. 4. Scanning electron micrographs of: (a) HP1150 and (b) HP1400 after heating in the dilatometer to 1500 °C.

1300 °C was significantly higher than the sample fired in the hot press furnace without applied pressure. That sample was so porous that no Archimedes measurement could be carried out (in fact it broke during handling). This verifies that an applied pressure during sintering will increase the density of the final product.

The dilatometer curves with end temperature 1500 °C are shown in Fig. 3. The curves for samples HP1150 and REF1500 are similar in shape. They exhibit large peaks around 1400 °C. This peak corresponds to the formation of Ti_3SiC_2; the shoulder-like feature just before the large peak is a result of $TiSi_2$ formation, as explored in earlier work [25,27]. The curves of samples HP1300 and HP1400 differ from the other two, since they do not show any expansion. This is in accordance with the fact that very small amounts of Ti_3SiC_2, if any, were formed in these samples.

The large difference in porosity is clearly visible with SEM. Fig. 4 shows micrographs of two samples hot pressed at different temperatures after heat treatment in the dilatometer up to 1500 °C.

4. Conclusions

Production of Ti_3SiC_2 by hot pressing TiC and Si powders is associated with difficulties caused by the presence of thin oxide

films on particle surfaces. When entrapped in the structure they act as diffusion barriers, significantly lowering the reactivity of the system.

The formation of Ti_3SiC_2 is promoted by a low partial pressure of carbon monoxide gas, as residual oxide films may be reduced and escape in the form of CO(g). A high partial pressure of CO(g) promotes the decomposition of Ti_3SiC_2 (by reversing Eqs. (1) and (2)). CO(g) may also act as a source of carbon, leading to the carburisation of Ti_3SiC_2 into TiC and Si(g).

Hot pressing at intermediate temperatures reduces porosity while leaving the microstructure sufficiently open to allow the CO gas to escape in a second pressureless heat treatment. Thus, Ti_3SiC_2 forms and such samples may be used as precursors for the production of relatively dense Ti_3SiC_2 composites.

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