Preparation and firing of a TiC/Si powder mixture

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Abstract. This paper describes how the preparation and heat treatment of TiC/Si powders influences the phase reactions during firing. The powders are prepared by milling and some effects of powder preparation are discussed. A solid state displacement reaction according to: $3\text{TiC} + 2\text{Si} \rightarrow \text{Ti}_3\text{SiC}_2 + \text{SiC}$ is a priori expected to take place during heat treatment. The firing procedure is investigated with respect to the effect of heat treatment time and temperature on the phases produced, especially Ti_3SiC_2 . Samples were heat treated in a graphite lined furnace. Heat treated samples are analysed by x-ray diffraction, scanning electron microscope and energy dispersive spectroscopy. Ti_3SiC_2 , TiC and SiC are dominant in the final products. The highest amount of Ti_3SiC_2 is achieved for short holding times (2-4 hours) at high temperatures (1350-1400°C). Ti_3SiC_2 appears to decompose at elevated temperatures or extended times, through a $\text{Ti}_3\text{SiC}_2 \rightarrow \text{TiC} + \text{Si(g)}$ type reaction. The activation energy of Ti_3SiC_2 phase formation is determined to be 289 kJ/mol, using the Mehl-Avrami-Johnson model.

1. Introduction

The ternary system Ti-Si-C has some interesting phases, for example a number of both binary and ternary intermetallics, see Figure 1. One of the most intriguing of these phases to materials scientists is the Ti_3SiC_2 , which is a ceramic compound that exhibits a unique set of properties. It combines thermal and electrical conductivity and relative softness with chemical and thermal stability, elastic stiffness and excellent high-temperature mechanical properties.[1-3] It is resistant to thermal shock, damage tolerant and it can be machined by use of conventional high-speed tools without lubrication or cooling, which is of great technological importance for its potential applications.[1, 3] It is commonly referred to as a so called MAX phase; the MAX phases being a family of layered, ternary carbides and nitrides of general chemical formula $\text{M}_{n-1}\text{AX}_n$ where M is an early transition metal, A is an element from groups 12-16 in the periodic table of the elements, X is either carbon or nitrogen and n is an integer 1-3.

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Figure 1. 1200°C isothermal section of the Ti-Si-C ternary phase equilibrium diagram by Arunajatesan & Carim. [4]

Bulk samples of Ti_3SiC_2 have been produced by different approaches based on powder metallurgical techniques such as vacuum sintering,[5, 6] hot pressing,[7-10] hot isostatic pressing,[3, 11] self-propagation high-temperature synthesis,[12] mechanical alloying,[7, 13] and spark plasma sintering.[14] A range of powder mixtures have been used such as $\text{TiH}_2/\text{Si}/\text{C}$,[7] $\text{Ti}/\text{SiC}/\text{C}$,[8, 15] $\text{Ti}/\text{Si}/\text{C}$ [4, 16] or $\text{Ti}/\text{Si}/\text{TiC}$. [5, 14] While some has attained single phase Ti_3SiC_2 , [3, 17] many attempts have resulted in samples containing secondary phases such as TiC_x , $\text{Ti}_5\text{Si}_3\text{C}_x$, Ti_5Si_3 , TiSi_2 or unreacted raw materials in the final products.[18-20] The presence of other phases is not necessarily detrimental however; 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 improved properties and enhanced oxidation resistance [21]. 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. [22-24]

Common in the synthesis of these materials is the use of starting powders containing pure titanium metal. Powdered Ti is highly reactive and must be handled with great care to safety measures [25] which is a disadvantage in terms of an up scaled production. If comparable material could be synthesised from cheaper and less hazardous starting powders it would be a great advantage for industrialised production.

There is consensus in the literature, with some minor variations, on the route of formation of Ti_3SiC_2 from powder mixtures including Ti metal, regardless of the sintering method of choice. This reaction pathway includes $\text{Ti}_5\text{Si}_3\text{C}_x$ as a necessary intermediate step for the formation of Ti_3SiC_2 . [6, 26] This reaction pathway is not, however, applicable to TiC/Si powders since $\text{Ti}_5\text{Si}_3\text{C}_x$ has not been observed. Yet, Ti_3SiC_2 has been reported to form in spite of the relatively low reactivity of TiC . [27]

In this paper we report on the sintering process of a TiC/Si powder mixture. The a priori expected reaction is:

The phase reactions are investigated with respect to the effect of sintering time and temperature on the phases produced, especially Ti_3SiC_2 .

2. Experimental

The powders used were TiC (Aldrich) and Si (Merck) and they were mixed with a molar ratio of 3:2, corresponding to the stoichiometry of the expected reaction in equation (1). One sample, here denoted P1, was ball milled (Siemens: Elektra Tailfingen T10) during 96 hours. Another powder, here denoted P2, was first ball milled for 96 hours and then transferred to an attritor (Walther Flender: 4AP) and attrition milled for 24 hours. Finally, a third powder, here denoted P3, was ball milled for 24h.

The as-milled powders were evaluated using a scanning electron microscope (SEM, JEOL: JSM – 6460LV), and by measuring the Brunaur-Emmett-Teller (BET) surface area (Micromeritics: ASAP 2000). The compaction of the green body was performed by the combination of two methods operating at room temperature: cold uniaxial pressing (MFL Systeme Prüf und Mess: UPD6) and cold isostatic pressing (Autoclave Engineers: STD). The compaction was performed under pressures of 10 MPa and 300 MPa respectively. The furnace experiments took place in a reaction sintering furnace with graphite heating elements (Conrad Engelko Technik) in which the samples were embedded in boron nitride. Furnace heat treatments were performed at different temperatures and with varying holding times, under a vacuum of approximately 0.02 mbar. Powder samples were sintered at varying temperatures and holding times. The parameters of the sintering experiments are summarised in Table 1. The as-sintered microstructure was evaluated with x-ray diffraction (XRD, Philips: MRD), using CuK_α radiation and a proportional detector and by SEM with energy dispersive spectroscopy (EDS).

The activation energy of Ti_3SiC_2 formation was calculated using the Arrhenius equation and Mehl-Avrami-Johnson (MAJ) theory. [15] The kinetics of Ti_3SiC_2 formation was modelled using the MAJ equation (2) and the activation energy of the process was calculated using the Arrhenius equation (3).

The MAJ equation: $f(t) = 1 - \exp(Kt)^n$ (2)

Where n is the Avrami exponent and K is the reaction rate constant.

The Arrhenius equation: $K(T) = K_0 \exp\left(\frac{-E}{kT}\right)$ (3)

Where K is the frequency factor, E is the activation energy, k is the Boltzmann constant and T is the temperature.

Table 1. Summary of the reaction furnace experiments.

Sample	Milling method	Temp. (°C)	Time (h)
P1	Ball mill 96h	1200, 1250	4
P1	Ball mill 96h	1300	1, 2, 3, 4, 5, 6, 8, 10, 12
P1	Ball mill 96h	1350, 1400	1, 2, 4
P1	Ball mill 96h	1500	8, 24
P2	Ball mill 96h + Attritor 24h	1500	8, 24
P3	Ball mill 24h	1250	2.5

3. Results and Discussion

The ball milled P1 had a BET surface area of $3,63 \text{ m}^2/\text{g}$ and the ball- and attrition milled P2 had a BET surface area of $11,25 \text{ m}^2/\text{g}$. P1 was significantly coarser than P2 and had a wider particle size distribution, see Figure 2. SEM images of the as-milled powders are displayed in Figure 2a) and c). The majority of the P1 particles were of sizes between 1 and $5 \mu\text{m}$ but also particles smaller than $0,5 \mu\text{m}$ and large particles up to $15 \mu\text{m}$ were observed. The P2 displayed a narrower particle size distribution and small particles, mainly ranging from $0,1$ to $1 \mu\text{m}$. SEM images of the as-sintered products after heat treatment in 1500°C for 24h are displayed in Figure 2b) & d). Both samples have a porous microstructure. The P1 sample has finer particles with more rounded shapes than the P2. The P3 powder turned out to be very similar to the P1.

Figure 2a

Figure 2b

Figure 2c

Figure 2d

Figure 2. SEM images of the raw powders and of products sintered in the graphite furnace at 1500°C for 24h. a): P1 raw powder; b): P1 sintered product; c): P2 raw powder; d): P2 sintered product..

After heat treatment in vacuum in the reaction sintering furnace, at 1500°C for 8 and 24 hours, the P1 samples contained TiC and Ti_3SiC_2 as the main phases with minor amounts of SiC , see Figure 3. The 8 hour sintering run rendered somewhat more Ti_3SiC_2 than the 24 hour run. The P2 samples sintered under the same conditions also contained TiC but there were no Ti_3SiC_2 or SiC present. The absence of Ti_3SiC_2 in the P2 samples is likely a consequence of reaction kinetics. As Ti_3SiC_2 has a tendency to decompose, it is likely to have formed and decomposed in the P2 samples at an earlier stage than in the P1. The particle size of the P2 powder was smaller than the P1, due to attrition milling and since a more finely divided powder exhibits shorter diffusion paths, the rate of reaction is higher. This kinetic effect has also been confirmed by thermal analysis, results of which will be

published elsewhere. An unknown phase was detected; it is likely a decomposition product and possibly a non-stoichiometric adaptation of the Ti_3SiC_2 phase.

The extra hours of attrition milling of the P2 powder produced no advantage in terms of the production of phases of interest, such as silicides or ternary or binary carbides. Therefore, the ball milled P1 powder was chosen for further furnace experiments.

Figure 3. X-ray diffractograms of the P1 and P2 samples after sintering at 1500 °C for 8 and 24 hours respectively. Ti_3SiC_2 peaks are denoted TSC in the figure.

Figure 4 shows x-ray diffractograms of P1 samples sintered at different temperatures and the phase composition is summarised in Table 2. These samples were sintered for 4 hours at 1200-1400°C, the diffractograms in Figure 4 show that the main phases are Ti_3SiC_2 , TiC and SiC with TiSi_2 present in samples sintered at the lower temperatures. More Ti_3SiC_2 was found in these samples compared to those sintered at 1500°C. These results are in agreement with those of Li et al.[19] and Córdoba et al.[18] who observed secondary phases SiC and TiC in their final products, prepared from TiC/Si powders by hot pressing and pressureless sintering in argon.

Samples sintered at 1200 and 1250°C produced significantly less Ti_3SiC_2 and SiC than samples sintered at 1300-1400°C. Titanium disilicide, TiSi_2 is present only at the lower temperatures and appears to be an intermediate phase to the Ti_3SiC_2 formation.

Although the presence of $\text{Ti}_5\text{Si}_3\text{C}_x$ cannot be completely ruled out, as its two main diffraction peaks overlap those of the Ti_3SiC_2 , no significant amount was detected in this study. This contradicts the hypothesis based on thermodynamical calculations presented by Li et al.[19] stating that $\text{Ti}_5\text{Si}_3\text{C}_x$ should be the main intermediate phase for the development of a Ti_3SiC_2 structure.

Figure 4. X-ray diffractograms of P1 samples sintered during 4 h at different temperatures. TiSi_2 and Ti_3SiC_2 peaks are denoted TS and TSC respectively.

Table 2. Phase composition of P1 samples sintered for 4 hours.

Temperature (°C)	Phases present
1200	TiC, TiSi_2 , (traces of SiC)
1250	TiC, TiSi_2 , SiC, Ti_3SiC_2
1300-1400	TiC, SiC, Ti_3SiC_2

The influence of sintering time is displayed in Figure 5, it shows x-ray diffractograms of P1 samples sintered at 1300°C and held for different times. Ti_3SiC_2 , TiC and SiC were the main phases and small amounts of TiSi_2 were traceable in samples held at temperature for 4h or less. Most Ti_3SiC_2 was attained when the sample was held at temperature for 3 hours. Generally, short holding times (2-4 hours) produced more Ti_3SiC_2 than longer, suggesting a breakdown of Ti_3SiC_2 over time. The SiC content appears to change very little with changes in holding time.

From these sintering experiments, it is clear that sintering time and temperature have a stronger effect on the formation of Ti_3SiC_2 and TiSi_2 ; whereas the binary carbides TiC and SiC are less reactive and therefore less dependent on time and temperature. In order to achieve large amounts of Ti_3SiC_2 the sintering time should be shifted towards shorter holding times as the sintering temperature is increased. In this study, most Ti_3SiC_2 was achieved when sintering at 1400°C with a hold for 1 hour. Most TiSi_2 was produced when sintering at 1200°C with a hold for 4 hours. The evolutions of the TiC and Ti_3SiC_2 phases are strongly interconnected; the amount of TiC decreases while the amount of Ti_3SiC_2 increases, but when the Ti_3SiC_2 amount is reduced during the decomposition reaction, the TiC content is raised again. These results confirm Ti_3SiC_2 decomposition into TiC and Si as proposed by Racault et al.[28]

Figure 5. X-ray diffractograms of P1 samples sintered at 1300°C for different times. Ti_3SiC_2 peaks are denoted TSC in the Figure.

Figure 6a) shows an SEM image of a P3 sample sintered at 1250°C for 2.5h. Figures 6b), c) and d) shows the EDX mappings of the same area. The samples were not perfectly homogeneous and the Figure shows an inhomogeneous area. EDS analysis of the area revealed different chemical compositions within different, well defined parts of the sample. This will naturally influence the phase composition of the samples. Areas rich in Si also tend to be poor in Ti and vice versa. This indicates that SiC and TiSi_2 are dominating in some, well defined areas rich in Si. Therefore, it requires a certain temperature and/or holding time (1300°C, 4h) to allow the diffusion of silicon to more Ti rich areas, which appears to be necessary for Ti_3SiC_2 to form in any significant amounts. The carbon distribution is relatively uniform, partly because of the low atomic number of carbon. From the phase diagram in Figure 1 however, it is also clear that the carbon content should not vary greatly with varying phase composition.

Further investigation showed that the powder inhomogeneity originates from segregation, caused by a degree of particle sedimentation in the drying step during powder preparation. This effect was found to be reduced by extensive mechanical stirring throughout the entire milling and subsequent drying processes.

The activation energy was found to be 289 kJ/mol, which is in good agreement with the value 380 kJ/mol reported by Wu et al.[15] for the Ti_3SiC_2 formation from Ti/SiC/C powders with intermediate phases TiC_x , $\text{Ti}_5\text{Si}_3\text{C}_x$ and free carbon.

Figure 6a

Figure 6b

Figure 6c

Figure 6d

Figure 6. SEM micrographs of P3 sintered at 1250°C for 2,5h; a) backscattered electron mode; b) EDS mapping of titanium showing light areas rich in Ti and dark areas poor in Ti; c) EDS mapping of silicon showing light areas rich in Si and dark areas poor in Si; d) EDS mapping of carbon showing a relatively uniform distribution of C.

4. Conclusions

It is possible to synthesise Ti_3SiC_2 phase by ceramic powder processing from a starting powder of $3\text{TiC}/2\text{Si}$, i.e. without the expensive and highly reactive Ti. The activation energy for the formation of Ti_3SiC_2 was found to be 289 kJ/mol from TiC/Si starting powders.

SiC and TiC were present in all furnace heated samples. TiC is present both as a reactant involved in the formation of the Ti_3SiC_2 and as a product of its decomposition.

No $\text{Ti}_5\text{Si}_3\text{C}_x$ was observed in this study, and it is unlikely to be a key feature to the formation of Ti_3SiC_2 from TiC/Si powders.

TiSi_2 is suggested to be an intermediate phase in the process of Ti_3SiC_2 formation from TiC/Si starting powders.

The Ti_3SiC_2 and the TiSi_2 are very sensitive to holding times and temperatures, decomposing if either is extensive. Short holding times at temperatures of 1300-1400°C are advantageous for the development of Ti_3SiC_2 , whereas temperatures must be limited to 1250°C for TiSi_2 . Ti_3SiC_2 decomposed into TiC and other decomposition products such as gaseous silicon.

The particle size influences the rates of reactions in the sintered samples. An uneven size distribution of the particles of the starting powder is not necessarily detrimental for the formation of Ti_3SiC_2 during sintering.

The homogeneity of the powders influences the time and temperature of the heat treatments required for substantial formation of Ti_3SiC_2 .

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