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Phase reactions associated with the formation of Ti_3SiC_2 from TiC/Si powders

Ida Kero *, Ragnar Tegman, Marta-Lena Antti

Luleå University of Technology, Department of Applied Physics, Mechanical and Materials Engineering,
Division of Engineering Materials, SE-97181 Luleå, Sweden

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Abstract

The objective of this paper was to investigate the high temperature phase reactions that take place in a 3TiC/2Si powder mixture during heating. Special attention was paid to the formation of Ti_3SiC_2 and to the evaporation of gases. Differential scanning calorimetry and thermogravimetry were used for *in situ* analysis of the phase reactions. Samples were heated at a rate of 5 K/min to various temperatures between 890 and 1450 °C and then cooled at a rate of 20 K/min. Heat treated samples were analysed by X-ray diffractometry. The first phase to form was $TiSi_2$, which was consumed in the Ti_3SiC_2 forming reactions. No decomposition of Ti_3SiC_2 was observed at temperatures below 1450 °C. Evaporation of CO(g) and small amounts of Si(g) were detected at 1430 °C.

Keywords: Ceramics; Transition metal compounds; Calorimetry; Thermal analysis; X-ray diffraction

1. Introduction

Ti_3SiC_2 is a ceramic compound with 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 [1–4]. It is resistant to thermal shock, damage tolerant and it can be machined by use of conventional high-speed tools without lubrication or cooling [3–6]. It is commonly referred to as a MAX phase, i.e. a layered, ternary carbide (or nitride) of general chemical formula $M_{n-1}AX_n$ 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.

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, such as Ti/SiC/C [7,8], Ti/C/SiC [6,9,10], Ti/Si/C [11,12], Ti/Si/C [13–15], Ti/Si/TiC [16,17] or Ti/Si/TiC [18–20]. This reaction pathway includes the formation of $Ti_5Si_3C_x$ as a necessary intermediate phase for the formation of Ti_3SiC_2 [9,10]. In TiC/Si powders, however, $Ti_5Si_3C_x$ has not been observed.

Powdered Ti is very reactive and must be handled with great care to safety measures [21]. This is a major disadvantage for up scaled, industrial production. The synthesis of comparable materials from the cheaper and less hazardous starting powders TiC/Si would be favourable for industrial production.

Ti_3SiC_2 has been reported to form in TiC/Si powder mixtures, in spite of the relatively low reactivity of TiC, and $TiSi_2$ has been suggested to be an intermediate phase [22–25]. Li et al. [26] postulated that the dominant intermediate phase would be Ti_5Si_3 and Hwang et al. [27] reported a solid state reaction between $TiC_{0.67}$/Si powders without intermediate phases. Panigrahi et al. [28] corroborated these results but when their published X-ray diffractograms are scrutinised, there appear to be some $TiSi_2$ peaks present (at low temperature with short holding times) which are not discussed by the authors. The authors do, however, consider the possibility of such a phase being present undetected and propose a reaction pathway which includes Ti_3C_2, $TiSi_2$ and Ti_5Si_3C as intermediate phases.

Racault et al. [29] were first to observe the decomposition of Ti_3SiC_2 into TiC_x and gaseous Si, which has been confirmed by others [13,20,30]. Racault et al. [29] and Radhakrishnan et al.

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* Corresponding author. Tel.: +46 920 492 269; fax: +46 920 491 084.
E-mail address: ida.kero@ltu.se (I. Kero).

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[13] reported that this reaction was promoted by the presence of carbon. El-Raghy et al. [31] essentially confirmed these findings and suggested a carburisation process as follows:

$$Ti_3SiC_2 + (3x-2)C \rightarrow 3TiC_x + Si \quad (1)$$

where $x > 0.8$. In previous studies, we have reported that silicon additions in the starting powder may increase the conversion of Ti_3SiC_2 [24,32], which agree well with the findings of Hwang et al. [27] and Córdoba et al. [33]. Furthermore, we observed no decomposition of Ti_3SiC_2 below 1450 °C. In this respect, the presence of carbon made no difference [34]. Gao et al. [16] observed a tendency for Ti_3SiC_2 to decompose into $TiSi_2$ at high temperatures. Li et al. [26] suggested yet another carburisation reaction for Ti_3SiC_2 where SiC would be produced.

Oo et al. [35] observed a dissociation process of Ti_3SiC_2 under vacuum at temperatures around 1400 °C, findings which agree with the vacuum decomposition of Ti_3SiC_2 thin films described by Emmerlich et al. [36].

This lack of consensus on the subject of Ti_3SiC_2 formation and decomposition indicates a need for further studies of the high temperature chemistry of this system and the thermal stability of Ti_3SiC_2. The objective of this work is to explore the high temperature phase reactions that take place in TiC/Si powders during heating, with special emphasis on the formation of Ti_3SiC_2.

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 corresponding to the stoichiometry of reaction (2):

$$3TiC + 2Si \leftrightarrow Ti_3SiC_2 + SiC \quad (2)$$

The powders were wet milled in a ball mill using propanol 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 dried and compacted by uniaxial pressing to 10 MPa, followed by cold isostatic pressing (CIP) to 300 MPa. The samples were dried at 70 °C for 24 h immediately prior to heat treatment.

All heat treatments were performed in a simultaneous thermal analyzer (STA; Netzsch 449C Jupiter). Samples of approximately 30–50 mg in mass were placed in alumina crucibles and heated under a dynamic argon atmosphere. All temperature programs included three segments: first heating from room temperature to 850 °C at a rate of 10 K/min, secondly a slower heating from 850 °C to the final temperature at a rate of 5 K/min and thirdly a cooling segment to 600 °C at a rate of 20 K/min. During the heat treatments in the STA, the calorimetric (DSC) and gravimetric (TG) responses were recorded. A zirconium getter was present in the STA furnace.

A first sample was heated to 1450 °C in order to obtain global TG and DSC curves. From the global DSC curve, a number of peaks were detected. In order to assess whether a DSC peak was accompanied by any phase change, new samples were heated to final temperatures between these peaks. The phase compositions of all heat treated samples were determined by X-ray diffractometry (XRD) using Cu Kα radiation and a scintillation detector. Heat treated samples were crushed into a powder before XRD analysis using an agate mortar.

The phase fractions were estimated from the X-ray diffractogram using Eq. (3):

$$W_{TSC} = \frac{1.8}{1.8 + C}, \quad \text{where } C = \frac{I_{TiC}}{I_{TSC}} \quad (3)$$

where W_{TSC} is the weight fraction of the Ti_3SiC_2 phase and I_{TiC} and I_{TSC} are the integrated diffraction intensities of the (2 0 0) peak of the TiC phase and the (1 0 4) peak of the Ti_3SiC_2 phase, respectively [37].

The STA furnace was connected to a quadrupole mass spectrometer (MS, Netzsch 403C Aëolos) which recorded the composition of the exhaust gases. The composition of the exhaust gas is detected by the ionization of gas molecules and quantified in terms of fragment ion mass numbers. The ion mass number is the mass of the recorded entity divided by its charge.

3. Results and discussion

During the first heating segment (not shown), the TG curve indicates mass losses between 300 and 400 °C and many ion mass numbers exhibit a peak at the same temperature. These ion fragments indicate that air and water molecules were adsorbed on the powder particle surfaces during storage and handling. The molecules originating from ambient air were primarily N_2, O_2, CO_2, H_2O and Ar. Some ion fragments of hydrocarbons originating from the slurry of the milling step (primarily from the isopropanol) were also detected.

Fig. 1 shows the MS curve of ion mass 28 and the DSC and the TG curves from 850 to 1450 °C. From the DSC curve, three endothermic peaks can be distinguished at 980, 1250 and 1380 °C. In order to determine whether these DSC peaks were accompanied by any phase change, green pellets were heated to 890, 1020, 1150, 1310 and 1415 °C. The X-ray diffractograms of these samples are shown in Fig. 2. At 890 and 1020 °C only TiC and Si peaks are visible, indicating that no phase reactions occur below 1020 °C. $TiSi_2$ is the first phase to form – peaks are present at 1150 and 1310 °C – and it is consumed as the temperature increases.

Ti_3SiC_2 is present at 1310 °C in small amounts; it is the dominant phase at 1415 °C and increases further to a weight fraction of 96.6% (which corresponds to a volume fraction of 96.9%) at 1450 °C. Some SiC is also present above 1310 °C which may be difficult to perceive from the figure as the peaks are partially overlapped by the TiC peaks. In a previous study, we have observed that Ti_3SiC_2 would start to form at the melting temperature of silicon, 1414 °C [34]. 1310 °C is significantly lower, but $TiSi_2$ and Si may form a eutectic liquid at 1330 °C, thereby introducing a means for faster diffusion which increases the reactivity of the system. Ti_3SiC_2 is likely to form primarily in this melt [19]. Residual TiC is present in all

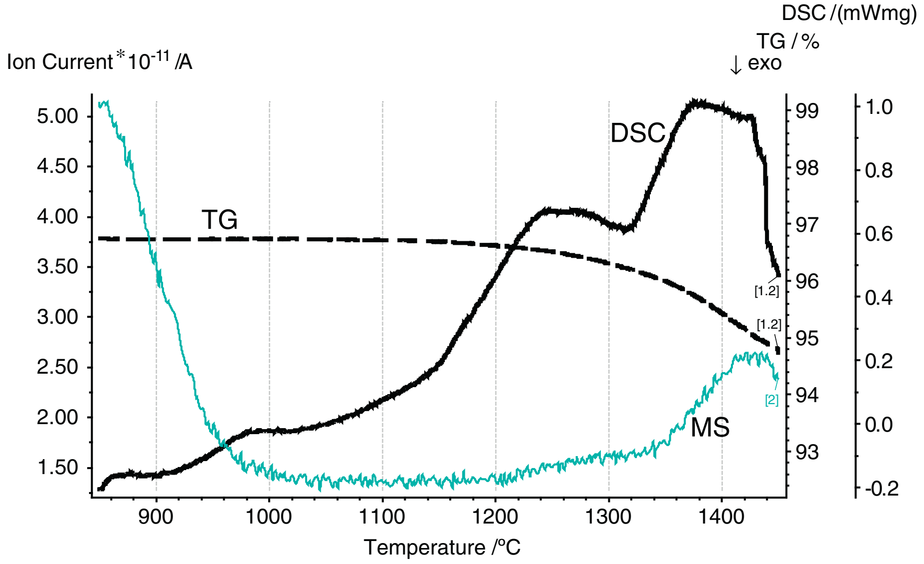

Fig. 1. TG, DSC and MS curves recorded during heating from 850 °C to 1450 °C. The blue/grey line is the MS curve of ion mass number 28; the black line is the DSC curve and the dotted line is the TG signal. The arrow indicates the direction of peaks due to exothermic reactions. (For interpretation of the reference to color in this figure legend, the reader is referred to the web version of the article.)

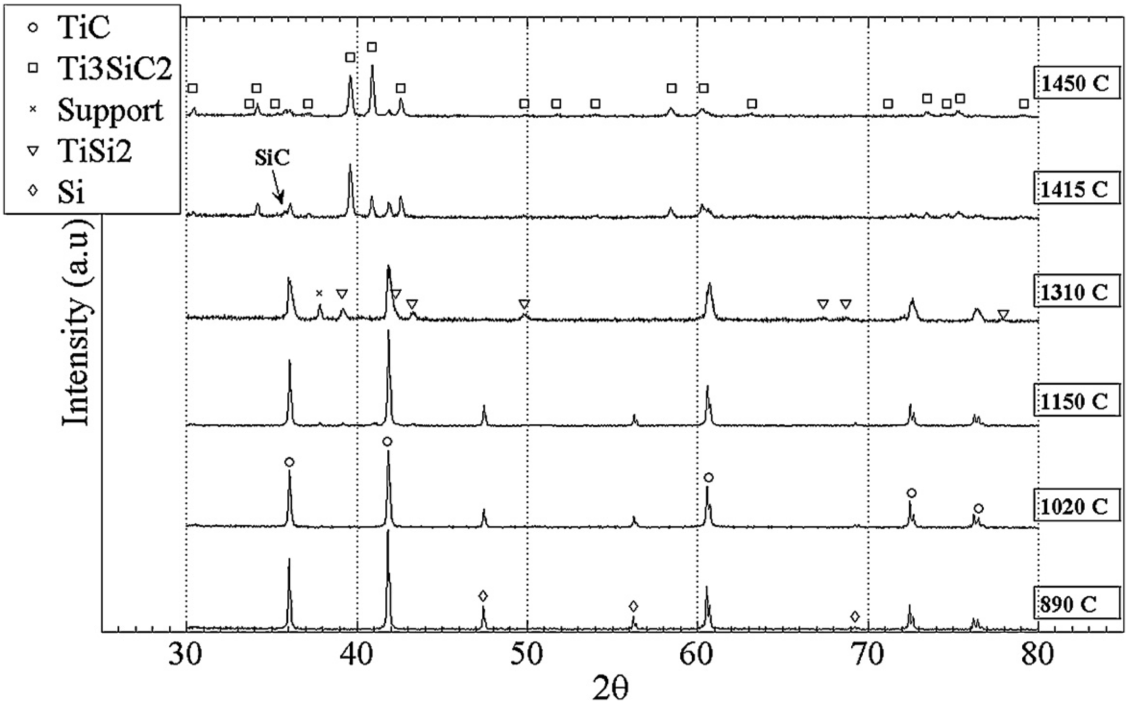

Fig. 2. X-ray diffractograms of samples heated to the indicated temperatures in the STA. Peaks marked with an × are from the sample holder.

samples but no decomposition of Ti_3SiC_2 was observed in this study.

We have previously observed decomposition of Ti_3SiC_2 in graphite furnace experiments [22]. When studying the phase reactions *in situ* by thermal analysis however, no decomposition has been detected, even in the presence of graphite [34]. This difference is most probably a result of differences in furnace construction. In the former [22], the experiments were performed using a relatively large chamber furnace in which the graphite heating elements and the samples were placed in the same chamber. This made furnace atmosphere control very difficult as there were many surfaces at varying distances from the heating elements where water molecules might adhere (for example furnace insulation). CO_2 and H_2O reacted with the carbon heating elements, producing CO and H_2 gases. These gases could cause the Ti_3SiC_2 to decompose in accordance with the thermal dissociation process in vacuum described by Emmerlich et al. [36].

In the furnaces used for thermal analysis, the furnace elements are separated from the sample chamber. The sample chamber is small, which enables a relatively uniform temperature throughout the chamber. This will limit the access to oxygen containing species, especially in the presence of graphite or a getter material (Zr). Adhered water molecules may still be present on powder particle surfaces, but these are likely to be given off at a relatively distinct temperature, as was detected by the TG and MS at 300 °C in this study.

The MS curve of ion mass number 28 is included in Fig. 1. Two ions, CO^+ and Si^+, both have ion mass 28 and therefore they are detected as the same curve. Hence, the interpretation of data from the MS must be based on the combination of the TG curve and other MS curves with different mass numbers. If a number of different ion mass numbers from the same parent molecule are detected and their curves exhibit peaks at the same temperature it can be concluded that this gas molecule was given off.

The TG curve is constant from 850 to approximately 1200 °C, where the mass loss rate is increased. Since the peak of the displayed MS curve at 850 is not associated with any mass loss from the sample, it is most likely a result of an expanding heat zone in the furnace. As temperature was increased in furnace parts and in the transfer line to the mass spectrometer, relatively cool surfaces may be heated sufficiently to give off adsorbed gases as discussed above. The MS curve peak at 1430 °C, on the other hand, is accompanied by a decreasing TG curve; therefore it is clear that gases are given off from the sample at this temperature. The displayed MS peak shown at this temperature is accompanied by slight increases in the curves of mass numbers 12 (C^+) and 16 (O^+) which indicate that CO gas molecules are given off and fragmented in the mass spectrometer. Si^+ ions may also be given off, but no increase in other Si ion fragments (such as Si^{2+} or SiO^+) could be detected to confirm it. Therefore, CO gas is likely to be the main feature responsible for the mass loss.

We thus propose the following set of phase reactions. At temperatures below 1310 °C:

$$TiC + 3Si \rightarrow TiSi_2 + SiC \tag{4}$$

At 1330 °C a eutectic liquid forms between residual Si and $TiSi_2$ and from this liquid, silicon may evaporate. The vapour pressure of Si is relatively low at these temperatures however (<1 Pa [38]), therefore no extensive evaporation is to be expected. Some SiC and relatively large amounts of Ti_3SiC_2 form:

$$7TiC + 2TiSi_2 \rightarrow 3Ti_3SiC_2 + SiC \tag{5}$$

Small amounts of oxides may be present in the samples. These oxides are residues from surface films that may have formed on the powder particles during handling and storage. In an open system at high temperature and low CO partial pressure, such oxides may be removed by the evaporation of CO gas:

$$6TiC + Si + SiO_2 \rightarrow 2Ti_3SiC_2 + 2CO(g) \tag{6}$$

$$8TiC + TiSi_2 + SiO_2 \rightarrow 3Ti_3SiC_2 + 2CO(g) \tag{7}$$

$$7TiC + TiSi_2 + SiC + TiO_2 \rightarrow 3Ti_3SiC_2 + 2CO(g) \tag{8}$$

4. Conclusions

$TiSi_2$ is an intermediate compound during the formation of Ti_3SiC_2. It forms a eutectic melt with Si from which Ti_3SiC_2 is produced. Some SiC forms simultaneously and CO gas is given off. No decomposition of Ti_3SiC_2 was observed in this study (at temperatures below 1450 °C) and this is likely to be an effect of furnace atmosphere control. Some silicon evaporation probably occurs concurrently with CO evaporation and Ti_3SiC_2 formation, but it is not likely to be a main feature at these temperatures.

The vapour pressure of silicon has been recognised as an important parameter to control in order to ensure the thermochemical stability of Ti_3SiC_2 [19,20]. This study shows that the high temperature chemistry may be more complex than previously thought and that it is equally important to limit the partial pressure of carbon monoxide. The formation of relatively large quantities of Ti_3SiC_2 can occur in parallel with the evaporation of CO(g) and small amounts of Si(g).

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