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ANALYSIS ON THE SEQUENCE OF FORMATION OF 
Ti$_3$SiC$_2$ AND Ti$_3$SiC$_2$/SiC COMPOSITES

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ABSTRACT

Ti$_3$SiC$_2$, a compound in the ternary Ti-Si-C system, is reported to be ductile. This paper reports the sequence of formation of Ti$_3$SiC$_2$ and Ti$_3$SiC$_2$/SiC composites involving either combustion synthesis or by displacement reaction, respectively. The onset of exothermic reaction temperatures were determined using Differential Thermal Analysis (DTA). The phases present after the exothermic temperatures were analyzed by X-Ray diffraction. Based on these observations a route to the formation of Ti$_3$SiC$_2$ and Ti$_3$SiC$_2$/SiC composites is proposed for the two synthesis methods.

INTRODUCTION

As potential candidates for high temperature applications, silicides (intermetallic compounds containing silicon) have generated increased interest due to a combination of interesting properties. These include high melting points, low density, good strength, creep resistance as well as excellent oxidation resistance [1]. Despite the above mentioned attributes, the low fracture toughness of silicides has limited their application as structural materials.

Titanium silicide (Ti$_5$Si$_3$) has been processed previously by combustion synthesis and further consolidated for mechanical property evaluation [2]. The measured fracture toughness value was 2.2 MPa.\(\sqrt{m}\), which may prohibit potential structural application. A method to increase the toughness of titanium silicides would be desirable. This paper presents the results of an extension of the previous experiments in the binary Ti-Si system to include the addition of carbon. The interest in the Ti-Si-C system followed reports of ductile behavior in the ternary compound Ti$_3$SiC$_2$ [3-5]. It has a melting temperature of 3000 C and is a "soft
ceramic" compound similar to BN or graphite in its behavior [3,4]. The crystal structure of Ti₃SiC₂ is hexagonal (D₄h \(-\) P6₃/mmc) with lattice parameters of a= 0.3064 nm and c= 1.765 nm.

The high melting point of Ti₃SiC₂ creates an obstacle for processing this compound by conventional melting techniques. Nickl et al. [3] were the first to report the synthesis of this compound by the chemical vapor deposition (CVD) route. Alternatively, combustion synthesis and displacement reaction processing can also be used. Combustion synthesis offers the ability to generate substantial heat in-situ, makes use of a simple reactor, can be scaled up and offers reduction in impurities over starting materials [6]. The process of combustion synthesis involves reacting elements to form compounds. In contrast displacement reactions use solid state diffusional reactions between compounds or compounds and an element, to yield thermodynamically stable phases. Displacement reactions generate reinforcements in-situ as well as tailored microstructures. The mechanical properties obtained in displacement reaction synthesized composites are equal to or better than to those processed by other routes [7-9].

In one case combustion of an elemental compact containing Ti, Si and C occurred at 1050 ± 50 C, during induction heating in a furnace. Conventional ignition in a loose powder mixture also yielded Ti₃SiC₂. The temperature of the combustion wave was measured to be 1830 C [5]. Combustion synthesis reactions have also been initiated using microwave energy [10]. In all cases Ti₃SiC₂ contained small quantities of titanium carbide.

Although compounds in the Ti-Si-C system frequently form as reaction products between silicon carbide and titanium (in fabrication of composites or in joining operations), discrepancies exist in the reported findings [11-15]. The reaction zones have been extensively characterized for the various phases that form and the sequence in which they are arranged. Ratliff et al. [11] and Martineau et al. [12] have both observed TiCₓ and Ti₅Si₃Cy, in a binary reaction sublayer during reaction between Ti and SiC fibers. This sublayer was separated from the SiC fiber by a thin layer of the ternary phase Ti₃SiC₂. According to Ratliff and Powell [11] the inner side of the binary layer was essentially made up of TiCₓ and not Ti₅Si₃Cy as reported by Martineau et al. [12]. In order to clarify this controversy, Choi et al. [13] reacted SiC and Ti powder compacts for several hours and characterized the reaction zone. The presence of Ti₅Si₃ and TiC rather than Ti₅Si₃Cy and TiCₓ further complicates the issue of phases that could possibly form in this case. But their observations on the phase that was closer to SiC supported the results of Ratliff and Powell [11]. Sambasivan et al. [14] investigated the phase relationships at 1200 C and 1350 C in the presence of high pressure (1.5 GPa). The phases and their sequence of arrangement for the samples reacted at 1350 were the same as those reported by Martineau et al. [12] except that an extra thin layer of Ti₅Si₃Cy was present in between the binary layer and Ti₃SiC₂. At 1200 C an additional phase, Ti₃Si formed. The absence of Ti₃Si beyond 1200 C was attributed to the fact that Ti₃Si is stable only up to a temperature of 1170 C. Pressureless sintering of polycrystalline SiC rods with titanium foil inserts resulted in the formation of Ti₃SiC₂ at the insert layer [15].
With single crystal SiC rods small amounts of Ti5Si3Cy and TiSi2 were additionally present.

The main objective of this work is to determine the sequence of phase formation during combustion synthesis and displacement reaction processing of Ti3SiC2 and Ti3SiC2/SiC composites, respectively. Several possible reaction mechanisms have been reported in the literature based on the reactions between titanium and silicon carbide [11-14]. These mechanisms are discussed and compared with the present observations. It should be emphasized at this juncture that the reactants used in the present investigation are a mixture of elemental powders for combustion synthesis (to obtain Ti3SiC2) and a mixture of TiC and Si for displacement reactions (to obtain Ti3SiC2/SiC composite).

EXPERIMENTAL PROCEDURE

Powders of titanium, silicon, carbon and titanium carbide were used as the starting materials. The particles sizes of the different powders are as follows: titanium and silicon < 44 μm, titanium carbide < 5 μm and carbon lampblack < 45 pm. The powders were then mixed in the ratios of 3Ti + Si + 2C and 3TiC + 2Si for several hours in a polyethylene jar filled with alumina grinding balls. Mixed powders were then compacted uni-axially at a load of 65 MPa. Small chips of the powder compact were chipped from the compact for Differential Thermal Analysis (DTA) experiments.

The DTA experiments were performed in an inert atmosphere at heating rates of 15, 30 and 45 C/min. After an initial scan from 50 C to 1400 C was obtained, further DTA experiments were stopped before and after the occurrence of exothermic peaks. X-Ray diffraction was performed in order to identify the phases that formed. Sodium fluoride was used an internal standard for X-Ray diffraction. Microstructural studies were performed using a Scanning Electron Microscope (SEM).

RESULTS AND DISCUSSION

The reaction mechanism for the formation of Ti3SiC2 and Ti3SiC2/SiC composites were determined based on the following reactions:

\[
\text{MA1 : } 3 \text{Ti} + \text{Si} + 2 \text{C} \rightarrow \text{Ti}_3\text{SiC}_2 \\
\text{MA2 : } 3 \text{TiC} + 2 \text{Si} \rightarrow \text{Ti}_3\text{SiC}_2 + \text{SiC}
\]

Tables 1 and 2 summarize the exothermic temperatures and the corresponding phases, for composition MA1 and MA2 respectively. The exothermic temperatures were similar irrespective of the heating rates (15, 30 and 45 C/min) used.

A DTA profile from 50 C to 1450 C for composition MA1 is shown in Figure 1. Titanium Carbide (TiC1-x) is the first phase to form accompanied by trace amounts of titanium silicide (Ti5Si3). The lattice parameter for TiC1-x was calculated to be
Table 1 Exothermic temperatures and corresponding phases for composition MA1

<table>
<thead>
<tr>
<th>Exotherm Temperatures (in C)</th>
<th>Phases Present</th>
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<tbody>
<tr>
<td>995</td>
<td>Ti, Si, TiC_{1-x}, Ti_5Si_3 (traces)</td>
</tr>
<tr>
<td>1135</td>
<td>Ti, Si, TiC_{1-x}, Ti_5Si_3</td>
</tr>
<tr>
<td>1318</td>
<td>Ti_5Si_3, TiC_{1-x}</td>
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</table>

Table 2 Exothermic temperatures and corresponding phases for composition MA2

<table>
<thead>
<tr>
<th>Exotherm Temperatures (in C)</th>
<th>Phases Present</th>
</tr>
</thead>
<tbody>
<tr>
<td>1170</td>
<td>TiC, Si, TiSi_2, SiC (traces)</td>
</tr>
<tr>
<td>1335</td>
<td>TiC, TiSi_2, SiC, Ti_3SiC_2</td>
</tr>
<tr>
<td>1370</td>
<td>Ti_3SiC_2, SiC, TiC_{1-x}</td>
</tr>
</tbody>
</table>
Figure 1. DTA profile from 50°C to 1450°C for composition MA1 (45°C/min)

Figure 2. SEM micrograph of compact heated to 1140°C. Areas of molten titanium silicide are indicated by arrows.
0.4317 nm. This corresponds to a carbon content of approximately 40 vol\%. [16]. With an increase in temperature, more titanium silicide forms. A micrograph of the compact heated to 1140 C is shown in Figure 2. Areas of molten titanium silicide can be seen in this micrograph. At this temperature unreacted titanium and silicon are still present along with titanium carbide and titanium silicide. A strong exotherm corresponding to the reaction between silicon and titanium to form titanium silicide was observed at 1320 C. Titanium carbide, once formed, remains stable even at 1450 C, due to its higher stability.

The absence of an exothermic peak corresponding to the formation of Ti₃SiC₂ is interesting. Pampuch et al. [5] have reported that ignition of an elemental compact of Ti, Si and C occurred at 1050 C in an induction furnace. This differing behavior in the DTA and furnace experiments can only be explained by further analysis of the kinetics involved in the reaction since a likely cause could be the absence of sufficient diffusional time to yield Ti₃SiC₂. To test this hypothesis, compacts were soaked at 1350 C for 1 hour in the DTA. An analysis by XRD indicated the presence of Ti₃SiC₂. However, the ternary compound was accompanied by TiC₁₋ₓ, a behavior which has been previously reported [5].

Based on these observations, a mechanism for the formation of Ti₃SiC₂ can be proposed. The first stage in the reaction between Ti, Si and C is the formation of titanium carbide. Upon saturation of titanium in carbon, the remaining titanium reacts with silicon to form titanium silicide. Further diffusion of titanium and carbon into Ti₅Si₃ causes a re-arrangement in the atomic ratio to form Ti₃SiC₂. This observation is similar to the one proposed by Ratliff et al. [11] and Choi et al [13]. The reaction layers in Ti-SiC composites treated at high temperatures revealed the presence of titanium carbide and titanium silicide adjacent to a thin layer of the ternary phase.

The DTA profile for composition MA2 is shown in Figure 3. The reaction between TiC and Si starts at 1170 C, with the formation of TiSi₂. With increasing temperature SiC and Ti₃SiC₂ begin to form. A sample taken at 1325 C indicated that TiSi₂, SiC and traces of Ti₃SiC₂ were present in addition to silicon and titanium carbide. More silicon was consumed at 1335 C leading to increased amounts of TiSi₂, Ti₃SiC₂ and SiC. After the next exotherm only Ti₃SiC₂ and SiC could be detected along with trace amounts of TiC. An isothermal hold at 1380 C caused some rejection of carbon resulting in TiC₁₋ₓ.

The Ti-Si-C phase diagram [3] is shown in Figure 4. A tie line connecting TiC and Si passes through 3 three-phase fields, namely Si + SiC + TiSi₂, TiSi₂ + SiC + Ti₃SiC₂ and SiC + Ti₃SiC₂ + TiC₁₋ₓ. Our observations are in accord with these phase fields. A different reaction mechanism than the one proposed for the combustion synthesis reaction is suggested for the formation of Ti₃SiC₂/SiC composites from the reaction of TiC with Si. Silicon diffuses into titanium carbide to form TiSi₂ and SiC. Once silicon is saturated in TiSi₂, it reacts with TiC and TiSi₂ to form Ti₃SiC₂. The ternary phase could be a little off-stoichiometric in terms of carbon content as indicated by peak shifts in XRD, but with time more carbon is rejected from
Figure 3. DTA profile of composition MA2. Shown here is the section from 1000 °C to 1450 °C (15 °C/min).

Figure 4. The Ti-Si-C phase diagram. Super-imposed on the phase diagram are the diffusional path for the reactants.
titanium carbide to attain complete stochiometry.

The diffusional path of silicon reacting with TiC in the Ti-Si-C system appears to follow the field SiC-TiSi$_2$-Ti$_3$SiC$_2$ and that of TiC with Si appears to follow SiC-Ti$_3$SiC$_2$-TiC$_{1-x}$. In the case of Ti reacting with SiC, the mechanism offered by Choi et al. [13] for the reaction zones does not follow the fields in the path of the tie line in the Ti-Si-C system. The absence of silicides other than Ti$_5$Si$_3$C lead to this conclusion. But for the reaction sequence determined in this paper, the behavior is similar to that indicated by the ternary system tie line. The diffusional path for the reactants in this study are superimposed on the ternary phase diagram in Figure 4.

CONCLUSIONS

An analysis on the sequence of formation of Ti$_3$SiC$_2$ and Ti$_3$SiC$_2$/SiC composites has been performed. The absence of a direct exothermic reaction during combustion synthesis of Ti+Si+C to yield the ternary phase leaves some unresolved issues. Further analysis of kinetics and thermodynamics could shed an insight to this difference in behavior during DTA. The final composition for MA2 indicates that it lies in the three phase field of Ti$_3$SiC$_2$+SiC+ TiC$_{1-x}$. Silicon appears to be the fastest diffusing species in the reaction between TiC and Si. Additional studies with increased soaking times need to performed in order to verify if titanium carbide can undergo complete reaction with Si to form SiC and Ti$_3$SiC$_2$.

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