Reaction synthesis of Ti$_3$SiC$_2$ phase in plasma sprayed coating

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**Abstract**

This investigation focuses on the feasibility of reaction synthesis of Ti$_3$SiC$_2$ phase using plasma spraying of powder mixture of Ti, SiC and graphite. In-flight particle diagnostics suggested that dwell (reaction) time of these powder mixture is very short ($\sim 10^{-4}$ s) during plasma spraying. Phase identification and microstructural characterizations of the as-sprayed coatings were conducted using X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Thermodynamic calculations on Ti–SiC–C system were also made. Reaction mechanism of Ti$_3$SiC$_2$ synthesis during plasma spray is proposed. Although relatively lower volume percentage of Ti$_3$SiC$_2$ ($\sim 15$–$19$%) phase was found in the plasma sprayed coating, reaction synthesis of Ti$_3$SiC$_2$ phase using plasma spray provides a potential processing technique to fabricate Ti$_3$SiC$_2$ as a protective coating on large engineering components.

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1. Introduction

Ternary titanium silicon carbide (Ti$_3$SiC$_2$) with a layered hexagonal crystallographic structure has attracted much attention by materials community, because it combines many excellent merits of metals and ceramics [1,2]. For example, it exhibits metal properties such as high electrical and thermal conductivity and is readily machinable [1,2]. It also possesses ceramic like properties such as high elastic modulus of 320 GPa, and high stability to at least 1700 °C in an inert atmosphere or under vacuum [3]. Therefore, Ti$_3$SiC$_2$ is expected to be a potential structural material candidate for high temperature applications such as bearings, engine linings, and turbine blades. Ti$_3$SiC$_2$ was first synthesized using sintering technique [4] and its structure was determined in the late 1960s. Since then, several processing techniques have been developed to synthesize single-phase, bulk, polycrystalline Ti$_3$SiC$_2$. These processing techniques include arc melting [5], direct sintering [6], reactive hot-pressing (HP) [1], hot-isostatic pressing (HIP) [3], spark plasma sintering (SPS) [7], pulse discharge sintering (PDS) [8] and self-propagating high-temperature synthesis (SHS) [9]. A variety of precursor materials viz. Ti–Si–C [4,5,9], Ti–Si–TiC [10,11], Ti–SiC–C [1], Ti–Si–C–SiC [12] and Ti–SiC–TiC [13] have been employed for synthesis of Ti$_3$SiC$_2$. Of these processing techniques, most of them are perceived to be energy intensive because of both requirement of high temperature ($\sim 1450$–$1700$ °C) and long processing time of approximately 4 h [3,5,6]. SPS and SHS techniques are rapid processing techniques, which have been reported to synthesize Ti$_3$SiC$_2$ within 10 min [7] and tens of seconds [9], respectively.

From the viewpoint of energy efficiency, development of a novel and rapid processing technique for synthesis of Ti$_3$SiC$_2$ compound is of significance. In addition, the nontrivial properties of Ti$_3$SiC$_2$ make it an excellent high temperature coating for applications such as jet engines, automobiles, aircrafts, and petrochemical installations. Recently, synthesis of Ti$_3$SiC$_2$ as coating has been reported using pulsed laser deposition [14] and dc magnetron sputtering techniques [15,16]. However, Eklund et al. have debated the formation of Ti$_3$SiC$_2$ by pulsed laser deposition technique [17]. In addition to slow deposition rate, the pre-requirement for abovementioned two processing methods is high vacuum ($10^{-7}$ Torr), which greatly limits coating deposition on large engineering components for aerospace and automotive applications. Plasma spraying is a well-established, versatile coating technique with high deposition rate, which can deposit a wide range of alloys, ceramics, and composites as functional coatings for thermal protection, oxidation and corrosion resistance, and wear resistance [18]. To the best knowledge of authors, there is little information available in the literature on the synthesis of Ti$_3$SiC$_2$ coating using plasma spray technique. One of the reasons could be the lack of commercial availability of Ti$_3$SiC$_2$ powder feedstock. Thereby, the objective of the present research is to investigate the feasibility of adopting plasma as the ignition source for the reaction synthesis of Ti$_3$SiC$_2$ phase in the coating through the self-propagation reactions in the Ti–SiC–C precursor system. The reaction mechanisms of Ti–SiC–C system under high heating and rapid cooling rate conditions experienced during plasma spraying is also discussed.

2. Experimental procedure

Trbochemically mixed Ti–SiC–C powders with composition of 74 wt.% Ti, 20 wt.% SiC and 6 wt.% graphite in the particle size of 40–50 μm were selected as...
the feedstock material. Plasma spraying was carried out using SG-100 gun (Praxair Surface Technologies, Indianapolis, IN). The processing parameters are listed in Table 1. Hereafter, coatings synthesized with plasma power of 24 and 32 kW are referred to as TSC24 and TSC32, respectively. Grit blasted AISI 1020 steel substrate was used for the coating deposition. The average surface temperature and velocity of these in-flight particles exiting from the plasma plume was measured using in-flight diagnostic Accuspray G3 optical sensor (Tecna Automation Ltd., QC, Canada). Powder morphology and coating microstructure were characterized using JSM-6330F field emission scanning electron microscope (SEM) and Philips PW 6601 transmission electron microscope (TEM). Metallographically polished samples in cross sections were etched using a HF:HNO3:H2O in the ratio 1:1:8 by volume. Elemental analysis was carried out using an energy dispersive X-ray spectroscopy (EDS). Phase analysis of powders and plasma-sprayed coatings was carried out with Siemens D500 X-ray diffractometer using Cu Kα radiation (\(\lambda = 1.54184 \text{ Å}\)) radiation and with DiffracPlus Release 2000 using Mo Kα radiation (\(\lambda = 0.70930 \text{ Å}\)), respectively.

3. Results and discussion

3.1. Powder feedstock characterization

Fig. 1a shows the morphology of Ti–SiC–C feedstock powder. Corresponding elemental X-ray maps of powder particle are shown in Fig. 1b–d. It is clearly seen from Fig. 1 that tribochemically blended powder is not homogeneously mixed and may lead to chemical segregation in the plasma sprayed coatings. Fig. 2 shows XRD results of the powder feedstock, depicting the presence of α-Ti, SiC and graphite phases, and no impurity or oxide is observed.

3.2. Phase and microstructure characterization of Ti3SiC2 based coatings

Fig. 3 shows X-ray diffraction patterns of plasma sprayed TSC24 and TSC32 coatings. As-sprayed coatings contain Ti3Si2, TiC, TiO and α-Ti and β-Ti besides Ti3SiC2 phase. The volume fraction of different phases in as-sprayed coating is quantified in Table 2, using the concept that volume fraction of a phase corresponds to the ratio of diffracted intensity of this phase to that of all phases. It is evident from Table 2 that higher plasma power leads to the increase in the amount of Ti3SiC2 in the as-sprayed coating.

Table 1
Plasma spraying parameters used for synthesizing Ti3SiC2 coatings.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Power (kW)</th>
<th>Primary gas, Ar (slm)</th>
<th>Secondary gas, He (slm)</th>
<th>Carrier gas, Ar (slm)</th>
<th>Standoff distance (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TSC24</td>
<td>24</td>
<td>32.1</td>
<td>59.5</td>
<td>19.8</td>
<td>101.6</td>
</tr>
<tr>
<td>TSC32</td>
<td>32</td>
<td>32.1</td>
<td>59.5</td>
<td>19.8</td>
<td>101.6</td>
</tr>
</tbody>
</table>

* Standard liters per minute.
Table 2
Relative percentages of the phases present in the coatings.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Ti₃SiC₂</th>
<th>TiC</th>
<th>Ti₅Si₃</th>
<th>TiO</th>
<th>α-Ti</th>
<th>β-Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>TSC24</td>
<td>~15.8</td>
<td>~11.1</td>
<td>~24.0</td>
<td>~18.5</td>
<td>~16.0</td>
<td>~7.1</td>
</tr>
<tr>
<td>TSC32</td>
<td>~19.1</td>
<td>~14.3</td>
<td>~18.3</td>
<td>~23.0</td>
<td>~8.9</td>
<td>~4.0</td>
</tr>
</tbody>
</table>

Fig. 3. XRD patterns of plasma sprayed TSC 24 and TSC 32 coatings using Mo Kα radiation.

Fig. 4. SEM micrograph showing cross-section overview of plasma sprayed coating (TSC 24).

Table 3
In-flight particle diagnostic data for plasma sprayed coatings.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Temperature (K)</th>
<th>Velocity (m/s)</th>
<th>Residence time (s)</th>
<th>Cooling rate (K/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TSC24</td>
<td>2898</td>
<td>114</td>
<td>8.91 × 10⁻⁴</td>
<td>3.25 × 10⁶</td>
</tr>
<tr>
<td>TSC32</td>
<td>3052</td>
<td>116</td>
<td>8.62 × 10⁻⁴</td>
<td>4.39 × 10⁶</td>
</tr>
</tbody>
</table>

Fig. 5. SEM micrographs showing the multiple characteristics of microstructure of plasma sprayed coating (a) TSC24 and (b) TSC32. EDS results for TSC24 coating from location 1 and 2 are shown in (c) and (d), respectively.
The most significant result of this research is that Ti$_3$SiC$_2$ phase can be reactively synthesized in a very short period using plasma spray technique. Therefore, it is necessary to understand the reaction mechanism of Ti$_3$SiC$_2$ formation using Ti–Si–C powder feedstock under rapid processing conditions of plasma spraying. Reaction mechanism has been elucidated based on the thermodynamic predictions and microstructural and phase characterization.

Gibbs free energies of formation ($G_f$) of different phases in Ti–Si–C ternary system were calculated using Kosalapova’s handbook of materials data [19]. The Gibbs free energy of formation for Ti–Si–C ternary system were calculated using Kosalapova’s handbook of materials data [19]. The Gibbs free energy of formation for TiC is approximately $-172$ kJ/mol, as shown in Fig. 6.

(1) Step 1: Two simultaneous reactions occur favorably as the first step in the plasma synthesis of Ti$_3$SiC$_2$. These reactions are (i) SiC sublimation: SiC → Si + (g) + C (s), and (ii) TiC formation: Ti + C → TiC$_2$. SiC sublimation occurs because the average temperature of in-flight particles is in the rage of 2898–3052 K. It has been reported that SiC sublimation occurs around 2540–3150 K [19,21]. Sublimation of SiC is also corroborated by TEM micrograph (Fig. 7) of as-sprayed TSC24 coating. It is clearly seen from Fig. 7 that particles are very fine with a diameter of 20–40 nm. Corresponding SAED pattern illustrates these nanosize powders are TiC and SiC. It should be noted that the original particle size of SiC is around 40–50 μm. The significant decrease in particle size (from 40 μm to 40 nm) sufficiently implies that SiC sublimes and vapors of Si condense to recombine with the free carbon to form nanosize SiC powder. This process is similar to gas condensation which is utilized for making nanopowders [22]. The existence of nanosize TiC particles indicates that Ti reacts with carbon. The Gibbs free energy of formation for TiC is approximately $-172$ kJ/mol, as shown in Fig. 6.

(2) Step 2: From the SEM micrograph and EDS analysis in Fig. 5, Ti–Si solid solution regions are observed in plasma sprayed coatings. Li et al. [23] reported that metallic reactants (Ti, Si) can rapidly melt and form a Ti–Si liquid phase under the condition of high heating rate of the reactants (500 K/s). It is well established that plasma spray technique combines high heating rate and rapid solidification. Therefore, it is proposed that Ti–Si liquid phase should form in the second step of the overall synthesis reaction. Also, it is necessary to note that during first step of the reaction sublimation of SiC will lead to depletion of Si content due to escape as vapor phase at 3000 K. Hence, Ti$_{rich}$–Si liquid phase forms during second step as the following reaction Ti (l) + Si (l, depletion) → Ti$_{rich}$–Si (l).

(3) Step 3: With further cooling of particles exiting from the plasma plume, TiC reacts with Ti$_{rich}$–Si liquid to form Ti$_3$SiC$_2$ as the following reaction TiC + Ti–Si (l) → Ti$_3$SiC$_2$. The reaction temperature range for the formation of Ti$_3$SiC$_2$ is around 1500–1900 K, which is supported by previous research done by Sun et al. [24] and Riley et al. [25] using pulse discharge sintering and SHS process, respectively, with precursor powders of Ti–Si–C. Meanwhile, it is evidenced both from Figs. 5a and b and 8 that Ti$_3$SiC$_2$ always coexists with TiC, which sufficiently implies that the reaction, TiC + Ti–Si (l) → Ti$_3$SiC$_2$, is incomplete under the condition of rapid cooling rate. Based on the binary Ti–Si phase diagram [26], eutectic reaction of L (Ti–11 atm% Si) → Ti–5 atm% Si (solid solution) + Ti$_5$Si$_3$ occurs at approximately 1609 K, which is within the temperature range of Ti$_3$SiC$_2$ (1500–1900 K). The eutectic reaction dissipates some
Ti–Si solid phase, leading to depletion in Ti–Si liquid phase in the peritectic reaction for the formation of Ti3SiC2. Hence, Ti3SiC2 phase is often found to grow along with TiC phase, as indicated in Fig. 8. Also, the eutectic products of Ti3Si and titanium solid solution are supported by XRD patterns (Fig. 3) and EDS result (Fig. 5d).

As compared with the results reported by Gauthier et al. [9], it is pointed out that the common characteristics in the present research are TiC and Ti3Si3 formed as impurity under the condition of rapid heating rate, but the amount of Ti3SiC2 in final plasma-sprayed product decreases dramatically, which strongly illustrates that processing time (reaction time) of precursor powders is vital factor affecting Ti3SiC2 formation. The amount of synthesized Ti3SiC2 phase depends largely not only on the reactant constituents (TiC and Ti–Si liquid phase) but also on the reaction time. The residence time of the Ti–Si–C feedstock in plasma plume is very short in the order of ~10−4 s, which greatly constrains the nucleation and growth of Ti3SiC2 phase, and subsequently leading to small amount of Ti3SiC2 formation. Based on the results listed in Tables 2 and 3, it is concluded that the volume fraction of Ti3SiC2 in the as-sprayed coating increases with the plasma power. It implies that an increase in the residence time and temperature of the powder particle in plasma plume would increase the amount of Ti3SiC2 phase formed. This could be achieved by optimizing the plasma processing variables that include higher plasma power (i.e., increase in the temperature), lower carrier gas flow rate (i.e. increase in the residence time of particles in the plasma) and low powder feed rate (i.e. increase in the temperature). Additional, powder pre-treatment such as spray drying would also assist in homogenous reaction throughout the coating, which will be employed in our future work. Spray drying of fine sized Ti + SiC + C powders would result in homogeneously mixed spherical agglomerates of the precursor that would lead to uniform heating in plasma spraying and homogeneous reaction throughout the molten droplet to increase the Ti3SiC2 content. Hence, amount of Ti3SiC2 phase is expected to be further increased by optimizing the plasma processing variables.

4. Conclusion

Reaction synthesis of Ti3SiC2 phase was achieved using plasma spraying of feedstock with the Ti + Si + C powder mixture. The dwell time (reaction time) of the Ti–Si–C powder mixture is estimated to be as short as ~10−4 s, leading to lower amount of Ti3SiC2 (~15–19 vol.%), in the as-sprayed coatings. In addition to Ti3SiC2 phase, intermediate phases such as TiC, Ti3Si3 and Ti–Si solid solution are also found in the coating. Based on the microstructural characterization and thermodynamic computations, the multiple steps formation mechanism of Ti3SiC2 phase is proposed. It is concluded that higher particle temperature (at higher plasma power) results in an increased percentage of Ti3SiC2 phase in the coating. It is proposed that by increasing the plasma power, increasing the residence time of the particles in the plasma, and using spray dried homogeneously mixed Ti + Si + C powder precursor, higher fraction of Ti3SiC2 phase in the as-sprayed coatings can be achieved. This will allow depositing Ti3SiC2 coatings on large engineering components, to achieve an unique protection of combining metal and ceramic properties.

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