Preparation of TiN–Ti$_5$Si$_3$ in-situ composites by Selective Laser Melting

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The Selective Laser Melting (SLM) Rapid Manufacturing (RM) of the high-energy ball milled Ti–Si$_3$N$_4$ composite powder with the mol ratio of 9:1 was performed in the present work. The microstructural characterizations revealed the formation of TiN reinforced Ti$_5$Si$_3$ matrix composites after laser processing via the in-situ synthesis reaction 9Ti + Si$_3$N$_4$ = 4TiN + Ti$_5$Si$_3$. The in-situ presented TiN reinforcing phase possessed a refined granular morphology and a uniform distribution throughout the Ti$_5$Si$_3$ matrix, showing a clear and compatible interfacial structure with the matrix. The metallurgical mechanisms for the in-situ synthesis of TiN reinforced Ti$_5$Si$_3$ matrix composites by SLM were also proposed.

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1. Introduction

The intermetallic compound Ti$_5$Si$_3$ has been considered as a promising candidate for high-temperature structural applications, because of its high melting temperature (2130 °C), low density (4.32 g/cm$^3$), capacity to retain high strength up to 1200 °C, and excellent oxidation and creep resistance [1]. However, due to its complex hexagonal structure, Ti$_5$Si$_3$ possesses considerably low fracture toughness at room temperature. Hence, a major challenge for a successful application of Ti$_5$Si$_3$ material is to reduce its room-temperature brittleness. From this point of view, the preparation of Ti–Ti$_5$Si$_3$ composites by incorporating TiN ceramic within Ti$_5$Si$_3$ intermetallics is an important way to improve the integrated mechanical properties (including fracture toughness) [2]. Such composite materials can be prepared with several conventional methods including mechanical alloying [3], self-propagating high-temperature synthesis (SHS) [4], and powder metallurgy [5]. However, the preparation of composites by these conventional processes is much likely to generate large agglomerates of reinforcing phases, thereby decreasing the degree of microstructural homogeneity. Alternatively, the production of composites by in-situ synthesis is regarded as a more promising method to obtain more homogeneous microstructures [6,7]. In-situ reinforcements mean that the reinforcing phases are formed via the reaction between the constituent elements of composites during fabrication process [7]. Moreover, the in-situ formed reinforcements are thermally stable and possess compatible interfaces with the matrix. On the other hand, conventional techniques, which generally need expensive and dedicated tools such as moulds or dies, are not suitable for small volume production and complex shapes. Therefore, novel processing methods for the net-shape fabrication of complex-shaped intermetallics-based composites parts should be innovatively designed.

Selective Laser Melting (SLM), as a typical Rapid Manufacturing (RM) technique, enables the quick production of three-dimensional components with complex configurations directly from metal powder [8–11]. SLM creates parts in a layer-by-layer fashion by selectively fusing thin layers of loose powder with a scanning laser beam. SLM, due to its flexibility in feedstock and shapes, also gives a high potential for producing complex-shaped intermetallics-based composites parts that cannot be easily developed by other conventional methods. Furthermore, with the material components tailored, the unique metallurgical process during high-energy SLM favors the formation of particular composite structures in an in-situ manner.

In this work, SLM of the high-energy ball milled Ti–Si$_3$N$_4$ composite powder was performed to prepare in-situ TiN–Ti$_5$Si$_3$ composite components. The phases, microstructures, and compositions of SLM processed composites were assessed and the formation mechanism of the in-situ composite structure was elucidated.

2. Experimental

The starting powder components were: 99.9% purity Ti powder having a polygonal structure and a mean particle size of 30μm and 99.5% purity Si$_3$N$_4$ powder possessing an irregular shape and an average size of 4μm. According to Ti:Si$_3$N$_4$ weight ratio of 75.45:24.55 (the equivalent mol ratio of 9:1), the two components were milled in a...
high-energy Pulverisette 6 planetary mono-mill, using a ball-to-
powder weight ratio of 10:1, a rotation speed of 250 rpm, and a milling
time of 8 h. In order to avoid the temperature rise within the grinding
bowl, 20 min ball milling was followed by 10 min interval. The
obtained Ti–Si3N4 composite powder particles became significantly
refined and homogeneous in their structures, with the mean particle
size of 2.5 μm (Fig. 1).

Details concerning SLM equipments and processing procedures
have been stated in literature [12]. Through a series of preliminary
experiments, the following suitable processing parameters were
chosen to prepare specimens with dimensions of 30×10×6 mm3:
spot size 0.30 mm, laser power 900 W, scan speed 0.10 m/s, scan line
spacing 0.15 mm, and powder layer thickness 0.15 mm.

Samples for metallographic examinations were cut, ground, and
polished according to standard procedures and etched in a solution
consisting of HF (4 ml), HNO3 (6 ml), and distilled water (100 ml) for
45 s. Microstructures were characterized using a Quanta 200 scanning
electron microscope (SEM). Chemical compositions were determined
by an EDAX energy dispersive X-ray spectroscope (EDS). Phase identi-
fication was performed using a Bruker D8 Advance X-ray diffrac-
tometer (XRD).

3. Results and discussion

3.1. Phases

Fig. 2 depicts the typical XRD spectrum of SLM processed sample.
The strong diffraction peaks corresponding to TiN and Ti5Si3 were
clearly observed, while no apparent diffraction peaks for the initial Ti
and Si3N4 phases were detected. Thus, it can be preliminarily
considered that TiN–Ti5Si3 composites are obtainable by SLM through
the following in-situ synthesis reaction:

\[ 9Ti + Si3N4 = 4TiN + Ti5Si3 \]  (1)

According to Table 1, the change in the Gibbs free energies (ΔG)
of reaction (1) is \(-1170.647\) kJ/mol. A negative ΔG leads to a
spontaneous occurrence of the above reaction. On the other hand,
the change in the enthalpy (ΔH) of reaction (1) is \(-1185.746\) kJ/mol.
The large negative ΔH also acts as the driving force for the proceeding
of reaction (1), favoring an exothermic, self-sustaining, and rapid
formation process of TiN–Ti5Si3 composites.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Ti</th>
<th>Si3N4</th>
<th>TiN</th>
<th>Ti5Si3</th>
</tr>
</thead>
<tbody>
<tr>
<td>G (kJ/mol)</td>
<td>9.171</td>
<td>-778.433</td>
<td>346.890</td>
<td>644.059</td>
</tr>
<tr>
<td>H (kJ/mol)</td>
<td>0</td>
<td>-744.752</td>
<td>-337.858</td>
<td>-579.066</td>
</tr>
</tbody>
</table>

Fig. 2. XRD spectrum of SLM processed composites.

3.2. Microstructures and compositions

The characteristic microstructure on the etched section of SLM
processed sample is provided in Fig. 3a. It was clear that the in-situ
synthesized reinforcing phase possessed a refined granular morphol-
ogy and distributed uniformly throughout the matrix. SEM character-
ization at a higher magnification revealed that the reinforcing phase
exhibited a smooth and round shape, possessing a clear and coherent
interfacial structure with the matrix (Fig. 3b). In order to further
determine the elemental distributions, EDS point measurements were
performed. The Ti and Si elements were detected within the matrix
(Point 1, Fig. 3b), with the Ti:Si atomic ratio of about 5:3 (Fig. 3c). The
reinforcing phase (Point 2, Fig. 3b) was composed of the Ti and N
elements with an equal atomic proportion (Fig. 3d). Combined with
XRD (Fig. 2), SEM, and EDS (Fig. 3) results, it was confirmed that the
in-situ TiN reinforced Ti5Si3 matrix composites were successfully
prepared by SLM of Ti–Si3N4 composite powder.

3.3. Formation mechanisms

A reasonable mechanism for the formation of TiN–Ti5Si3 in-situ
composites by SLM of Ti–Si3N4 composite powder (Fig. 4a) is
proposed. During the line-by-line laser processing, the absorbed
energy heats up the powder particles speedily, leading to the complete
melting of Ti matrix as the operating temperature reaches its
melting point (~1670 °C). With the sufficient wetting of the Ti
liquid in laser molten pool, coupled with the exothermic character of
the material system (Table 1), the Si3N4 component tends to
decompose and release atomic Si and N, due to its relatively low
decomposition point of 1900 °C (Fig. 4b). With the laser beam moving
away, the molten composite system enters a rapid solidification
process. The N atoms preferentially combine with Ti to form high-
temperature phase TiN possessing a melting point of 2930 °C, thereby
beginning the precipitation of TiN reinforcing phase (Fig. 4c). The TiN
precipitates grow subsequently by grain boundary diffusion and,
meanwhile, the Si atoms dissolve into the residual Ti melt to form
Ti5Si3 matrix, giving rise to the in-situ formation of TiN–Ti5Si3
composite system (Fig. 4d). Since the laser-induced cooling rate can
reach a high value of \(10^6\) K/s [14], the TiN reinforcing phase has
insufficient time for a significant grain growth, retaining a refined morphology after solidification (Fig. 3a).

4. Conclusions

Selective Laser Melting (SLM) was introduced to process high-energy ball milled Ti-Si3N4 composite powder with the component mol ratio of 9:1. The TiN reinforced Ti5Si3 matrix composites were successfully prepared by SLM through the in-situ synthesis reaction $9\text{Ti} + \text{Si}_3\text{N}_4 = 4\text{TiN} + \text{Ti}_5\text{Si}_3$. A uniform distribution of the in-situ formed TiN reinforcing phase and a compatible interfacial structure between TiN reinforcement and Ti5Si3 matrix were obtainable in SLM processed composites.

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References