Synthesis of Al-TiAl₃ compound by reactive deposition of molten Al droplets and Ti powders

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Abstract: The Al-TiAl₃ compound materials were prepared by depositing molten Al droplets onto the Ti powders layer at 350 °C. The results show that the stoichiometric TiAl₃ phase is the only Ti-Al intermetallic compound formed during the reaction process. The microstructure analysis shows that the TiAl₃ particles disperse in an Al matrix. The results of the compressive tests of the specimens at room temperature show that the reacted Al-TiAl₃ compound has higher compressive strength of 594.7 MPa and fracture strain of 13.5 %.

Key words: Ti-Al intermetallics; TiAl₃; molten Al droplets; synthesis; compressive properties;

1 Introduction

Recently, ordered Ti-Al intermetallic compounds, especially the stoichiometric compounds TiAl₃, TiAl(γ) and Ti₃Al(α₂), have attracted extensive attention of many researchers, because of their excellent properties, such as the superior specific stiffness, high melting point, good oxidation resistance at high temperature[1]. Therefore, these Ti-Al based intermetallic alloys are considered as one of the most promising candidate materials as the structural components used at high temperature[2–3]. Among these compounds, TiAl₃ has the lowest density of 3.4 g/cm³, the highest micro hardness of 465–670 kg/mm² and the best oxidation resistance even at 1 000 °C[4]. However, the applications of TiAl₃ in the engineering and aerospace fields are limited by its poor ductility. In addition, the loss of ductility at ambient temperature is usually accompanied by a change of fracture mode from ductile transgranular to brittle intergranular or to brittle cleavage[5]. Despite the fact that a lot of toughening strategies have been developed to improve their toughness, machining quality is still a difficult problem to tackle. Near-net shape manufacturing technology is considered as one of the best choices for preparing such materials[6–7].

As an emerging near-net shape manufacturing technology, the uniform droplet-based spray forming (UDS) technique has attracted more and more attentions[7–14]. During this process, molten metal are dispersed into uniform micro-droplets by a vibration of a rod immerged in the metals melt or by an inert gas pulse. Successive droplets are delivered precisely onto a movable substrate in X, Y, and Z directions to build a three-dimensional (3D) component layer by layer in the light of computer-aided designing (CAD) information. Therefore, UDS technique can accomplish rapid prototyping (RP) of products. Additionally, the UDS technique could be theoretically applied to any metal that can be contained in a crucible in its molten state[11].

The UDS technique had been applied for the solder printing[15] and preparing metal droplets with higher melting point, for example, Al alloys. Al-4.5%Cu (mass fraction) droplets with 295 μm in size and Al-4.3% Fe droplets with 250 μm in diameter were fabricated by UDS technique[12]. Besides, a droplet-based rapid prototype technique for making metallic structural components directly from their CAD models was developed by ORME et al[13–14]. A 3D Al parts prepared by depositing molten Al droplets had been

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studied by CAO et al[9]. They also attempted to deposit molten Al droplets onto Ti powder bed with the result that the two elements exothermically reacted, intermetallic beads were produced[7]. By repeating this process, a 3D structural component with Ti-Al intermetallics would be eventually fabricated. Additionally, a heterogeneous structural component could be fabricated by selection of fall point of molten Al droplets. To date, there is little reported information about the synthesis and mechanical properties of Ti-Al intermetallics prepared through the UDS technique.

The aim of the present work was to investigate the synthesis technology of Ti-Al intermetallics through molten Al droplets depositing on Ti powders layer. The reaction mechanism by thermodynamic calculation and compressive properties of fabricated Ti-Al intermetallics were also discussed.

2 Experimental

A schematic diagram of UDS apparatus for molten Al droplet generation and deposition is shown in Fig.1. During this process, 30 g pure Al rod was placed in a graphite crucible and heated to 950°C, which was implemented in a glove box full of 99.999% purity argon gas to avoid oxidation of Al liquid. A nozzle of 0.5 mm in diameter was located at the bottom of the crucible. Molten Al droplets were ejected out of the nozzle under an argon gas pulse that was controlled by a solenoid valve. The pressure and duration time of the argon gas pulse were 0.5−1 MPa and 1−1.5 ms, respectively. The frequency range of droplet formation was occurring at rates between 1 and 10 Hz. The as-received Ti powders (99.3%, mass fraction) passed through the sieve of 325 meshes and were deposited onto the substrate to make a powder bed. The powders were fed by ultrasonic vibration[16]. The distance between the nozzle and the surface Ti powders bed was approximately 10 mm. Two experiments under conditions of Ti powders at room temperature and heated to 350 °C were implemented, respectively.

The microstructure and phase distribution of reaction product in the Ti-Al system were identified by X-ray diffraction (XRD, X’Pert Pro MPD, PANalytical BV, the Netherlands), optical microscope (OM) and field emission scanning electron microscope (FESEM, SUPRA55, ZEISS, Germany) with back scatter electron (BSE) detector. The approximate composition of reaction product was identified by an energy dispersive spectroscopy (EDS). The determination of Ti-Al intermetallics in reaction product and the reaction mechanism between molten Al droplet and Ti powders were investigated by a simultaneous TG-DTA (TGA/SDTA851e, Mettler Toledo, USA) machine. In the first DTA test, about 12 mg sample of reaction product was heated at the rate of 30 °C/min from room temperature to 1 500 °C. In the second DTA test, approximate 17 mg sample was heated with the rate of 10 °C /min from room temperature to 1 000 °C. The operation was conducted under argon atmosphere. The mechanical properties of the specimens machined from the product were evaluated. Rectangular specimens with dimension of 1.6 mm×1.6 mm×2.4 mm were used for the compression tests. The tests were implemented on an Instron−5848 microtester with a static load of 2 kN at an initial strain rate of 4×10^{-3} s^{-1}.
3 Results and discussion

The diameter of an aluminum droplet ejected was about 1 mm in this case. The deposited molten Al droplets solidified instantly and cannot infiltrate into Ti powders bed and engulf Ti particles at room temperature. When molten Al droplets were deposited onto the Ti powder layer at 350 °C, an exothermic reaction between Al liquid and Ti powders occurred, which induced the propagation of a combustion wave. The XRD pattern of reaction product is shown in Fig.2. It can be found that a new phase of TiAl₃ forms due to the violent reaction between Al liquid and Ti powders, and the peak of the TiAl₃ phase is very strong. In addition, still redundant Al and trace amount of Ti exist in the reaction product. The reasons for this phenomenon will be given below.

Figure 3(a) shows the morphology of the Ti powders as received. The Ti particles exhibit irregular shape and are 5–50 μm in size. Fig. 3(b) shows the morphology of Al balls collected in the UDS process. The size of Al balls is uniform and about 1 mm in diameter. The optical microstructure images of the reaction product are shown in Figs. 3(c) and (d). White irregular Ti powders with the size of 40 μm nearly reacted completely, except for separated gray cores. And the grey area represents residual Al. According to the EDS results of the product in Fig. 4, bright white phase should be TiAl₃ derived from the smaller Ti particles enveloped by Al liquid. Fig. 4(a) shows a BSE image of the product. Three kinds of phases marked with different colors are found in the sample. By EDS and XRD, the three phases could be characterized as Ti (A), TiAl₃ (B) and Al (C). The Ti-rich phases give rise to the brightest image because Ti has the highest atomic number (22) of the elements present. Al-rich areas give rise to the darkest image because it has the lowest atomic number (13). TiAl₃ phases present gray image due to Ti atoms replaced by Al atoms from liquid aluminum.

![Fig.2 XRD patterns of Ti powders (a) and reaction compound (b) of Ti powders and Al droplets](image)

![Fig.3 Morphologies of Ti powders(a), solidified Al droplets(b), and reaction compound ((c), (d))](image)
DTA had been employed to identify the compounds of TiAl₃ and discuss the reaction mechanism between liquid Al droplet and Ti particles. The DTA curve of the product containing TiAl₃ is shown in Fig.5(a). A sharp endothermic peak at 670.0 °C was due to the melt of Al, which is consistent with the redundant Al in the XRD pattern. Another endothermic peak is located at 1388.4 °C, which approaches to the melting point of TiAl₃ (1340 °C). This indicates the existence of TiAl₃ in reaction product. The offset of peaks towards high temperature in the DTA curve may result from the larger heating rate of 30 °C/min.

To understand the reaction between Al liquid and Ti powders, the sample of the second DTA test is a mixture of Ti powders and pure Al balls collected in UDS experiment as shown in Fig.3(b). Fig.5 (b) shows the DTA curve of the mixture of Al balls and Ti powders. During the sample being heated, two endothermic peaks and two exothermic peaks appear, respectively. However, the peak refers to the reaction between liquid Al and solid Ti particles is at 939.5 °C. There were solid Ti particles and liquid Al at this temperature. The possible reactions are as follows:

\[
\begin{align*}
\text{Ti} + 3\text{Al(ℓ)} &\rightarrow \text{TiAl}_3 \\
\text{Ti} + \text{Al(ℓ)} &\rightarrow \text{TiAl} \\
2\text{Ti} + \text{Al(ℓ)} &\rightarrow \text{Ti}_2\text{Al}
\end{align*}
\]

According to the binary Ti-Al phase diagram[17], \(\text{Ti}_2\text{Al}\) cannot exist stably. So the possible TiAl₃ and TiAl

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**Fig.4** BSE image of reaction compound(a) and EDS patterns corresponding to spots A(b), B(c) and C(d)

**Fig.5** DTA curves of reaction compound (a) and mixture of Ti powders and solidified Al droplets (b)
compounds were considered. Free energies of reactions were calculated using the following formula[18–19]:

\[ H^\circ_f(T) = \Delta_r H^\circ_f + \int_{T_{298.15}}^{T} c_p dT + \sum \Delta H^\circ_i \] (4)

where \( \Delta_r H^\circ_f \) was the standard enthalpy of formation from the elements in their reference phases at \( T=298.15 \) K; \( \Delta H^\circ_i \) was the standard enthalpy of transition at the transition temperature.

The calculation of the entropy function was as follow [18–19]:

\[ S^\circ_f(T) = S^\circ_f + \int_{T_{298.15}}^{T} c_p d \ln T + \sum \frac{\Delta H^\circ_i}{T_i} \] (5)

where \( S^\circ_f \) is the standard entropy of the substance at \( T=298.15 \) K; \( \Delta H^\circ_i / T_i \) was the entropy of phase change.

The molar heat capacities of pure substances can be described with sufficient accuracy over a relatively wide range of temperature by means of the following polynomial[19].

\[ c_p = a_i + b_i \times 10^{-3} T + c_i \times 10^5 T^{-2} + d_i \times 10^{-6} T^2 \] (6)

where \( c_{p,i} \) is the standard heat capacity of the substance concerned over the temperature range under consideration; \( a_i, b_i, c_i, d_i \) were the temperature dependence of the heat capacity of the substrate.

At certain temperature, the Gibbs free energy of the reaction system can be expressed as follow:

\[ \Delta G^\circ_f = \Delta H^\circ_f - T \Delta S^\circ_f \] (7)

where \( H, S \) and \( T \) stand for the enthalpy, entropy and thermodynamic temperature, respectively. The thermochemical data of pure substances adopted in this calculation was from[19–20]. The calculation results of reaction enthalpies and free energies at 939.5 °C are listed in Table 1. It can be seen that reaction enthalpy and free energy of reaction (1) are both less than that of reaction (2) at 939.5 °C. So the reaction between the molten Al droplets and heated Ti powders took place as the reaction (1).

<table>
<thead>
<tr>
<th>Temperature/°C</th>
<th>Reaction (1)</th>
<th></th>
<th>Reaction (2)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \Delta H^\circ ) (kJ·mol(^{-1}))</td>
<td>( \Delta G^\circ ) (kJ·mol(^{-1}))</td>
<td>( \Delta H^\circ ) (kJ·mol(^{-1}))</td>
<td>( \Delta G^\circ ) (kJ·mol(^{-1}))</td>
</tr>
<tr>
<td>939.5</td>
<td>−182.76</td>
<td>−105.53</td>
<td>−107.34</td>
<td>−61.65</td>
</tr>
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</table>

From the binary Ti-Al phase diagram[17], it can be seen that several intermetallic compounds, such as Ti3Al, TiAl, TiAl2, and TiAl3, form in the Ti-Al system. Among these compounds, TiAl3 belongs to Ti-rich compounds and exist over a range of composition. In contrast with these Ti-rich compounds, TiAl2 exists as a line compound and crystallized in the tetragonal D0\(_{22}\) unit cell. Many studies involving synthesis of titanium aluminides showed that TiAl3 formed prior to the formation of any other titanium aluminides present in this system[17, 21]. Furthermore, SUJATA et al[4, 22]. proved that TiAl3 was the only compound formed during reaction between Ti and Al in the temperature range of 973–1 273 K. The phenomena appeared in our experiments accorded with this viewpoint. In addition, TiAl3 layer surrounding bigger Ti particles hindered direct contact between residual liquid Al and Ti cores. Due to the lower temperature and shorter time of the reaction, liquid Al could not diffuse through TiAl3 layer and react with the Ti core. Therefore, the residual Al and...
trace amount of Ti appeared in the reaction compound and other compounds, such as TiAl and TiAl₂ were not formed in the Ti-Al system.

Based upon the results of X-ray diffraction and microscopic observations (SEM and OM), the reaction product can be characterized as TiAl₃ particles dispersed in an Al matrix. Uniaxial compression tests of the Al-TiAl₃ composites were performed. This specimen shows an edge fracture with an angle of about 45º with respect to the compressive direction (Fig.6). The measured compressive stress—strain curve of the sample at room temperature is shown in Fig.6. The specimen exhibits high compressive strength of 594.7 MPa and fracture strain of 13.5%. This character might be related to the chemical composition consisting of Al and TiAl₃. The existence of TiAl₃ and Al in the specimen contributed to the strength and fracture strain, respectively [1]. Fig.6 shows SEM image of the fracture surface of the specimen after the compressive test. The Al-TiAl₃ composite fractured with high-density tear edges and cleavage steps, which were typical feature of quasi-cleavage fracture.

4 Conclusions

1) The Al-TiAl₃ compound materials were prepared by uniform droplet spraying technology under the conditions of droplets temperature of 950 °C and the Ti powders heated to 350 °C.

2) The stoichiometric TiAl₃ was the only Ti-Al intermetallic in the reaction product. Most Ti powders on the order of 40 μm reacted with liquid Al completely.

3) According to the calculation results of enthalpy and free energy, the reaction mechanism was considered as that liquid Al droplets reacted with solid Ti powders by Ti+3Al(l)→TiAl₃. The fabricated composite consisted of TiAl₃ particles dispersed in an Al matrix and exhibited high compressive strength of 597.4 MPa and fracture strain of 13.5% at room temperature.

References


