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Reaction mechanism in an Al-TiO_2-C system for producing *in situ* Al/(TiC + Al_2O_3) composite

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In the last decade, production of particulate reinforced metal matrix composites (MMCs) through *in situ* reaction has attracted much attention due to its many advantages, e.g., low production costs, clean particle-matrix interfaces, over conventional methods [1–4].

Particulates used for reinforcement mainly include TiC [2–4], Al_2O_3 [1], TiB_2 [1], etc. In a typical *in situ* reaction, one or more particles is formed through direct chemical reaction in the melt of the metallic matrix. The preparation of Al_2O_3/TiC ceramic composites through SHS (self-propagating high-temperature reaction) in the TiO_2-C-Al system has been extensively studied recently [5–7], but little work has been conducted to prepare TiC and Al_2O_3 particle reinforced Al matrix composites through *in situ* reaction of the three starting materials. Aiming to providing a basis for the production of Al/(TiC + Al_2O_3) composites, this letter mainly deals with the reaction process in an Al-TiO_2-C system by using DSC, XRD and TEM.

A mixture of 15 g Al, 5 g TiO_2, and 0.75 g C powders (99.0% purity or better), i.e., 72.3 wt%Al-14.1 wt% TiO_2-3.6 wt% C, was sealed in a vacuum stainless steel vial together with steel balls ten times the weight of the powder mixture, and then ball milled for 9 h using a QM-1SP2 planetary-type ball mill with a planetary rotation speed of 450 rev min^{-1}. About 0.35 g of ball-milled powders were heated under argon in a Netzsch 404 differential scanning calorimeter (DSC) at a rate of 20 °C/min, from 25 °C to the desired temperatures and then cooled to the ambient temperature. The heated powders were analyzed using a Rigaku *D*/max-rB X-ray diffractometer (XRD) with Cu K_α radiation or a H-800 transmission electron microscope (TEM) to detect phases formed during heating.

Fig. 1 presents the DSC traces of the powder mixture heated to 1300 °C and cooled to ambient temperature, both at a rate of 20 °C/min. An endothermic peak during heating, with peak temperature at 667.8 °C, and an exothermic peak during cooling are visible. They are obviously caused by the melting and solidification of Al, respectively. No other thermal effects could be observed during cooling besides the solidification of Al, indicating that phases formed during heating are thermodynamically stable. In the heating curve, another endothermic peak with peak temperature at 886 °C and an exothermic peak soon after the melting of Al with peak temperature at 706 °C are also evident.

To determine reaction events at different peaks, the powders were heated in the DSC to different temperatures shown in Fig. 1 and then subjected to XRD or TEM analysis. Fig. 2 shows the X-ray diffraction patterns of the powder mixture without heating or heated to different temperature points. Fig. 2a reveals the existence of the three starting materials: Al, TiO_2, and C. Because the amount of carbon is small in the mixture and it is easy to ball mill into small crystallites while being mixed with Al, which has been reported previously [8, 9], only a very low carbon peak can be observed.

In the XRD pattern of the powder mixture heated to point A, the intensity of TiO_2 was greatly reduced, and peaks of $TiAl_3$ appeared. In the mixture heated to point B, the intensity of $TiAl_3$ peaks was further increased, while peaks of TiO_2 disappeared completely and those of α-Al_2O_3 appeared too. TEM observations of the two heated powders often revealed the ring-like diffraction patterns of α-Al_2O_3 (Fig. 3a). This indicates that most of the α-Al_2O_3 particles formed at these temperatures were too small to be revealed in the XRD analysis, resulting in the very low peaks in the XRD patterns. As seen in Fig. 2d, the diffraction peaks of α-Al_2O_3 become much stronger after heating to 915 °C, this suggests that Al_2O_3 underwent grain growth during the subsequent heating. The above results clearly reveal that the following reaction occurred at the exothermic peak:

$$3TiO_2 + 13Al \rightarrow 3TiAl_3 + 2\alpha\text{-}Al_2O_3 \qquad (1)$$

Both of the powder mixtures heated to point A and B revealed the presence of Al_4C_3. This shows that the formation of this compound from the reaction between Al and C also occurred at the exothermic peak:

$$4Al + 3C \rightarrow Al_4C_3 \qquad (2)$$

This exothermic reaction, occurring soon after the melting of Al, has also been confirmed in previous studies of Al-Ti-C [2, 8] and Al-C systems [9].

After heating to point C (915 °C), the intensity of $TiAl_3$ phase was greatly reduced and strong peaks of TiC appeared. $TiAl_3$ can react with either carbon or

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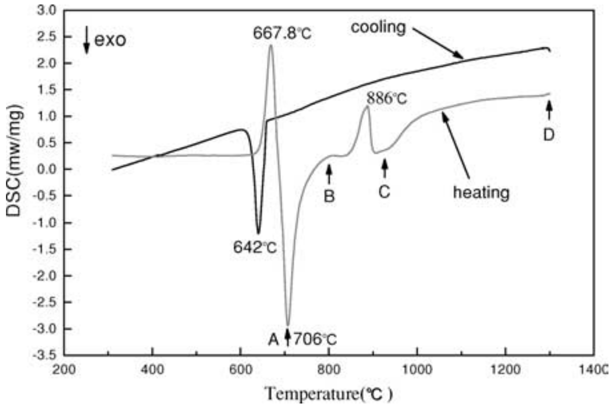

Figure 1 DSC trace of the powder mixture heated to 1300 °C at the rate of 20 °C/min, followed by cooling at the same rate.

Al_4C_3 to form TiC [2, 3, 8], with the former reaction event being exothermic, the latter endothermic [2]. The endothermic peak with peak temperature at 886 °C apparently involves the formation of TiC through the following equation:

$$3TiAl_3 + Al_4C_3 \rightarrow 3TiC + 13Al \qquad (3)$$

This is in agreement with the previous observations in the Al-Ti-C system of this endothermic reaction event with peak temperature at 881 °C [8] or near 900 °C [2], respectively.

Sometimes carbon could be found through TEM of the mixture heated to point B (Fig. 3b). XRD analysis of the mixture heated to 915 °C still reveals the existence of Al_4C_3 and $TiAl_3$. These indicate that both reaction (2) at the exothermic peak and reaction (3) at the second endothermic peak were not completely finished over these temperature ranges, as in the case of the Al-Ti-C system [2, 8]. The reason might be that the presence of large amounts of α-Al_2O_3 particles, which formed according to Equation 1 and thus around Al and $TiAl_3$ particles, hindered the diffusion of elements or the contact of different phases during the reaction.

After heating to 1300 °C, $TiAl_3$ and Al_4C_3 completely disappeared, and the powder mixture only reveals the existence of TiC and α-Al_2O_3 in the Al matrix. It is clear that Al_4C_3 and $TiAl_3$ revealed in Fig. 2d continued to react to form TiC according to Equation 3 during the subsequent heating. The peaks of TiC are broad in Fig. 2d but become sharper and stronger in Fig. 2e, indicating the growth of TiC particles during heating between points C and D.

The weight ratio between TiO_2 and C in the powder mixture has been prepared according to the stoichiometric value in the following equation:

$$3TiO_2 + 3C + 4Al \rightarrow 3TiC + 2Al_2O_3 \qquad (4)$$

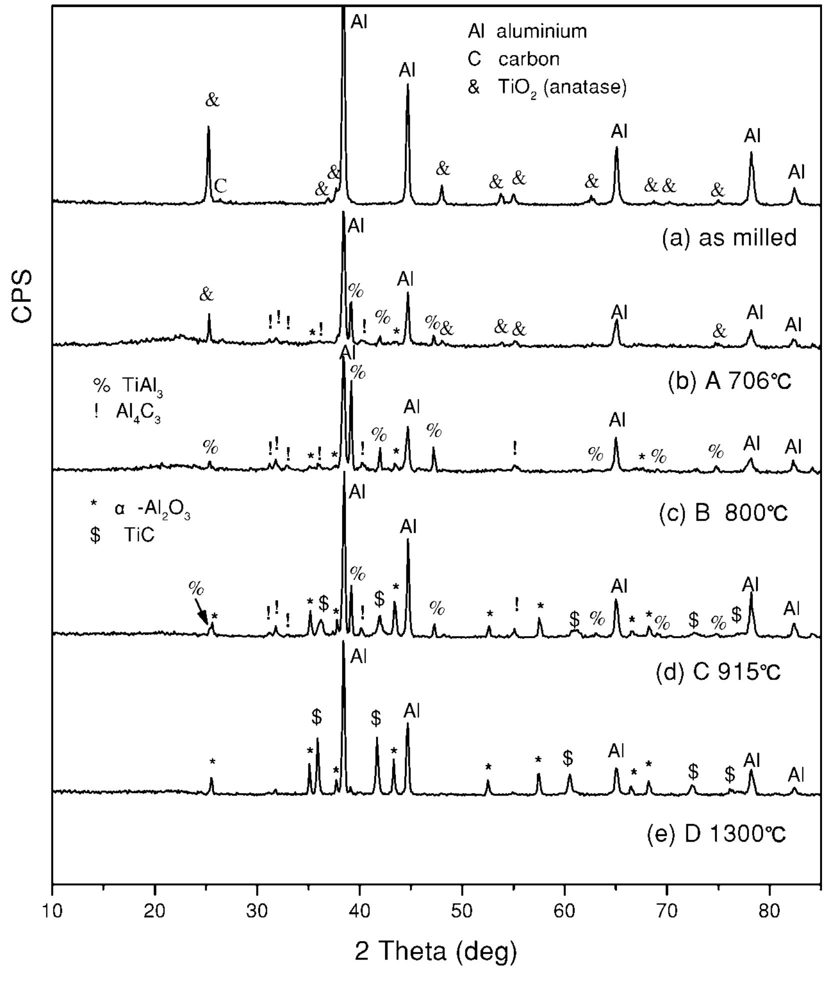

Figure 2 XRD analysis of the powder mixtures heated to different temperature points in Fig. 1.

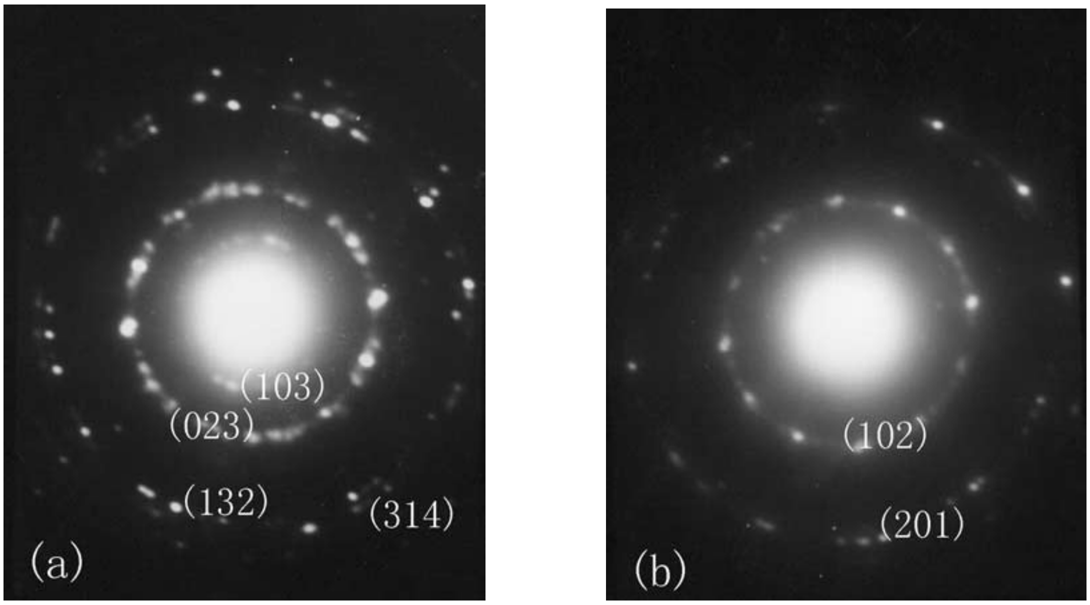

Figure 3 TEM selected area electron diffraction (SAED) patterns of (a) α-Al_2O_3 particle, (b) carbon particle

From the above results it is apparent that all the Ti content in the starting TiO_2 phase has been transformed into TiC phase, indicating no loss of carbon content through the formation of carbon oxide gases during the whole heating process, as suggested next in Equations 5–8. If there had been loss of C content, there should have been $TiAl_3$ phase present in the final product. Furthermore, no other intermediate phases such as γ-Al_2O_3 [1], Ti_2O_3 [1, 10], Ti_3O_5 [10], and TiC_xO_y [11], were detected through either XRD or TEM in the products heated to different temperature points. These rule out the possibility of TiO_2 reacting directly with C according to

$$3TiO_2(s) + C(s) \rightarrow 3Ti_3O_5(s) + CO(g) \tag{5}$$

$$2Ti_3O_5(s) + CO(g) \rightarrow 3Ti_2O_3(s) + CO_2(g) \tag{6}$$

$$\text{or}\ TiO_2(s) + 3C(s) \rightarrow 3TiC(s) + 2CO(g) \tag{7}$$

$$aTi_3O_5(s) + bC(s) \rightarrow cTi_2O_3(s) + dTiC_xO_y(s) + eCO(g) \tag{8}$$

as suggested in [10, 11], or Al according to

$$6TiO_2 + 2Al \rightarrow 3Ti_2O_3 + \gamma\text{-}Al_2O_3 \tag{9}$$

as reported in [1].

In summary, the reaction process in the 72.3 wt%Al-14.1 wt%TiO_2-3.6 wt%C system has been studied by using DSC, XRD and TEM. TiC and α-Al_2O_3 are finally formed in the Al matrix, $TiAl_3$ and Al_4C_3 are found to be transitional phases during the *in situ* reaction process, which involves two steps as follows:

$$(1)\ 3TiO_2 + 13Al \rightarrow 3TiAl_3 + 2\alpha\text{-}Al_2O_3$$
$$4Al + 3C \rightarrow Al_4C_3$$
$$(2)\ 3TiAl_3 + Al_4C_3 \rightarrow 3TiC + 13Al$$

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