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Study of the reaction mechanism in the Al-C binary system through DSC and XRD

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Al-Ti-C master alloy grain refiner for Al and its alloys [1, 2] and TiC reinforced aluminum matrix composite [3–5] have been extensively studied. The preparation of both of the products involves the addition of C into Al-Ti melt to react with Al or Ti. Experience has shown [1–5], however, that it is especially difficult to add carbon particles into Al or Al-Ti melts. So special techniques, such as pressing of carbon and aluminum powders into pellet [3, 4], mechanical stirring of carbon powders into Al-Ti melt [1] and infiltration of carbon-containing gases into Al-Ti melt [5], have been applied to produce the Al-Ti-C products. Despite several studies of the reaction mechanism in this system [1–7], the reaction behavior of carbon in Al or Al-Ti melts still remains controversial. For a better understanding of the reaction mechanism in the Al-Ti-C ternary system, it is important and necessary to study the reaction in Al-C binary system. Aiming to this objective, the present investigation was carried out in ball milled Al-C powders and pressed Al-C pellets using DSC and XRD.

Pure Al (100–200 mesh, 99.8 wt% purity) and C (600 mesh, 99.9 wt% purity) elemental powders with a composition of Al-10 wt%C (all compositions are in weight percent) were mixed and then ball milled for different times using a QM-1SP2 planetary-type ball mill with a planetary rotation speed of 450 rev min^{-1}. The mixed Al-10C powders were also cold-pressed into pellets in a 5 mm diameter die. The as-mixed powders, as-milled powders and pressed pellets (about 0.35 mg) were heated, under argon, in a Netzsch 404 differential scanning calorimeter (DSC), at a rate of 20 °C/min, from 25 °C to desired temperatures, and then naturally cooled to the ambient temperature. The heated products along with the ball milled powders were analyzed using a Rigaku D/max-rB X-ray diffractometer with Cu K_α radiation.

Fig. 1 shows the X-ray diffraction patterns of Al-10C powders ball milled for 1, 5, and 20 h, respectively. Peaks of carbon become weak and fairly broad after 5 h of milling, and disappear completely after 20 h. This indicates that the size of carbon particles was greatly reduced to nanometer scale during milling through the repeated plastic deformation, fracturing and cold-welding.

DSC traces of as-milled and as-mixed Al-10C powders heated to 1000 °C are presented in Fig. 2. The only endothermic peak with peak temperature at 659–681 °C in each curve corresponds to the melting of Al. Besides this, no other peaks appear in the curve of the as-mixed powder, and the heated product is found to be a metallic sphere surrounded by black powders, indicating that Al and C powders have separated from each other during the heating process due to their especially poor contacting/wetting and no reaction occurred. An exothermic peak soon after the melting of Al can be found in the curves of the three ball milled powders, it is clear from the presence of Al_4C_3 in the heated products (Fig. 3) that this is caused by the reaction between aluminum and carbon to form Al_4C_3, but the exothermic peak in Fig. 2b is not as sharp as that in c and d. Fig. 3a reveals the diffraction peaks of carbon, showing that C in Fig. 2b has just partly reacted with Al. Carbon X-ray diffraction peaks are not presented in the heated products of Fig. 2c and d. Further investigation through transmission electron micrograph (TEM) on the two products was performed to examine the existence of carbon and none was found, revealing that the carbon had completely reacted with Al and formed Al_4C_3. An exothermic peak before the melting of Al can also be observed in Fig. 2d, this shows that the reaction between Al and C in this sample starts at the peak onset temperature (T_o) of 551 °C. It is possible that the two exothermic peaks are a united one interrupted by the endothermic peak due to the melting of Al.

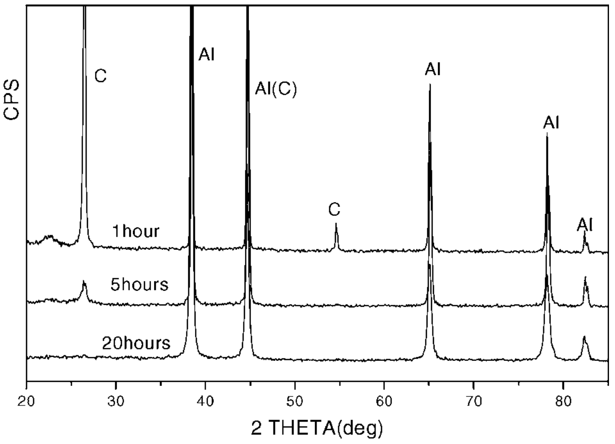

Figure 1 X-ray diffraction patterns of Al-10C powders ball milled for different times.

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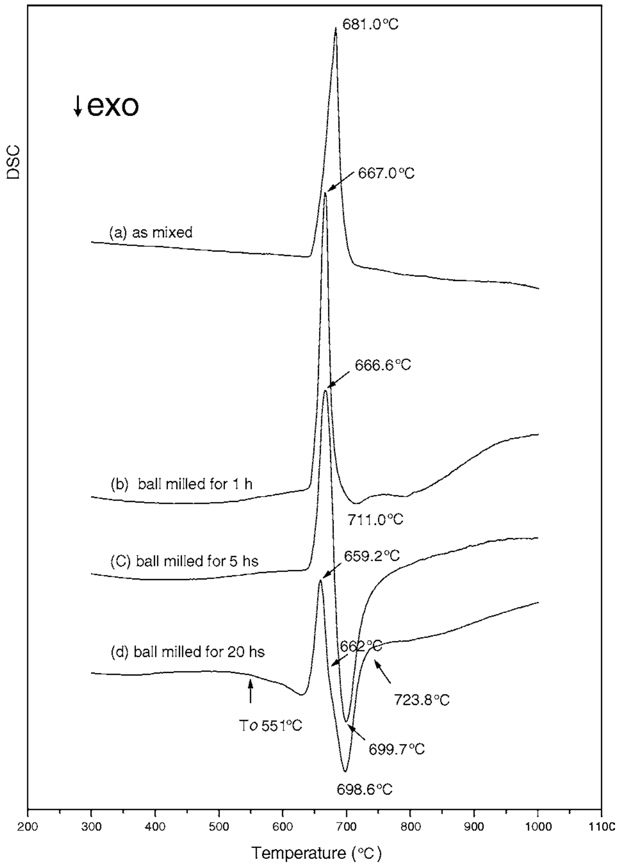

Figure 2 DSC traces of Al-10C powders.

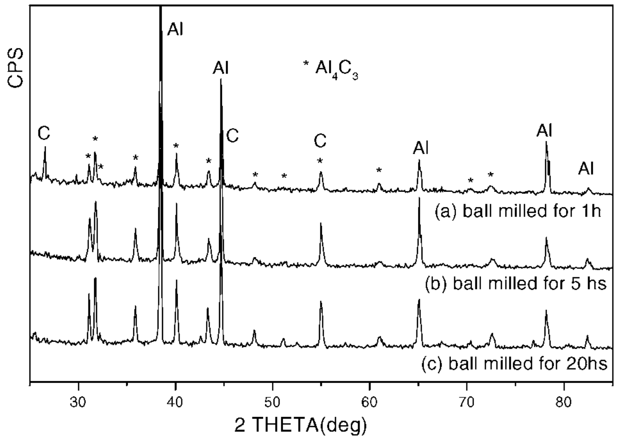

Figure 3 XRD patterns of ball milled Al-10C powders heated to 1000 °C.

The DSC trace of the pressed Al-10C pellet is shown in Fig. 4. As in Fig. 2d, two exothermic peaks due to the formation of Al_4C_3 can be found before and after the Al melting peak. The first exothermic peak indicates that the reaction between Al and C has begun at 580 °C (T_o). The second exothermic peak with peak temperature at 907 °C has a larger temperature range, between 688 and 1122 °C, than that in Fig. 2d between 662 and 723 °C. It is noticed that peak temperatures of the exothermic peaks in the ball milled powders (Fig. 2b–d) are about 200 °C lower than that in the pressed pellet.

Fig. 5 shows the XRD patterns of Al-10C pellet annealed for 1.5 h at different temperatures. It is clear that more carbon reacted with aluminum with the increase of temperature. The peak temperature 907 °C appears to be a critical point only over which could the reaction between Al and C be fully completed during the given annealing time.

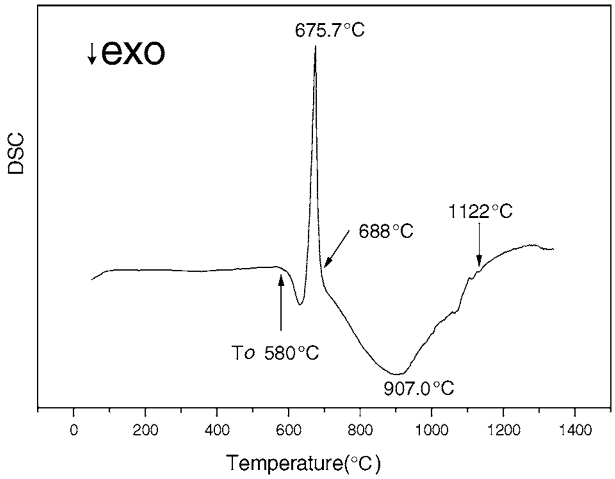

Figure 4 DSC trace of the pressed Al-10C billet.

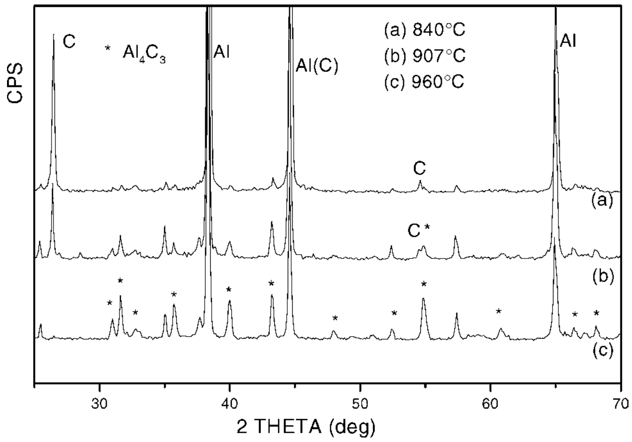

Figure 5 XRD patterns of Al-10C billet annealled for 1.5 h at different temperatures.

According to thermodynamic prediction [7], carbon can react with aluminum to form Al_4C_3 at any temperature under1500 °C. In the study of reaction in Al-Ti-C system, Kennedy reported [6] that the Al-C reaction occurs at 705 °C, but the DSC trace therein showing the reaction event is not very distinct due to the low carbon content used (2%). It is evident from the above results that this reaction occurs before or soon after the melting of Al, provided that the two reactant particles closely contact each other during the reaction process, as in the cases of ball milled powders and pressed pellets. The earliest starting reaction temperature found in this work is 551 °C, and it is likely that this can be even lower since different pre-processing methods or conditions of the mixed powders resulted in different starting reaction temperatures (as clearly suggested in Figs 2 and 3).

Compared with the ball milled powders, both a higher peak temperature and a wider reaction temperature range (and hence a longer reaction time) are evident in the pellet reactants. This is apparently caused by the relatively larger starting carbon and aluminum particles. The high defect densities as well as the nanocrystalline carbon particles induced in the ball milling can ensure large reaction interface areas between C and Al particles and enhance their diffusion rates through the product phase. The combination of factors greatly decrease the reaction temperature and the temperature range (Fig. 2). The differences in the two reaction cases suggest a strong kinetic dependence of the Al-C reaction process.

In conclusion, the reaction between carbon and aluminum to form Al_4C_3 may start before Al melts based on DSC data, under the condition that carbon particles closely contact with aluminum. The starting reaction temperature, the peak reaction temperature and the reaction temperature range depend greatly on the starting particle size and contact conditions of the two reactants, revealing a strong kinetic reaction process.

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