In situ synthesis of Al_2O_3 particulate-reinforced Al matrix composite by low temperature sintering

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The powder mixture of Al-10 wt.% SiO_2 was selected as a research system. Compared with an as-mixed powder, the phase structure and microstructure of an as-milled powder was investigated, and the temperature of the displacement reaction in the two kinds of powder was determined by thermal analysis. The preforms of the two kinds of powder were sintered based on the result of thermal analysis. The results indicate that the particle size of the Al-SiO_2 powder was refined greatly after 4 h of high energy ball milling, and diffusion couples were formed due to SiO_2 particles embedded in the Al matrix. The displacement reaction did not occur between Al and SiO_2 for the as-mixed powder, while it occurred in the range of 560–680°C for the as-milled powder. For the as-milled powder, an aluminum matrix composite reinforced with Al_2O_3 particles, which were homogeneously distributed in the Al matrix, can be fabricated by sintering at 640°C for 2 h.

1. Introduction

Al matrix composites, which possess superior properties, such as high strength, high hardness and high-specific elastic modulus etc, are widely used in the aerospace and automobile industries [1]. Traditionally, the Al matrix composites are produced by directly adding reinforcements, fiber, whisker and particulates, to the Al matrix [2]. Recently, some *in situ* methods based on the reaction between metal and oxides, such as CuO [3], ZnO [4] and TiO_2 [5] have been developed and employed in the production of Al matrix composites.

Silicon is one of the most popular additions to the aluminum alloys, which will impart fluidity to the alloys in welding and high mechanical properties through the formation of compounds that make the alloys heat treatable. Thus, silicon oxide is one promising candidate to produce *in situ* Al matrix composites, because Al will react readily with SiO_2 at a certain range of temperatures, and the Si derived from the reaction will have the above-mentioned benefit to the Al alloys. As for the Al-SiO_2 system, only some aluminum melting infiltration processes were reported to fabricate the Al matrix composite, which were usually performed at very high temperatures [6, 7], and few work was conducted based on the displacement reaction at low temperature. In this study, we report that Al_2O_3 particulate reinforced Al (Si)-matrix composite was fabricated by low temperature sintering using the uniaxial pressed green preform, made of the high energy ball milled Al-10 wt.% SiO_2 powder.

2. Experimental procedure

The nominal composition of Al-SiO_2 powder mixture was Al-10 wt.% SiO_2. The as-mixed powder was blended for 24 h with a self-made rotation mixer. To produce the as-milled powder, 7 g of a mixture of elemental Al and SiO_2 compound powder with a purity of 99.5%, was loaded in a hardened steel vial together with sixteen stainless steel balls in diameter of 8.0 mm. The ball to powder weight ratio was 4:1. The vial was then sealed in a glove-box filled with high purity argon. The ball milling was performed using a SPEX8000 Mixer/Mill

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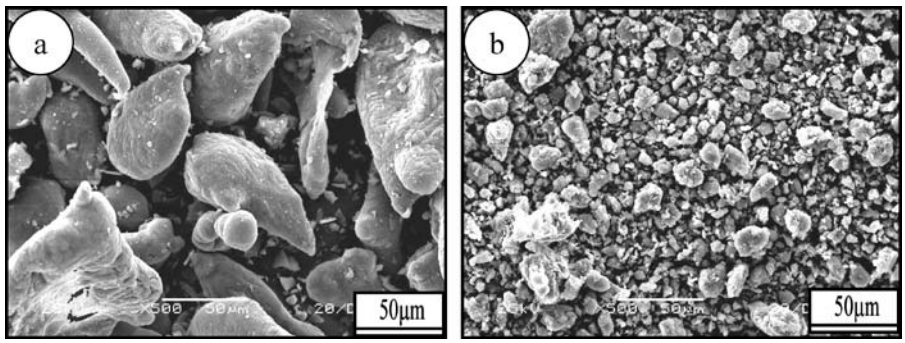

Figure 1 SEM micrographs of the as-mixed powder (a) and the 4 h-milled powder (b).

machine. After milling, the powder was analyzed using X-ray diffractometry (XRD) and differential thermal analysis (DTA). The XRD analysis was performed in a Philips X-pert system diffractometer with Cu Kα radiation and copper single crystal monochromator. The differential thermal analysis was performed using a TGD 9000 MTS 9600 instrument under flowing argon. The heating rate used for the thermal analysis was 10°C/min. Both the as-mixed and the as-milled powders were uniaxially pressed at 30 MPa to form green compact discs in diameter of 13 mm. Then, the green compacts were sintered at 600 and 640°C for 2 h in a tube furnace under flowing argon to fabricate the bulk samples based on the DTA analysis. The microstructure and elements distribution of the sintered products were examined by SEM, equipped with the energy dispersive X-ray spectroscopy (EDX). The density of the compact discs before and after sintering was measured by Archimedean principle of buoyancy.

3. Results and discussion

Fig. 1a shows the microstructure of the as-mixed powder. The average particle size of aluminum was about 60 μm. The fine SiO_2 particles were homogeneously dispersed on the surface and the interstice of aluminum particles. Fig. 1b shows the microstructure of the as-milled powder. After 4 h of ball milling, the aluminum and SiO_2 particles were obviously refined. There also existed some relatively large particles, which were the result of the cold welding between aluminum particles during ball milling. In addition, some SiO_2 particles were embedded in the aluminum matrix. This can be verified by TEM micrograph in Figs 2a and b, which show the bright-field image (BFI) and the corresponding selected-area diffraction pattern (SADP) of the as-milled powder. Obviously, some SiO_2 particles, average size of 40 nm, were embedded in the Al matrix. The SADP shows a ring-spot pattern that is characteristic of the simultaneous diffraction of crystal SiO_2 (fcc) and Al (fcc). This suggests that Al/SiO_2 diffusion couples were formed during ball milling, and their size was in the scale of nanometer. The formation of Al/SiO_2 diffusion couples is beneficial to the displacement reaction in the Al-SiO_2 system.

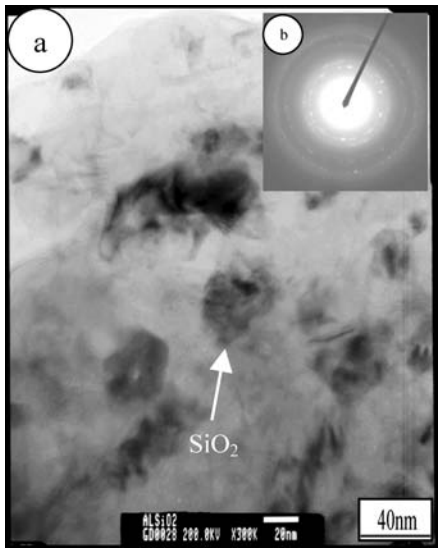

Figure 2 BFI (a) and the corresponding SADP (b) of the 4 h-milled powder.

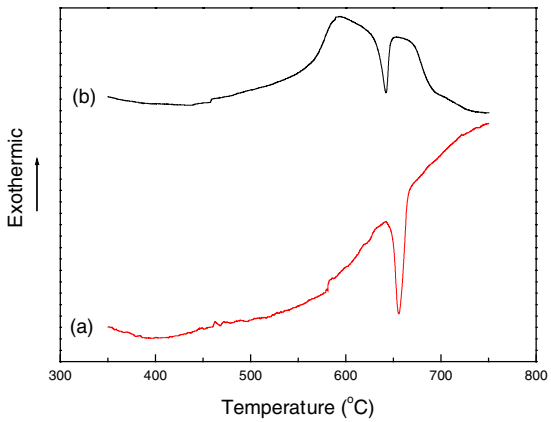

Figure 3 DTA traces of the as-mixed powder (a) and the as-milled powder (b).

Figs 3a and b show the DTA traces of the as-mixed and the as-milled powder, respectively. For the as-mixed powder, only one sharp endothermic peak appeared during heating from ambient temperature to 750°C. The onset and peak temperatures of this endothermic peak were 640 and 656°C, respectively. The endothermic peak was caused by the melting of aluminum. No other reactions

took place in the process of heating of the as-mixed powder. However, for the as-milled powder, the DTA trace exhibited both endothermic and exothermic peaks. The onset and peak temperatures of the endothermic peak were 620 and 640°C, respectively, which was due to the melting of the Al composite particles. The SiO_2 particles embedded in the aluminum matrix facilitated the decrease in melting point. In addition, the refinement of the aluminum particles was beneficial to the decrease in melting point. The exothermic peak was located in the temperature range between 560 and 680°C, and it was split into two parts by the endothermic peak. Such an exothermic peak probably corresponded to the displacement reaction between Al and SiO_2 predicted according to the composition of this system. The reaction is described by the following equation.

$$4\mathrm{Al}(s,l) + 3\mathrm{SiO_2}(s) \rightarrow 2\mathrm{Al_2O_3}(s) + 3\mathrm{Si}(s) + Q \quad (1)$$

where the subscripts "s" and "l" stand for the solid and the liquid form of the substances. Furthermore, calculation according to Equation 1, the change of enthalpy for the displacement reaction was about −208 KJ/mol SiO_2 in the temperature range of 527–727°C. However, the heat of fusion of pure Al is only 10.7 KJ/mol, thus, the reaction enthalpy released was much more than the heat of fusion of Al. When the exothermic and the endothermic reactions occurred in the same temperature range, the endothermic peak was superimposed on the exothermic peak, and appeared as the shape of Fig. 3b.

To identify the reaction corresponding to the exothermic peak shown on the DTA trace, the as-milled powder was analyzed using XRD before and after DTA analysis, as shown in Figs 4a and b. For the as-milled powder, the diffraction peaks corresponded to Al and SiO_2, respectively. This indicated that no reaction occurred between Al and SiO_2 during ball milling, i.e. the strain energy accumulated during the milling can not induce a displacement reaction. After analysis of DTA, the intensity of SiO_2 diffraction peaks decreased, and the diffraction peaks corresponding to Si and Al_2O_3 appeared. This indicated that the *in situ* reaction between Al and SiO_2 occurred during heating of DTA analysis. In the meantime, this verified that the exothermic peak on the DTA trace was due to the *in situ* displacement reaction.

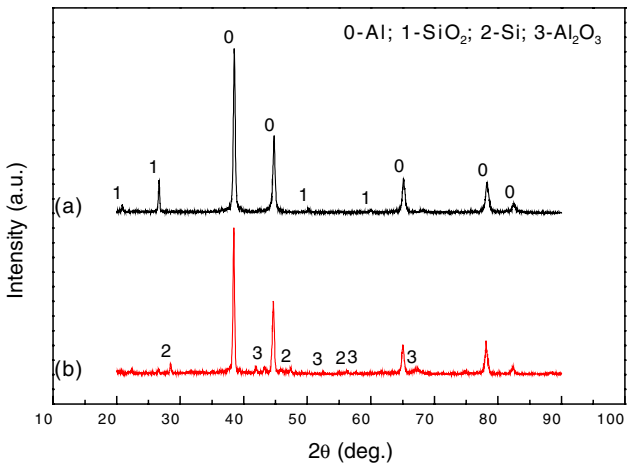

Figure 4 XRD patterns of the as-milled powder before (a) and after (b) DTA analysis.

Figs 5a and b show the cross section of the as-mixed powder preforms sintered at 600 and 640°C for 2 h, respectively. From these images, it is evident that the preforms can be sintered well, and the powder particles were integrated by metallurgy. However, the SiO_2 particles segregated on the grain boundaries, which implied that the displacement reaction between Al and SiO_2 particles did not occur during sintering. A microstructure such as this deteriorates the mechanical properties of the sintered products obviously. Calculation according to the nominal composition, the theoretical density of the Al-10 wt.% SiO_2 system should be 2.69 g/cm^3. For the as-mixed powder preform, the real density measured by Archimedean principle of buoyancy was about 2.32 g/cm^3, and the relative density was 86.2%; after sintering at 600 and 640°C for 2 h, the real density increased to 2.54 g/cm^3 and 2.58 g/cm^3, respectively. The relative density was 94.4% and 95.9%, respectively. Figs 6a and b show the cross section of the as-milled powder preforms sintered at 600 and 640°C for 2 h, respectively. For the former, the preform can not be fully sintered, and it was impossible to polish it for observation of microstructure. Thus, only one optical micrograph at low magnification of the sintered specimen was given to show the layered structure. The outer layer was better than the inner layer. However, for the latter, the Al_2O_3 particles were homogeneously dispersed in the matrix. These Al_2O_3 particles had a rather narrow size distribution and an average size of about 5 μm. This was attributed to the displacement reaction between Al and SiO_2 under this sintering condition. Si formed from the *in situ* reaction dissolved into the aluminum matrix and formed the Al-Si eutectic phase, as shown in Fig. 6b. No pores or other defects were found in the sintered product. According to the result of DTA analysis, the former sintering should be classified as solid state sintering, while the latter sintering should be classified as solid-liquid state sintering for the as-milled powder. In the case of sintering at 640°C for 2 h, the melting of aluminum occurred, which will contribute to the diffusion of the elements and enhance the sintering ability of the preform. Due to the melting of aluminum being involved in the course of sintering, thus, the deformation of the preforms will occur after sintering. Assuming that Al-10 wt.% SiO_2 being fully converted to Al_2O_3 and Al (Si) solid solution, the volume shrinkage was 3.12% and the theoretical density was 2.78 g/cm^3. In order to check the deformation degree of the preforms during sintering, various heights of compact discs were sintered, in height of 3.0 mm, 5.5 mm and 10.0 mm, respectively. The results indicated that the shape change decreased greatly with increasing the height

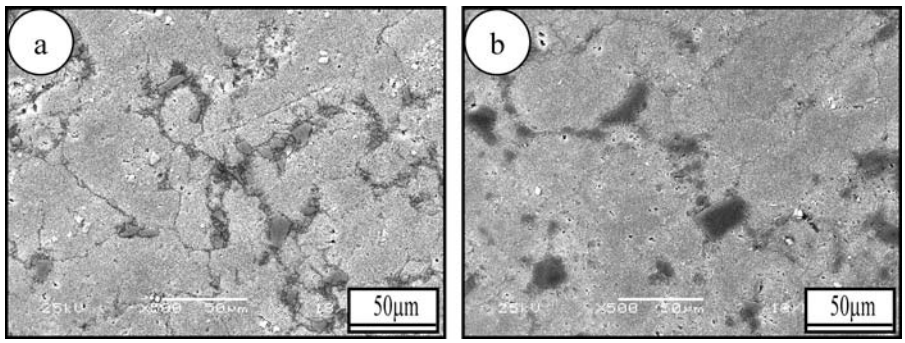

Figure 5 SEM micrographs showing the cross section of the as-mixed powder preforms after sintering at 600 (a) and 640°C (b) for 2 h.

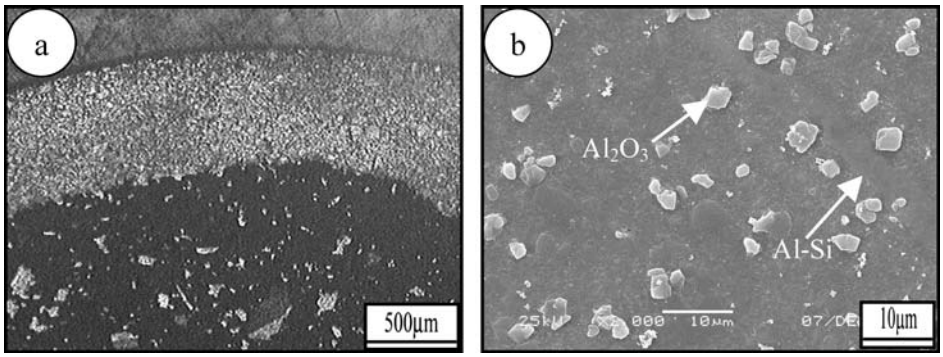

Figure 6 Optical and SEM micrographs of the cross section of the as-milled powder preforms after sintering at 600 (a) and 640°C (b) for 2 h.

of preform. For the case of height of 3.0 mm, the shape change was relatively serious, and a little crack occurred on the top surface of the preforms, however, for the case of height of 10.0 mm, the shape change was not obvious, and just a little recess of the top surface and a little decrease in height occurred for the sintered preforms. After sintering, the real density measured by Archimedean method was 2.76 g/cm^3, thus, the relative density reached 99.3%, suggesting the formation of fully dense of Al/Al_2O_3 composite.

When compared to the process of aluminum melting infiltration [6, 7], it was very attractive that Al matrix composite reinforced with Al_2O_3 particles can be fabricated by sintering at a very low temperature. In addition, it was well-known that the pressure employed to preform played a great role on the sintering of powder. HIP (hot isostatic pressing) and CIP (cold isostatic pressing) were often applied to obtain an ideal sintering product. However, for the as-milled Al/SiO_2 powder, a perfect sintered product could be fabricated with the green compacts prepared at small uniaxial pressure, 30 MPa. This indicated that high energy ball milling improved the sintering ability of the composite powder. In fact, two essential processes occur during ball milling-cold welding between the different particles and fracturing of the cold welded particles due to high energy collision [8]. The cold welding minimizes the diffusion distance between the atoms of the different components. The fracturing of the welded particles impedes the clustering of the particles and promotes the transfer of the high collision energy to all particles and produces new, clean surfaces without oxide layers increasing the atomic activity. Through continuous plastic deformation, fracture and cold welding in an inert atmosphere, mechanical milling of a powder mixture can result in the formation of numerous diffusion couples in the starting phases. Because the diffusion couples are formed in an inert atmosphere, they are free of contamination and the size of the diffusion couple decreases to sub-micrometer scale, or nanometer scale through high energy ball milling. In the mean time, the atomic diffusivity of the diffusion couples is also enhanced through the introduction of a lot of structural defects, such as vacancies, dislocations, and grain boundaries. When the mechanically prepared diffusion couples are heated to a certain temperature, some displacement reactions can be activated. Consequently, the aluminum matrix composite reinforced with ceramic particles can be fabricated by low temperature sintering the green preform, made of the high energy ball milled powder.

4. Conclusions

For the ductile/brittle Al-SiO_2 system, the particle size of the Al-SiO_2 powder was significantly refined after 4 h of high energy ball milling, and diffusion couples were formed due to SiO_2 particles embedded in the Al matrix. The displacement reaction did not occur between Al and SiO_2 for the as-mixed powder, while it occurred in

the range of 560–680°C for the as-milled powder. Thus, it was not suitable to fabricate the particulate reinforced Al matrix composite with the as-mixed powder. For the as-milled powder, an aluminum matrix composite reinforced with Al_2O_3 particles, which were homogeneously distributed in the Al matrix, was fabricated by solid-liquid state reaction sintering at 640°C for 2 h. The relative density of the sintered compact discs reached 99.3%, suggesting the formation of fully dense Al/Al_2O_3 composite.

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