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Effect of high energy ball milling on the displacement reaction in particulate reinforced Al–Si–Cu alloy matrix composite powders

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Abstract The displacement reaction between Al and SiO_2 in an Al–3wt%Cu–3wt%Si–9wt%SiO_2 powder mixture has been studied when the mixture had been ball-milled, and compared with the reaction in the as-mixed powder. Diffusion couples consisting of Al/SiO_2 were formed during ball milling. The size of the composite powder particles and the diffusion couples was reduced by increasing the ball milling time. Differential thermal analysis and X-ray diffraction results showed that the displacement reaction between Al and SiO_2 did not occur in the as-mixed powder, but occurred in the as-milled powders in the temperature range of 640–680 °C. Furthermore, the onset temperature of the displacement reaction shifted to lower temperatures after increasing the ball milling time. On the basis of these results the milled powder was sintered at 640 °C in order to produce an Al–Cu–Si matrix composite reinforced with homogeneously distributed submicron-sized Al_2O_3 particles. This is much lower than the temperature required for the same reaction in other processes which are used to produce such composites, such as the melting infiltration process.

Introduction

It has been well established that high energy ball milling is an effective technique to facilitate formation of composite powder particles from elemental powders [1–3]. Once the composite structure is established, each powder particle consists of numerous diffusion couples for solid state reactions during further ball milling or subsequent heat treatment of the as-milled powders.

Solid state reactions in diffusion couples which are comprised of multi-elemental phases or oxides are complex and interesting as there are a lot of possibilities in terms of the first phase to be formed and the sequence of phase formation. A great deal of research has been devoted to understanding the phase formation during ball milling and subsequent heat treatment of a mixture of elemental phases or oxides [4, 5]. In addition, by combining the short time of mechanical alloying with low-temperature isothermal annealing, various metal matrix composites (MMCs) reinforced with ceramic particulates can be produced based on the displacement reaction between metal oxides and pure metals [6, 7]. Thus, it is very attractive to investigate the effect of high energy ball milling on the displacement reaction in particulate reinforced metal matrix composite powders. In this paper, Al–Cu–Si/SiO_2 composite powders were prepared by high energy ball

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milling. Subsequently, the as-milled powders were isothermally annealed under flowing argon. The displacement reaction that occurred while heating the powders was investigated in detail. The main purpose was to clarify the effect of high energy ball milling on the displacement reaction in Al–Si–Cu alloy matrix composite powders and to provide some guidance for the subsequent sintering of these powders.

Experimental procedure

The composition of the powder sample was Al–3wt%Si–3wt%Cu–9wt%SiO_2. The mixed powders were placed into a hardened steel vial, together with 18 stainless steel balls having a diameter of 8.0 mm. The total mass of the powder was 7 g, and it consisted of a mixture of Al, Si, and Cu elemental powders and SiO_2 compound powder. 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 SPEX-8000 Mixer/Mill. After ball milling, the powders were 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-K_α radiation and copper single crystal monochromator. The DTA was performed using a TGD 9600 Instrument under flowing argon. The heating rate used for the thermal analysis was 10 °C/min. The microstructure of the powder particles was examined using scanning electron microscopy (JSM-5900 SEM) and transmission electron microscopy (JEM-2010 TEM). TEM specimens were prepared by dipping a copper grid in a dispersion solution of the as-milled powders, which was dispersed by supersonic vibration for 15 min in alcohol.

Results and discussion

Phase of the as-milled powders

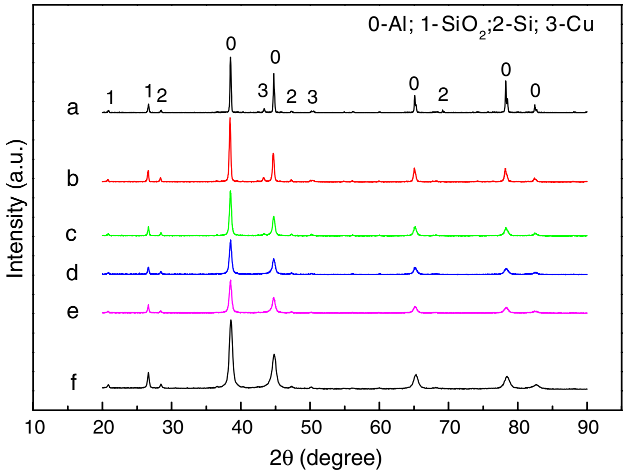

Fig. 1 XRD patterns of the as-mixed Al–Cu–Si/SiO_2 powder (**a**) and the corresponding powders milled for various milling times: (**b**) 1 h, (**c**) 4 h, (**d**) 8 h, (**e**) 12 h, (**f**) 24 h

XRD patterns of the as-mixed Al–Si–Cu/SiO_2 powder and the corresponding powders milled for 1, 4, 8, 12 and 24 h are shown in Fig. 1. In all cases, no new phase appeared, indicating that no chemical reactions occurred during either mixing or milling. For the as-mixed powder, all phases present were detected by the XRD analysis. For the as-milled powders, with an increased milling time, the intensity of the Al diffraction peaks decreased gradually and the peaks were broadened significantly, indicating that the grain size of Al was reduced greatly. In the meantime, the Al peaks also shifted to a higher 2θ diffraction angle, indicating that the lattice parameter of the Al phase decreased as a result of the high energy ball milling. The decrease in the lattice parameter of the Al phase, and the corresponding disappearance of the Si and Cu peaks revealed that the ball milling lead to solution of Cu and Si phases in Al to form an α-Al (Cu, Si) solid solution. The crystallite size of the α-Al (Cu, Si) phase was estimated using the Scherrer formula [8]. It was reduced greatly compared to that of the as-mixed powder, and was 20 nm after 8 h of milling.

Morphological and microstructural observations

Figure 2 a–f shows the SEM micrographs of the as-mixed Al–Si–Cu/SiO_2 powder and the corresponding powders milled for 1, 4, 8, 12 and 24 h, respectively. For the as-mixed powder, the fine particles of Cu, Si and SiO_2 were distributed in the interstices of coarse aluminum particles. The size of the aluminum particles ranged from 50–100 μm. In the early stages of ball milling, the coarse particles of Al were soft, and their tendency to weld together and form large particles was high. Thus, after 1 h of ball milling, the size of a few particles was increased. In the meantime, the particles got work hardened and fractured by a fatigue failure mechanism and/or by the fragmentation of fragile flakes during the milling, which resulted in significant refinement of most of particles. After 4 h of milling, it is clear that the particle size was further refined, and the size distribution became narrow. At this stage, the tendency to fracture predominated over cold welding.

With further ball milling up to 24 h, due to the continued impact of grinding balls, it was inevitable that the structure of the particles was steadily refined, but the particle size remained constant. The particle size distribution at this stage was narrow, because the particles which were over the average size were refined at the same rate as the fragments with size below the average grew through agglomeration of smaller particles. In order to identify microstructure details of the as-milled powders, some were examined by TEM. Figure 3 a–d shows bright field image (BFI) and the corresponding selected area diffraction patterns (SADP) of the powders milled for 1, 4, 12 and 24 h, respectively. It is clear that various amounts of brittle particles embedded in the matrix for the as-milled powders. 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. With the aid of image analysis software (Image Pro Plus), the particle sizes embedded in the matrix were measured. After 1 h of milling, the number of particles embedded in the matrix was sparse, and the mean particle diameter was 85 nm. After 4 h of milling, the amount of embedded particles was increased, and the mean particle diameter was decreased to 55 nm. After 12 h of milling, it was obvious that the volume fraction of the embedded particles significantly increased, and the mean particle diameter was decreased to 22 nm. After 24 h of milling, although there was no obvious increase in the volume fraction of the embedded particles, the mean particle diameter was further decreased to 15 nm. Thus, with an increase in milling time, the size of the diffusion couples was reduced, and the volume fraction of the diffusion couples was increased.

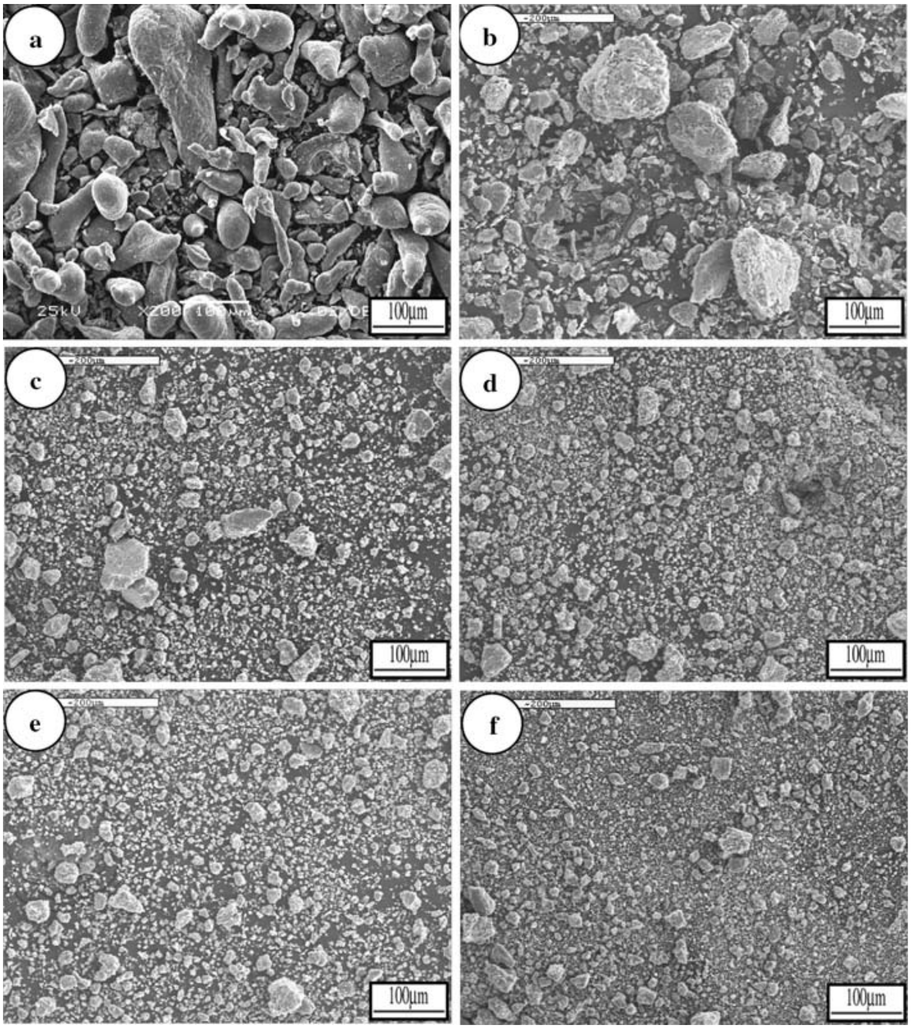

Fig. 2 SEM micrographs of the as-mixed Al–Cu–Si/SiO_2 powder (**a**) and the corresponding powders milled for various milling times: (**b**) 1 h, (**c**) 4 h, (**d**) 8 h, (**e**) 12 h, (**f**) 24 h

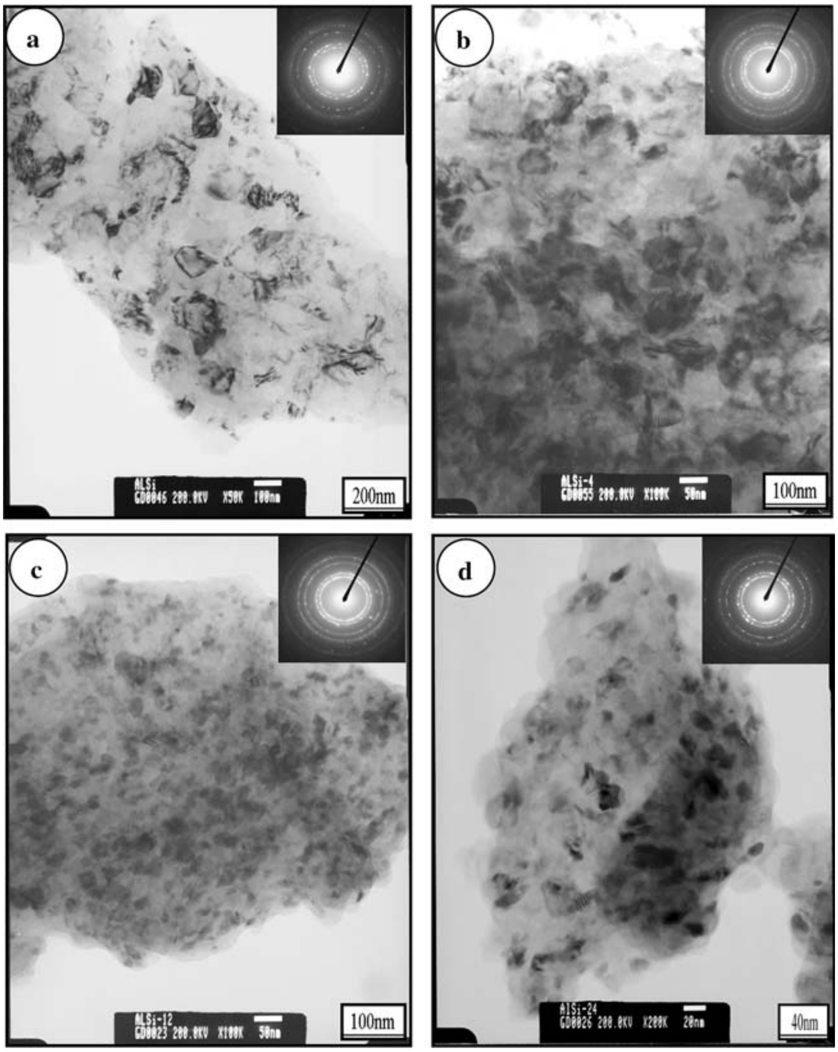

Fig. 3 Bright field image and the corresponding SADP of the Al–Si–Cu/SiO_2 powders milled for 1 h (**a**), 4 h (**b**), 12 h (**c**) and 24 h (**d**)

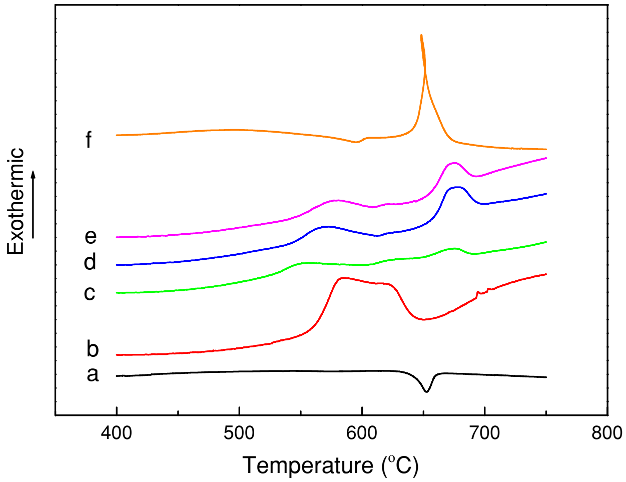

Fig. 4 DTA traces of the as-mixed powder (**a**) and the corresponding powders milled for various milling times: (**b**) 1 h, (**c**) 4 h, (**d**) 8 h, (**e**) 12 h, (**f**) 24 h

Displacement reactions during sintering

Figure 4 a–f shows the DTA traces of the as-mixed Al–Si–Cu/SiO_2 powder and the corresponding powders milled for 1, 4, 8, 12 and 24 h, respectively. During DTA, the trace will depart from the base line and form a negative or a positive peak when a phase transition occurs. Thus, the onset temperature can be determined by extrapolation. The extrapolated onset is the point of intersection between the tangent drawn at the point of greatest slope on the leading edge of the peak and the extrapolated base line. The peak temperature is the temperature at which the maximum temperature difference between the sample and the reference is reached. The onset and peak temperatures extracted from Fig. 4 are listed in Table 1. For the as-mixed powder, the DTA trace showed only one endothermic peak, which was mainly due to the melting of aluminum.

Table 1 The onset and peak temperatures of DTA traces of the as-mixed Al–Si–Cu/SiO_2 powder and the corresponding powders milled for 1, 4, 8, 12 and 24 h

Powder	Endothermic peak		1st exothermic peak		2nd exothermic peak	
	T_{onset} (°C)	T_{peak} (°C)	T_{onset} (°C)	T_{peak} (°C)	T_{onset} (°C)	T_{peak} (°C)
As-mixed	635	650	–	–	–	–
1 h-milled	–	–	560	588	–	–
4 h-milled	–	–	525	548	650	673
8 h-milled	–	–	545	567	650	675
12 h-milled	–	–	550	576	650	675
24 h-milled	–	–	–	–	640	655

The onset temperature of this peak was 635 °C, which was lower than the melting point of pure Al. This might be due to the diffusion of Cu and Si into Al particles during heating of the powder in the course of DTA, which caused the melting temperature of Al to be lowered. No other reactions occurred in the process of heating the as-mixed powder. The DTA trace of the 1 h-milled powder exhibited one large exothermic peak, the onset and peak temperatures of which were 560 and 588 °C, respectively. Furthermore, there was a small, but sharp exothermic peak superimposed on the exothermic peak. The DTA traces of the 4, 8 and 12 h-milled powders were similar to each other, but they differed from the DTA trace of the 1 h-milled powder. They showed two exothermic peaks in the temperature range of 520–680 °C. With 4 h of milling, the onset and peak temperatures of the first exothermic peak were 525 and 548 °C, respectively, while the onset and peak temperatures of the second exothermic peak were 650 and 673 °C, respectively. With 8 h of milling, the two exothermic peaks became much larger compared to those of the 4 h-milled powder, and the onset and peak temperatures of the first exothermic peak increased to 545 and 567 °C, respectively. In the meantime, the second exothermic peak became much sharper, but its onset and peak temperatures were similar to those of the 4 h-milled powder. With 12 h of milling, the onset and peak temperatures of the first exothermic peak changed to 550 and 576 °C, respectively, while the second exothermic peak remained almost unchanged compared to that of the 8 h-milled powder. After 24 h of milling, the first exothermic peak disappeared, but the intensity of the second exothermic peak was increased, and the onset and peak temperatures were reduced to 640 and 655 °C, respectively.

The powders from these DTA runs were then used for a second set of DTA runs. The traces are shown in Fig. 5. For all the as-milled powders, only an endothermic peak appeared in the temperature range of 540–580 °C. This revealed that one of the exothermic peaks in the first run was due to the formation of Al_2O_3 and Si by the displacement reaction between Al and SiO_2. After the first run, the displacement reaction was completed and resulted in the formation of Al_2O_3 and Si. Therefore, in the second run, the corresponding exothermic peak disappeared, and only one endothermic peak occurred, which was due to the melting of the eutectic phase of Al–Si formed in the first DTA run.

To identify the reaction related to each of the exothermic peaks shown on the DTA traces, the as-milled powders were heated to various temperatures in a DTA instrument with argon protection, and then cooled to room temperature. XRD was used to analyze the phases formed during heating. Figure 6 a shows the XRD pattern of the powders milled for 1 and 12 h and then heated to 600 °C, i.e., after the first exothermic peak but before the second exothermic peak. The XRD pattern showed peaks of the Al_2Cu intermetallic phase (θ phase). This indicated that the first exothermic peak on the DTA trace was due to the precipitation of θ phase while heating the as-milled powders. At the same time, the absence of Al_2O_3 peaks indicated that the displacement reaction did not occur below 600 °C. Figure 6b shows the XRD pattern of the

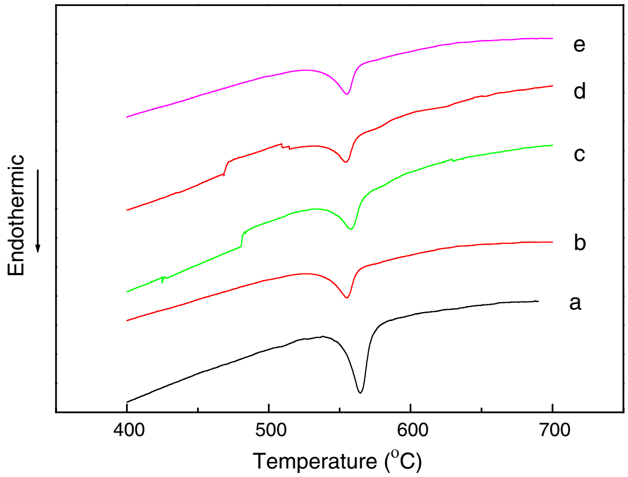

Fig. 5 DTA traces of the powders milled for (**a**) 1, (**b**) 4, (**c**) 8, (**d**) 12 and (**e**) 24 h in the second run

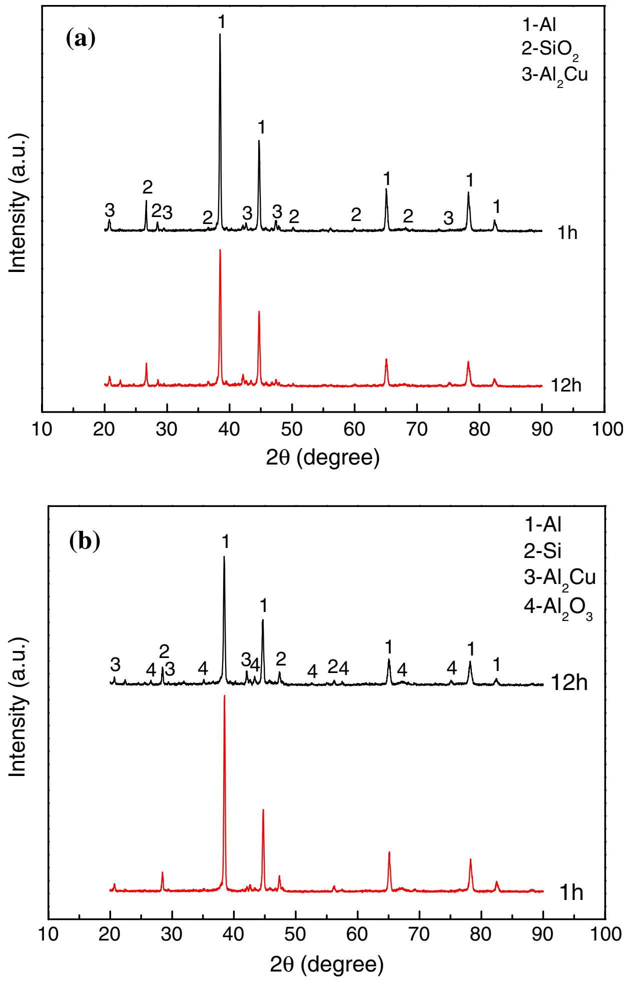

Fig. 6 XRD patterns of the 1 and 12 h-milled powders heated to 600 °C(**a**) and 650 °C (**b**)

powders milled for 1 and 12 h, and then heated to 650 °C. Al_2O_3 and Al_2Cu diffraction peaks appeared on this pattern and the intensity of Si peaks was increased, whilst the SiO_2 peaks disappeared. This suggests that the second exothermic peak was initiated by the reaction between Al and SiO_2. The reaction is described by the following equation.

$$4Al(s,l) + 3SiO_2(s) \rightarrow 2Al_2O_3(s) + 3Si(s) + Q \qquad (1)$$

where the subscripts "s" and "l" stand for the solid and liquid forms of the substances. For the 1 h-milled powder, some Al_2O_3 peaks were also detected after heating to 650 °C, which demonstrates that the displacement reaction also occurred. The small but sharp exothermic peak superimposed on the broad exothermic peak may be attributed to this reaction. This also indicated that 1 h of ball milling was not enough to produce the composite powder, in which the displacement reaction could be fully activated. For the 24 h-milled powder, the exothermic peak was mainly due to the displacement reaction between Al and SiO_2. The disappearance of the first exothermic peak was attributed to the overlap of the precipitation of θ phase and the displacement reaction. The longer milling time, the more diffusion couples were formed, and the size of the diffusion couples was much finer, which was beneficial to the displacement reaction, thus the precipitation of θ phase was retarded. According to the above analysis, it can be claimed that the second exothermic peak on the DTA traces of the as-milled powders was due to the displacement reaction between Al and SiO_2. From 4 to 24 h of milling, the onset temperature of the displacement reaction shifted to lower temperatures, and the intensity of the peaks increased. This is attributed to the microstructure of the as-milled powders as shown in Fig. 3. With an increase in milling time, the size of the diffusion couples was reduced, and the volume fraction of the diffusion couples was increased. Thus, the displacement reaction was activated at lower temperatures and increased amounts of Al and SiO_2 reacted to form Al_2O_3.

Once the reaction (or reactions) corresponding to each of the exothermic peaks was identified, information on the reaction kinetics was extracted from the exothermic peaks. The onset temperature of the exothermic peak represents the critical temperature required to activate the reactions for a given heating rate, while the peak temperature represents the temperature at which the reaction rate reaches a maximum value. This information is pertinent for the subsequent sintering to produce the Al–Cu–Si alloy matrix composites reinforced with the particulates formed from the in situ displacement reaction. The results of DTA, for the powders milled for more than 4 h, revealed that the displacement reaction between Al and SiO_2 can be activated at 640 °C, which is much less than the required temperature of 1000 °C in the process of melting infiltration to produce the Al matrix composite reinforced with ceramic Al_2O_3 particulates [9]. This is attributed to the formation of diffusion couples during high energy ball milling, where the size was reduced by increasing the ball milling time. Through continuous plastic deformation, fracture and cold welding in an inert atmosphere, mechanical milling of a powder mixture of Al–Si–Cu/SiO_2 can result in the formation of numerous Al/SiO_2 diffusion couples. Since the diffusion couples are formed in an inert atmosphere, they are free of contamination. With further milling, the size of the diffusion couple decreases from a micron scale to a submicron and/or nanometer scale. In the mean time, introducing a large number of structural defects such as vacancies, dislocations and grain boundaries also enhances the atomic diffusivity of the diffusion couples. When the mechanically prepared diffusion couples are heated, the in situ reactions can be activated, causing exothermic peaks at low temperature.

Conclusions

From these results, the following conclusions can be drawn:

1. For the ductile/brittle Al–Cu–Si/SiO_2 powder mixture, no new phase was generated during high energy ball milling, but it was transformed into a composite powder with numerous diffusion couples consisting of nano-sized SiO_2 particles embedded in the Al (Si, Cu) alloy matrix. With an increased milling time, the composite particle size decreased, and the volume fraction of diffusion couples increased
2. For the as-mixed powder, no reaction between the original phases occurred during the DTA run. The displacement reaction between Al and SiO_2 in the Al/SiO_2 diffusion couples of the as-milled powders was activated at low temperatures, and the exothermic peak was located in the temperature range of 640–680 °C, which is much less than the temperature of >1000 °C which is required for the processes which are currently used to produce Al matrix composites reinforced with ceramic Al_2O_3 particulates. Therefore, an Al–Cu–Si matrix composite reinforced by submicron sized, homogeneously distributed Al_2O_3 particulates can be fabricated by low-temperature sintering

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