JTTEE5 13:214-222
DOI: 10.1361/10599630418130
1059-9630/$19.00 © ASM International

Peer Reviewed

Al-SiC Powder Preparation for Electronic Packaging Aluminum Composites by Plasma Spray Processing

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(Submitted 4 September 2002; in revised form 10 December 2002)

Powders of pure aluminum (Al) with 55 and 75 vol.% SiC particles were ball milled in a conventional rotating ball mill with stainless steel and ZrO_2 balls for 1-10 h. The morphology and microstructure of the milled powders have been observed and analyzed by scanning electron microscopy (SEM) and energy dispersive x-ray (EDX). The milled powders were plasma sprayed onto a graphite substrate to obtain Al matrix composites with high SiC volume fraction. SiC particles in the milled powders existed in two forms; i.e., the combination of Al into composite powder and individual. Plastic Al particles were broken during ball milling, and fine Al particles can be coated onto the surface of SiC particles. Iron contamination in the milled powders occurred when stainless steel balls were used. The iron level can be effectively controlled by using ZrO_2 ball media. The milling efficiency by ZrO_2 balls is inferior to that by stainless steel balls. Longer milling time was required with ZrO_2 balls to achieve the same effect as obtained with stainless steel balls. SiC particles in the sprayed composites from the milled powders exhibited a reasonably uniform distribution and high volume fraction.

Keywords aluminum matrix composite, ball milling, plasma spraying, powder, silicon carbide particle

1. Introduction

There are several requirements to be considered for electronic packaging, such as low coefficient of thermal expansion (CTE), superior thermal conductivity, and high elastic stiffness. These properties can be reasonably well realized in the Al/SiC composite systems by tailoring the aluminum (Al) alloy and SiC parameters based on these requirements. In addition, Al/SiC composites have low density as a superior character, in contrast to the conventional package materials, such as Invar, Kovar, and W/Cu alloys. Thus, Al/SiC composites, especially SiC particle reinforced Al matrix composites, have emerged as a novel electronic package material.[1-4] For applications of Al/SiC composites in electronic packaging, 60-65% SiC volume fraction in the composites is necessary to obtain close CTE matching between the composites and integrated circuits and electronic components.

Plasma spray processing has been used to produce particle-reinforced Al matrix composite (AMC) coatings.[5-10] This process is also a feasible way of producing bulk, near-net-shape form of AMCs.[11-14] Besides plasma spray parameters, powder preparation is also an important step, especially for a multi-element powder consisting of an Al and SiC mixture. In practice, SiC particles always appeared to be preferentially lost compared with the metallic Al particles during plasma spraying if the feedstock was prepared by blending SiC with Al particles. This phenomenon is more seriously demonstrated for a powder with high SiC level. Meanwhile, the further increase of the level of SiC particles in the feedstock no longer increases the SiC volume fraction in the sprayed composites when the SiC level in the feedstock exceeds some value. Excess SiC particle added onto the feedstock to compensate for the SiC loss in the sprayed composite is not an effective way, especially for high SiC level powders. This behavior is probably related to the large difference in melting temperatures between SiC and Al, and poor wettability of SiC by Al. Thus, the volume fraction of SiC particles in the sprayed composites is less than that in the original powders. Therefore, the loss of SiC particles should be effectively controlled if the plasma spray process is expected to be as an effect method to produce AMCs with high SiC volume fraction as electronic packaging.

Mechanical alloying (MA), or ball milling processes[5,10,15-19] have been widely used to prepare powders for fabricating AMCs or AMC coatings with particle reinforcement, such as SiC particles, by powder metallurgy or by the plasma spray process. During ball milling, two essential processes can happen to the powders. The constituent powder particles are repeatedly fractured and subsequently cold-welded. In a metal-ceramic system, the hard ceramic particles do not undergo any cold welding, and may be trapped into the soft metal matrix. Ball milling enables powders with a homogenous structure to be obtained; hence improving the uniformity of SiC particle distribution in the Al matrix in the final solid materials. However, most work performed in this field was related to relatively low SiC volume fractions. In this study, pure Al powders with 55 and 75 vol.% SiC particles were synthesized by ball milling, and the milled powders were plasma sprayed to form free-standing bulk composites. The aim of the present work is to improve uniformity of SiC particle distribution and to increase the SiC volume fraction in

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Table 1 Ball Milling Conditions

Classification	Condition
Mill jar	Stainless steel
Milling media	Stainless steel, ZrO_2
Atmosphere	Air
Weight ratio of media to powder	10:1
Mill times	1–10 hrs
Mill speed	90 rpm

Table 2 Conditions for Plasma Spraying Process

Parameters	Al-55SiC	Al-75SiC
Voltage, V	50	70
Current, A	400	500
1st gas, Ar, l/min	52	52
2nd gas, H_2, l/min	1.5	7.5
Powder feed rate, g/min	20	20
Spray distance, mm	100	100

the plasma sprayed composites by employing feedstocks prepared by ball milling.

2. Experimental Procedures

The 99.7 wt.% pure Al powders with an average size of 45 μm were used as matrix material. The reinforcement material was SiC particles with an average size of 17 μm. Al powders with 55 and 75 vol.% SiC particles; i.e., Al-55SiC and Al-75SiC powders, were prepared by ball milling process. Stearic acid of 1.5 wt.% was added as a process control agent (PCA). The mill jar, made of stainless steel, was a cylindrical container of 3.8 L with an inner diameter of 157 mm. The ball milling process was carried out in a conventional rotating ball mill. The jar containing ball media and powder was put on two horizontal rollers, and driven by them on a rotating run. For all experiments to prepare feedstock, the jar was kept at the same rotational speed of 90 rpm, which corresponds to 84% of its critical rotational speed (a speed in which centrifugal motion occurs for milling balls). This critical rotational speed N_c was calculated by formula: $N_c = 42.3D^{-0.5}$, where D is the diameter of a jar in meters.[20] The stainless steel balls were 16 mm in diameter, whereas a mixture of 10 and 15 mm diameter ZrO_2 balls were used. The milling balls were occupied half the volume of the jar. The feedstock processing size when using stainless steel balls was 800 g, while it was 600 g when using ZrO_2 balls. The ball milling lasted different times. Ball milling conditions are summarized in Table 1. The Al-55SiC and Al-75SiC powders were also prepared by a blending process for a comparative analysis.

The ball-milled powders were analyzed with a JEOL 8600 (Tokyo, Japan) scanning electron microscope (SEM) equipped with energy dispersive x-ray (EDX) analysis. Prior to plasma spraying, the stearic acid and moisture were drawn off from the ball-milled powders by treating at 150 °C for 4 h under an air atmosphere. Powder agglomerations formed at the dry treatment were destroyed by sieving to a final size of 80 mesh. Atmospherical plasma spraying (APS) was carried out using LCP REM.A type Sulzer Metco (New York, NY) plasma equipment. The composites were deposited onto graphite substrates and then mechanically removed to obtain freestanding plates. The sprayed composite plates are 100 × 100 mm and about 2 mm in thickness. Plasma spray conditions are listed in Table 2. Specimens for microstructural observation were prepared from the cross sections of the composite plates. A Nikon Epiphot 200 optical microscope attached with image analysis (IMT2.0™, IMTechnology, Co. Ltd., Daejeon, Korea) was used to observe microstructure and to quantitatively evaluate the SiC volume fraction and porosity in the composites. Three samples and five random areas for each sample were tested for the evaluation of SiC and porosity levels.

3. Results and Discussion

3.1 Powder preparation and analyses

The morphologies of the Al and SiC powders are shown in Fig. 1. The Al powders demonstrate a spherical morphology, whereas the SiC particles are angular with smooth facets.

SEM micrographs in Fig. 2 show the typical morphologies of the milled powders with 55 vol.% SiC_p by stainless steel ball at milling time of 3 and 5 h. It can be seen from Fig. 2(a) and 2(d) that the ball milled powders are composed of larger particles and some small particles. The larger powders are composite in nature and consist of SiC and plastic Al (Fig. 2b and 2e). The amount of SiC in the composite powders by EDX quantitative analysis was found to increase with milling time. Small particles were mostly individual SiC particles, while a few Al particles were also found. Al powders tend to be broken and become fine during the milling process. In general, Al powders with an average initial size of 45 μm were reduced to about 5 μm after 5 h. From Fig. 2(c) and 2(f), it can be found that the broken fine Al powders can be attached onto the surface of SiC particles, and the amount of the fine Al powders on the surface increases with increasing milling time. Observation of milled powders indicates that the SiC particles did not undergo significant fracture as exhibited by the Al particles. These features are also reflected in the microstructures of the sprayed composites.

The powders with 75 vol.% SiC_p milled by stainless steel balls have similar characteristics to those with 55 vol.% SiC_p. The amount of large composite powders in the milled powders was, however, evidently less than that in the case of 55 vol.% SiC_p. Figure 3 shows the typical morphologies of the milled powders with 75 vol.% SiC_p by stainless steel ball at milling times of 5 and 10 h. Regarding ZrO_2 ball milling, morphology and structure of the milled powders are compatible to those milled by stainless steel balls irrespective of SiC levels. It should be mentioned, however, that Al particle fracture and the attachment of fine Al particles to the surface of SiC proceed slowly in the ZrO_2 ball milling process compared with the milling process with stainless steel balls. This effect arises due to different material densities between stainless steel and ZrO_2.

Ball milling consists of two movement processes. One is relative rolling and friction occurring between the balls and the inner wall of jar. The other is collision between balls. The latter is a more effective way to fracture and cold weld particles. The rotational speed determines the dominant movement process during ball milling. In the present work, the collision process dominates because a high rotating speed was used. During ball milling, plastic Al particles are deformed and hardened, and hard SiC particles are random inserted into the Al particles

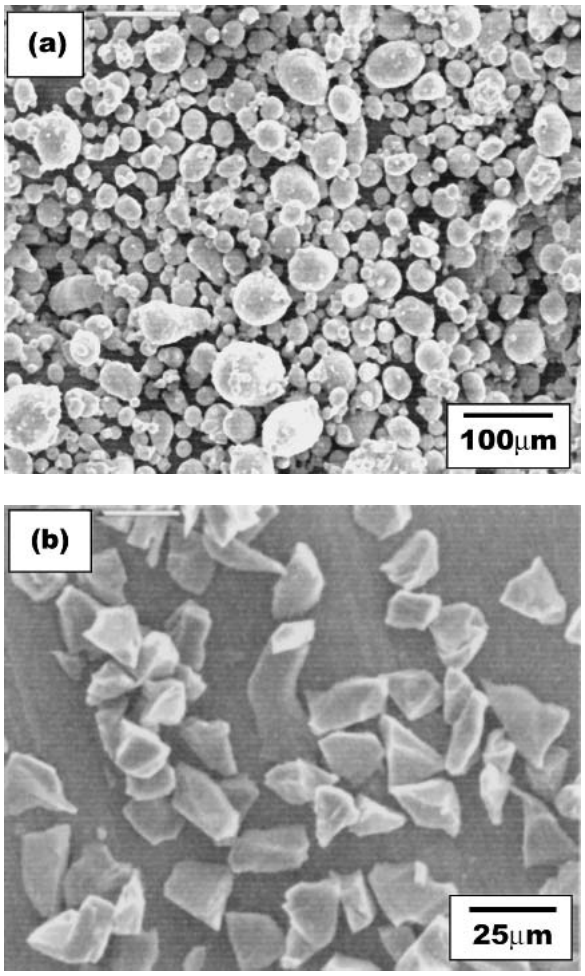

Fig. 1 Morphologies of initial particles of **(a)** pure Al and **(b)** SiC

due to the collision between balls. The SiC particles entrapped into the Al particles would form the composite powders. The hard SiC particles may also function as a micro-cutter to cleave plastic Al particles into smaller ones. In addition, due to deformation and work hardening, the Al particles would be broken after some repeated collisions. The collisions during milling can create cold welding between Al particles together with SiC particles and provide another way to form composite powders in the milled powder. The fine Al particles can be cold welded onto the surface of SiC particles (Fig. 2c and 2f). The attachment of fine Al particles onto the SiC surface in the milled powders would improve the wettability of SiC by Al, promoting a uniform SiC distribution and high SiC volume fraction in the sprayed composites. Therefore, this phenomenon during ball milling is quite important for plasma sprayed composites. To evaluate this phenomenon, some micro areas, where only individual SiC particles can be seen, with a high magnification of 2000 times under SEM observation were chosen and analyzed quantitatively by EDX. Figure 4 shows the Al levels with ball milling time obtained in this way for Al-55SiC and Al-75SiC powders demonstrating the attachment degree of fine Al particles onto the surface of SiC particles. In general, stainless steel balls can facilitate more Al particles to be attached on the SiC surface for the same milling time as ZrO_2 balls. From this viewpoint stainless steel balls demonstrate a better milling efficiency than ZrO_2 balls.

There is an iron increase in the milled powders when stainless steel balls were used as milling media. The iron (Fe) level in the milled powders was analyzed by EDX under 100 times magnification. Figure 5 shows the Fe levels in the powders milled by stainless steel and ZrO_2 balls with respect to the ball milling time. In the case of stainless steel balls, a certain amount of Fe in the milled powders can be detected by EDX analysis. The level of Fe increased significantly with milling time and exceeded 5 wt.% after 7 h milling time. This Fe contamination would perhaps degrade certain physical properties of the sprayed composites, such as the thermal conductivity. Besides primitive content in raw materials, the Fe in the milled powders came from the ball media and milling jar due to their abrasive grinding with hard SiC particles. The Fe level can be effectively controlled to about 0.5 wt.% by using ZrO_2 balls irrespective of milling time. However, a small amount of Zr in the milled powders can be also found, which originates from the ZrO_2 milling media. Figure 6 shows the Zr level in the ZrO_2 ball milled powders with ball milling time using the same EDX analysis mentioned above.

Regarding the function of PCA, it has been reported that the addition of PCA reduces the rate of cold welding and promotes fracture of Al particles.[5,15] Therefore, PCA may affect the size spectrum of milled powders and the homogeneity of distribution of SiC in the Al matrix. In the present ball milling process, PCA not only promoted significantly Al particle fracture but also promoted finer Al particles to be attached to the surface of SiC particles. The same powders with 75 vol.% SiC without PCA were milled with stainless steel and ZrO_2 balls for 10 h for comparison purposes. As a result, only 10.1 and 4.75 wt.% Al were detected on the SiC particles without PCA by EDX analysis, while 21.6 and 14.3 wt.% with PCA for stainless steel and ZrO_2 balls, respectively, under the same milling conditions.

Figure 7 indicates x-ray diffraction (XRD) patterns of blended and milled powders with 55 and 75 vol.% SiC particles. The milling time was 5 and 10 h for Al-55SiC and Al-75SiC powders, respectively. It was found that ball milling minimally changed peak spectrums under comparison with the blended mixture; especially for Al-55SiC powders milled for 5 h. For the Al-75SiC powders, the last two peaks from high crystal plane index of Al were weaker and broadened, indicating Al particles to be finer to a certain extent after 10 h milling. It is difficult to determine whether pure Fe phase exists in the powders milled by stainless steel balls because three main peaks from pure Fe phase are coincident with peaks of pure Al phase in the XRD pattern.

It has been found that milling time has a significant influence on SiC distribution and volume fraction in the spray formed composites. In the present milling conditions, 3–5 h milling times are necessary to obtain uniform SiC distribution and high SiC volume fraction for Al-55SiC powders, and 5–7 h for Al-75SiC powders. Among them, stainless steel ball milling can be successful in a relatively short time, while ZrO_2 ball milling should use relatively long times because the milling efficiency is inferior to that of stainless steel balls.

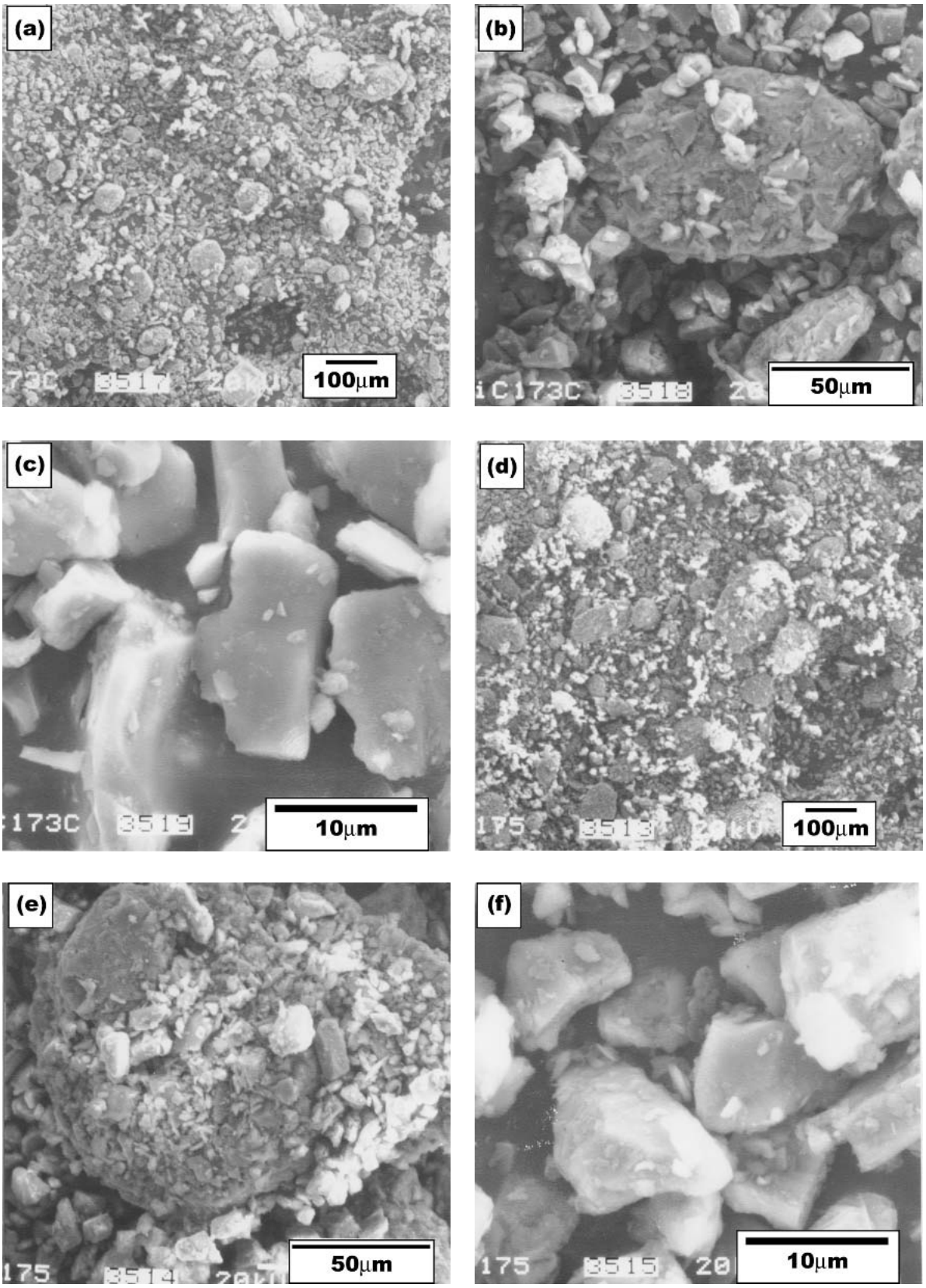

Fig. 2 SEM micrographs showing morphologies of stainless steel ball milled Al-55SiC powders at milling time of 3 and 5 h: **(a)** low magnification, **(b)** showing composite powder, and **(c)** showing SiC_p state for 3 h milling time; **(d)** low magnification, **(e)** showing composite powder, and **(f)** showing SiC_p state for 5 h milling time

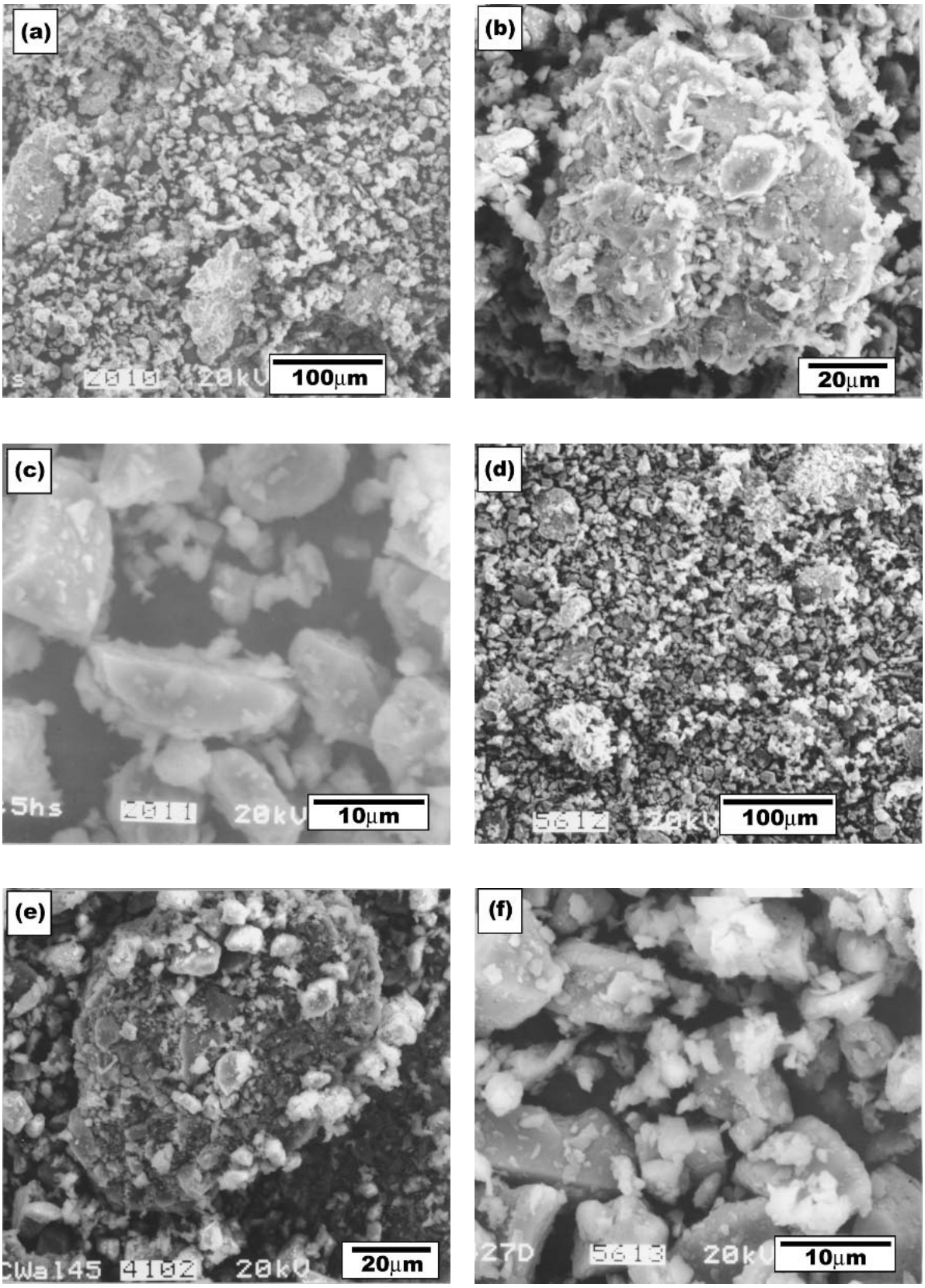

Fig. 3 SEM micrographs showing morphologies of stainless steel ball milled Al-75SiC powders at milling time of 5 and 10 h: **(a)** low magnification, **(b)** showing composite powder, and **(c)** showing SiC_p state for 5 h milling time; **(d)** low magnification, **(e)** showing composite powder, and **(e)** showing SiC_p state for 10 h milling time

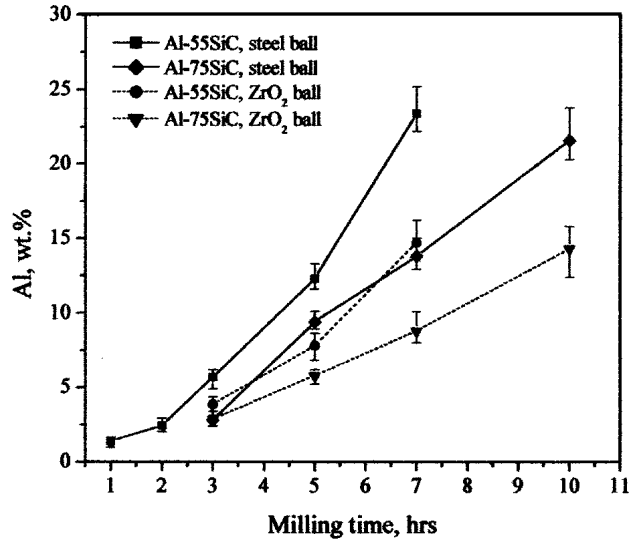

Fig. 4 Attachment degree of aluminum on the SiC surface with milling time for Al-55SiC and Al-75SiC powders

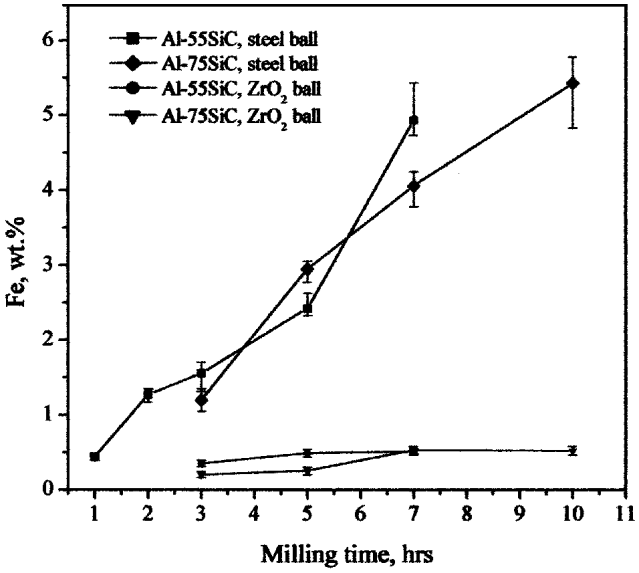

Fig. 5 Fe levels in the powders milled by stainless steel and ZrO_2 balls with milling time by EDX analysis

3.2 Sprayed Composite Characteristics

The ball-milled powders have been used as feedstock for the plasma spray process. The plasma spray test was carried out repeatedly with the conditions shown in Table 2. Figure 8 and 9 show the microstructures of composites sprayed from Al-55SiC and Al-75SiC powders, respectively.

In the composite sprayed from Al-55SiC powders, SiC particles exhibit a uniform distribution and SiC volume fraction is about 50–55% with a lower porosity of about 1–2%. In the composite sprayed from Al-75SiC, the distribution of SiC particles is also reasonably uniform. And SiC volume fraction is about 65–70% with a relatively high porosity of 4–6%. The SiC volume

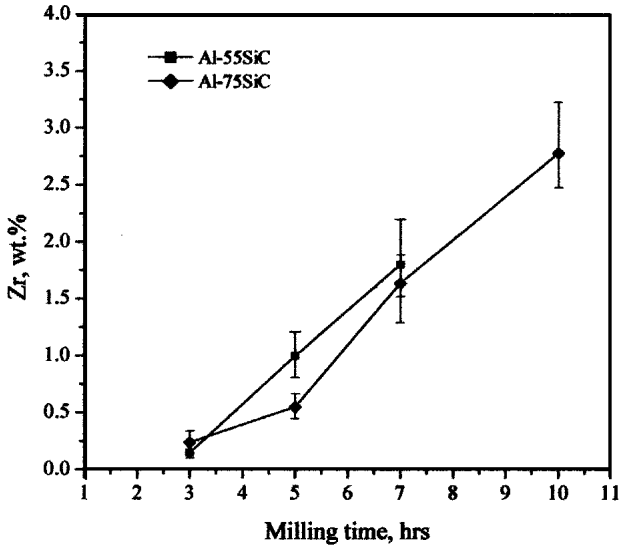

Fig. 6 Zr level in the ZrO_2 ball milled powders with ball milling time by EDX analysis

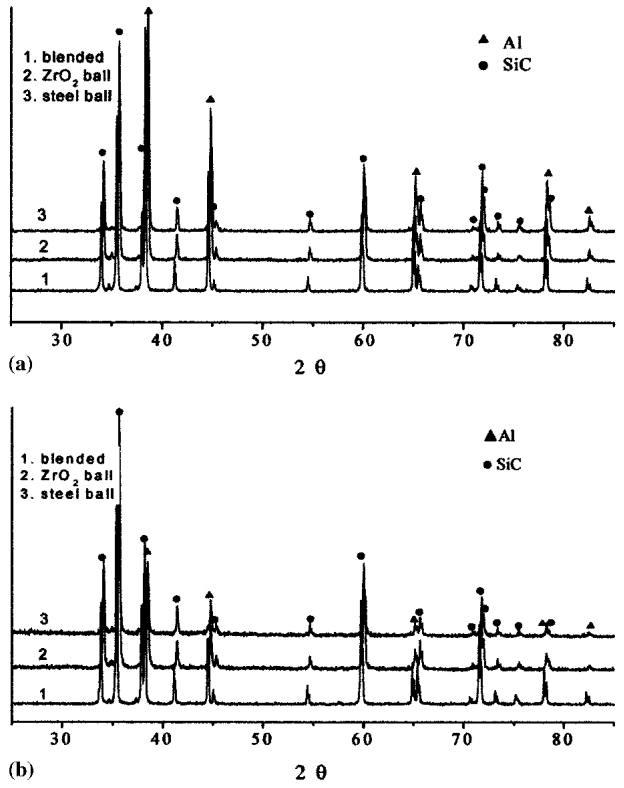

Fig. 7 XRD patterns of blended powders and milled powders by stainless steel and ZrO_2 balls: **(a)** Al-55SiC powders, milling time 5 h and **(b)** Al-75SiC powders, milling time 10 h

fraction in the composite sprayed from Al-55SiC powders is close to that in the original powders, whereas it is 5–10 vol.% less than the original powders in the composite sprayed from Al-75SiC powder. Figure 10 shows the SiC volume fractions and porosity of the composites sprayed from Al-55SiC and

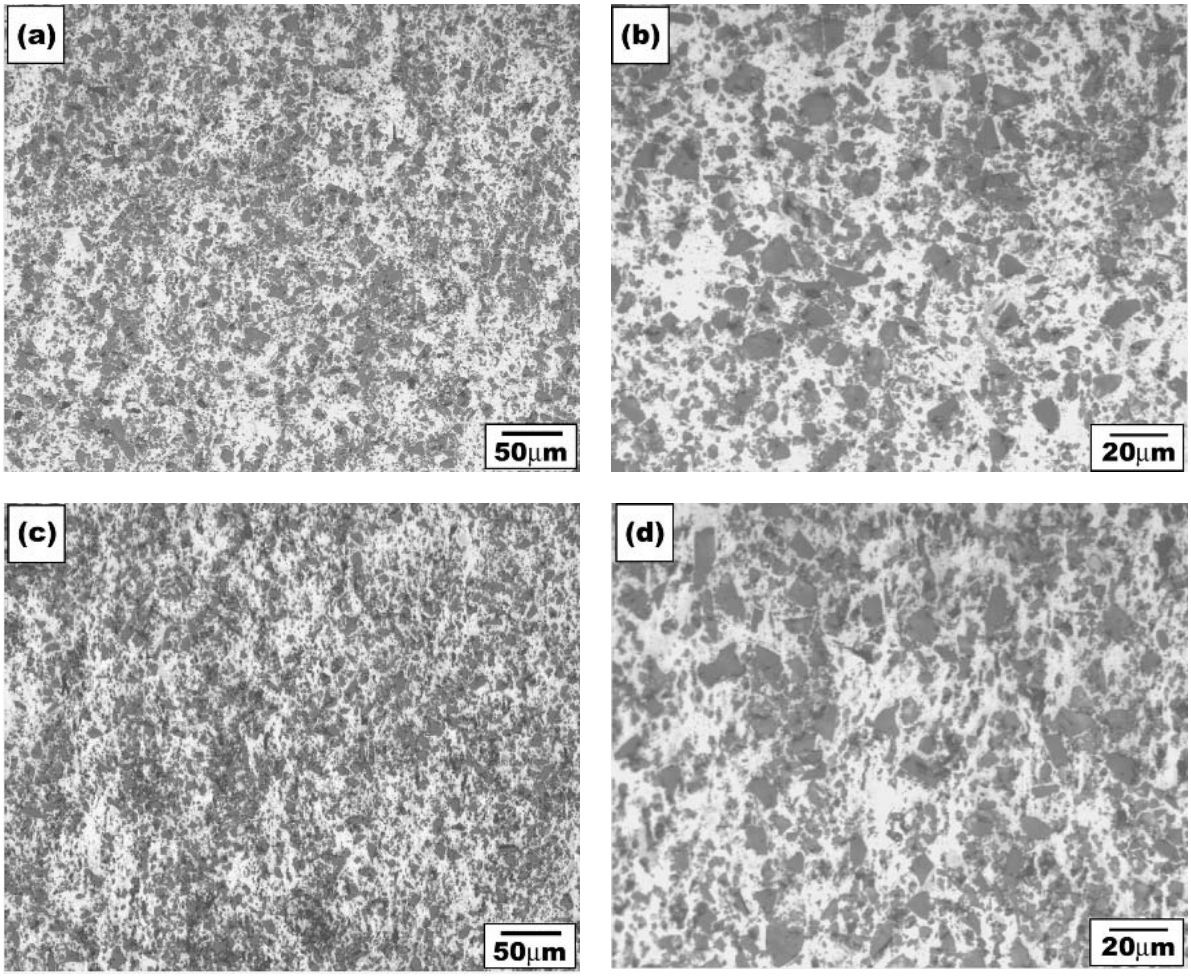

Fig. 8 Microstructures of composites sprayed from milled Al-55SiC powders: **(a)** low magnification and **(b)** higher magnification by stainless steel ball for 3 h; **(c)** low magnification and **(d)** higher magnification by ZrO_2 ball for 5 h

Al-75 SiC powders. At the present experiments, the sprayed composite plates were formed through repeated plasma spray deposition, and consisted of a couple of sprayed layers. A pore in the composites may appear inside layer or be located at the border between two layers. As for the inside layer pore, it was formed due to the deficiency in the flow and filling of liquid Al. The surface of the sprayed layer was relatively rough. Pores would be formed in the layer interface when gaps on the sprayed surface cannot be filled or compacted during next plasma spray deposition. The high porosity in the composites sprayed from Al-75SiC powders is related to inner-layer solidification and interlayer bonding characteristics. Due to more SiC particles in the sprayed composite of Al-75SiC powder than Al-55SiC powder, the flow and filling of liquid Al becomes difficult, resulting in the increase in the inner-layer porosity. In addition, the composite sprayed from Al-75SiC powder possesses larger stiffness; the filling of the spraying feedstock into the gaps on the sprayed surface becomes difficult, meanwhile the probable compaction of the gaps is also prohibited, which is created from local deformation because the high-speed feedstock clashes. These factors can result in higher interlayer porosity in the sprayed composite of Al-75SiC powder. The porosity in the sprayed composites may be reduced by a post-treatment process, such as hot isostatic pressure (HIP). This study will be carried out in the future.

4. Conclusions

The Al-55SiC and Al-75SiC powders were milled by stainless steel and ZrO_2 balls in a conventional rotating ball mill for 1-10 h. The milled powders were plasma sprayed onto graphite substrates, and Al matrix composites with high volume fraction and uniform distribution of SiC particles have been obtained. The following conclusions can be drawn:

1. There are two existing forms of SiC particles in the milled powders; i.e., the combination of Al into composite powder and individual. Plastic Al particles are broken during ball milling, and fine Al particles can be coated onto the surface of SiC particles.
2. The Fe contamination occurs to the milled powders when stainless steel balls are used. A certain amount of Fe can be detected in the stainless steel ball milled powders by EDX analysis, and it increases significantly with milling time. The Fe level can be effectively reduced by using

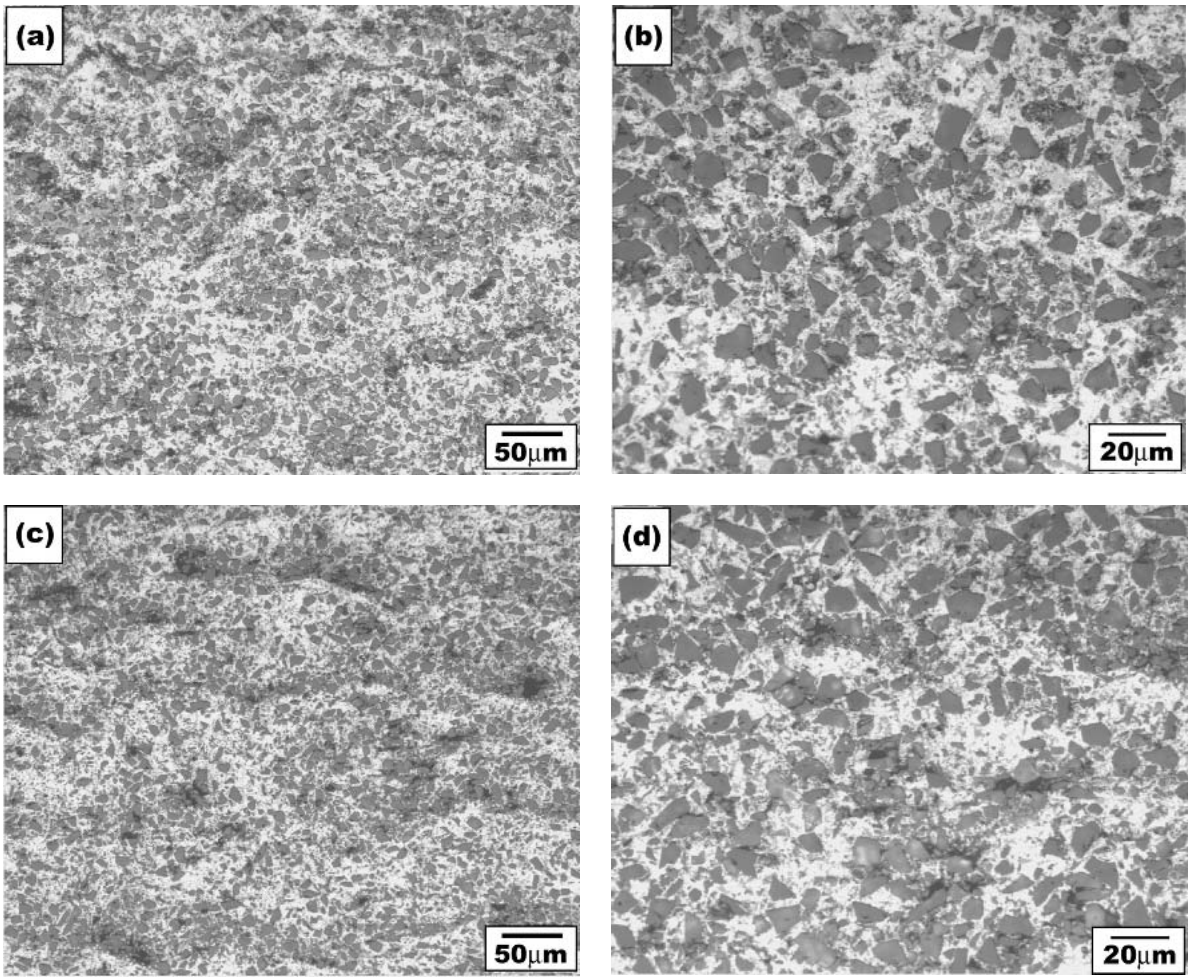

Fig. 9 Microstructures of composites sprayed from milled Al-75SiC powders: **(a)** low magnification and **(b)** higher magnification by stainless steel ball for 5 h; **(c)** low magnification and **(d)** higher magnification by ZrO_2 ball for 7 h

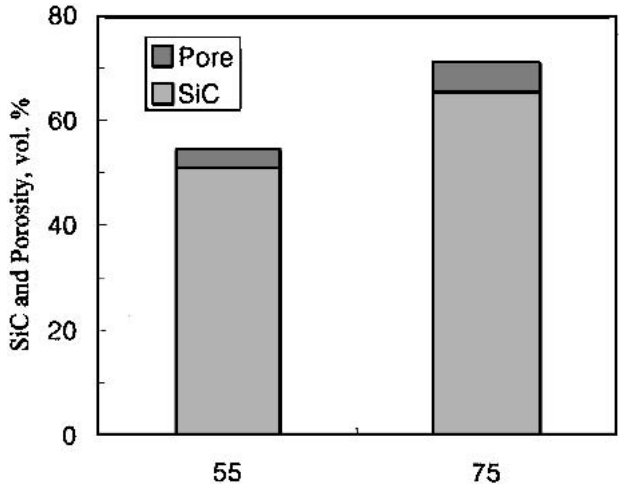

Fig. 10 SiC volume fractions and porosity in the composites sprayed from of 55 vol.% SiC_p and 75 vol.% SiC_p

ZrO_2 balls. A small amount of Zr can be detected in the powders milled by ZrO_2 balls.

3. The milling time of 3–5 h is necessary to obtain a uniform SiC distribution and high SiC volume fraction for Al-55SiC powders, and the milling time for Al-75SiC powders is 5–7 h. Stainless steel ball milling is appropriate for relatively short processing times, while ZrO_2 ball milling requires a relatively long time since the milling efficiency by ZrO_2 balls is inferior to that by stainless steel balls.
4. The SiC particles exhibit a reasonably uniform distribution in the composites sprayed from the milled powders. The SiC volume fraction is about 50~55% in the composite sprayed from milled Al-55SiC powders and about 65–70% from milled Al-75SiC powders.

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