Effect of CuO Particle Size on the Microstructure Evolution of Al₂O₃p/Al Composites Prepared Via Displacement Reactions in the Al/CuO System

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Abstract An Al₂O₃p/Al composite was successfully synthesized using a displacement reaction between 80 wt% Al and 20 wt% CuO powders at a heating rate of 5 °C/min. Two different sizes CuO particles were used, and all the experiments were conducted under an argon atmosphere. To analyze the microstructural evolution during synthesis, the Al–20 wt% CuO samples were heated to the temperatures selected according to the differential scanning calorimetry curve and then immediately quenched with water. The phase composites and microstructure of the water-quenching samples were investigated using X-ray diffraction, optical microscopy, scanning electron microscopy and energy-dispersive spectrometry. The results indicate that the CuO particle size has a significant effect on the microstructural evolution of the samples during the heating stage and on the microstructure of synthesized composites. Smaller CuO particles can decrease the reaction temperature, narrow the reaction temperature range at the different reaction stages during the heating stage and make the size and distribution of in situ Al₂O₃ particles more uniform. The reaction between Al and CuO can be complete as the temperature rises to 900 °C. The size of the in situ Al₂O₃ particles is approximately 5 μm when the size of the CuO particles is less than 6 μm. This sample has a relatively high Rockwell hardness of 60 HRB.

KEY WORDS: Al₂O₃p/Al composite; Displacement reaction; CuO particles; Particle size; Microstructure evolution

1 Introduction

Particle-reinforced aluminum-based metal matrix composites (Al-MMCs) are of interest in various applications such as the aerospace, military, electronic devices and automobile industries due to their high specific strength and stiffness, good wear resistance, a low thermal expansion coefficient and traditional preparation processes [1–4]. In situ synthesis has been extensively utilized to produce particle-reinforced metals for strong interfacial contact

between the reinforcement and the Al matrix, effective control of the size of the in situ particles as well as the level of reinforcement, which yields better tailorability of the properties [5]. One commonly adopted in situ method involves a reaction between Al and a metal oxide, such as CuO [6], Fe₂O₃ [7], Ti₂O [8] and ZnO [9], to produce Al₂O₃ particle reinforcements. CuO is one of the most widely used metal oxides because fine in situ Al₂O₃ particles can be successfully synthesized in the Al/CuO systems and the reduced Cu can react with Al to form intermetallic phases that can act as reinforcements in the composite matrix [10].

The reaction mechanism of the Al/CuO system has been studied extensively. It is generally accepted that there are two main chemical reactions during synthesis: $6\text{CuO} + 2\text{Al} = 3\text{Cu}_2\text{O} + \text{Al}_2\text{O}_3$ and $3\text{Cu}_2\text{O} + 2\text{Al} = \text{Al}_2\text{O}_3 + 6\text{Cu}$ [11], but the chemical reaction can be

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explained as $\text{CuO} + \text{Al} \rightarrow \text{Cu} + \text{Al}_2\text{O}_3$ when the reduction rate is sufficiently high [12]. Reaction rate increases as the sintering time increases [11]. As the sintering time increases, reaction rate increases and the dissolution of CuO and the precipitation of Al_2O_3 is more rapid, which results in the formation of fine Al_2O_3 particles [12, 13]. During the reaction, amorphous Al_2O_3 is formed below 700 °C and crystallized Al_2O_3 particles at 900 °C [14]. These studies also revealed that in situ Al_2O_3 particles segregated in the eutectic structure due to the redistribution of the particles during solidification. However, as previous studies were focused on the microstructures of the samples that were synthesized, the microstructural evolution during the reaction has not been dynamically observed and the effect of the CuO particle size on the microstructure of the composite has not been reported.

In this study, the Al–20 wt% CuO samples were heated to temperatures selected according to a differential scanning calorimetry (DSC) curve and then immediately quenched with water. The objective was to study the effect of the CuO particle size on the microstructural evolution that occurs during the reaction and on the microstructure of $\text{Al}_2\text{O}_3/\text{Al}$ composites.

2 Experiments

All of the experiments were carried out with a powder mixture containing 80 wt% Al and 20 wt% CuO for the preparation of the in situ composite. Two different particle sizes of CuO powders (referred to as CuO I and CuO II, AR) and one Al powder (<50 µm, AR) were used as the raw materials. The particle sizes of the CuO powders were less than approximately 6 and 50 µm for CuO I and CuO II, respectively. The powder mixture was milled using a planetary mill (QM-BP) at 40 RPM for 2 h and then cold pressed under 400 MPa of pressure to form compact disks with a diameter of 10 mm.

Differential scanning calorimetry (DSC) (Netzsch STA409 PC) was conducted to determine the Al/CuO reaction temperatures. Two pieces of the samples (ϕ 4.0 mm $\times$ 1.0 mm) were obtained from two different (CuO + Al) green compacts (corresponding the two different CuO powders). These two sample pieces were heated at an argon atmosphere in the differential scanning calorimeter where the temperature was increased from ambient temperature to 900 °C at a heating rate of 5 °C/min.

The green samples were heated in a tube furnace under an argon atmosphere and immediately quenched with water at the selected temperature according to the DSC curves, and two other green samples (corresponding the two different CuO powders) were synthesized at 900 °C for 1 h to compare the microstructure with water-quenching samples

heated to 900 °C. X-ray diffraction (XRD, D/MAX-2500/PC, 40 kV, 20 mA, Cu-K α radiation), optical microscopy (MO), scanning electron microscopy (SEM) and energy-dispersive spectrometry (EDS) were used to investigate the phase and microstructure in all water-quenching samples.

3 Results and Discussion

3.1 DSC Results

The DSC curves of the two Al–20 wt% CuO samples are shown in Fig. 1. An independent exothermic peak was observed between 540 and 620 °C, which is not in agreement with previous results [9, 11, 12, 15]. Although these studies indicated that the initial reaction occurred as a solid–solid reaction, the corresponding exothermic peak partially overlaps with the aluminum melting peak in their results.

An endothermic peak appears at approximately 670 °C, which corresponds to the melting of Al. The CuO particle size does not influence the melting of Al at the same heating rate. The second exothermic peak is located in the temperature range below 720 and 750 °C for CuO I and CuO II, respectively, and this peak partially overlaps with the endothermic peak of Al, which is similar to previous results [9, 11, 12, 15]. Two additional independent exothermic peaks were observed at 740–800 and 830–900 °C in the CuO I DSC curve. However, only one independent exothermic peak was observed at 760–900 °C in the CuO II DSC curve.

It is obvious that the CuO particle size has a significant effect on the reaction of Al/CuO during heating stage, especially when the temperature is higher than the melting point of Al. To analyze this effect, four CuO I green samples were heated to 620, 710, 790 and 900 °C, three CuO II green samples were heated to 620, 740 and 900 °C, and all samples were water quenched.

Fig. 1 DSC curves of the CuO I and CuO II samples at a heating rate of 5 °C/min

3.2 XRD Results

The diffraction patterns of the green sample and the sintered samples are shown in Fig. 2. Only peaks that correspond to Al and CuO are observed in the pattern from the green sample (Fig. 2a).

The XRD results for the CuO I sample are shown in Fig. 2b–e. In the XRD result for the sample heated to 620 °C (Fig. 2b), the peaks corresponding Al, CuO and Cu₂O were observed. When the green sample was heated to 710 °C (Fig. 2c), the products of the reaction are Cu₂O and Cu. Only the Al₂Cu and Al phases appear in the 790 °C sample (Fig. 2d), which means that the reducing reaction of Al/CuO is complete at this temperature. However, the phase containing O was not detected during XRD analysis. The results in Fig. 2e indicate that Al₂O₃ is present in the sample heated at 900 °C, which suggests that the fourth exothermic peak in the DSC curve corresponds to the crystallization temperature of amorphous Al₂O₃.

The CuO II samples heated at 620 and 740 °C exhibit diffraction patterns that are similar to the CuO I samples heated at 620 and 710 °C, respectively. Therefore, the corresponding diffraction patterns are not shown. The results in Fig. 2f indicate that the sample heated at 900 °C contains Al₂Cu, Al₂O₃ and Al. The relative intensity of the Al₂O₃ diffraction peaks is much lower than that shown in Fig. 2e.

In the XRD patterns of the samples sintered at higher temperatures, the peaks corresponding Al are slightly shifted to higher angles compared with those in the XRD

pattern of the green sample. It should be noted that the location of the diffraction peak depends on the crystallite size [16], which suggests that the Al lattice parameters in the samples decreased after synthesis. The calculated values of the Al lattice parameters in the different samples are listed in Table 1. The calculated lattice parameter of the Al matrix in the green sample was 0.405375 nm. In comparison with the lattice parameter ($a = 0.40497$ nm) in the PDF card, there is some deviation. The Al lattice parameters in the CuO I samples heated at 620 and 710 °C are 0.40535 and 0.405327 nm, respectively, and the Al lattice parameters in the CuO II samples heated at 620 and 740 °C are 0.405287 and 0.405300 nm, respectively. It is reasonable to postulate that Cu does not dissolve into the Al at lower temperatures because these four values are very similar. However, at the 790 and 900 °C for CuO I samples, as well as at 900 °C for CuO II sample, the changes in the lattice parameter are relatively large. The lattice parameters for these samples are 0.404407, 0.404423 and 0.404883 nm, respectively. Because both Al and Cu have face-centered cubic structures and the difference between their lattice parameters is not very large, Cu has a relatively high solubility in Al. Based on the deviation of the calculated lattice parameters, the accurate solubility of Cu in Al has not been calculated. However, the trend in the change in the lattice parameters can be estimated according Vegard's law (i.e., at high temperatures during the heating stage, Cu dissolves into the molten Al).

Fig. 2 Phase analysis of the green sample and evolution of the phases in the samples heated at different temperatures and then immediately water quenched: **a** green sample; **b–e** XRD results for the CuO I sample heated at 620, 710, 790 and 900 °C, respectively; **f** CuO II sample heated at 900 °C

Table 1 Lattice parameters of the Al (0.1 nm) in the matrix of the Al–20 wt% CuO samples heated to different temperature [$a = 0.40497$ nm for pure Al Ref. Swanson, Tatge, Natl. Bur. Stand. (U.S.), Circ. 539, 1, 11 (1953)]

Temperature	Green sample	620 °C	710 °C	740 °C	790 °C	900 °C
CuO I	4.05375	4.053504	4.05327		4.04407	4.04423
CuO II	4.05375	4.05287		4.05300		4.04883

Fig. 3 SEM images of the CuO I **a** and CuO II **b** green samples. The corresponding size of the CuO particles is less than approximately 6 and 50 μm. **c** Optical micrograph of the Al matrix formed by the Al particles

3.3 Microstructure

3.3.1 Green Sample

The microstructures of the CuO I and CuO II green samples are shown in Fig. 3a, b. The bright patches are the CuO particles, and some of these particles form clusters. Figure 3c shows an optical micrograph of the Al matrix formed by the Al particles. The CuO particles and clusters are distributed between the Al particles. Nearly all of the Al particles are in contact with CuO particles in the CuO I sample, and there is direct contact between most of the Al particles in the CuO II sample.

3.3.2 Microstructures of the Water-Quenched CuO I Samples

The microstructures of the CuO I samples heated at 620, 710, 790 and 900 °C are shown in Fig. 4. The sizes of the bright patches in the samples heated at 620 and 710 °C are similar to that observed in the green sample (Fig. 3a). Based on the XRD result, these bright patches consist of Cu₂O and CuO in the sample heated to 620 °C and Cu₂O and Cu in the sample heated to 710 °C. In contrast to the green sample, some small dark patches appear and attach themselves to the bright patches in the two samples and a bright network appears in the latter. To determine the elemental composition of the black patches, an EDS map was prepared (Fig. 5), and the results indicate that these dark patches primarily contain O and Al. The O concentration in the black patches is higher than that in the bright

patches. The phase containing the Al and O elements could not be detected by XRD, which may be due to its relatively low content or amorphous phase. The results in Fig. 5 also indicate that the bright network is composed of Cu and O elements, which indicate that a portion of the Cu and O that was reduced by reducing CuO was located on the boundaries of the Al particles.

The bright patches consisting of Cu₂O and Cu do not appear, and only many black patches containing Al and O elements appear in the sample heated to 790 °C (Fig. 4c). The corresponding phase containing the Al and O elements were not detected by XRD (Fig. 2d). Other studies [12, 13, 15] confirmed the presence of amorphous Al₂O₃ before Al₂O₃ particles are formed, which postulate that the black patches are amorphous Al₂O₃. The size and distribution of the amorphous Al₂O₃ are similar to that of the CuO particles and clusters in the green sample (Fig. 3a), which indicates that most of the O atoms in the CuO particles were incorporated into the Al via diffusion [17] to form amorphous Al₂O₃ and then attaching themselves to the reaction fronts. The Cu atoms diffused into the molten Al, and the bright fine network of Al(Cu)–Al₂Cu eutectics was formed after cooling.

Figure 4d showed that the Al₂O₃ particles (bright dots) are embedded in the Al(Cu)–Al₂Cu eutectic microstructure. Their distribution is not similar with that of amorphous Al₂O₃, which indicates that the Al₂O₃ particles are redistributed during crystallization. The size of Al₂O₃ particles is less than approximately 5 μm. It is obviously that all amorphous Al₂O₃ are transformed to the Al₂O₃ particles by heating to 900 °C. In addition, some cracks

Fig. 4 SEM images of the CuO I sample heated at 620 °C **a**, 710 °C **b**, 790 °C **c** and 900 °C at different magnifications **d**, **e**

Fig. 5 EDS analysis of the CuO I sample heated to 710 °C, the EDS spectrum and element distribution are from the bright point in the dark patch in the image

appeared in the sintered sample due to the detachment of Al_2O_3 particles from the sample during polishing [11] and the sharp temperature gradient during rapid cooling [18].

3.3.3 Microstructures of the Water-Quenched CuO II Samples

The microstructures of the CuO II samples heated to 620, 740 and 900 °C are shown in Fig. 6. The distribution of bright patches at the 620 and 740 °C samples is similar to that observed in the green sample (Fig. 3b). The microstructures of these two samples are comparable to the CuO I samples heated at 620 and 710 °C. In contrast to the CuO I sample, most of the amorphous Al_2O_3 remained in the CuO II sample and a small quantity of it crystallized Al_2O_3 particles in the green samples were heated at 900 °C, which can explain the relative low-intensity diffraction peak of Al_2O_3 particles in the XRD result (Fig. 2f). The size and distribution of the amorphous Al_2O_3 in Fig. 6c are similar to that of the CuO particles in the green sample (Fig. 3b). The distribution of $\text{Al}(\text{Cu})\text{--Al}_2\text{Cu}$ is similar to that observed in the CuO I sample (Fig. 4d), which means that the size and distribution of the second phase, including amorphous Al_2O_3 and Al_2O_3 particles, have no effect on the diffusion of Cu atoms in the water-quenching samples.

3.3.4 Microstructures of the Samples Held at 900 °C for 1 h Followed by Furnace Cooling

An additional two green samples (i.e., one for CuO I and CuO II) were held time at 900 °C for 1 h followed by furnace cooling. The microstructures are shown in Figs. 7 and 8.

Fig. 6 SEM images of the CuO II sample heated at 620 °C **a**, 740 °C **b** and 900 °C at different magnifications **c**, **d**

Fig. 7 SEM images of the CuO I sample sintered at 900 °C for 1 h at different magnifications **a**, **b**

The results in Fig. 7 indicate that the cracks disappeared in the CuO I sample. Therefore, the holding time can increase the interface bonding strength between Al and the Al_2O_3 particles. The Al_2O_3 particles have a rather uniform size of 5 μm . The particles synthesized in the study of Yu *et al.* [15] were as approximately 10 μm . Compared with the water-quenched sample (Fig. 4e), it can be observed that the finer Al_2O_3 particles were coarsened, but the bigger particles were remained.

The results in Fig. 8 indicate that most of the amorphous Al_2O_3 crystallizes to form Al_2O_3 particles, and the size of these particles ranges from submicron to approximately 6 μm . The Al_2O_3 particles, which have an approximate size

of 6 μm , are dispersed, and the fine particles aggregate. These aggregations are detrimental to the properties of the composite because it is difficult to break even in subsequent processing, such as extrusion or rolling [19].

As far as the $\text{Al}(\text{Cu})\text{--Al}_2\text{Cu}$ eutectic is concerned, they become coarser due to sufficient diffusion time during furnace cooling in comparison with that of water-quenching samples. The eutectic network in the CuO II sample is coarser than that in the CuO I sample, which means that the Al_2O_3 particles act as an obstacle to the diffusion of Cu atoms during furnace cooling. Most of Al_2O_3 particles and aggregates are segregated in the eutectic structure, and a similar result was observed in previous studies [14].

Fig. 8 SEM images of the CuO II sample sintered at 900 °C for 1 h at different magnifications **a**, **b**

Fig. 9 HRB of the samples heated at 5 °C/min

3.3.5 Hardness

Mechanical hardness tests were performed on all samples using a HRB-100 tester. The overall average was obtained using a 100 KG-F load indenter over random regions for the mechanical hardness. The mechanical hardness as a function of the heating temperature is shown in Fig. 9. The minimum HRB values were obtained for both the CuO I and CuO II samples heated to 710 and 740 °C, respectively. The decrease in the hardness value may be caused by the residual stress owing to the difference in thermal expansion between ductile matrix and brittle inclusions [20, 21]. The network Al(Cu)–Al₂Cu eutectic is formed as the temperature increases, which can increase mechanical hardness. The hardness value decreases due to the crack occurrence as the CuO I sample was heated to 900 °C. The maximum HRB values of 60 and 54 are obtained from the CuO I and CuO II samples sintered at 900 °C for 1 h. It is concluded that the holding time can increase the mechanical hardness because the porosity of the sintered samples decreases as the sintering time increases [22]. In addition, the HRB value of the former is higher than that of the latter, which is a result of the dispersion of Al₂O₃

particles, i.e., Al₂O₃ particles is dispersed in the former and aggregated in the latter.

3.4 Discussion

The initial reaction of Al/CuO is controlled by the CuO decomposition followed by the diffusion of reacting species through the amorphous material and subsequent crystallization of Al₂O₃ particles [23]. During the decomposition process, a small amount of O and Cu atoms decompose from CuO and diffuses along the Al grain boundaries. However, most of the O atoms were incorporated into the Al and then attached themselves to the reaction fronts for their slow diffusion rate at lower temperature. The concentration of O atoms makes the atoms ratio of Al and O do not correspond to that of Al₂O₃ crystal causing the formation of amorphous Al₂O₃. According to the EDS maps in Fig. 5, the O concentration in amorphous Al₂O₃ is higher than that in Cu and Cu₂O, which prevents the O atoms in CuO from transferring from CuO into the Al matrix across the amorphous Al₂O₃. Therefore, it can be postulated that after the amorphous Al₂O₃ forms, further reaction of Al/CuO results from diffusion of the Cu atoms in the CuO particles across the amorphous Al₂O₃ into the Al melt and Al atoms across the amorphous Al₂O₃ to combine with O atoms, which can explain the appearance of Cu in the EDS map of amorphous Al₂O₃ (Fig. 5). Thus, the reduction reaction depends on the diffusion rate of Cu atoms after the formation of amorphous Al₂O₃.

The smaller CuO particles have a relatively short distance from the center of the CuO particle to the Al matrix. Therefore, a short time is required to complete the diffusion of Cu atoms during the reaction. In our study, O and Al form amorphous Al₂O₃, and the Cu atoms completely dissolve in the Al melt when heated to 790 °C in the CuO I sample, while this process occurs as the temperature increases to 900 °C in the CuO II sample. Amorphous Al₂O₃

completely transformed to Al_2O_3 particles as the temperature was increased to 900 °C in the CuO I sample, while the amorphous Al_2O_3 is gradually crystallized during the holding time at 900 °C in the CuO II sample. The above analysis indicated that the small CuO particles can lower reaction temperatures and narrow the reaction temperature range during the heating process.

The size distribution of the Al_2O_3 particles can be explained by the result reported by Song *et al.* [17], that is, as the oxygen concentration decreased, the size of the Al_2O_3 particles increased. In addition, the Al_2O_3 particle size increased as the oxidation time increased due to the influence of Ostwald ripening. In this study, the O concentration in amorphous Al_2O_3 is much higher than that in the regions far away from amorphous Al_2O_3 , leading to large Al_2O_3 particles forming in the Al matrix and tiny Al_2O_3 particles forming in the amorphous Al_2O_3 during amorphous Al_2O_3 crystallization. The tiny Al_2O_3 particles become coarser with the increase in heating time, which is similar to those of others reports [18, 24].

4 Conclusions

- (1) The size and distribution of amorphous Al_2O_3 are similar to that of CuO particles. Smaller amorphous Al_2O_3 is in favor of the formation of in situ Al_2O_3 particles with a uniform size distribution and good dispersion.
- (2) When the size of the CuO particles is less than 6 μm , the Al/CuO reaction is complete when the sample was heated to 790 °C. Then, amorphous Al_2O_3 was transformed to dispersed Al_2O_3 particles that were less than 5 μm as the temperature was further increased to 900 °C.
- (3) When the size of the CuO particles is less than 50 μm , the Al/CuO reaction is complete, and a small amount of amorphous Al_2O_3 crystallized into Al_2O_3 particles as the temperature increased to 900 °C. The relatively larger amorphous Al_2O_3 gradually transformed to Al_2O_3 particles when the sample was held at 900 °C. The Al_2O_3 particles ranged from submicron to

approximately 6 μm in size, and most of them agglomerated.

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