FABRICATION AND CHARACTERIZATION OF AL-AL₄C₃ NANOCOMPOSITE BY MECHANICAL ALLOYING

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Aluminum carbide (Al₄C₃) seems to be an ideal reinforcement for producing aluminum matrix composites. Al₄C₃ has high hardness and shear strength as well as a high melting point. The dispersion of Al₄C₃ particles in the matrix produces a pinning effect that reduces aluminum grain growth, which improves the mechanical properties. In this study, aluminum powders were mixed with 4.5 wt.% graphite and mechanically alloyed using a high-energy ball mill in order to produce Al-Al₄C₃ nanocomposite. The structural evaluation of powder particles after different milling times was studied by X-ray diffractometry, scanning electron microscopy and microhardness measurements. The aluminum crystallite size estimated with broadening of XRD peaks by Williamson–Hall formula. XRD results suggested that the grain size of aluminum decreased to nanometer range (30 nm) during ball milling. No Al₄C₃ formed during the mechanical alloying process. Milled powders were then annealed at 300–600 °C for 1 h under argon atmosphere. Annealing at temperatures higher than 300 °C led to formation of Al₄C₃ phase which increased as annealing temperature increased. Aluminum grain size remained in nanometer range after annealing process. The microhardness of powder particles increased after annealing. Both effects are due to the formation of nanosized Al₄C₃ particles.

Keywords: Aluminum; Al₄C₃; Nanostructured materials; Mechanical alloying.

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1. Introduction

Aluminum matrix composites are important applicable materials for automotive and aerospace industries.¹ Lightweight, environmental resistance, high specific strength and stiffness, good wear resistance and high thermal and electrical conductivity are characteristics that promote research and development to extend their applications by further improvement in the properties. Ceramic particles, mainly SiC and Al₂O₃, are the most widely used materials for reinforcing aluminum alloys. More recently, Considerable attention has been paid to Al-Al₄C₃ composites.²⁻⁵ Fine and homogeneously distributed Al₄C₃ particles provide very effective obstacles to dislocation motion and consequently improve the creep strength significantly in addition to excellent room temperature properties.⁶⁻⁷

In fact, there are several techniques available to preparation of aluminum matrix composites. The fabrication methods can be divided into three types. These are solid phase process, liquid phase process and semi-solid fabrication process. Mechanical alloying (MA) is a solid-state powder processing technique which has been widely used to synthesis a variety of materials, such as amorphous alloys, nanocrystalline materials, intermetallic compounds and nanocomposites. This technique can lead to formation of interpenetrating phase composites with nanosized microstructures. An important characteristic of such phases is that they exhibit properties and performance much improved over their conventional microcrystalline counterparts.⁸ In addition, unfavorable phenomena associated with liquid techniques including reaction between matrix alloy and reinforcement and formation of undesirable phases, clustering of reinforcements, etc. can be eliminated via this method.⁹⁻¹⁰

The reinforcement particles can be directly added to matrix (ex-situ technique) or they can be formed by an in-situ reaction during MA or with subsequent heat treatment. It is known that the in-situ procedure yields finer reinforcement particles with more uniform size distribution. In addition, this technique provides effective control of the reinforcement volume fraction with an improved interfacial boundary with the matrix.¹¹ Ultrafine and in-situ Al₄C₃ particles can be readily introduced in Al matrix by reaction milling process involving either milling of Al-graphite powder mixture or milling of Al powder with organic compounds. Although a subsequent heat treatment was reported to be necessary to obtain Al₄C₃ phase.²⁻⁵

In this work, fabrication of Al-Al₄C₃ nanocomposite powder was investigated by utilizing MA process starting from graphite and Al powder mixtures. In meantime, the structural evolutions occurred during MA process and subsequent heat treatment were studied.

2. Experimental Procedure

The morphology of elemental Al (99.5% purity) and graphite powders are shown in Fig.1. As seen, as-received Al powders had a random morphology and average particle size was about 60 μm (Fig. 1.a). The graphite particles were angular and flaky in shape

with a mean particle size of 30 μm (Fig. 1.b). Al and graphite powders were mixed and milled in order to produce Al–20 vol.% Al_4C_3 composite. To minimize the extreme cold welding of aluminium powders, 0.6 wt% of stearic acid was used as a process control agent (PCA).

Fig. 1. SEM micrographs of as-received elemental powder particles: (a) Al and (b) graphite.

Ball milling of powder mixture was carried out in a planetary ball mill at room temperature and under argon atmosphere. The ball milling media were hardened chromium steel vial (150 ml) with five steel balls (20 mm). The ball-to-powder weight ratio and the rotational speed of vial were 10:1 and 600 rpm, respectively. The ball milling was interrupted at selected times and a small amount of powder was removed for further characterizations. Phase transformation and crystallite size evaluation during ball milling were determined by X-ray diffraction (XRD) with Cu $K\alpha$ radiation ($\lambda = 0.15406$ nm). The morphology of the milled powder particles was examined by scanning electron microscopy (SEM) in a Philips XL30 at an accelerating voltage of 30 kV. The hardness of powder particles was determined by microhardness measurements using a Vickers indenter. Ten indentations were made on each sample to obtain an average value of hardness. The crystallite size and internal strain of powders was estimated using the Williamson-Hall method:¹²

$$\beta \cos \theta = \frac{K\lambda}{D} + 2A\sqrt{\varepsilon^2} \sin \theta \quad (1)$$

Where θ is the Bragg diffraction angle, D the average crystallite size, ε the average internal strain, λ the wave length of the radiation used (0.15406 nm), β the diffraction peak width at half maximum intensity, K the Scherrer constant (0.9) and A is the coefficient which depends on the distribution of strain; it is near to unity for dislocations.

Prepared Al–graphite powders were isothermally annealed to study the thermal behaviour of milled powders. Powder samples were sealed and then annealed under flowing argon atmosphere in a conventional tube furnace. The structural evolutions during annealing were determined by XRD.

3. Results and Discussion

3.1. Phase evolution during milling

The XRD patterns of the structural evolution of the mechanically alloyed Al-C powders are shown in Fig. 2. The principle change observed consisted of a broadening of the Al peaks and a decrease of their peaks intensities. The crystalline graphite peaks disappeared after 10 h of milling time. This noticeable change in the XRD pattern can be attributed to the fact that within this short duration of milling, the crystalline graphite powder may either (i) transform to an amorphous state due to high-energy impact or (ii) carbon atoms diffuse into the Al-lattice and as a result a Al-C solid solution alloy is formed or (iii) graphite layers are being distributed as thin layer around the grain boundaries of Al particles. No traces of the diffraction peaks of Al₄C₃ phase were evident on the XRD patterns even after 60 h of milling time. This suggests that the mechanical alloying process for Al-C system is essentially a mixing process, which additionally involves a high density of lattice defects and progress refinement of Al crystallite size.

Fig. 2. XRD patterns taken from Al-4.5 wt.% C powder mixture milled for different hours.

The Al crystallite size was estimated from broadening of XRD peaks using Williamson-Hall method. Fig. 3 plots the Al crystallite size as a function of milling time. The initial crystalline size of as-received aluminum was about 340 nm. As a result of ball milling Al readily achieved a nanocrystalline structure. The Al crystallite size after 2 h of milling time were about 58 nm which changed to 30 nm as milling time increased to 40 h. The Al crystallite size appeared to approach a constant value, saturated value, as ball milling proceeds.

Ball milling is characterized by intensive plastic deformation of powder particles at extremely high strain rate and therefore, creation of a high density of lattice defects, mainly dislocations. At the same time recovery phenomena can take place, reducing the

density of lattice defects. The progressive accumulation and interaction of dislocations lead to formation of dislocation cell structure which subsequently creates low-angle grain boundaries. With prolonged processing, this structure is transformed to a fully nanocrystalline structure.¹³⁻¹⁴ The observed initial sharp decrease in Al crystallite size during the initial milling stage and the ultimate crystallite size achieved can be discussed with respect to the competing rates of creating dislocations due to work hardening and recovery phenomena.¹⁴⁻¹⁵ The former has a higher rate at initial stage of ball milling leading to a rapid decrease in crystallite size. Thereby, the ultimate crystallite size achieved by ball milling is determined by the balance between creation and annihilation of dislocations.¹³⁻¹⁶

Fig. 3. Reduction of Al crystallite size versus ball milling time.

3.2. Effect of heat treatment

Although there was no new phase formation after MA, it was believed that high deformation during MA process resulted in high internal energy; which most probably acted as driving force for the formation of Al_4C_3 during subsequent annealing. It was observed that longer MA together with higher annealing temperature caused an increase in the formation of Al_4C_3 phase.³

Figure 4 shows the XRD patterns from the Al-C powder mixture as-milled for 60 h after subsequent heat treatment at 300-600 °C for 1h. The lines of Al_4C_3 phase appear for the first time on the XRD patterns, when the heating temperature reaches 400°C. The effect of annealing temperature on the amount of Al_4C_3 formed during heating can be evaluated by plotting the ratio of intensity of Al_4C_3 (110) and Al (111) peaks versus annealing temperature (Fig. 5). As seen increasing the annealing temperature from 400 °C to 600 °C led to increase on the fraction of Al_4C_3 phase.

According to thermodynamic prediction¹⁷, carbon can react with aluminum to form Al_4C_3 at any temperature under 1500 °C. The high defect densities, large amount of created grain boundaries due to the formation of nanostructured aluminum as well as the

nanocrystalline carbon particles produced during milling can ensure large reaction interface areas between C and Al and enhance their diffusion rates through the product phase. The combination of the above factors greatly decreases the reaction temperature and the temperature range.

Fig. 4. The XRD patterns of Al-4.5 wt.% C powder mixture milled for 60 h followed by annealing at different temperatures for 1 h.

Fig. 5. Relative intensity of Al₄C₃ (110) and Al (111) XRD peaks as a function of annealing temperature.

The Al and Al₄C₃ grain size after annealing was estimated using Williamson–Hall method. Al grain size remained almost constant after heat treatment (30 nm). Al₄C₃ particles formed during heat treatment appeared to have the size of about 10 nm, which remained unchanged upon heating. Presence of nanosized Al₄C₃ particles appeared to hinder effectively the grain growth phenomenon.

3.3. Microhardness measurements

Figure 6 plots the average value of microhardness of Al-4.5 wt.% graphite powder particles as milled for 60 h and also after annealing for 1 h at different temperatures. The

value of microhardness for as-milled powder was 90 HV. As can be seen annealing at 300 °C had no significant effect on the hardness value. Increasing annealing temperature to 400 °C and then 500 °C and 600 °C however, resulted in increasing the hardness value. This is caused by the development of nanosized Al_4C_3 particles, consistent with XRD results.

Fig.6. Microhardness values of Al-4.5 wt.% C powder mixture as-milled for 60 h and after annealing for 1 h at different temperatures.

3.4. Morphological analysis

Figure 7 shows SEM images of Al-4.5 wt.% graphite powder particles after different milling times. During high-energy milling the powder particles change their morphology and size as a result of repeated deformation, fracturing and welding processes. Fig. 7a shows that after 2 h of milling time the aluminum powder particles are extensively flattened. By increasing milling time to 10 h, the powder particle sizes were decreased due to predominance of the powder particles fracturing over the cold welding process (Fig. 7b). Further milling led to a significant decrease in powder particle sizes (Fig. 7c and d). After 60 h of milling, the powder particles became equiaxed in shape with a mean size of 3 μm .

4. Conclusions

Al-C powders were mechanical alloyed and the following results were obtained:

1. After 60 h milling of Al-C powder mixture, no traces of the diffraction peaks of Al_4C_3 phase were observed in XRD pattern.
2. The nanostructured Al particles, which formed during MA, increased the internal energy and acted as a driving force during subsequent annealing and enhanced the formation of Al_4C_3 particles.
3. Al grain size remained almost constant after heat treatment. It seems that presence of nanosized Al_4C_3 particles effectively hinder the grain growth phenomenon.

4. The microhardness of Al-C powder particles increased after heat treatment due to the formation of nanosized Al₄C₃ particles.

Fig. 7. SEM micrographs of Al-4.5 wt.% C powder mixture particles after (a) 2h, (b) 10h, (c) 40h and (d) 60h of milling time.

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