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Preparation and surface modification of submicron YAl_2 particles by mixed milling with magnesium for fabricating $\text{YAl}_{2\text{p}}/\text{MgLiAl}$ composites

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Abstract: A new process for the preparation and surface modification of submicron YAl_2 intermetallic particles was proposed to control the agglomeration of ultrafine YAl_2 particles and interface in the fabrication of $\text{YAl}_{2\text{p}}/\text{MgLiAl}$ composites. The morphological and structural evolution during mechanical milling of YAl_2 powders ($<30\text{ }\mu\text{m}$) with magnesium particles ($\sim 100\text{ }\mu\text{m}$) has been characterized by scanning electron microscopy, transmission electron microscopy, and X-ray diffraction. The results show that YAl_2 particles are refined to submicron scale and separately clad in magnesium coatings after mixed milling with magnesium particles for 20 hours. Mechanical and metallurgical bonds have been found in YAl_2/Mg interfaces without any interface reactions. Both the refining and mechanical activation efficiencies for YAl_2 particles are enhanced, which may be related to the addition of magnesium

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particles leading to atomic solid solution and playing a role as “dispersion stabilizer”.

Keywords: Magnesium alloys; Composites; Intermetallics; Electron microscopy; Bonding; Interfaces

1. Introduction

Mg-Li based alloys and composites, known as the lightest metallic structural materials, have great potential for use not only in aerospace and military but also in automobiles and electrical appliances, due to their attractive features of high values of specific strength, specific modulus, and electromagnetic shielding properties [1–3]. SiC, Al₂O₃ fibers, and Mg₂Si particles [4–6] have been used to reinforce Mg-Li based alloys recently. The results show that the ceramic reinforcements are harmful to the ductility of the composites, as the chemical incompatibility between ceramic reinforcements and Mg-Li alloy matrix remains a critical problem.

Wang et al. showed that YAl₂ intermetallics have good physical and chemical compatibility with MgLiAl matrix, in Mg-Li matrix composites strengthened with the intermetallic compound YAl₂ (25~37.5 μm) [7]. With the addition of 20% volume fraction YAl₂ particles, the tensile strength increases to 225 MPa and the elongation remains at 9%. However, the strength is still low compared to some commercial aluminum alloys. When the volume fraction increases to 40%, the advantage of low density for Mg-Li fades.

The composite mechanical properties increase with the decrease of reinforcement particle size, especially when the particle size is in submicron or nano range [8,9].

However, fine reinforcement particles are easy to agglomerate in matrix which may seriously affect the mechanical properties of the composites [10–12]. To overcome this problem, many methods were used to control micro particle agglomeration, such as mechanical stirring [13], ultrasonic dispersion [14], surface coating [15], and dispersing agents [16]. However, it is still a challenge for submicron or nano-sized particles. Mechanical alloying method was used to improve the reinforcement distribution in particle-reinforced metal matrix composites, especially for the nano-sized particles [17,18]. However, Mg-Li matrix composites could not be prepared by mechanical alloying, because the powders can be easily oxidized. How to control the agglomeration for ultrafine particle-reinforced Mg-Li composites is crucial. Zhang et al. proposed a pre-milling followed by stir casting method to control the agglomeration of ultrafine YAl_2 particles in $YAl_{2p}/MgLiAl$ composite. The strength was significantly improved to 220 MPa with the addition of 5vol% YAl_2 particles ($<3\ \mu m$) [19]. It shows a very good prospect for the Mg-Li matrix composites development. However, neither the pre-milling process nor control mechanism in the method has been further studied.

In the present work, submicron YAl_2 particles have been prepared by mechanical milling with and without magnesium particles at ambient temperature. The effects of milling on the surface modification and dispersion of YAl_2 particles in YAl_2/Mg mixture were characterized. The influence of the milling time on the particles size and crystal structure during mechanical milling was investigated by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray diffraction (XRD). The YAl_2/Mg interfacial evolution was observed. The effect of magnesium

particle addition on the morphological and structural evolution is further discussed.

2. Experimental methods

2.1 Materials and milling procedure

YAl₂ ingots (99.9% pure) were obtained from General Research Institute for Nonferrous Metals by melting pure yttrium and aluminum. The ingots were crushed and then mechanically milled to about 30 μm in a planetary ball milling device (QM-1SP). Agate balls and tanks were used. The ball to powder weight ratio was approximately 4:1. The rotation speed (cup speed) was 400 rpm. The magnesium particles (99.9% pure, $\sim 100\ \mu\text{m}$) were sawn from magnesium ingots.

The YAl₂ particles ($\sim 30\ \mu\text{m}$) were further milled at ambient temperature in the same milling device and parameters, without (route 1) and with magnesium particles (route 2). The ball to powder weight ratio was approximately 8:1, and the rotation speed (cup speed) was 400 rpm. The mixed materials were ball-milled up to 30 h with several interruptions to open the vial and take out a small portion of particles for analysis. Samples were collected at shorter milling times (2, 10, 20, and 30 h), so that the evolution of the particles during milling could be followed.

2.2 Microstructure characterization

The morphological evolution of particles during milling was characterized by SEM (S-4800) and TEM (JEM-2100). The particle size evolution was characterized using IPP software based on five SEM images, for each condition. For microstructural study on the cross-section and interface of the YAl₂/Mg mixed particles, the mixed

particles were hot mounted with bakelite powders. Then, the samples were ground by No. 2000 sandpaper and polished with 0.5 μm Al_2O_3 slurry. An SEM (Quanta 200F) was used to observe the section morphology of the mixed particles. There is no bakelite showing in micrographs because all the particles were pressed to a block sample before hot mounting. All SEM samples were gold coated to make them conductive.

Following the milling, the particles were characterized by XRD with $\text{Cu K}\alpha$ radiation (XRD-MAC Science M21X). The crystallite size and lattice strain of specimens were calculated from XRD patterns using the Williamson–Hall method as follows [20]:

$$B\cos\theta = 0.9\lambda/D + 2\varepsilon\sin\theta \quad (1)$$

where B , θ , λ , D , and ε are full width at half maximum (FWHM), peak position, the wave length (0.15406 nm), crystallite size, and lattice strain, respectively.

3. Results and discussion

3.1 Morphological changes

Fig. 1 presents the morphology of particles before mixed milling. The initial YAl_2 powder consists of irregular shaped particles with various sizes from 1 to 30 μm . The magnesium particles are in polyhedral shape with particle sizes of about 50~100 μm .

The morphological evolution of YAl_2 particles after milling respectively through route 1 and route 2 is shown in Fig. 2a and Fig. 2b. For route 1, after milling, the YAl_2 particles are refined in a regular-rounded morphology. In route 2, the YAl_2/Mg mixed

particles appear similar to that of route 1 but with a smaller particle size. The variation in the surface morphologies of the particle samples after being ball-milled is shown in higher magnification. Compared to route 1 (Fig. 2a), we can see that YAl_2 is cladded by Mg scraps, forming a kind of mixed particles with rough surface (Fig. 2b), for the reason that ductile Mg particles underwent intense plastic deformation and formed layers of wrapping due to the ball impact.

The morphology and cross-section micrographs of the YAl_2/Mg mixed particles during the mixed milling are presented in Fig. 3. After milling for 10 h, YAl_2 was cladded in magnesium wrapping, forming series of coarse mixed particles with irregular shape (Fig. 3a). These mixed particles had a mean diameter of about $10\text{ }\mu\text{m}$ and consisted of two phases (Fig. 3b). Further, continuous and severe repetitive impacts of the milling media in longer milling times caused the particles to break into smaller pieces. Partially agglomerated YAl_2 particles were deagglomerated. At the milling of 20 h, the mixed particles were refined with a mean diameter of about $1\text{ }\mu\text{m}$ (Fig. 3c). The corresponding energy dispersive spectrometry analyses, Fig. 3e and Fig. 3f, respectively, of positions A and B in Fig. 3d suggest that the white phase is YAl_2 because of the higher content of yttrium element with a higher atomic weight compared to magnesium. It can be seen that YAl_2 particles are refined to submicron scale and separately cladded in magnesium coatings after mixed milling for 20 h. The morphology of mixed particles changes to very homogeneous near-spherical shape, and good metallurgical bond is obtained between YAl_2 particles and elemental magnesium.

In the samples for cross-section observation, the interface mixed milled for 10 h after hot mounting is still at the mechanical embedding stage, which means that the hot mounting could not change the interface bonding from mechanical to metallurgical bonding. This means that the effect of hot mounting on the YAl_2/Mg interface is limited, and maybe very small. The metallurgical bonding resulted from the milling process. Although hot mounting reached $140^\circ C$ with forces, it lasted for only less than 10 min. Under this condition, the effect on the interfaces may be neglected.

3.2 Interfacial evolution for YAl_2/Mg

Further characterization of the YAl_2/Mg interface of mixed particles during mixed milling is shown in Fig. 4. During the milling process, the ductile Mg particles underwent intense plastic deformation and formed layers of wrapping due to the ball impacts. YAl_2 particles adhered and were mechanically embedded into the magnesium wrapping, forming mechanical bond interface (Fig. 4a). With further milling, element diffusion might have happened between YAl_2 intermetallics and magnesium coatings.

The SEM-BSE imaging, in Fig. 4b, suffers from a resolution issue, because the backscattered electrons can come from sub surface, after the incident electron beam has scattered. So, the gradual contrast, between the particle and Mg, labeled “bond” in Fig. 4b, in a brightness between that of the particle and that of Mg, could be the result of averaging.

Meanwhile, coarse YAl_2 particles fracture and some interface decohesion appear to have happened between YAl_2 and Mg matrix during further milling (Fig. 4b). When welding and fracture mechanisms reach a balance, YAl_2/Mg interface bond will

gradually change from mechanical bond to metallurgical bond. If the mixed particles are added into the melted LA143 matrix, the coatings would (partially) dissolve first. Then, the YAl_2 particles may adhere better to the metal matrix, resulting in stronger particle/matrix interface formation.

TEM observation indicates that after milling for 20 h, the brittle phase (YAl_2 particles) is incorporated in the ductile phase (Mg) through ball milling. Good metallurgical bond is obtained between YAl_2 particles and elemental magnesium. The YAl_2/Mg interface is clear and free from any interfacial reactions and bonds directly (Fig. 5a). Fig. 5b gives HRTEM image of the YAl_2/Mg mixture along the $[\bar{1}14]$ orientation of the YAl_2 particles and the $[2\bar{1}\bar{1}0]$ orientation of the elemental magnesium. It can be seen that the YAl_2 particle and magnesium coating bond on the atomic scale, and some atomic disorder exists in the interface region (marked by the arrow) that may be generated by ball milling.

3.3 Particle size distribution

Fig. 6 shows the frequency distributions of YAl_2 particle size milled in route 1 and route 2 for different times. It can be seen that, for route 1 (Fig. 6a), as the milling time increases from 0 h to 20 h, not only does the frequency distribution peak shift to smaller particle size regions, but also the particle size distributes more narrowly. After milling for 10 h, the particle mean diameter is 0.9 μm . Compared to the trend in route 1, the frequency distribution of YAl_2 particle size in route 2 (Fig. 6b) shifts to smaller particle size regions with an anomaly at the milling time of 10 h, because the hard fine YAl_2 particles are randomly embedded into the deformed, soft magnesium matrix to

form coarse mixed YAl_2/Mg particles at the milling time of 10 h, as shown in Fig. 3. Fracturing becomes a significant process for mixed particles with further milling, which leads to a decrease in particle size. Beyond the milling of 20 h, the particle size virtually has no change.

Moreover, detailed analysis for Fig. 6a and Fig. 6b reveals a variation of frequency distribution of submicron particle size after milling for 30 h. The frequency distribution peak shifts to and stabilizes at the 0.5-1 μm position in route 1, while the peak stabilizes at the $<0.5 \mu\text{m}$ position in route 2, which supports the SEM observations in Fig. 2. It reveals that the addition of magnesium particles improves the refining of YAl_2 particles.

3.4 Structural evolution

The XRD patterns of particles produced from routes 1 and 2 at various milling times are shown in Fig. 7. No oxidation reaction or new phases can be detected after milling in both routes. Severe plastic deformation of the particles can lead to grain refining, accumulation of internal stress, change of the lattice parameter, and formation of cell structure [21]. It is observed that the XRD peak of YAl_2 and magnesium particles are lowered and broadened during the milling process, which indicates that both routes have significant effect in reducing the crystallite size and accumulation of lattice strain. This can also be revealed from the TEM and HRTEM morphology as shown in Fig. 5. The absence of the diffraction peaks of magnesium element is probably due to its small amount and weak X-ray scattering intensity.

The lattice strain and grain size of YAl_2 as a function of milling time were

calculated according to the Williamson–Hall method, and the results are shown in Fig. 8. It can be seen that the crystallite size decreases (Fig. 8a) but lattice strain increases (Fig. 8b) with increasing milling time. The two parameters appear to approach a constant value after the milling time of 10 h in route 1. Compared to route 1, approaching steady state is delayed to after the milling time of 20 h in route 2. Meanwhile, smaller crystal size and higher lattice strain of YAl_2 particles in route 2 are obtained than those of route 1. Surface modification through ball milling has a significant effect on the structure evolution and particle distribution in the matrix due to the atomic solution or dispersion stability [22-24]. Magnesium coating on the YAl_2 particles might have diffused into YAl_2 during the ball milling, and might also play a role of “dispersion stabilizer”, which can promote both the refining and mechanical activation behavior. As a result, the efficiency of mechanical activation for YAl_2 particles is enhanced by ball milling with the addition of magnesium particles. Submicron YAl_2 particles and surface modification, produced by mixed milling with magnesium particles for 20 hours, should be beneficial to the wettability and interface bonding between YAl_2 reinforcements and MgLiAl matrix. When the YAl_2/Mg mixed particles are used as reinforcements in the composites fabrication, they should more uniformly distribute in the matrix and should result in excellent mechanical properties.

4. Conclusions

In this study, a new process for preparation and surface modification of submicron YAl_2 particles by mixed milling with magnesium particles was developed

for the fabrication of $\text{YAl}_2/\text{MgLiAl}$ matrix composites. The main results are as follows:

- (1) The YAl_2 particles were refined to submicron scale and separately cladded in magnesium coatings after mixed milling for 20 hours. After that, the morphology of the YAl_2/Mg mixed particles changed to homogeneous spheres with a mean size below 1 μm .
- (2) Mechanical and metallurgical bonds have been found in YAl_2/Mg interfaces without any interface reactions. After long mixed milling, mechanical bond transformed into metallurgical bond possibly by element diffusion between YAl_2 intermetallics and magnesium coatings.
- (3) The efficiencies of both refining and mechanical activation are enhanced by the milling with magnesium particles, which may be related to the addition of magnesium particles leading to atomic solid solution and playing a role as “dispersion stabilizer”.
- (4) It may be possible to achieve uniformly distributed microstructure of the $\text{YAl}_2/\text{LA143}$ composites and excellent mechanical properties with the submicron YAl_2 particles and surface modification produced by mixed milling with magnesium particles.

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Figure captions

Fig.1. SEM micrographs for particles before mixed milling. (a) YAl_2 , (b) magnesium.

Fig.2. SEM micrographs for particles milled for 20 h. (a) YAl_2 ; (b) YAl_2/Mg particles.

Fig.3. SEM micrographs and EDS analyses of the mixed particles after mixed milling for different times. (a) Morphology image, 10 h; (b) cross-section BSE image, 10 h; (c) morphology image, 20 h; (d) cross-section BSE image, 20 h; (e) EDS of location A; (f) EDS of location B.

Fig.4. SEM micrographs of the YAl_2/Mg interface of mixed particles during surface modification. (a) Morphology image; (b) BSE image.

Fig.5. TEM (a) and HRTEM (b) images of YAl_2/Mg particle after mixed milling.

Fig.6. Frequency distributions of YAl_2 particle size in route 1 (a) and in route 2 (b), after different milling times. The distribution in (b) at 0 h is for YAl_2/Mg mixed particles that include both YAl_2 particles and Mg particles. At the beginning of mixed milling, the plastic Mg was deformed more severely. There were no Mg particles remaining after milling for 20 h.

Fig.7. XRD pattern evolution during milling for route 1 (a) and route 2 (b).

Fig.8. Crystal size (a) and lattice strain (b) evolution of YAl_2 during milling for route 1 and route 2.

20 μm

Magnesium
coatings

0.5 μm

2 μm

2 μm

A black and white micrograph showing a distribution of bright, irregularly shaped particles (YAl₂) within a darker, textured matrix. The particles vary in size and are scattered throughout the field of view. A scale bar in the bottom right corner indicates a length of 2 μm.

YAl_2

2 μm

YAl_2

Mechanical
embedding

Mg

500nm

Particle
fracture

Interface
decohesion

bond

YAl_2

Mg

$1\text{ }\mu\text{m}$

a

YAl_2

Mg

30 nm

b

YAl_2

220

511

$3\bar{1}1$

Mg

0002

$01\bar{1}1$

4 nm