Preparation and mechanical properties of in situ Al_2O_3/Al composites by adding $NH_4AlO(OH)HCO_3$

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Abstract: Aluminium matrix composite reinforced by Al_2O_3 particles was produced by adding $NH_4AlO(OH)HCO_3$ into molten aluminum. The mechanical properties and wear behavior of the as-fabricated composites were studied. The results show that during stirring γ-Al_2O_3 particles were formed via decomposition reaction of $NH_4AlO(OH)HCO_3$, and the distribution of Al_2O_3 particles is more uniform in the matrix aluminum than directly added Al_2O_3 into molten aluminum. The density and the hardness values of the as-fabricated composites increase with increasing the particle volume fraction, while the tensile strength of the composites decreases with increasing the volume fraction of the Al_2O_3 particles. The wear rate of the composites decreases with increasing the volume fraction of the particle and loading. The in situ formed Al_2O_3/Al composite by adding $NH_4AlO(OH)HCO_3$ shows more superior mechanical and wear behaviors than that prepared by directly adding Al_2O_3 particles.

Key words: aluminum matrix composite; $NH_4AlO(OH)HCO_3$; Al_2O_3 particles; microstructure; hardness; tensile strength; wear behavior

1 Introduction

Particle reinforced aluminum matrix composites (Al-MMCs) have attracted much attention due to their excellent performance, such as lower density, high specific stiffness, high specific strength and good thermal stability compared with pure aluminum and aluminum alloys [1−3]. The Al-MMCs can be prepared by in situ or ex situ synthesis. In ex situ methods, the particles must be prepared prior to the fabrication of the composites. There are some defects and difficulties in fabricating composites by ex situ methods. For example, the particle size is difficult to be controlled. Furthermore, the distribution of fine particles in matrix is generally inhomogeneous. These disadvantages bring about a detrimental effect on material properties [4]. To overcome these problems, in situ technique has been proposed to fabricate composites where the reinforcement phases are in situ formed within the matrix [5].

Recently, several in situ technologies of producing ceramic particles in metals have been proposed, e.g. direct melt reaction (DMR) process [1, 2, 6], direct decomposing reaction (DDR) process [7], reactive hot pressing (RHP) [8−9] and self-propagating high temperature synthesis (SHS) [10−11]. The DMR and DDR are considered one of the most promising in situ synthesizing techniques for commercial applications due to their simplicity, low cost and near net-shape forming capability [1].

In the present paper, Al_2O_3/Al composites were fabricated by a new in situ synthesizing technique where the reinforced phase Al_2O_3 particles were introduced by DDR process. In this process, the in situ Al_2O_3 particles were obtained from decomposition of $NH_4AlO(OH)HCO_3$ by adding it to aluminium melt. The microstructure was examined using scanning electron microscopy (SEM). Physical and mechanical properties of the composites were evaluated and the wear behavior was also investigated.

2 Experimental

2.1 Materials and processing

The raw materials used in this study were commercial purity Al (99.5% purity) and $NH_4AlO(OH)HCO_3$ (99.5% purity), which were employed as the matrix metal and in situ formed reinforcement phase by decomposing $NH_4AlO(OH)HCO_3$, respectively. In order to get a better comparison with Al_2O_3 reinforced pure aluminum composites, alumina(<1 μm, 99.7% purity) was used as comparative reinforcement. After melting at 667 °C, the molten metal was continuously reheated and stirred at a rotating speed of 200 r/min and 850 °C. Preheated powder of $NH_4AlO(OH)HCO_3$ was gradually added to the swirl of molten metal during stirring. As a result, in situ formed Al_2O_3 from $NH_4AlO(OH)HCO_3$ was produced within the metal matrix, and a molten composite formed. As the reaction was completed, the agitating was stopped for a while to let the gas out and the molten was then cast in the pressure die-machine with a maximum locking force of 1.5 MN. A comparative study was performed to prepare Al_2O_3/Al composite by directly adding superfine Al_2O_3 into molten Al under the same testing condition.

2.2 Material characterization

Specimens for SEM observations were taken from the as-cast composites. The specimens were polished in a conventional manner and the microstructure was observed on a SSX−550 scanning electron microscope (SEM). Philips PW 1840 X-ray diffractometer with a Cu K_α radiation was used to characterize the phase composition of the as-prepared composites.

The densities of the composites were measured using the water displacement technique. The theoretical density of composite can then be calculated according to the rule of mixtures. Brinell hardness (HBN) measurements were carried out using a ball of 5 mm in diameter under load of 498 N for 30 s. A Hounsfield H25KS tensile machine was used to evaluate the tensile behaviors in accordance with ASTM standard E−8−81. The strain rate was maintained to be 0.1 mm/min in tensile test till rupture. Wear tests were carried out using a pin-on-disk tester with the aluminum or composites as the pin and GCr15steel as the disk. The disk specimen was 70 mm in diameter and 5 mm in thickness. The pin test piece had a flat surface with a diameter of 6 mm. The diameter of the wear track was 60 mm. The surfaces of both the disk and the pin were polished with #1500 emery paper. The wear tests were performed under dry sliding conditions at loads of 5, 10 and 15 N, respectively.

3 Results and discussion

3.1 Microstructure and density

Figure 1 shows the microstructures of the composites prepared by adding $NH_4AlO(OH)HCO_3$ powder and the traditional composites by adding superfine Al_2O_3 particles at 8% (volume fraction), respectively.

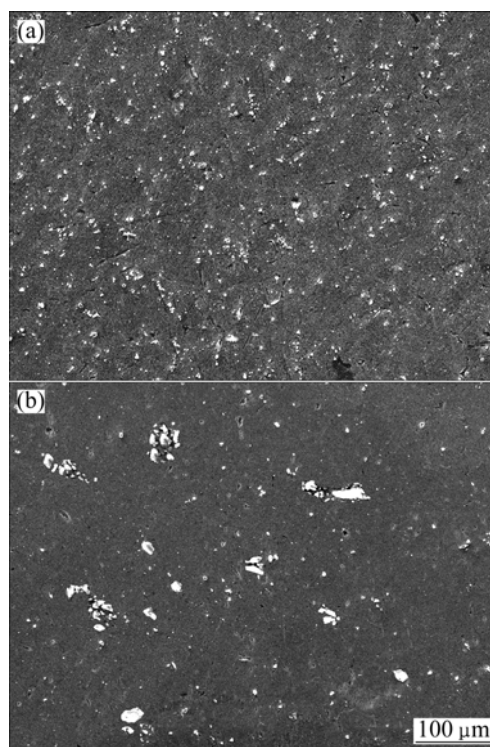**Fig. 1** SEM images of Al_2O_3/Al composites with 8% (volume fraction) Al_2O_3: (a) Composite by adding $NH_4AlO(OH)HCO_3$; (b) Composite by directly adding Al_2O_3

From Fig. 1(a), we can see that the Al_2O_3 particles in situ produced from $NH_4AlO(OH)HCO_3$ are uniformly distributed in the Al matrix. The particulate size of the Al_2O_3 was measured to be 0.5−2 μm in diameter, although some of them were much smaller. Figure 1(b) indicates that the Al_2O_3 particles agglutinate and distribute non-uniformly in the matrix.

The XRD pattern in Fig. 2 can be used to analyze reaction process, which reveals that γ-Al_2O_3 is the only resultant in the composite and residual $NH_4AlO(OH)HCO_3$ does not exist. According to XRD result, the in situ decomposition reaction in aluminum matrix can be expressed as the following reaction:
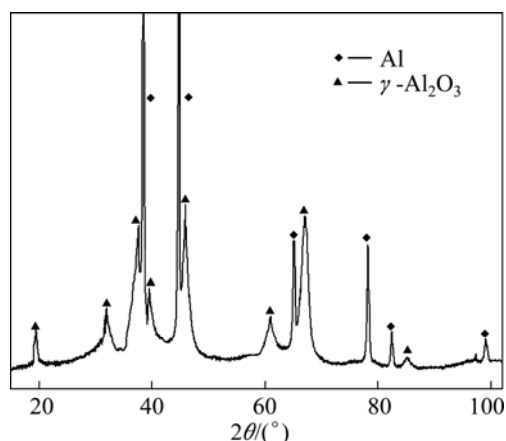
$$2NH_4AlO(OH)HCO_3(s) \rightarrow$$
$$Al_2O_3(s) + 2NH_3(g) + 2CO_2(g) + 3H_2O(g) \qquad (1)$$
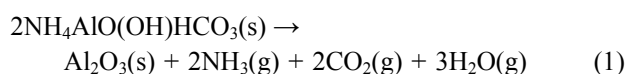
Fig. 2 XRD pattern of composite fabricated by adding $NH_4AlO(OH)HCO_3$

$NH_4AlO(OH)HCO_3$ is known to be one of the raw materials for fabricating commercial superfine high-pure Al_2O_3 [12−13]. The mode of decomposition from $NH_4AlO(OH)HCO_3$ is γ-Al_2O_3 with a high specific surface area and sorption capacity [14]. At the same time, the Al_2O_3 particles are in spherical shape, which have better wettability with the molten aluminum, so they could bond firmly with the aluminum matrix. The morphology of this kind of composites is able to reduce stress concentration and easy to transfer load, so the properties of the composites could be improved.

The density was measured using the water displacement technique. The results of the density measurements of the matrix and the composites are presented in Fig. 3. Using the law of mixtures, the theoretical densities of the composites were calculated. Figure 3 shows the relationship between the densities and volume fraction of the Al_2O_3 particles. It can be observed from Fig. 3 that the densities of the composites increased by adding Al_2O_3 particles. According to Ref. [15], the matrix aluminium and Al_2O_3 particle have
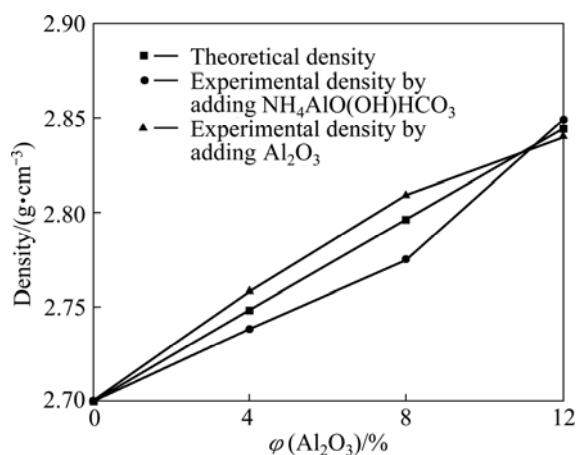

Fig. 3 Density as function of volume fraction of Al_2O_3 for composites obtained under different conditions

the densities of 2.7×10^3 and 3.9×10^3 kg/m³, respectively. Therefore, the density values of the composites increased by adding Al_2O_3 particles. Figure 3 also shows that while experimental and theoretical results are close to each other, there is a little deviation of the measured densities from theoretical calculations. This could be attributed to the change of volume fraction of matrix or Al_2O_3 particle in the sample. Figure 1 shows that there is no porosity in the composites, so it can be deduced that such a little divergence in the volume fraction of Al_2O_3 particle has no effect on the properties of the composites.

3.2 Hardness and tensile strength

After polishing, the hardness values of the composites and matrix were measured. The relationship between the particle volume fraction and the hardness of the composites is plotted in Fig. 4. Figure 4 shows that the hardness of the composites is increased with increasing particle volume fraction. The hardness of composites obtained by adding $NH_4AlO(OH)HCO_3$ is higher than that by directly adding Al_2O_3 particles. This is due to the fact that the small decomposed particles have more surface area in the matrix.
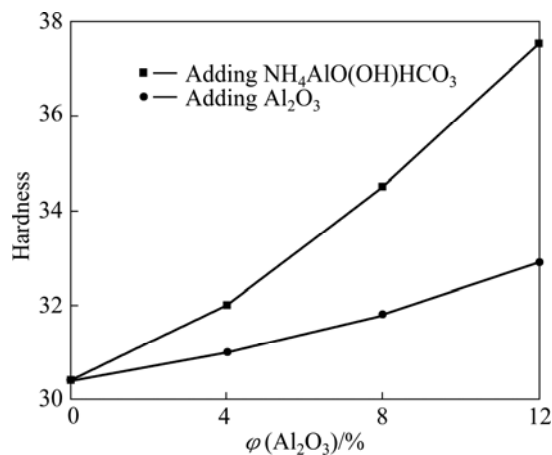

Fig. 4 Relationship between volume fraction of Al_2O_3 and hardness of composites

The ultimate tensile strength (UTS) of the composites is presented in Fig. 5, which shows that the Al_2O_3 in the matrix aluminium leads to a reduction in the tensile strength. The decrease in UTS of the MMCs with increasing Al_2O_3 particle content may be attributed to the fracture of the surfaces between Al_2O_3 and matrix Al during tensile loading. On the other hand, the lower UTS values were obtained in the composites by directly adding Al_2O_3 particles. This is due to the fact that large particles or agglomerated particles could have some flaws with respect to small ones and easily crashed under loading. In such cases, this may be another reason why large particle reinforced composites show lower hardness than composites with small particles.
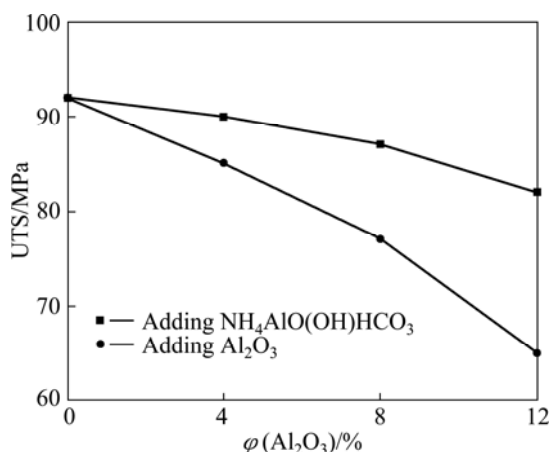
Fig. 5 Relationship between volume fraction of Al_2O_3 particles and ultimate tensile strength of composites

3.3 Wear behavior

Dry sliding wear tests were carried out at a sliding velocity of 0.5 m/s. Figure 6 shows the variation in mass wear rates of two kinds of MMC pin specimens as a function of the volume fraction of Al_2O_3 under different loads. It is observed that the wear rate of the matrix aluminium was more than that of the composite under all loads; the wear rates of the composites decrease with increasing particle volume fraction and the wear rates of the composites increase with the increase of the load. From Fig. 6, it can be observed that the wear rate of the composite prepared by adding $NH_4AlO(OH)HCO_3$ is smaller than that of the composite prepared by adding Al_2O_3. So the composite prepared by adding $NH_4AlO(OH)HCO_3$ is more wearable than the composite prepared by directly adding Al_2O_3. The main reason is that the Al_2O_3 particles decomposed from $NH_4AlO(OH)HCO_3$ are fine and uniform, and the bonding between the Al_2O_3 reinforcement and the Al matrix is improved.

4 Conclusions

1) An in situ Al_2O_3 reinforced Al matrix composite was successfully fabricated by adding $NH_4AlO(OH)HCO_3$, where γ-Al_2O_3 particles distribute uniformly. Alumina particles in aluminium matrix lead to the increased density of the composites.

2) The hardness of the composites increases with increasing particle volume fraction, and is higher by adding $NH_4AlO(OH)HCO_3$ than by directly adding Al_2O_3 particles. The ultimate tensile strength is decreased with increasing the particle volume fraction.

3) Wear rate of the γ-Al_2O_3/Al composites decreases with increasing the volume fraction of the reinforced particles and the load applied. The composite prepared
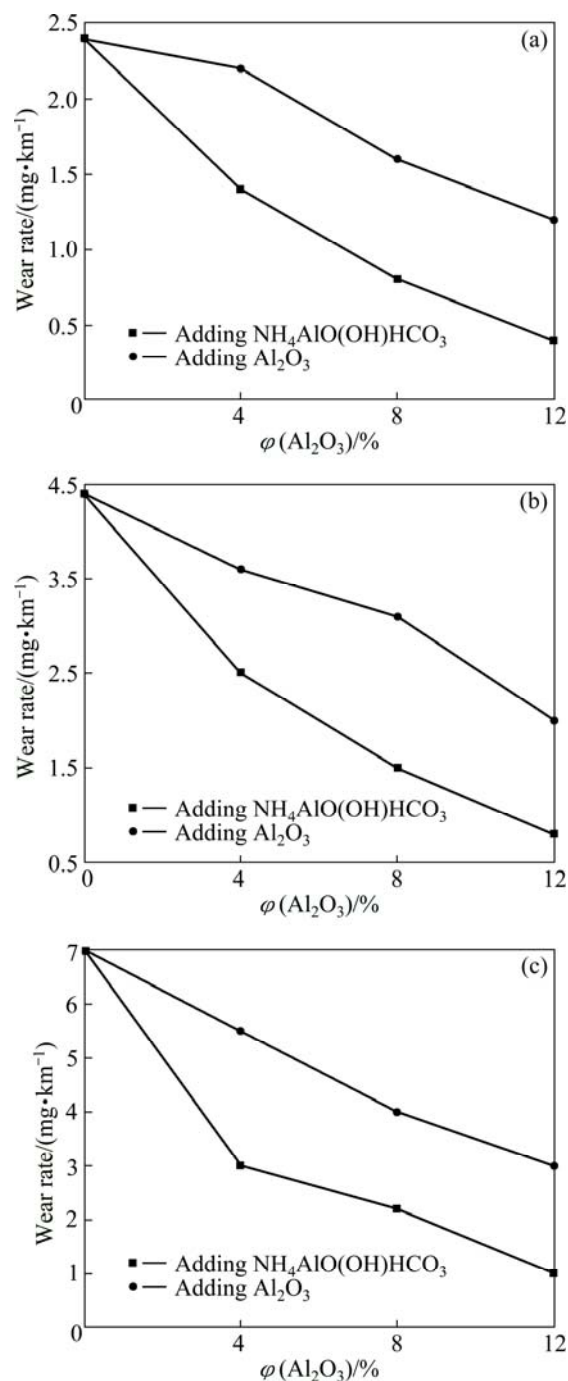

Fig. 6 Wear rate of Al matrix and composites as function of volume fraction of Al_2O_3 at loads of 5 N (a), 10 N (b) and 15 N (c) at sliding velocity of 0.5 m/s

by adding $NH_4AlO(OH)HCO_3$ is more wearable than the composite prepared by directly adding Al_2O_3.

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添加 NH₄AlO(OH)HCO₃ 原位生成 Al₂O₃/Al 复合材料的制备及其性能

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摘 要：碳酸铝铵与熔融的铝液反应原位生成颗粒增强铝基复合材料，对复合材料的力学性能和摩擦磨损行为进行研究。结果表明：在搅拌的铝熔体中碳酸铝铵发生分解反应生成 γ-Al₂O₃；该原位反应的增强颗粒比直接添加的 Al₂O₃ 在铝熔体中分布得更均匀；复合材料的密度和硬度随着增强相加入量的增加而提高， 而强度则随着增强相加入量的增加而降低；磨损率随着增强相加入量的增加和载荷的增加而提高；原位反应生成的复合材料的力学性能和耐磨性明显优于直接添加 Al₂O₃ 颗粒形成的复合材料的。

关键词：铝基复合材料；NH₄AlO(OH)HCO₃；氧化铝颗粒；微观组织；硬度；抗拉强度；摩擦磨损性能

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