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# The Influence of Cu Content on the Aging Behavior of $Al_2O_{3P}$/Al-Cu-Mg Composite

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The 30 vol.% $Al_2O_{3p}$/Al-5.46Cu-Mg composites were fabricated by Pressure Infiltration Method for investigating aging behavior of the composites which within sub-micron $Al_2O_3$ particles. its corresponding matrix alloy was obtained by adjusted the Cu content of 2024Al. Brinell hardness test, differential scanning calorimetry(DSC) and transmission electron microscopy(TEM) were used for investigated the aging behaviors of composites and the corresponding matrix alloy. Results show that the aging behavior of the matrix alloy of Al-5.46Cu-Mg is visible and the peak-aging time put ahead with aging temperature rises. The best aging effect appears at 190℃. The addition of sub-micron alumina particles improves the thermal-diffusion activation energy of precipitates and strongly restrains the precipitation within the matrix and the G.P. zones are completely invisible. Addition of Cu content results in the increase of HBS value in the composites and the decrease of that in the matrix alloy. It is indicated that increment of Cu content results in the formation of high dense Cu-vacancy pair, the decrease of density of vacancy and that of Cu atoms used for precipitation, the improvement of activation energy of G.P. zones strongly dependent on vacancy and finally the difficulty in precipitating. In the composites, a few of dislocations and some interfacial reactions are observed in the matrix alloy, which makes the precipitations finer.

***Keywords:*** *Sub-micron; $Al_2O_3$; Cu content; Al-Cu-Mg alloy; Composites; Aging.*

## 1. Introduction

Studies on the reinforcement size of particle reinforced composite transform from micron to sub-micron. In recent years, studies on sub-micron particle reinforced aluminum matrix composite have shown that[1-7] characteristic of microstructure and mechanical properties in sub-micron particle reinforced composite is obviously different from that of the micron particle reinforced composite. Studies on aging behavior of sub-micron $Al_2O_{3P}$/6061Al composites revealed that[8] there is nearly no precipitation in the matrix alloy. Investigations showed that the content of element in the matrix alloy had a great impact on aging behavior of composites. By adding Cu content to the Al-Cu-Mg system, the author prepared the 0.15μm-$Al_2O_{3P}$/Al-5.46Cu-Mg composite with the volume fraction of 30% .Then the influence of Cu content on the aging behavior of $Al_2O_{3P}$/Al-Cu-Mg composites was investigated by HBS testing, DSC analysis and TEM observation.

## 2. Materials and methods

Sub-micron $Al_2O_{3P}$/Al-5.46Cu-Mg Composites with 30% volume fraction were fabricated by squeeze casting technology. $Al_2O_3$ particles are nearly spherical and their sizes are about 150 nm. And the matrix was obtained by adjusting the Cu content of 2024Al alloy.

All specimens were solution treated at 495℃ for 1h and water quenched at room temperature. After that,the alloy and composite were aged at 130, 160 and 190℃ for periods up to 50 h.

The microstructure of composite was observed by Hitachi S-4700 SEM, as shown in Fig.1. No obvious holes and bright aluminum bands could be seen in in the field of vision. The particles are nearly spherical with uniform distribution and no obvious segregation. So the composites have high quality.

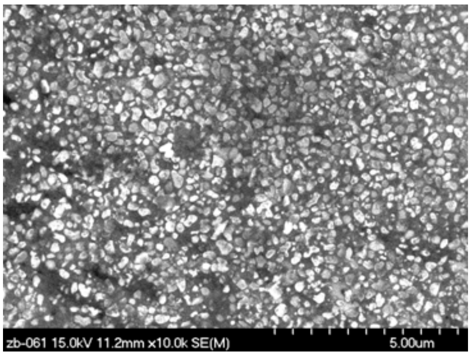



Fig.1 SEM microscopy of the $Al_2O_{3p}$/Al-5.46Cu-Mg composite

The age-hardening responses of composite and unreinforced matrix alloy were characterized using Brinell hardness(HB) measurement, with triplicate specimens and five measurements per condition to ensure the accuracy of results. DSC experiments were conducted on DSC141 thermal analyzer, and the size of samples is Φ5×3mm. All DSC tests were started under the protection of $N_2$ at room temperature and terminated at 400 ˚C using $Al_2O_3$ as the reference sample. Foils of the composite for TEM analysis were examined in a Philips CM-12 and JEOL200CX transmission electron microscope (TEM). The TEM samples were ion milled as follows: The samples were ion milled on Gattan-600 ion milled machine, the working conditions is 4kv, 0.5mA; ion beam glancing angle is 7 ˚ ~ 15 ˚, the cooling medium is liquid nitrogen (-196 ℃). Foils of the matrix alloy were jet-polished with a solution of one third nitric acid and two-thirds methanol at −20 ˚C.

## 3. Results and discussions

### 3.1 Hardness testing

Fig.2 gives hardness measurements as a function of aging time for $Al_2O_{3P}$ /Al-5.46Cu-Mg and matrix alloy at 130, 160,190 ◦C, respectively. Hardness of the two materials increases monotonically as a function of aging time before reaching peak hardness and then gradually decreases. The two composites also behave softening phenomena during initial aging stage. The peak values and peak aging time for matrix alloy increase when the aging temperature rises, which shows that raising the temperature of the matrix alloy plays an obvious role in accelerating aging behavior. The hardness of composites is significantly higher than that of matrix alloy. Taking the 130 ℃ for example, the peak hardness of composites is about 1.93 times compared to the matrix alloy. However, the age-hardening

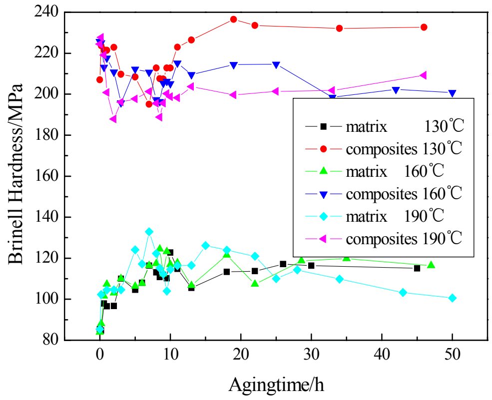



Fig.2 Aging hardening curves of 0.15μm-$Al_2O_{3P}$/ Al-5.46Cu-Mg composite ($Al_2O_{3P}$ volume fraction: 30%) and matrix alloy at different aging temperatures

efficiency of composites is not obvious. There is not obvious aging hardness peak at 160 ℃ and 190 ℃, only with an increase of 19% at 130 ℃. Meanwhile, the increment is much lower than that of matrix alloy. It shows that the dispersion strengthening by adding sub-micron $Al_2O_3$ particles has much more effect than the aging strengthening. The strengthening mechanism is different from the micron particle reinforced aluminum matrix composites which have significant increase in the hardness after aging treatment[10].

In addition, JIANG Long-tao[9] have studied the age-hardening behavior of the 30% - 0.15μm-$Al_2O_{3P}$/2024Al composite and 2024Al alloy in details. $Al_2O_{3P}$/Al-5.46Cu-Mg composites at various aging temperature have a higher hardness value than that of $Al_2O_{3P}$/2024Al composites, while the hardness values of the matrix alloy at all aging temperatures were lower compared with 2024Al alloy. With the increase of Cu content, the aging precipitation of the composite has been promoted , but the aging precipitation of the matrix alloy is suppressed.

### 3.2 DSC analysis

In order to investigate the effect of Cu content on thermodynamics behavior during aging in composites and matrix alloy, DSC curves of the as-quenched specimens of sub-micron $Al_2O_{3P}$/Al-5.46Cu-Mg composite and matrix alloy at heating rates of 0.05 K/s, 0.83 K/s, 0.167 K/s and 0.25 K/s were obtained by DSC141 analyzer(see Fig.3). Furthermore, Thermal-diffusion activation energies for the precipitation in composites and matrix alloy were calculated by DSC curves.

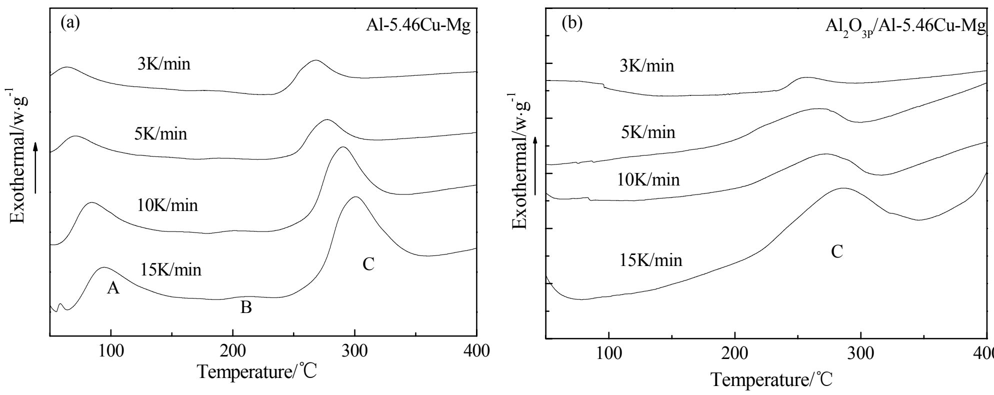



Fig.3 DSC curves at different heating rates for Al-5.46Cu-Mg alloy and the composites treated by solution quenching
(a) Al-5.46Cu-Mg alloy; (b) $Al_2O_{3p}$/ Al-5.46Cu-Mg composite

A, B and C three exothermic peaks in Fig.3(a) were respectively associated with the formation of G.P.B (I) zones, G.P.B (II) zones and s′ phase. It can be seen from Fig.3 that reactive exothermic peaks move to high temperature gradually and become sharp with the increase of heating rate. In addition, It is obvious to observe the presence of three exothermic peak on the curve of 15K/min. However, no obvious peak associated with G.P. zones in composite is noted and there is only one gentle exothermic peak associated with metastable phase between the regions of 500 and 600K in Fig. 3(b). Exothermic peaks temperature of composites are lower and the precipitation temperature range is wider than that in matrix alloy by comparing DSC curves in Fig. 3(a) and Fig. 3(b). Reactive exothermic peaks of DSC curves in sub-micron $Al_2O_{3P}$/Al-5.46Cu-Mg composite are sharper than those in sub- micron $Al_2O_{3P}$/2024Al[9].

According to the equation of Augis and Bennett [9] and DSC results listed in Tab.1, the thermal-diffusion activation energies at every stage during precipitation process can be calculated. Fig.4 presents the calculated results. Thermal-diffusion activation energy of G.P.B( Ⅰ) zone is lower than that of G.P.B(Ⅱ) zone and that of s′phase is highest(119.7KJ/mol) in matrix alloy, which indicates that G.P.B( Ⅰ ) zone precipitates first and s′ phase precipitates last. Hence it can be concluded that the increase of Cu content has no effect on the order of precipitation in matrix alloy

Thermal-diffusion activation energy of s′phase is 128.7KJ /mol, which is higher that in matrix. As a result, Thermal-diffusion activation energy of s′phase in the sub-micron $Al_2O_{3P}$/Al-5.46Cu- Mg is increased, which makes the precipitation of s′ phase more difficult.

Table.1 exothermic peak positions of Al-5.46Cu-Mg alloy and the composites at different heating rates

| Materials | Heating rate (℃/min) | Peak temperature (℃) | | |
|---|---|---|---|---|
| | | G.P.B( Ⅰ ) zone | G.P.B( Ⅱ ) zone | S' |
| Al-5.46Cu-Mg | 3 | 64.21 | 187.95 | 266.86 |
| | 5 | 70.96 | 189.42 | 276.26 |
| | 10 | 83.40 | 200.12 | 289.40 |
| | 15 | 93.67 | 210.45 | 299.38 |
| $Al_2O_{3p}$/Al-5.46Cu-Mg | 3 | -- | -- | 254.76 |
| | 5 | -- | -- | 259.60 |
| | 10 | -- | -- | 269.83 |
| | 15 | -- | -- | 282.53 |

From Jiang Long-tao' research[9], thermal-diffusion activation energies of G.P.B( Ⅰ ) zone and G.P.B( Ⅱ ) zone are 25KJ/mol and 39.7KJ/mol respectively. By comparing with her results, thermal-diffusion activation energies at every stage during precipitation process are all heightened, especially that of G.P.B( Ⅱ ) zone duo to the increase of Cu content, which makes the precipitation more difficult. Meanwhile, thermal-diffusion activation energy of s′ phase in $Al_2O_{3P}$/2024Al composite is 133.5KJ/mol in Jiang Long-tao' research, which is slightly higher than that in sub-micron $Al_2O_{3P}$/ Al-5.46Cu-Mg. It is indicated that addition of Cu has slight effect on the suppression of precipitation in sub-micron $Al_2O_{3P}$/ Al-5.46Cu-Mg.

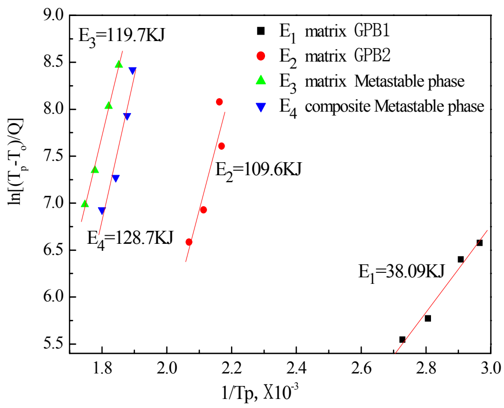



Fig.4 Thermal diffusion activation energy of $Al_2O_{3P}$ / Al-5.46Cu-Mg composites and the matrix alloy

What needs to point out is that exothermic peaks temperatures and thermal-diffusion activation energies are not accurate in the present work, but the tendency of formation difficulty of precipitates at every stage during precipitation process should be accurate.

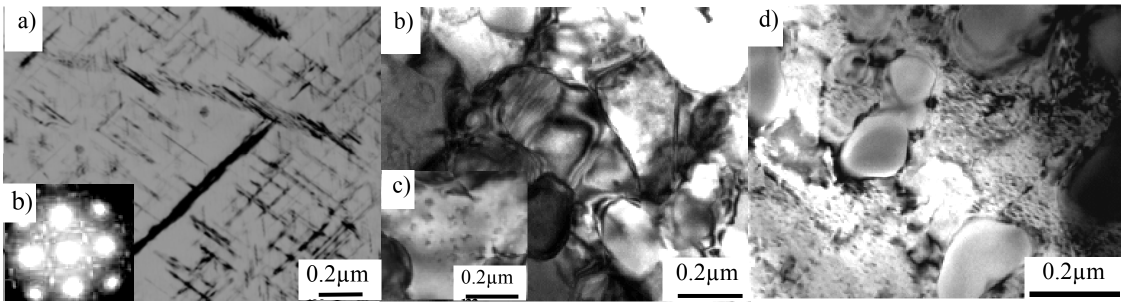
**3.3 TEM observation**

In order to further investigate the micro-mechanism of the effect of the Cu content on the aging behavior of the composite and matrix alloy, TEM was employed to observe the composite and the matrix alloy after typical heat treatment. Fig.5 shows the microstructure of the composite and matrix alloy after typical aging treatment.

It shows from Fig.5(a) that the size of the precipitates in the matrix alloy is about 0.2～0.6μm after aging at 190℃ for 25h.

Some precipitates distributed in a oblique crossing way connect together with each other and grow up to about 1.5μm. From the electron diffraction spots of precipitates in Fig.5(b), S' phase and θ' phase precipitate simultaneously, and their structure varies from coherent one to non-coherent one. In the composite of $Al_2O_{3P}$/Al-5.46Cu-Mg, $Al_2O_3$ particles in nearly spherical shape distribute homogeneous in matrix. As can be showed in Fig.5 (b), the contrast of strain field in the composite does not disappear completely, linear dislocations can still be observed in some area and a certain amount of subgrain structure with size of 0.6~1.5μm occur at under-aged condition(160℃/1h). Besides, G.P. zones with a demission of 10~30nm (see Fig.5 (c)) precipitate from the interior of grain and precipitates also appear at the subgrain boundary. It can be concluded that the addition of sub-micron particles and the increase of Cu content refine the matrix grains and promote the early formation of G.P. zones.

After aging for 34h at 160℃, a great number of precipitates, with size of up to about 20 nm and density much more higher than that of $Al_2O_{3P}$/2024Al composite, dispersed in the matrix in the shape of fine needle or rod (see Fig.5(c)). According to the component of the material and the morphology of the precipitates, precipitates may be determined to be θ' phase or mixture of S' phase and θ' phase. Meanwhile, a thin layer of reactants about 10 nm occurs at the surface of particles, which is inferred to be $Al_2Cu$. In addition, no subgrain morphology is observed.




a）Al-5.46Cu-Mg, 190, 25h; b) c）$Al_2O_{3P}$/Al-5.46Cu-Mg, 160, 1h; d）$Al_2O_{3P}$/Al-5.46Cu-Mg, 160, 34h

Fig.5 Microstructure of typical aged state for $Al_2O_{3P}$/Al-5.46Cu-Mg composites and the matrix alloy

### 3.4 Aging behavior of sub-micron $Al_2O_{3P}$/Al-5.46Cu-Mg composite

In ternary Al-Cu-Mg alloy, s' phase and θ' phase are the main strengthen phases and the composition and structure of precipitates will be different when the ratio of Cu and Mg varies. In the present work, mass ratio of Cu/Mg equals to 6.5,which is between 2.67 and 8. Therefore, precipitates are the $CuMgAl_2$ phase and $CuAl_2$ phase. However, aging behavior of sub-micron $Al_2O_{3P}$/Al-5.46Cu-Mg composite will become more complex.

Cu solute atoms are prone to combined with vacancies in matrix alloy. As a result, increment of Cu content results in the formation of high dense Cu- vacancy pair, the decrease of density of vacancy and that of Cu atoms used for precipitation, the improvement of activation energy of G.P. zones strongly dependent on vacancy and finally the difficulty in precipitating. In addition, the lower density of dislocation reduces the positions for nonuniform nucleation of s' phase and the higher density of Cu atoms universally existed in the matrix increases the possibility of uniform nucleation. So the thermal-diffusion activation energy of precipitates is higher and they precipitate uniformly from the interior of grain, which results in the lower density of precipitates and lower aging hardness than that of 2024 aluminum alloy.

As a result of the addition of sub-micron $Al_2O_3$ particles, the matrix is strongly segmented, which blocks the long-rage diffusion of alloying atoms[5,8-10]. Due to the volume effect and surface effect, vast interfaces provide a lot of positions for trapping vacancies and concentration of Cu atoms to interfaces and interface reactions consume lots of Cu atoms(see Fig.5), which reduces the amount of vacancies and Cu atoms. As a result, the formation of G.P. is suppressed completely. However, finer dislocations resulted from strain field provides lots of positions for nonuniform nucleation for precipitation of metastable phases. Besides, the Cu content of $Al_2O_{3P}$/Al-5.46Cu-Mg composite is higher than the $Al_2O_{3P}$/2024Al composite， so the thermal-diffusion activation energy is lower than the $Al_2O_{3P}$/2024Al composite, which promotes the aging precipitation of composite。

## 4. Conclusions

(1) Aging behavior of the matrix alloy of Al-5.46Cu-Mg is visible and the peak-aging time decreases with aging temperature rises. The best aging effect appears at 190℃. The addition of sub-micron alumina particles restrains the precipitation strongly.

(2) In the Al-5.46Cu-Mg alloy, addition of Cu improves the thermal-diffusion activation energy of precipitates and restrains the precipitation. Precipitates in the Al-5.46Cu-Mg alloy precipitate from the interior of grain and number and size of them are relatively less and smaller at under-aged condition.

(3) In the sub-micron $Al_2O_{3P}$/Al- 5.46Cu-Mg composites, addition of sub-micron $Al_2O_3$ particles introduces vast interfaces and finer dislocation , which results in the consumption of Cu atoms, suppression of the formation of G.P. and prohibition of precipitation of s' phase.

## References


[1] ZHAO Min, WU Gaohui and JIANG Longtao:Acta Mater. Compos. Sin.3(2004) 91-95.
[2] BAI Pucun and DAI Xiongjie:Acta Mater. Compos. Sin.25(2008) 88-93.
[3] Ou Yang Liuzhang and Luo Chengping:Journal of Chinese Electron Microscopy Society. 22(2003) 50-55.
[4] ZHU Jianhua and LIU Lei: :Acta Mater. Compos. Sin.23(2006)65-71.
[5] Jiang Longtao, Wu Gaohui and Sun Dongli: *J Mater Sci Lett*. 21(2002) 609-611.
[6] J.H. Wang and D.Q. Yi:J Materia Eng Perform .15( 2006) 596-600.
[7] Cai QingKui and He ChunLin: Acta Metall. Sin.39( 2003) 865-869.
[8] Su-Shen Chu, Kuo-Shung Liu and Jien-Wei Yeh: Scr. Mater. 45(2001)541-546.
[9] Jiang Longtao, Zhao Min, Wu Gaohui and Zhang Qiang : Mater. Sci. Eng. A.392(2005)366-372.
[10] Taya M and Mori T:Acta Metall.35(1987)155-162.