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ARTICLE

Effect of Cu Content on Microstructure and Properties of AI-2.5Mg-xCu-0.2Si Alloy

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Abstract: Effect of Cu content on microstructure and properties of Al-2.5Mg-xCu-0.2Si alloys was investigated in this research. Results show that the microhardness of the alloy with Cu addition has an obvious rapid hardening effect due to the clustering of Cu and Mg at the early stage of aging. With further aging, the microhardness of the alloy increases again and reaches an obvious second peak due to the formation of S' phase and Guinier-Preston-Bagaryasky (GPB) zone. The increasing amount of Cu content results in a significant increase in tensile strength and yield strength while a reduction of elongation and intergranular corrosion performance. With the increase of Cu content, the intergranular corrosion performance of the alloy becomes worse. The alloy has a reasonably well corrosion performance when the Cu content is less than 1.14wt%. However, there is a significant reduction when the alloy contains 2.10wt% Cu. Based on these results, the alloy containing 1.14wt% Cu has better mechanical properties and corrosion resistance.

Key words: Cu content; heat treatment; strength; corrosion

Automobile body is the most important component for a vehicle's safety, which accounts for about 30% of the total mass of automobile. Therefore, it is rather important if the body frame can be light-weighted. Currently, the majority of automobiles are made by steels. Hypothetically, using aluminum to substitute steel can reduce the body mass and vehicle mass by 40%~50% and 10%, respectively. Aluminum alloys exhibit bright prospects in vehicle lightweight industry with a capability of high specific strength, super corrosion resistance and recycling ability^[1-3]. However, aluminum alloy plate changes due to the natural aging during the time elapsing between the processing and paint baking. The effect of room temperature storage causes the formation of early phases (metastable clusters), which decreases the concentration of Mg and Si in solid solution. Because the clusters dissolve slowly at typical aging temperatures, which results in a loss in the paint bake response^[4-6].

To meet the requirements of high strength and high surface quality of automotive aluminum plates, some researchers have added a trace amount of Cu to Al-Mg alloys to produce Al-Mg-Cu alloys with rapid aging hardening effect^[7-10]. It solves the problem of insufficient strength and softening of Al-Mg alloys during paint baking treatment^[11-13]. Addition of Si can further accelerate the aging hardening process and increase the aging hardening level of the Al-Mg-Cu alloy^[14,15]. Li et al^[11-13] studied the effect of Si element on the precipitation behavior of Al-4Mg-1Cu alloy. They found that Mg₂Si phase forms in the high Mg alloy with addition of Si, which makes Si fail to play a corresponding role in the acceleration of aging hardening^[16]. Moreover, the corrosion problems occur in the long-term use when the Mg content is higher than 3.5wt%^[17]. Therefore, the content of Mg in the alloy in this research is controlled at 2.5wt%. In the previous investigation, it was found that Al-2.5Mg-0.1Cu-0.2Si has a good precipitation

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hardening effect, especially a rapid hardening phenomenon.

In terms of Al-Mg-Cu-Si alloys, the aging strengthening effect is weak when the Cu content is low. However, the increase of Cu content reduces the corrosion resistance and accelerates the natural aging process of the alloy^[12]. Hence, the influence of Cu content on the properties of the alloy needs to be further explored. The effect of Cu content on microstructure and properties of Al-2.5Mg-*x*Cu-0.2Si alloy was investigated in this research.

1 Experiment

The experimental alloys were cast into slab ingot from pure aluminum, pure magnesium, Al-50wt% Cu and Al-24wt% Si master alloys using a resistance furnace at 780 °C. The melt was poured into an iron mold at room temperature to produce a 20 mm×150 mm×200 mm plate. The chemical composition of the investigated alloys (alloy A, B, C, D) is given in Table 1.

After surface milling, the ingots were homogenized at 470 °C for 2 h, and subsequently cooled naturally. The ingots were then hot and cold rolled to sheets of 4 mm in thickness. The cold rolled samples were solution heat treated at 560 °C for 2 h followed by immediate quenching in cold water. Artificial aging was carried out at 175 °C, and the temperature error was ± 1 °C. The age-hardening response was monitored by Vickers hardness measurements using HXD-1000 microhardness machine. The tensile strength, yield strength and elongation were tested by WDW-10E machine. Tensile samples were prepared according to GB/T 228.1-2010. Specimens for transmission electron microscope (TEM) were ground to less than 70 µm, mechanically punched into discs of 3 mm and twin-jet electropolished in a 7:3 (volume ratio) methanol-nitric acid solution cooled to -30 °C. The specimens were analyzed by JEOL 2100 microscope with an operating voltage of 200 kV. The intergranular corrosion (IGC) testing was performed according to the ASTM G67-04 standard. According to this standard, the sample size is 50 mm×6 mm×4 mm and the temperature is 30±0.1 °C. After the test, the specimens were cleaned in water and dried, and then the intergranular corrosion depth is measured using metalloscopy.

2 Results and Discussion

2.1 Aging hardening behavior

 Table 1
 Practical composition of the experiment alloy (wt%)

Alloy	Mg	Cu	Si	Al
А	2.56	-	0.20	Bal.
В	2.57	0.57	0.28	Bal.
С	2.45	1.14	0.25	Bal.
D	2.59	2.10	0.22	Bal.

The hardness curves of A, B, C and D alloys under solution treatment at 560 °C for 2 h and artificially aging treatment at 175 °C are provided in Fig.1. It can be seen that the age-hardening response of the alloys is enhanced by the addition of Cu. Compared with the Cu-free alloy, the time taken to the first peak hardness reduces for the Cu-containing alloys. With the increase of the Cu content, the rapid aging hardening effect is more obvious ($0\sim10$ min). Although the Si content of B alloy is a little bit more and may have a positive effect on cluster and precipitation, it does not change the overall increase trend of the hardness curve with the increase of the Cu content.

After the process of rapid hardening, the hardness increases very slowly and then reaches the second peak (48~192 h). This phenomenon is similar to the that of Al-Cu-Mg alloys reported by Gupta et al^[13]. The second stage of hardening for the alloys involves a relatively steady rise to the peak hardness followed by over-aging. Both the rapid hardening values and the second peak hardness increase with the increase of the Cu content.

2.2 Tensile properties

The tensile properties of A, B, C and D alloys aged for various time periods are presented in Fig.2. It is worth noting that the addition of Cu leads to a distinct improvement of the tensile strengths. With increasing the Cu content, the tensile strengths increase.

As shown in Fig.2a, the strength of A alloy is very low while the elongation is very high when A alloy is only solution treated or solution+short-aging treated. Fig.2b shows the tensile properties of B alloy. After solution treatment, the strength of the alloy is low, but the elongation is high. When aging time is prolonged to 16 h, the strength of alloy significantly improves, and the elongation does not decrease. When aging time is prolonged to 96 h, the strength and elongation decrease comprehensively. Fig.2c shows the tensile properties of C alloy. The tensile strength and yield strength increase with increasing the aging time. The peak ten-



Fig.1 Microhardness curves of A, B, C and D alloys with isothermal aging at 175 °C after solution treatment at 560 °C for 2 h

sile strength and peak yield strength are reached at aging time of 96 h. The elongation of the alloy does not show much difference when aging time is prolonged from 0 h to 0.5 h, but declines with further aging. Fig.2d shows the tensile properties of D alloy. Compared with Fig.2a~2c, the strength is higher and the elongation is lower which restricts the application of D alloy in automobile plate.

2.3 TEM observation of precipitate of alloy

Bright-field (BF) TEM images of alloys under different age conditions and a selected-area electron diffraction (SAED) pattern of the B alloy are shown in Fig.3.



Fig.2 Tensile test results of A (a), B (b), C (c), and D (d) alloys with artificial aging



Fig.3 TEM bright field images (a~c) and SAED pattern (d) of B alloy after aging at 175 °C for different time: (a) 0 h, (b) 6 h, and (c, d) 96 h

Mg₂Si phase can be observed in the matrix after solution treatment. After aging for 10 min, the microhardness of the alloy increases rapidly, but there are no obvious precipitates. The rapid hardening of the alloy is responsible to cluster hardening by clustering of Cu, Mg and vacancy^[18]. The precipitated phase is first observed at dislocation area in the alloy, as shown in Fig.3b. This phase should be S phase which nucleates at dislocations^[14]. As shown in Fig.3c, Guinier-Preston-Bagaryasky (GPB) zones and S phases are observed in the matrix after 96 h aging. And the volume fraction of the S phase is too small to be resolved clearly in the corresponding SAED pattern. During the aging process, the GPB zone, which appears a very fine and uniform dispersion, continuously forms^[12].

Fig.4 shows TEM bright-field images and an SAED pattern of C alloy. Fig.4a is the TEM picture of C alloy after aging for 6 h, which shows that very few S phases can be found to nucleate at dislocations. As shown in Fig.1, aging time of 6~48 h of the alloy is considered to be the incubation period of the second hardening period of the alloy^[7-10,19-21]. Fig.4b shows TEM observation of the alloy after aging for 96 h. It can be found that the second hardness peak corresponds to the lath-shaped S' phase with GPB zones. The precipitate S' phase is distributed uniformly with the length of 8~9 nm. As shown in Fig.4c, the coarse S phase and a large number of GPB zones are observed in the matrix after aging for 240 h.



Fig.4 TEM bright field images (a~c) and SAED pattern (d) of C alloy after aging at 175 °C for different time: (a) 6 h, (b, d) 96 h, and (c) 240 h

TEM images of D alloy with different aging time and a selected-area electron diffraction pattern are shown in Fig.5. Comparing with B and C alloys, the rapid aging hardening effect is more obvious in D alloy. As shown in Fig.5a, a large number of S phases can be observed in the alloy after aging at 175 °C for 96 h. The coarse S phase and the fine GPB zone can be observed in Fig.5b and 5c. It can be seen that the original S phase coarsens which consequently causes a reduction of the hardness of the materials. Comparing the TEM micrographs of B, C and D alloys after aging for 96 h, it can be found that the density of the S phase and GPB zone increases with increasing the Cu content, indicating that the number of precipitated phases increases when the Cu content is higher. The GPB zones and the S

phase coexisting in the Al-2.5Mg-*x*Cu-0.2Si alloy serve as the effective strengthening precipitates.

2.4 Intergranular corrosion

Fig.6 shows the intergranular corrosion mass loss curves of A, B, C and D alloys after artificial aging at 175 °C. It can be seen from Fig.6 that the mass loss of D alloy is 36.8 mg/cm² after solution treatment, which is greater than 25 mg/cm². According to the American standard ASTM G67-04, intergranular corrosion may occur in the D alloy. With the increase of aging time, the intergranular corrosion of the alloy becomes worse. After aging for 64 h, the mass loss of the alloy reaches \geq 75 mg/cm² which enters the severe corrosion zone of intergranular corrosion, indicating that high Cu content causes serious intergranular corrosion.



Fig.5 TEM bright field images (a~c) and SAED pattern (d) of D alloy after aging at 175 °C for different time: (a, d) 96 h and (b, c) 240 h



Fig.6 Mass loss curves of A, B, C and D alloys after artificial aging

The other three alloys have good resistance to intergranular corrosion. It can be seen from the Fig.6 that the mass loss of A and B alloys is lower than 15 mg/cm^2 during the aging process. After aging for 64 h, the mass loss of C alloy reaches 20.8 mg/cm², which is at meso-sensitive zone of intergranular corrosion. Fig.7 shows the optical micrographs of cross-sectional corrosion morphologies of C alloy after aging for 64, 96 and 384 h.

The corrosion of C alloys after aging for 64 and 96 h is pitting dominated, as shown in the Fig.7a and 7b. IGC occurs in limited area with pitting, and the IGC develops at the pit wall, i.e., this corrosion mode is defined as local IGC with pitting (Fig.7c). The sample has the maximum corrosion depth of 13.6 μ m, which belongs to intergranular corrosion level 2.



Fig.7 Intergranular corrosion depth of C alloy after aging at 175 °C for 64 h (a), 96 h (b), and 384 h (c)

Based on the above analyses, the alloy with 0.57wt% Cu has poor hardness and strength with good elongation and corrosion resistance. Alloy with 2.10wt% Cu has high hardness and strength, but poor elongation and corrosion resistance. Therefore, the alloy with 1.14wt% Cu has comprehensively better performance.

3 Conclusions

1) During artificial aging, with the increase of Cu content, the effect of early rapid aging hardening becomes more obvious. The increasing amount of Cu content results in a significant increase in tensile strength and yield strength while the elongation and intergranular corrosion performance reduces.

2) TEM observation results show that there are two main strengthening phases of the alloy, namely the GPB zone and S phase. The GPB zone exists stably during the aging process. The higher the Cu content, the more the number of precipitated phases, the higher the hardness of the alloy.

3) With the increase of Cu content, the intergranular corrosion performance of the alloy becomes worse. The alloy has a reasonably well corrosion performance when the Cu content is less than 1.14wt%, however there is a significant reduction when the alloy contains 2.10wt% Cu. The corrosion performance of alloy with 2.10wt% Cu is very poor, When the Cu content less than 1.14wt%, the alloy has good corrosion performance.

4) The alloy containing 1.14wt% Cu has comprehensively better mechanical properties and corrosion resistance.

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Cu含量对 Al-2.5Mg-xCu-0.2Si 合金微观组织和性能的影响

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摘 要:研究了 Cu 含量对 Al-2.5Mg-xCu-0.2Si 合金微观组织和性能的影响。结果表明:由于形成 Cu、Mg 原子团簇,加入 Cu 的 合金的显微硬度在时效初期有明显的快速硬化。随着时效时间的延长,由于 S'相和 GPB 的形成使得合金的硬度再次提高,并达到 硬度峰值。快速硬化的硬度值和峰值硬度值均随铜含量的增加而增加。铜含量增高,合金的抗拉强度和屈服强度增加明显,延伸 率降低。含铜量增高,合金的抗晶间腐蚀能力变差。当 Cu 含量低于 1.14% (质量分数,下同)时,合金具有良好的抗晶间腐蚀性 能;但含铜 2.10%的合金抗晶间腐蚀性能显著降低。实验结果表明:含铜量为 1.14%的合金具有较好的机械性能和抗腐蚀能力。 关键词:铜含量;热处理;强度;腐蚀

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