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# Influence of Cu addition on microstructure and hardness of near-eutectic Al-Si-*x*Cu-alloys

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Abstract: The influence of Cu content on the microstructure and hardness of near-eutectic Al-Si-xCu (x = 2%, 3%, 4% and 5%) was investigated. After melting Al-based alloys with different Cu contents, alloys were cast in green sand molds at 690 °C and solidified. The solution treatment was performed at 500 °C for 7 h and then the specimens were cooled by water quenching. The samples were respectively aged at 190 °C for 5, 10 and 15 h to observe the effect of aging time on the hardness of matrix. Also differential thermal analysis was used to obtain the transition temperature of the equilibrium phases at cooling rate of 30 K/min and to determine the effect of Cu content on the formation of quaternary eutectic phases and the melting point of  $\alpha$ (Al) + Si. The results show that as Cu content in the alloy increases, the hardness of matrix increases due to precipitation hardening, the melting point of  $\alpha$ (Al) + Si decreases and the amount of these eutectic phases increases, quaternary eutectic phase with melting point of 507 °C forms when Cu content is more than 2%.

Key words: near-eutectic Al-Si-xCu-alloys; Cu content; DTA; hardness

# **1** Introduction

Aluminium-silicon based alloys are well-known casting alloys with high wear resistance, low thermal expansion coefficient, good corrosion resistance and improved mechanical properties in a wide range of temperature. These properties lead to the application of Al-Si alloys in automotive industry, especially for cylinder blocks, cylinder heads, pistons and valve lifters [1-10].

Heat treatment is generally carried out to obtain an optimum combination of strength and ductility in Al-Si-Cu-Mg alloys. The steps for the heat treatment consist of solution treatment, quenching and artificial aging [3]. The age-hardening mechanisms responsible for strengthening are based on the formation of intermetallic compounds during decomposition of a metastable supersaturated solid solution obtained by solution treatment and quenching (precipitation hardening). The mechanical properties of these alloys are significantly influenced by the presence of precipitates.  $W(Al_xCu_4Mg_5Si_4)$  and  $S(Al_2CuMg)$  phases coexist with  $\theta(Al_2Cu)$  and Mg<sub>2</sub>Si phases in aged Al-Si-Cu-Mg alloys.

 $\theta'$  phase preferentially precipitates on the dislocations introduced around eutectic Si particles in the Al-Si-Cu based alloys, while  $\lambda'$  (Al<sub>5</sub>Cu<sub>2</sub>Mg<sub>8</sub>Si<sub>5</sub>) phase homogenously precipitates in the  $\alpha$  matrix, regardless the sites of dislocations, and therefore these precipitates significantly raise the age-hardening ability. *Q* (Al<sub>5</sub>Cu<sub>2</sub>Mg<sub>8</sub>Si<sub>6</sub>) phase exhibiting an effect on age-hardening may exist in aged Al-Si-Cu-Mg alloys [5, 11].

In this study, the effect of Cu content on the microstructure and hardness of Al-Si-*x*Cu alloys was studied. Copper promotes the development of matrix hardness by precipitation hardening in aluminum based alloys.

# **2** Experimental

The solidification of near-eutectic Al-Si alloys including 2%, 3%, 4%, 5 % Cu was realized by melting in a gas crucible furnace and casting in green sand molds at 690 °C. The small samples with dimensions of 30 mm $\times$ 30 mm $\times$ 2 mm were cut from solidified castings. To avoid the effect of casting size on cooling rate and microstructure, all the castings were cut in the same

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dimensions, and the specimens used in this study were taken from the same parts of the castings. To understand the effect of casting dimensions on microstructure, further study is needed. The solution treatment was composed of heating at 500 °C for 7 h and then quenching in water at room temperature. The samples were aged at 190 °C for 5, 10 and 15 h to observe the aging effect on the hardness of the alloys. The compositions of the Al-Si alloys used in this study are listed in Table 1. The analyses were performed by optical emission spectroscopy (OES).

**Table 1** Chemical compositions of alloys used in experiment

Alloy	w(Cu)/ %	w(Si)/ %	w(Fe)/ %	w(Mg)/ %	w(Ti)/ %	w(Zn)/ %	w(Al)/ %
1	2.0	10.8	0.8	0.1	0.02	0.08	Bal.
2	3.1	10.7	0.6	0.1	0.01	0.005	Bal.
3	3.9	10.8	0.6	0.1	0.07	0.04	Bal.
4	5.0	10.6	0.6	0.1	0.07	0.03	Bal.

Differential thermal analysis (DTA-Netzsch STA 409 PG) was performed to obtain the transition temperature of the equilibrium phases at cooling rate of 30 K/min under argon atmosphere. Microstructure observations were carried out with the combination of optical microscope (OM, Zeiss Axiotech 100) and scanning electron microscope (SEM-Jeol 6060) with an energy dispersive X-ray spectrometer (EDS). An image analyzer (Leica Quantimet 501) was used to determine the influence of Cu content on the microstructure of near-eutectic Al-Si alloys.

# **3 Results**

#### 3.1 Microstructural observations

Figure 1 represents the optical micrograph of as-cast microstructure of alloy 1.  $\alpha$ (Al) face-centered-cubic solid solution is the predominant phase (light grey) in the as-cast microstructure of these alloys.  $\alpha$ -phase forms dendritic network, usually cores, and also participates in several multiphase eutectic reactions. The silicon-phase which is soluble into aluminium, and the other alloying elements form a binary eutectic with  $\alpha$ (Al). In the as-cast alloys, the morphology and orientation of dendritic  $\alpha$ (Al) are non-uniform. There are some primary silicon particles, whereas the eutectic silicon is present as coarse plates. Accurate identification of the relatively coarse iron-rich intermetallic phases commonly found in Al-Si casting alloys is important, since some of these phases are associated with reduced mechanical properties. Identification of these intermetallic phases is usually based upon the morphology because of their characteristic shapes. Early research identified two important phases with optical microscope as Chinese script  $\alpha$ (Fe,Si) and needle-shaped  $\beta$ (Fe,Si). Although the needle-shaped  $\beta$ -phases have negative effects on the mechanical properties, the dendritic  $\alpha$ -phase shows a positive effect [12].

The microstructure of as-cast alloy 1 consists of large grains, including the dendrites of the aluminium matrix, interdendritic networks of eutectic silicon plates and other large intermetallic compound particles present between the aluminium dendrite arms, as shown in Fig. 1.



**Fig. 1** Optical micrograph of as-cast alloy 1 etched with light grey: (a)  $\alpha$ (Al) phase surrounded by eutectic; (b) Eutectic phases at higher magnification

Cu is soluble to a low concentration in  $\alpha$ (Al) (5.65% in the binary alloy) [13] and is a major constituent in the intermetallic phase CuAl<sub>2</sub> ( $\theta$ -phase). After the precipitation of CuAl<sub>2</sub> at  $\alpha$ -grain boundaries in Al-Si-*x*Cu alloy, the microstructure becomes brittle and fails intergranularly.

CuAl<sub>2</sub> phase cannot be quantified by using an optical microscope due to color-contrast problems. Instead of this imaging technique, SEM secondary-electron micrographs are used. Figure 2(a) represents the SEM micrographs of heat-treated microstructure of alloy 2. Some network structures are observed. The bright particles (CuAl<sub>2</sub> phases) appear at the boundaries of eutectic cells. Figure 2(b) represents

the energy dispersive X-ray analysis of  $\beta$ -needles. The EDX result indicates that these needles contain Al, Si and Fe ( $\beta$ -Al<sub>5</sub>FeSi).

Figure 2(c) shows the EDX analysis of the  $\theta$ -phase (see Fig. 2(a)), which proves that contained in Al and Cu contained in equal to CuAl<sub>2</sub>.



**Fig. 2** SEM image (a), EDS spectra of  $\beta$ -phase (b) and  $\theta$ -phase (c) in heat-treated alloy 1

As seen from Fig. 3, many intermetallic phases dissolve and the eutectic silicon particles tend to spheroidize after the heat treatment. The mechanical properties of Al-Si alloys not only depend on the chemical composition, but also on the microstructural features such as morphologies of dendritic  $\alpha$ (Al),

spheroidization of eutectic silicon and other intermetallics within the microstructure. The improvement in mechanical properties is generally attributed to the variation of the morphology and size of the eutectic silicon phase particles [8].



Fig. 3 Optical micrograph of heat treated alloy 3

The microstructural investigations show that the shape of the eutectic Si particles changes to granular type in all alloys after heat treatment. Figure 3 shows the microstructural change of Si particles in alloy 3. It is observed a very remarkable spheroidization of eutectic Si particle in comparison to plate shaped as-cast specimen in Fig. 1. The particle distribution including eutectic silicon and intermetallic compounds is more homogenous after heat treatment.

After the heat treatment, most of the intermetallic phases dissolve and the Fe-rich  $\beta$ -needles appear in the structures prominently (Fig. 4). These Fe-rich  $\beta$ -needles are very hard and brittle [8]. The Fe-containing phase ( $\beta$ -Al<sub>5</sub>FeSi) is the most harmful to the mechanical properties of Al-Si based alloys [4].



Fig. 4 SEM image of alloy 4

As known in Al-Cu alloys, rapid cooling after a solution treatment makes GP zones form disc shape and consist of about 90% Cu. These zones with a uniform distribution in the  $\alpha$ (Al) matrix form preferentially with

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copper atoms in the aluminium lattice. A general characteristic of these zones is to have a coherent interface within the matrix, which results in local strain and provides higher hardness. As Cu content increases, the formation of GP zone is promoted due to rapidly cooling with homogenous nucleation [14]. Furthermore, the effect of these zones on hardness under aging condition is emphasized in section 3.3.

#### 3.2 DTA analysis

Figure 5 represents the DTA curves of near-eutectic Al-Si alloys with different Cu contents. It is obvious that Peak I appears when Cu content is higher than 2 %. Moreover, the amplitude of Peak I increases with increasing Cu content. This means that quaternary eutectic phases with low melting point are formed when Cu content is higher than 2% and its amount increases with increasing Cu content [6]. The height of Peak I increases due to increasing Cu content.



Fig. 5 DTA curves for as-cast samples of Al-Si-*x*Cu alloys at 30 K/min

The solidification point of  $(\alpha(AI)+AI_2Cu+Si+AI_5Mg_8Cu_2Si_6)$  signed by Peak I is 507 °C, which is obtained by using Fig. 5. With increasing the Cu content, the melting point of  $(\alpha(AI)+Si)$  decreases and quaternary eutectic phase with melting point of 507 °C forms [3]. The formation of these phases at 507 °C is dependent on the solidification rate (the amount of Cu and Mg can be kept in solid as the alloy cools).

#### 3.3 Age-hardening of alloys and hardness variation

The solution treatment was performed at 500 °C for 7 h and then quenched in water at room temperature. The samples were aged at 190 °C for 5, 10 and 15 h, which is customary for industrial practice to observe the effect of aging on hardness. In Al-Si-xCu alloys, the temperature for solution treatment is usually limited to about 500 °C, because higher temperature leads to incipient melting of

Cu-rich phases and lowers the mechanical properties of casting [5].

Hardness change of alloys 1, 2, 3, and 4, due to aging at 190 °C depending on aging time is given in Fig. 6. Increasing Cu content leads to an increase in hardness and this relationship between the hardness of the matrix of similar alloy and Cu content is in agreement with that in Refs. [8, 11]. It is found that increasing Cu content from 3% to 5% increases the hardness from HB 55 to HB 118. This hardening mechanism suggests the formation of GP zones in the early stage of aging. In the course of aging, this is followed by the precipitation of  $\theta$  " and  $\theta$ '. At long aging time, overaging occurs and the hardness drops due to extensive aging, when the precipitation turns the equilibrium phase  $\theta$ . The hardness drop is due to long mean free path between the  $\theta$  precipitates [11].



**Fig. 6** Hardness change versus aging time for alloys aged at 190 °C

# 4 Conclusions

1) The mechanical properties of Al-Si-xCu alloys largely depend on the heat treatment. Thus, the characteristics of heat treatment play a vital role in a good combination of microstructure and mechanical properties. Cu content in Al-Si-xCu alloys affects the mechanical properties. With increasing Cu content, the hardness increases due to precipitation hardening. It is found that increasing Cu content from 3% to 5% increases the hardness from HB 55 to HB 118.

2) The improvement in mechanical properties is generally attributed to the variation of the morphology and size of the eutectic silicon phase particles. The Fe-containing phase ( $\beta$ -Al<sub>5</sub>FeSi) is the most harmful one for the mechanical properties of Al-Si based alloys. After the heat treatment, most of the intermetallic phases dissolve and the eutectic silicon particles tend to spheroidize.

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3) The quaternary eutectic phases with low melting point are formed when Cu content is more than 2% and its amount increases with increasing Cu content. With the increase of Cu content, the melting point of ( $\alpha$ (Al)+ Si) decreases and quaternary eutectic phase with melting point of 507 °C forms.

4) More researches are necessary for better understanding of the mechanisms responsible for hardness increase in Al-Si-*x*Cu alloys.

## References

- LIAO H, SUN Y, SUN G. Correlation between mechanical properties and amount of dendritic α-Al phase in as-cast near-eutectic Al-11.6%Si alloys modified with strontium [J]. Materials Science and Engineering A, 2002, 335(1–2): 62–66.
- [2] KILAAS R, RADMILOVIC V. Structure determination and structure refinement of Al<sub>2</sub>CuMg precipitates by quantitative high-resolution electron microscopy [J]. Ultramicroscopy, 2001, 88(1): 63–72.
- [3] LASA L, RODRIGUES-IBADE J M. Wear behaviour of eutectic and hypereutectic Al-Si-Cu-Mg casting alloys tested against a composite brake pad [J]. Materials Science and Engineering A, 2003, 363(1–2): 193–202.
- [4] LASA L, RODRIGUES-IBADE J M. Characterization of the dissolution of the Al<sub>2</sub>Cu phase in two Al-Si-Cu-Mg casting alloys using calorimetry [J]. Materials Characterization, 2002, 48(5): 371–378.
- [5] REIF W, DUTKIEWICZ J, CIACH R, YU S, KROL J. Effect of aging on the evolution of precipitate in AlSiCuMg alloys [J].

Materials Science and Engineering A, 1997, 234-236(30): 165-168.

- [6] WANG G, BIAN X, WANG W, ZHANG J. Influence of Cu and minor elements on solution treatment of Al-Si-Mg-Cu cast alloys [J]. Materials Letters, 2003, 57(24–25): 4083–4087.
- [7] ASHTARI P, TEZUKA H, SATO T. Influence of Li addition on intermetallic compound morphologies in Al-Si-Cu-Fe cast alloys [J]. Scripta Materialia, 2004, 51(1): 43–46.
- [8] SAHEB N, LAOUI T, DAUD A R, HARUN M, RADIMAN S, YAHAYA R. Influence of Ti addition on wear properties of Al-Si eutectic alloys [J]. Wear, 2001, 249(8): 656–662.
- [9] TOMIDA S, NAKATA K, SHIBATA S, ZENKOUJI I, SAJI S. Improvement in wear resistance of hyper-eutectic Al-Si cast alloy by laser surface remelting [J]. Surface and Coatings Technology, 2003, 169–170(1): 468–471.
- [10] HAGUE M M, MALEGUE M A. Effect of process variables on structure and properties of aluminium-silicon piston alloy [J]. Journal of Materials Processing Technology, 1998, 77(1-3): 122-128.
- [11] LI R X, LI R D, ZHAO Y H, He L Z, Li C X, GUAN H R, HU Z Q. Age-hardening behavior of cast Al-Si base alloy [J]. Materials Letters, 2004, 58(15): 2096–2101.
- [12] KRAL M V, MCINTYRE H R, SMILLIE M J. Identification of intermetallic phases in a eutectic Al-Si casting alloy using electron backscatter diffraction pattern analysis [J]. Scripta Materiallia, 2004, 51(15): 215–219.
- [13] YU P, DENG C J, MA N G, YAU M Y, NG D H L. Formation of nanostructured eutectic network in *a*-Al<sub>2</sub>O<sub>3</sub> reinforced Al-Cu alloy matrix composite [J]. Acta Materilia, 2003, 51(12): 3445–3454.
- [14] VERHOEVEN J D. Fundamentals of physical metallurgy [M]. New York: Wiley & Sons Publishers, 1975: 487.

# 铜添加对近共晶 Al-Si-xCu 合金的 微观组织和硬度的影响

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**摘 要:**研究铜含量对 Al-Si-*x*Cu (*x* = 2%, 3%, 4% and 5%)合金的微观组织和硬度的影响。不同铜含量的铝合金 经熔炼后于 690 °C 铸造成湿砂模并固化,于 500 °C 保温 7 h 进行固溶处理后对样品进行水冷。随后于 190 °C 进行时效处理,分别保温 5,10 和 15 h,研究时效时间对基体硬度的影响。采用差热分析法,在冷却速度 30 K/min 下确定平衡相的转变温度,并研究铜含量对四元共晶合金的形成和α(Al) + Si 熔点的影响。结果表明,随着铜含量的增加,发生析出硬化从而导致基体硬度增加,α(Al) + Si 的熔点降低,共晶相的含量增加。当铜含量超过 2% 时,生成熔点为 507 °C 的四元共晶相。

关键词:近共晶 Al-Si-xCu 合金;铜含量;DTA;硬度

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