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Boundary trend of $\alpha_1/(\alpha_1+\alpha_2)$ phase region at lower Cu side in Al-Zn-Cu system①

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Abstract: The range of miscibility gap above 300 ℃ at low Cu side in Al-Cu-Zn ternary system was obtained by EPMA of the designed alloys and diffusion-couples treated for equilibrium. The results about the boundary trend of the $\alpha_1/(\alpha_1+\alpha_2)$ phase region was obtained. The $\alpha_1/(\alpha_1+\alpha_2)$ boundary moves towards the lower Zn side with the increase of Cu content. The results are opposite to traditional phase diagrams obtained by experiments, but consistent with recent thermodynamic calculations.

Key words: Al-Zn-Cu system; miscibility gap; $\alpha_1/(\alpha_1+\alpha_2)$ boundary
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1 INTRODUCTION

Al-Zn-Cu ternary system is an important practical one. This system was studied by Kóster, Moeller and Gebhardt in 1941 - 1942[1]. The crystal structure of ternary compound(T' phase)[2] was determined in 1975. The equilibrium relationship between T' phase and the phases in low Cu side at room temperature[3, 4] and microstructure of discontinuous precipitation[5-11] were also investigated. However, it's an unfathomable problem that how copper atoms influence the miscibility gap of Al-Zn system in the Al-Zn-Cu system[1, 12-15], and the results were conflictive with each other. Even the experimental results reported by the Ternary Alloys Phase Diagrams[1, 12] are conflictive with the recent thermodynamic calculation[13-15]. The early experiment results based on alloy method showed that the range of miscibility gap gradually reduced and finally disappeared with the increasing of Cu content at lower Cu side. The thermodynamic calculation on the metastable miscibility gap in Al-Zn-Cu system showed that the range of miscibility gap increased slightly and moved towards the lower Zn side with the increase of Cu content, and that two phase ($\alpha_1+\alpha_2$) field continuously transitted from Al-Zn system to Al-Cu system. If the early experiment results are correct, the solubility of Zn in α(Al) phase will increase, and the addition of Cu atoms can increase the solubility of Zn in α(Al) phase, and decrease the driving force of spinodal decomposition and the distributive ratio of Cu in the phases α_1 and α_2. If the shape of the miscibility gap is consistent with the thermodynamic calculation, the addition of Cu atoms will decrease the solubility of Zn in α(Al) phase, the driving force of spinodal decomposition will hardly change and the Cu atoms mainly exist in phase α_2. The trend of the boundary of $\alpha_1/(\alpha_1+\alpha_2)$ will affect the design of the Al-alloys and the heat-treatment procedure. It is also important for the analysis of the metastable precipitation in supersaturated solid solution.

2 EXPERIMENTAL

The experimental alloys were made of pure Al (99.999%), Zn(99.999%) and Cu(99.999%), melted in an alumina crucible and casted in the steel die. The compositions of the alloys are shown in Table 1. The experimental alloys were hot rolled to 4mm in thickness.

Table 1 Compositions of alloy(mass fraction, %) and finally treatment schedule

Alloy	Al	Zn	Cu	Finally heat treatment schedule
0Cu	60	40	0	Water quench after being kept at 300, 320, 340 ℃ for 400, 300, 200 h, respectively
2Cu	59	39	2	Water quench after being kept at 300, 320, 340 ℃for 400, 300, 200 h, respectively
5Cu	75	20	5	Water quench after being kept at 300, 340 ℃ for 400, 200 h, respectively

The alloys were treated under the following condition: 400 ℃, 48 h(homogeneous treatment) + 200 ℃, 1 h + 100 ℃, 0.5 h + furnace-cooling to room

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temperature (equilibrium treatment).

Different kinds of diffusion-couples were made by 0Cu and 2Cu alloys in order to obtain the boundary compositions of $\alpha_1/(\alpha_1+\alpha_2)$. The preparation process of the diffusion-couple was schematically shown in Fig. 1. The diffusion-couple and alloy samples were sealed in a vacuum quartz tube for heat-treatment. The vacuum was 1 Pa. The final heat-treatment conditions of the samples were shown in Table 1.

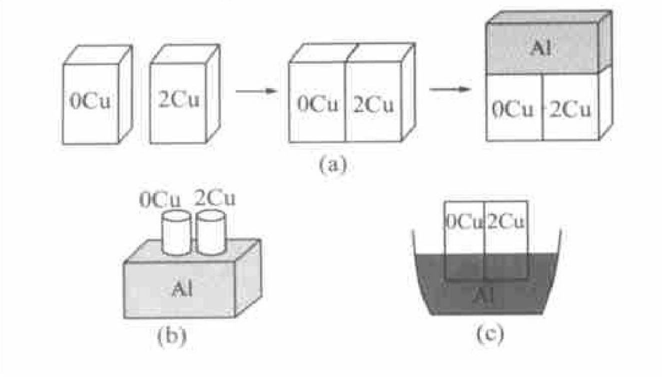

Fig. 1 Preparation process of diffusion couples
(a) —Extrusion; (b) —Embedment;
(c) —Merged melting

After being ground and polished by MgO suspending liquid, the samples were etched by the aqueous solution of mixed acid (2 mLHF+ 3 mLHCl+ 5 mLHNO_3+ 250 mLH_2O). The microstructures of alloys were observed by Versamet-2 optical microscope and Philips XL30 FEG SEM. The compositions of the samples were analyzed by EPM-810Q. The diameter of the electro beam spot was 2 μm, and the voltage was 25 kV. X-ray diffractions of the sheet samples were made by D/Max-Ra X-ray diffractometer of RIGAKU, and K_α diffraction rays of Cu target was adopted. The voltage was 50 kV, current was 15 mA and the scanning speed was 4(°)/min.

3 RESULTS AND DISCUSSON

The representative microstructures of various diffusion couples are shown in Fig. 2. When the alloy 0Cu is embedded in pure Al, the Al_2O_3 film is broken and the two alloy is welded to form the diffusion couple. The bright layer(α_1 phase) results from the diffusion of the element Zn in the alloy 0Cu into pure Al. The coarsened microstructure consists of α_1 and α_2 phases in the alloy 0Cu. The equilibrium composition at the $\alpha_1/(\alpha_1+\alpha_2)$ boundary was measured with infinitely approaching to the boundary along α_1 phase by means of EPMA. The size of α_1 phase in the alloy 2Cu is large enough to directly analyze the composition of α_1 phase in the equilibrium of α_1 and α_2 phases. The compositions of the $\alpha_1/(\alpha_1+\alpha_2)$ boundary at various temperatures are listed in Table 2.

The alloy 2Cu is located in the three phase region of $T'+\alpha_1+\alpha_2$. According to the data of Table 2, the trend of $\alpha_1/(\alpha_1+\alpha_2)$ boundary and the location of the $T'+\alpha_1+\alpha_2$ region at 300 ℃ and 340 ℃ are illustrated in Fig. 3. Because the miscibility gap is connected with the three phase region, the trend of $\alpha_1/\alpha_1+\alpha_2$ boundary is determined by the composition of α_1 phase in the three phase region. It can be clearly seen that the Zn content in α_1 phase decreases due to the addition of Cu.

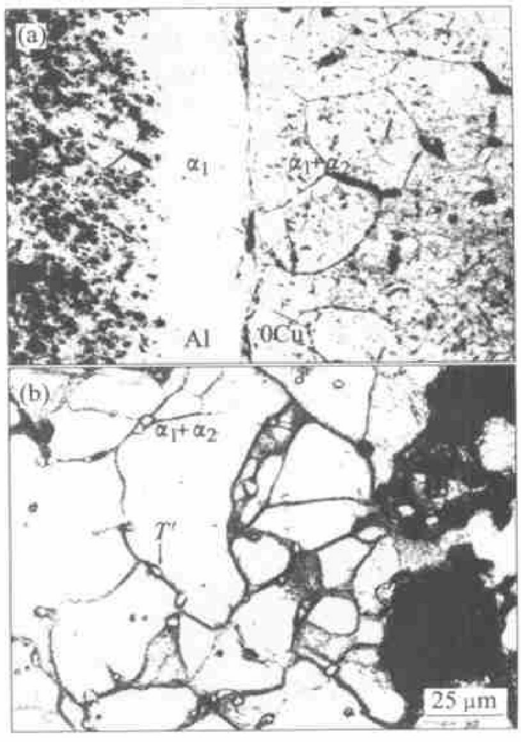

Fig. 2 Microstructures of diffusion couple made of 0Cu and 2Cu alloys (320 ℃, 300 h)
(a) —Pure Al and 0Cu side after diffusion;
(b) —Inside 2Cu

Table 2 Boundary compositions of $\alpha_1/(\alpha_1+\alpha_2)$ in Al-Zn-Cu system at different temperatures(mass fraction, %)

Temperature/ ℃	0Cu			2Cu			5Cu		
	Al	Zn	Cu	Al	Zn	Cu	Al	Zn	Cu
300	78.1	21.9	0	81.7	17.6	0.75	81.42	17.83	0.75
320	74.8	25.2	0	78.25	20.43	1.32	–	–	–
340	67.3	32.7	0	68.82	29.74	1.44	74.06	24.15	1.79

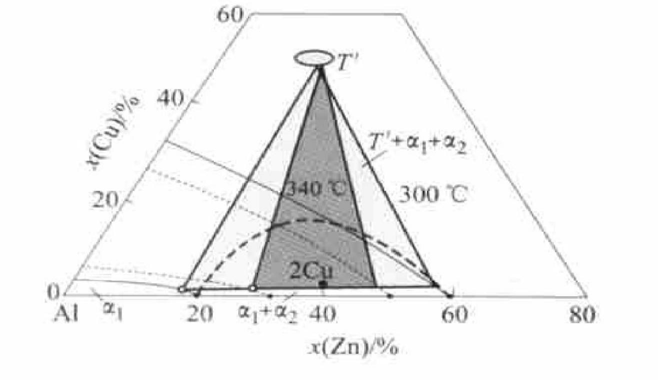

Fig. 3 Trend of $\alpha_1/(\alpha_1+\alpha_2)$ boundary in Al-Zn-Cu system at lower Cu side

The alloy 5Cu is also in the ternary phase region of $T' + \alpha_1 + \alpha_2$. The volume fraction of phase α_1 is expected to be larger. It is suitable for direct detecting the compositions of equilibrium phase α_1. The X-ray diffraction pattern of the alloy 5Cu treated by equilibrium treatment at 300 ℃ is shown in Fig. 4. It can be seen that phase constitutes of the alloy are consistent with what have been expected. Fig. 4(b) shows the separation of the diffraction peak caused by the different composition of α_1 and α_2. Phase α_2 is a Zn-rich phase. the volume fraction of phase α_2 is smaller, but the diffraction factor of phase α_2 is more larger than that of phase α_1. The diffraction peak caused by phase α_2 is high.

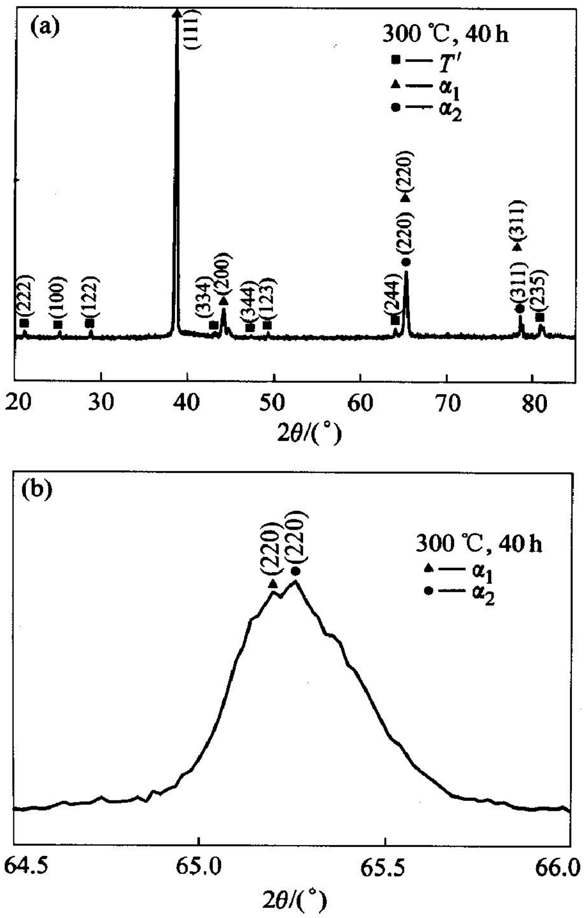

Fig. 4 X-ray diffraction spectrums of 5Cu alloy through equilibrium treatment (a) and diffraction peak separation of α_1 and α_2 phase due to different compositions (b)

The compositions of the Al-rich phase α_1 in the alloy 5Cu treated at 300, 340 ℃ for equilibrium were detected by EPM. The results are shown in Table 2. According to these data, the trend of the $\alpha_1/(\alpha_1+\alpha_2)$ boundary and the position of the $T' + \alpha_1 + \alpha_2$ ternary phase region are drawn in Fig. 5. The characteristics of the trend of the $\alpha_1/(\alpha_1+\alpha_2)$ boundary can be seen more obviously at 300, 340 ℃. It fits the data of alloy 2Cu in equilibrium (Table 2) very well. It is shown that the trend of the $\alpha_1/(\alpha_1+\alpha_2)$ boundary detected in alloy 2Cu is credible. The sizes of the phases T' and α_2 are small, and the composition of these phases can not be detected by EPM. The main reason that the miscibility gap in Al-Zn system was believed to decrease with Cu addition and the boundary of $\alpha_1/(\alpha_1+\alpha_2)$ was believed to move towards the Zn-rich side till 1980s is that this boundary is short at 300 ℃, ie it exists when the Cu content is less than 2% (mole fraction). The alloy with more than 2% Cu is in $T' + \alpha_1 + \alpha_2$ phase region, and the sizes of the phases are small. It is not suitable for the determination of the composition.

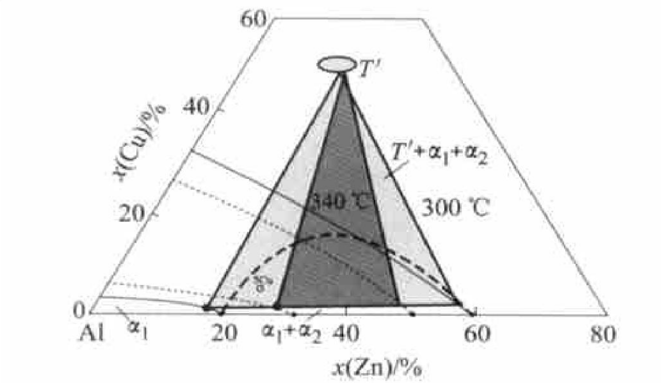

Fig. 5 Trend of $\alpha_1/(\alpha_1+\alpha_2)$ boundary in Al-Zn-Cu system at lower Cu side

The change of Cu content in α_1 phase is very small during 300 - 340 ℃. If the content of Cu in α_1 phase is set to fix, the vertical section of temperature - composition can be obtained by the composition of phase α_1 detected in ternary alloys at different temperatures. It is shown obviously that the addition of Cu decreased the solubility of Zn in phase α_1 (Fig. 6).

4 CONCLUSIONS

By EPM analysis of the isothermally treated alloys and diffusion-couples in Al-Zn-Cu system, the composition characteristic of the miscibility gap with

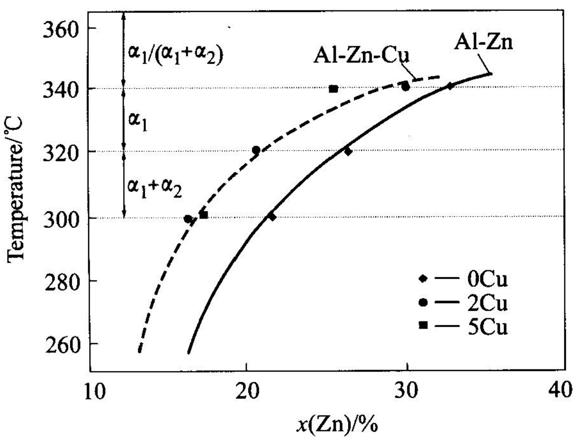

Fig. 6 Effect of solubility of Zn in α_1 phase joined Cu

low Cu content at 300 - 340 ℃ is confirmed, ie, the trend of the boundary of the $\alpha_1/(\alpha_1+\alpha_2)$ is obtained. This boundary moves to low Zn side with the increase of the Cu content, while doesn't move to high Zn side shown by previous studies. The result is contrary to the traditional experimental phase diagram, but consistent with the recent thermodynamic calculations.

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