Journal of University of Science and Technology Beijing
Volume 12, Number 2, April 2005, Page 155

Materials

Effect of electric field on the activity and quenching structure of liquid Cu-Al alloys

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(Received 2004-05-12)

Abstract: The activity coefficient of Al in molten Cu decreases with the increasing of electric current applied to the liquid alloy of Cu-0.2wt%Al. To investigate the mechanism, the quenching experimental results of the liquid Al-Cu alloy show that there is a remarkable change in structure, in which the solute congregates along the current direction especially for DC current. The mechanism of the activity coefficient change of Al in molten Cu-0.2wt%Al alloy treated by electrical field was discussed. Further, the results also provide an evidence for the short-range-ordered liquid metal.

Key words: electrical field; activity; liquid metal quenching structure; liquid metal structure

[This work was financially supported by the National Natural Science Foundation of China (No. 30160186).]

1 Introduction

At present, many works on the aspect of solidification in the electromagnetic field were conducted. And it is sure that the solidification structure is modified by electric field. As to the mechanisms and the way in the solidification affected by electric field, there are many different opinions, one of which put forward by J.Z. Wang [1] is that the nucleus number increases when the current passes through the molten metal during the process of solidification, hence a fine solidification structure can be gained. On the basis of the classical thermodynamics and the electro-dynamics of continuous medium, an equation about the relationship between the nucleation rate and the current density was deduced by R.S. Qing [2], however the mechanisms were not concerned. Also the vapor-liquid equilibrium is also affected by electric field [3]. The content of substance with a larger dielectric constant in the system will be increased in an electric field (when the electric field implies on the gas phase), and with the difference of the dielectric constant between substances increases, the polarization separation will be easier.

To further investigate the effect of electric field on the liquid metal structure, the activity of Al in a liquid Cu-Al alloy in the electric field was studied and the change of the liquid metal structure was recorded by the liquid metal quenching sample.

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2 Experimental procedure and apparatus

2.1 Test of activity

In this experiment the activity was measured according to the following procedure: first the activity a_i of a solute i was measured by the way of chemical equilibrium, then the density *(%i)* of the solute was measured, so the activity coefficient f_i can be deduced by the formula of $a_i = f_i \cdot (\%i)$. Therefore, the change of the solute activity affected by electric field can be obtained if only the solute activity with or without electric field can be measured.

$$2[\mathrm{Al}]+3[\mathrm{O}] \Leftrightarrow \mathrm{Al_2O_3(s)}$$

$$K_1=\frac{a_{\mathrm{Al_2O_3}}}{a_{[\mathrm{Al}]}^2 \cdot a_{[\mathrm{O}]}^3} \tag{1}$$

where

$$a_{Al}=f_{Al}\cdot[\%\mathrm{Al}] \tag{2}$$

For Al_2O_3 is solid phase, then

$$a_{\mathrm{Al_2O_3}}=1 \tag{3}$$

Since the content of [O] in the molten alloy is very low, which in the concentration range of Henry law, then:

$$f_{[\mathrm{O}]}=1, \quad a_{[\mathrm{O}]}=f_{[\mathrm{O}]}\cdot[\%\mathrm{O}]=[\%\mathrm{O}] \tag{4}$$

Substituting equations (2)-(4) into (1), we can deduce

$$K_1 = \frac{1}{f_{Al}^2 \cdot [\%Al]^2 \cdot [\%O]^3} \quad (5)$$

According to

$$\Delta G^{\ominus}_{Al_2O_3} = -RT \ln K_1 \quad (6)$$

That brings

$$K_1 = e^{\frac{-\Delta G^{\ominus}_{Al_2O_3}}{RT}} \quad (7)$$

where R is the gas constant, 8.314 J/(mol·K), T the temperature, K.

Substituting equation (7) into (5), the activity coefficient can be expressed as

$$f_{Al} = \left(\frac{1}{e^{\frac{-\Delta G^{\ominus}_{Al_2O_3}}{RT}} \cdot [\%Al]^2 \cdot [\%O]^3} \right)^{\frac{1}{2}} \quad (8)$$

2.2 Quenching experiment and material of the liquid alloy in electric field

A bar specimen with a radius of 4 mm was made from the alloy of Al-wt5%Cu, then put into a corundum tube of which the inner radius is 4 mm. Heat the specimen with a vertical resistance directional furnace to 800°C and let the current pass through the specimen. Holding for 20 min then the molten specimen was quenched into the water of 20°C, after that, the specimen was sectioned along the center for metallographic study.

The main apparatus in both experiments includes as follows: quartz tube, vertical resistance furnace, directional furnace, electric field triggering unit, electrode, corundum pot, analytical balance, electrolyte oxygen tester. And the material used in the experiment includes Cu (99.99% in purity), Al (99.99% in purity), and Ar (99.999% in purity).

3 Results

The data from **table 1** indicate that the activity of Al was notably decreased with the increase of the current density when an electric field was imposed on the specimen. In this experiment, it is noticed that when the electric field was withdrawn from the specimen, the activity of Al recovered to the initial level after holding for 15 min. Though the initial concentration of Al in the solution is different, the activity coefficients of Al under the three electric fields have an identical trend of change.

Table 1 Effects of electric field and current density on the activity of Al in the Cu-Al alloy

Pulse electric field		AC field		DC field	
Current / A	Activity coefficient of Al	Current / A	Activity coefficient of Al	Current / A	Activity coefficient of Al
0	2.77×10^{-5}	0	1.89×10^{-5}	0	1.56×10^{-5}
17	2.32×10^{-5}	20	1.91×10^{-5}	12	1.38×10^{-5}
51	2.17×10^{-5}	40	1.16×10^{-5}	21	9.08×10^{-6}
68	1.35×10^{-5}	60	6.52×10^{-6}	38	1.16×10^{-5}
102	1.13×10^{-5}	80	6.04×10^{-6}	50	1.35×10^{-5}
Recover	2.00×10^{-5}	Recover	9.08×10^{-6}	Recover	1.47×10^{-5}

Though it is difficult to observe the structure of the liquid metal, the experimental results show that the structure of the liquid alloy must be changed when the electric field was imposed on the specimen. By X-ray diffraction, H. Li and X.F. Bian [4] at east China's Shandong University found that the dimension of the atom group increased with the decrease of temperature. This indicates that the structure of the liquid metal is not completely disorder. Actually, atoms in the liquid metal are in a motive state, and to a given atom the number of the atoms around it is changing. And the order of the liquid metal's structure is only limited to few layers of the atom. By means of quenching from liquid metal, the structure of the molten metal can be recorded generally. Though there are some differences between the molten metal and the quenching solid metal in structure caused by diffusion, the distribution of the solute can be seen on the whole.

Figures 1 and 2 are the metallography of the liquid quenching sample, and the electric field is along the vertical direction. Specimen (a) without electric field in figure 1 is generally composed of globular grains and some dendritic grains with short arms, and the structure of specimen (b) treated by 50 A of AC current is almost composed of dendritic grains of which the primary dendritic arms are longer and the secondary dendritic arms are shorter than that of sample (a). The structures of the specimens treated by electric field in figure 1 is all refined to some degree, and with the increase of the current, the structure turns fine. It is also noticed that the solidification structure also turns fine with the increase of the frequency. In other words, the frequency has great effect on the structure of the molten alloy.

For the phase rich in Cu distributes uniformly, the metallography photos treated by the electric field in figure 2 are all in dark color. The reason is that $CuAl_2$ or rich Cu is dispersed. The liquid part of specimen (c) was connected to the cathode, where the white stripe zone is the Al-rich phase. The structure of the specimen treated by AC current or pulse electric current such as (b), (e) and (f) is not in strip distribution, and only some solute atoms get together locally. When the liquid part of the sample connected to the anode, the direction of the electrical transport is different from that of the specimens in which the liquid part connected to the cathode. So the solid part blocked the diffusion of the solute, therefore the structure is not in strip. During the solidification process, most probably the white stripes (Al-rich phase) are prior to forming the arm of the primary dendritic grain.

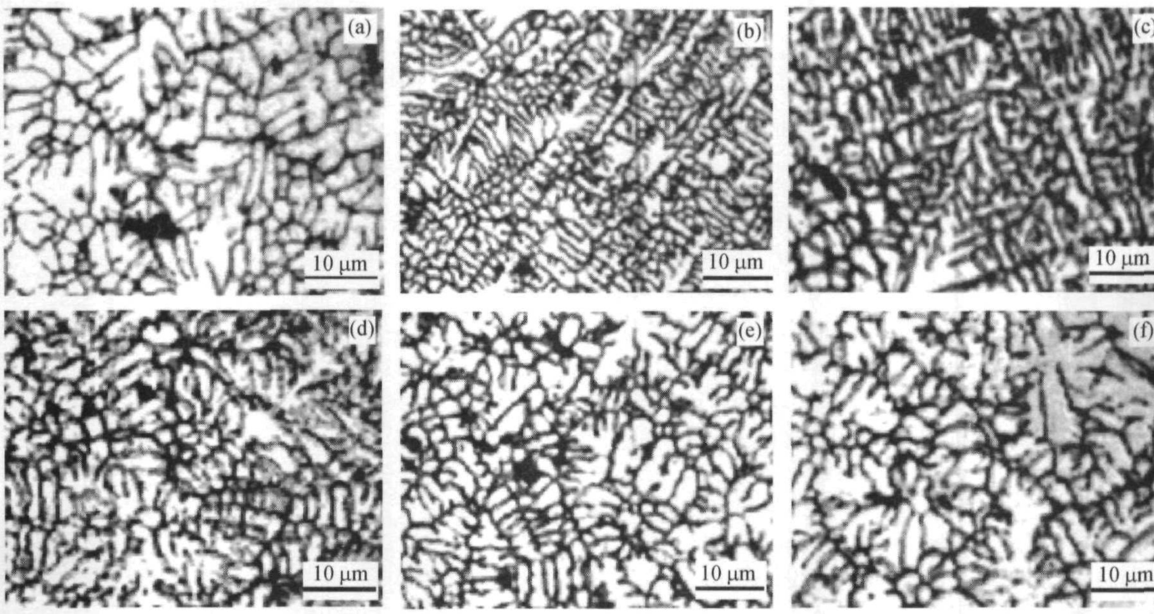

Figure 1 Liquid quenching structures of the Al-5%Cu alloy modified by different electric fields: (a) without electric current; (b) AC current (50 A); (c) DC current (48 A, the liquid part connected with the cathode); (d) DC current (24 A, the liquid part connected with the anode); (e) pulse current (102 A, 10 Hz); (f) with pulse current (102 A, 0.5 Hz).

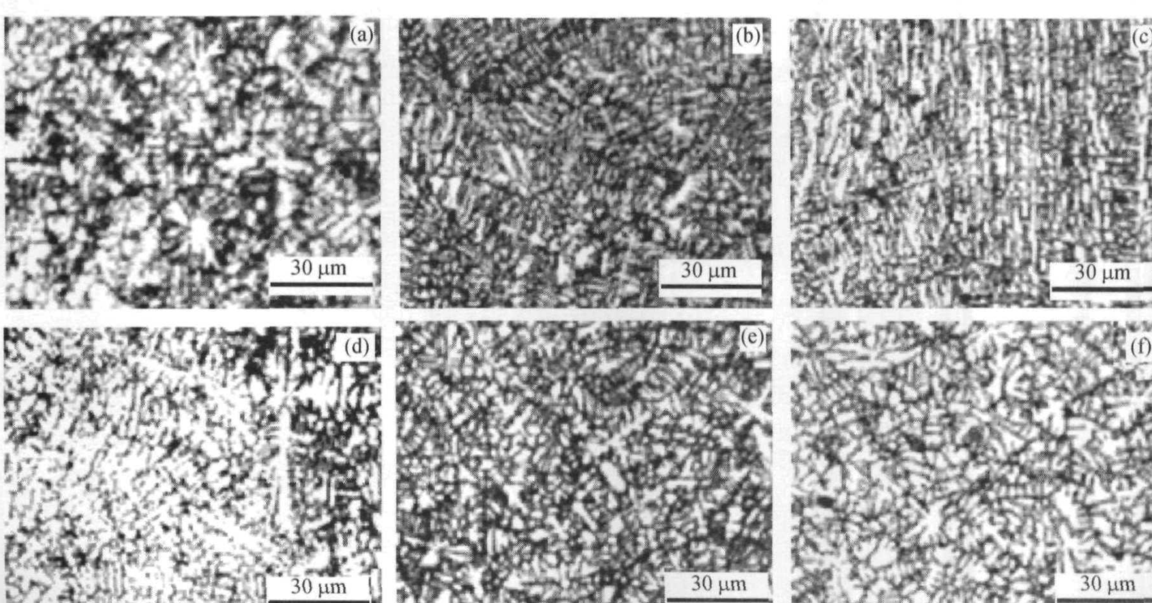

Figure 2 Liquid quenching structures of the Al-5%Cu alloy modified by different electric fields: (a) without electric current; (b) AC current (50 A); (c) DC current (48 A, the liquid part connected with the cathode); (d) DC current (24 A, the liquid part connected with the anode); (e) pulse current (102 A, 10 Hz); (f) the specimen with pulse current (102 A, 0.5 Hz).

4 Mechanisms analysis

Since the electron density and the work function is different, when metal Al contacts with Cu, a potential will be produced at the interface. And the potential difference can be expressed as:

$$V_{AB} = V'_{AB} + V''_{AB} = V_B - V_A + \frac{kT}{e}\ln\frac{n_A}{n_B} \quad (9)$$

where V'_{AB} is the potential difference caused by different work functions of Al and Cu; V''_{AB} the potential difference caused by different electron densities of Al and Cu; V_A and V_B are the potentials of metals A and B, respectively; n_A and n_B the electron densities of metals A and B, respectively; k is the Boltzman constant; T the temperature; e the charge of an electron. Generally, the potential difference caused by the work function of different alloys is not more than 10 V, while the potential difference caused by the electron density of different alloys is much smaller than the former.

If there are no electric fields, Cu atoms are surrounded by Al atoms; when an electric field is imposed on the alloy, for the potential of Cu is higher and the insulate constant is smaller than those of Al, the electrons are easy to pass through the group of Cu, then the electric field is changed. Assume the group of Cu is fixed, when the electric current passes through the bulk alloy, the initial electric field between group A and group B, which caused by the electron density and the work function, is distorted as shown in figure 3. Due to the asymmetric deforming, force F_4 is larger than F_2, then produce a force to drag B toward A (assume A is fixed) till in line with A. So the applied electric field can change the solute distribution and make the atom in a line. Though the solute distributes in line, the photos treated by the electric field in figure 2 show that the solute is more uniform than those not treated by electric field. The main reason is that the distance between lines is smaller than that of the solute atom group in a solution without electric field, and during the solidification process the solute diffuses toward both sides. The strips of the solute will promote the formation of the primary dendritic grain, therefore the primary dendritic grain arms of the quenched liquid alloy treated by the electric field are longer, but more narrow than those in the quenched structure without electric field. In addition, the primary arms are all parallel to the direction of the electric field on the whole especially for the DC field, and the secondary dendritic arms turn short.

At the same time, some other results can support the above mechanism, for instance the electrorheological fluid (ER) composed of solid polymer with high insulation substances and the oil with low insulation substances can flow like water and turn into solid when an electric field is applied for the viscosity is proportional to the current density, and the particles will be arranged in chain by the force of electric field. When the electric field was removed, the ER will turn into liquid again [5]. J.S. Wang found that the pulse electric field can promote the transition of carbon to graphite in cast iron during the solidification process, and the longer time treated, the more transited of the graphite [6]. Y. Tang found there exist three kinds of atom groups in the molten hypereutectic alloy of Al-Si which are Al-Al group, Al-Si group and Si-Si group [7]. When the molten hypereutectic alloy of Al-Si was treated by an electric field, Si-Si group increased remarkably. These results indicate that the solute and the solvent have a tendency of separation when the alloy treated by electric field.

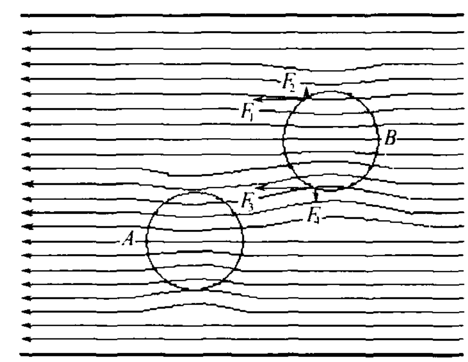

Figure 3 Mechanism sketch of the atom group distribution caused by electric field.

To a molten alloy treated by electric field, when the electric field was cancelled and then holding for 15 min at 800°C, the solidification structure would be same as that of the specimen without electric field. This is a spontaneous process, so the Gibbs free energy of the system will decrease in this process. Suppose the energy of the system is composed of the free energy G_0 and ΔG_E generated by the work of the electric field, when an electric field is imposed on the molten alloy, the energy of the system will increase. Though the total energy of the system increases, for ΔG_E is used to tie the atoms, the free energy of the system with electric field can be expressed as:

$$G = G_0 - \Delta G_E \quad (10)$$

In a word, the force of the electric field as shown in figure 3 binds up the solute atoms in a line, therefore the reaction of Al in the liquid alloy will decrease and the activity of Al will decrease accordingly.

5 Conclusions

(1) When the liquid Cu-Al alloy treated by electric field, the activity coefficient of the solute atoms will decrease.

(2) Electric field can change the molten alloy's structure obviously, and the solute atoms have a ten-

dency to get together in a line especially for the DC field.

(3) The stronger the electric field intensity, the more obvious the liquid alloy's structure change.

(4) The dendritic of the structure treated by electric field is more developed, while it turns fine on the whole.

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