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Effect of current density on distribution coefficient of solute at solid-liquid interface①

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Abstract: When current passes through the solid-liquid interface, the growth rate of crystal, solid-liquid interface energy and radius of curvature at dendritic tip will change. Based on this fact, the theoretical relation between the distribution of solute at solid-liquid interface and current density was established, and the effect of current on the distribution coefficient of solute through effecting the rate of crystal growth, the solid-liquid interface energy and the radius of curvature at the dendritic tip was discussed. The results show that as the current density increases, the distribution coefficient of solute tends to rise in a whole, and when the former is larger than about 400 A/cm^2, the latter varies significantly.

Key words: solidification of metals; distribution coefficient; current density; rate of crystal growth; solid-liquid interface energy; radius of curvature at dendritic tip

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1 INTRODUCTION

The authors have studied the effects of current on the stability of solid-liquid interface and columnar dendrite spacing in detail[1-3], and the effect mechanism of current has been discussed[4, 5]. But the effect of the current on the distribution coefficient of solute at solid-liquid interface was not considered in the previous studies. The distribution coefficient of solute at solid-liquid interface is one of the important parameters in the process of solidification. Therefore, the study of the effect of current on it will help us fully understand the solidification behavior under the action of current. Based on the previous studies, the authors aim to explore the variation of the distribution coefficient of solute at solid-liquid interface with current in this paper and then understand the acting mechanisms.

2 WAYS FOR CURRENT TO AFFECT DISTRIBUTION COEFFICIENT OF SOLUTE AT SOLID-LIQUID INTERFACE

For binary alloys, the distribution coefficient of solute at solid-liquid interface is related with the rate of crystal growth, the pressure of system and the radius of curvature at solid-liquid interface. Under constant pressure, the distribution coefficient of solute at solid-liquid interface considering the effect of the radius of curvature of solid-liquid interface can be expressed as follows[6]:

$$k^* = k_0 + \frac{\sigma V^{s}_{m,A} k}{R T_m x_l} + \frac{v_c (1 - k^*)}{\beta v_d} \qquad (1)$$

where k^* is the distribution coefficient of solute at solid-liquid interface with consideration of the radius of curvature of solid-liquid interface, R is the universal gas constant, T_m is the melting point of pure solute, σ is the solid-liquid interface energy, $V^{s}_{m,A}$ is the molar volume of solute constituent in the solid phase, k is the radius of curvature of solid-liquid interface, x_l is the molar fraction of solute in the liquid, k_0 is the equilibrium distribution coefficient of solute when the solid-liquid interface is planar, v_c is the rate of crystal growth, β is the desorption constant of adsorbed atoms, and v_d is the diffusion rate of atoms.

The results of previous studies show that when the current passes through the solid-liquid interface, the solid-liquid interface energy, the radius of curvature of solid-liquid interface and the rate of crystal growth are related with the current density[1-3]. Therefore, it can be seen from Eqn. (1) that the current can affect k^* by affecting k, σ and v_c.

2.1 Effect of current density on k^* through affecting rate of crystal growth

Derivation of Eqn. (1) to v_d shows that k^* increases with v_d. When the current passes through the solid-liquid interface, the relation between current density J and growth rate v_c can be expressed by[3]

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$$v_{\mathrm{c}}=[q-\frac{\pi}{4}a^2h(\frac{1}{k_{\mathrm{e}}^{\mathrm{s}}}+\frac{1}{k_{\mathrm{e}}^{\mathrm{l}}})J^2]/[\frac{\pi}{4}a^2(h\rho_{\mathrm{l}}G_{\mathrm{l}}c_{\mathrm{pl}}+L)] \qquad (2)$$

where q is the heat released in unit time in the process of solidification, a is the diameter of sample, h is the length of sample with current passing it, $k_{\mathrm{e}}^{\mathrm{l}}$ and $k_{\mathrm{e}}^{\mathrm{s}}$ are the electric conductivities of liquid and solid phases, ρ_{l} is the density of molten metal, G_{l} is the temperature gradient in front of the solid-liquid interface, c_{pl} is the specific heat capacity of molten metal, and L is the latent heat of solidification.

It is clear from Eqn. (2) that when the experimental conditions are determined, the degree of effect of current density on the rate of crystal growth depends on the characteristics of the materials. For Cu-5% Al, under the condition of unidirectional solidification, substituting the corresponding parameters and the data of G_{l} in Table 1 from Ref. [7] into Eqn. (2), one can know from the calculation results that as the current density increases from zero to 1 000 A/cm^2, the rate of crystal growth decreases only by about 0.26×10^{-2} mm/s. Therefore, for metallic materials with little resistance, the effect of current density on the distribution coefficient of solute at solid-liquid interface through affecting the growth rate of crystal can be neglected. But for metallic materials with large resistance, the effect of current density should be taken into consideration.

2.2 Effect of current density on k^* through affecting solid-liquid interface energy

The relation between current density and solid-liquid interface energy is given by[8]

$$\sigma=\sigma_0+wJ^2 \qquad (3)$$

where σ_0 is the solid-liquid interface energy without the action of current, w is a coefficient related with solute concentration and electric parameters of solid and liquid phases.

Combining Eqns. (3) and (1), it can be known that as current passes through the solid-liquid interface, the distribution coefficient of solute at solid-liquid interface tends to rise, and its varication depends on w. w and σ are of orders of magnitude of 10^{-10} and 10^{-5}, respectively[8, 9].

The theoretical variation of σ with J is displayed in Fig. 1. It can be seen that when the current density is larger than about 200 A/cm^2, the effect of current density on distribution coefficient of solute at solid-liquid interface is obvious.

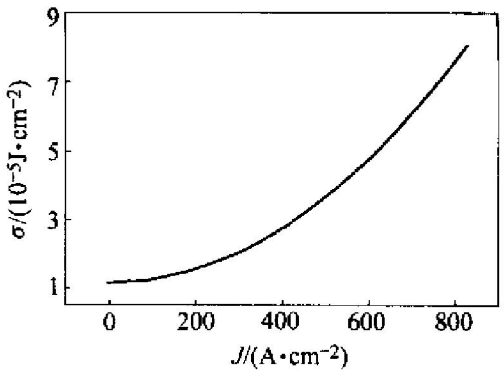

Fig. 1 Variation of solid-liquid interface energy(σ) with current density(J)

2.3 Effect of current density on k^* through affecting radius of curvature of solid-liquid interface

By assuming the cross-section of dendritic tips plus major axis to be semi-ellipse, Kurz and Fisher[10] established the relation between the first dendritic spacing d_1 and the radius of curvature of dendritic tip by using the geometric relation as follows:

$$d_1=(3\Delta T^1)^{1/2}G_{\mathrm{l}}^{-1/2}R^{1/2} \qquad (4)$$

where ΔT^1 is the temperature difference between the dendritic tip and the non-equliblium solidus.

There is a complex functional relation between the first dendritic spacing and current density. By simplifying this function and contrasting the experimental data, a simpler relation may be obtained[3], i. e.

$$d_1=a-bJ-cJ^2 \qquad (5)$$

where a, b and c are constants which depend on solidification temperature. For the Cu-5% Al alloy, under the conditions of sub-rapid and rapid solidification, $a=79$, $b=0.046$, $c=0.56\times10^{-5}$; under the condition of slow solidification, $a=79$, $b=-0.25$, $c=3.6\times10^{-4}$.

Substituting Eqn. (5) into Eqn. (4), the relation between the radius of dendritic tip and current density can be obtained, i. e.

$$R=(a-bJ-cJ^2)^2\frac{G_{\mathrm{l}}}{3\Delta T^1} \qquad (6)$$

It can be seen from Eqn. (6) that, under the conditions of sub-rapid and rapid solidification, the larger the current is, the smaller the radius of dendritic tip, thus the larger the corresponding curvature. Therefore, k^* increases with increasing current density. Under the condition of slow solidification, the larger the current density is, the larger the radius of dendritic tip is, then the smaller

Table 1 Temperature gradient in front of solid-liquid interface

Current density/(A·cm^{-2})	0	64	128	192	256	320	384	448	512	573	637	700	764	828
Temperature gradient/(K·cm^{-1})	75.5	74	75	76	77.5	80	82	85	88.5	92	96	101	107	115

the corresponding curvature. Therefore, k^* decreases with increasing current density. Flemings[11] pointed out that only when the radius of curvature of dendritic tip is smaller than 10^{-6} cm, can it play an obvious role on the distribution coefficient of solute; when the radius of curvature is larger than 10^{-4} cm, it almost has no effect on the distribution coefficient of solute. Therefore, the degree of effect of current density on the distribution coefficient of solute by affecting the curvature of the solid-liquid interface must be determined based on calculation.

For the Cu-5%Al alloy, ΔT^1 may take a value of 12 K[9], G_l takes the experimental values listed in Table 1, and its solidification rate is about 3 K/s which belongs to sub-rapid solidification[12]. It can be decided by calculation using Eqn. (6) that under the conditions of sub-rapid and rapid solidification, R decreases with increasing current density, as shown in Fig. 2. It can be seen that when the current density is larger than 200 A/cm², R reduces to below 10^{-4} cm, and it will produce obvious effect on the distribution coefficient according to the point of view of Flemings[11]. Comparatively, under the condition of slow solidification, when the current passes through the solid-liquid interface, it is not easy to produce effect on the distribution coefficient of solute by affecting the curvature of the solid-liquid interface.

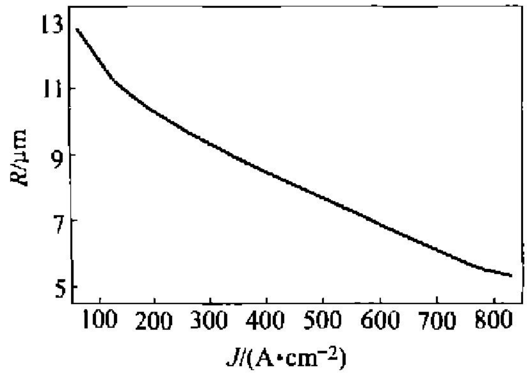

Fig. 2 Variation of radius of dendritic tip(R) with current density(J) under sub-rapid and rapid solidification

3 LAW OF EFFECT OF CURRENT DENSITY ON DISTRIBUTION COEFFICIENT OF SOLUTE AT SOLID-LIQUID INTERFACE

Substituting Eqns. (2), (3) and (5) into Eqn. (1) yields

$$k^* = k_0 + \frac{3V^{\mathrm{s}}_{\mathrm{m,A}}\Delta T^1(\sigma_0 + wJ^2)}{RT_{\mathrm{m}}x_{\mathrm{L}}G_{\mathrm{l}}(a - bJ - cJ^2)} + \frac{(1 - k^*)[4q - \pi a^2 h(1/k^{\mathrm{s}}_{\mathrm{e}} + 1/k^{\mathrm{l}}_{\mathrm{e}})J^2]}{\beta v_{\mathrm{d}}[\pi a^2(h\rho_{\mathrm{l}}G_{\mathrm{l}}c_{\mathrm{pl}} + 4L)]} \tag{7}$$

Eqn. (7) comprehensively reflects the effect of current density on the distribution coefficient of solute at solid-liquid interface.

If the effect of current density on k^* through affecting the growth rate of crytal is neglected, then Eqn. (7) can be rewritten as

$$k^* - \frac{\beta v_{\mathrm{d}}}{\beta v_{\mathrm{d}} + v_{\mathrm{c}}}k_0 = \frac{v_{\mathrm{c}}}{\beta v_{\mathrm{d}} + v_{\mathrm{c}}} + \frac{\beta v_{\mathrm{d}}}{\beta v_{\mathrm{d}} + v_{\mathrm{c}}} \cdot \frac{3V^{\mathrm{s}}_{\mathrm{m,A}}\Delta T^1(\sigma_0 + wJ^2)}{RT_{\mathrm{m}}x_{\mathrm{L}}G_{\mathrm{l}}(a - bJ - cJ^2)} \tag{8}$$

Eqn. (8) shows that the difference between k^* and k_0 will rise as v_c increases. If v_c is determined, when no current passes through the solid-liquid interface, then $k^* - k_0$ is a determined value. When current passes through the interface, the value of $k^* - k_0$ only depends on $[3\Delta T^1(\sigma_0 + wJ^2)]/[G_l(a - bJ - cJ^2)]$ on the right side of Eqn. (8), namely on the vriation of σk with current density. Therefore, the law of effect of current density on k^* can be known from the variation of σk with current density as shown in Fig. 3. The variation of σk with J indirectly reflects the law of effect of current density on k^*. It can be seen that when the current density rises to about 400 A/cm², σk shows a tendency of rapid increase. Compared with the above analysis, it can be known that the effect of current density corresponding to rapid solidification on k^* is increased significantly, which shows that the comprehensive effect of σ and k is more notable than those of single factors.

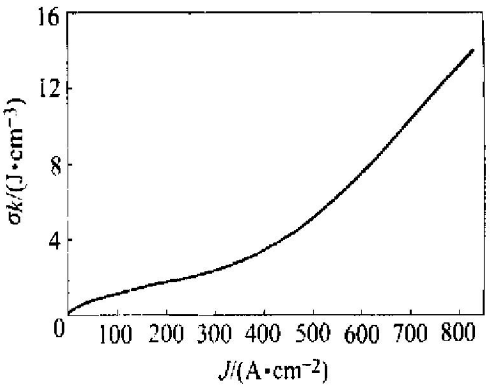

Fig. 3 Variation of σk with current density(J)

4 CONCLUSIONS

1) The theoretical relation between the distribution coefficient of solute at solid-liquid interface and current density can be expressed by

$$k^* = k_0 + \frac{3V^{\mathrm{s}}_{\mathrm{m,A}}\Delta T^1(\sigma_0 + wJ^2)}{RT_{\mathrm{m}}x_{\mathrm{L}}G_{\mathrm{l}}(a - bJ - cJ^2)} + \frac{(1 - k^*)[4q - \pi a^2 h(1/k^{\mathrm{s}}_{\mathrm{e}} + 1/k^{\mathrm{l}}_{\mathrm{e}})J^2]}{\beta v_{\mathrm{d}}[\pi a^2(h\rho_{\mathrm{l}}G_{\mathrm{l}}c_{\mathrm{pl}} + 4L)]}$$

2) The current density affects the distribution coefficient of solute at solid-liquid interface by changing the rate of crystal growth, solid-liquid interface energy and the curvature of solid-liquid interface. The distribution coefficient of solute at solid-liquid interface shows an increasing tendency with current density increasing generally.

3) When the current density is larger than about 400 A/cm^2, the distribution coefficient of solute at solid-liquid interface changes rapidly.

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