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Formation mechanism of anomalous eutectics in highly undercooled Ag–39.9 at%Cu alloys*

Zhao Su(赵 素), Li Jin-Fu(李金富)†, Liu Li(刘 礼), and Zhou Yao-He(周尧和)

State Key Laboratory of Metal Matrix Composites, School of Materials Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, *China*

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This paper investigates the solidification behaviour of the Ag–Cu eutectic alloy melt undercooled up to 100 K. It is revealed that lamellar eutectics grow in a dendritic form in the Ag–Cu eutectic melt with undercooling equal to or greater than 76 K. As undercooling increases, the remelted fraction of the primary eutectics during recalescence rises. The severe remelting and the subsequent ripening of the primary eutectic dendrites lead to the formation of anomalous eutectics.

Keywords: rapid solidification, undercooling, Ag–Cu eutectic alloy, anomalous eutecitcs
PACC: 6125M, 6150J, 6155H, 6470D

1. Introduction

While experimentally investigating the microstructural evolution of eutectic alloys with undercooling prior to nucleation, many researchers[1−9] have revealed a transition from lamellar to anomalous eutectics. Considering that the copper particles in the anomalous Ag–Cu eutectics were discontinuously distributed in the silver matrix, Powell[2] and Hogan[10] proposed that the discontinuous phase in anomalous eutectics was formed by repeated nucleation. Kattamis and Flemings[3] found that both eutectic phases in an anomalous Ni–Sn eutectic region were continuously interconnected along a polyhedral network. They therefore concluded that the formation of anomalous eutectics was due to the dendritic growth of the segregation-free α-Ni phase and its subsequent decomposition into equilibrium α-Ni and β-Ni_3Sn. Such a point of view was supported by Walder and Ryder.[11,12] Jones[4] and Li and Kuribayashi[13] ascribed the formation of anomalous eutectics in undercooled Ni–Sn alloys to the uncoupled growth of two eutectic phases, that is, during solidification of an eutectic alloy undercooled substantially, one constituent phase will grow significantly faster than the other, which breaks the stability of a coupled interface. Wei *et al*[14] assumed that independent nucleation and cooperative branched growth of two eutectic phases should be responsible for the formation of anomalous eutectics at large undercoolings. Since the reduction of interface energy of the lamellae is also a driving force for microstructural evolution, Goetzinger *et al*[15] proposed that the segmentation of primary eutectic lamellae by remelting and subsequent ripening should be responsible for the formation of anomalous eutectics. Recently, Li *et al*[16] advanced that both coupled and decoupled growths of eutectic phases in undercooled eutectic alloy melts could result in anomalous eutectics. In the present paper, we are going to investigate the mechanism which dominates the formation of anomalous eutectics in highly undercooled Ag–39.9 at%Cu alloy.

2. Experimental procedure

Eutectic alloy samples of Ag–39.9at%Cu with a mass of 6 g were prepared by the glass flux method[17,18] from 99.999% pure Ag and Cu slabs. The glass was made by melting a mixture of 12.3 wt% B_2O_3, 17.7 wt% $Na_2B_4O_7$ and 70 wt% Na_2SiO_3 which had been kept at 1273 K for 6 hours. In an experiment, the pure metals were put into a quartz crucible and covered with 0.6 g glass flux. The quartz crucible was then placed in a foamed alumina base inserted in a high-frequency induction heating coil in a vacuum chamber. After the vacuum chamber was evacuated to 2×10^{-3} Pa and backfilled with ultra pure argon, the metals were molten and cyclically superheated and cooled until the desired undercooling was acquired. The experimental samples were solidified

*Project supported by the National Natural Science Foundation of China (Grant No 50571068).
†E-mail: jfli@sjtu.edu.cn

spontaneously without any arbitrary stimulation, and taken out from the vacuum chamber after being cooled to room temperature. A two-colour infrared pyrometer with an accuracy of 1 K and a response time of 1 ms was utilized to monitor the thermal history of the sample during the entire experimental cycle. Chemical analysis indicated that the glass fluxing technique did not change the composition of the alloy. Without any etching, the surface structure was directly examined by a scanning electron microscope (SEM). Then the sample was sectioned, mounted in epoxy, polished, and etched with a mixture of 4% alcoholic picric acid. The microstructure was observed with an optical microscope, and the compositions of the phases were determined by energy dispersive x-ray.

3. Results

A large undercooling level up to 100 K was achieved. Two types of eutectic growths were observed. When the undercooling is less than 76 K, the eutectic lamellae grow in a cellular interface. Except for an anomalous zone near the nucleation site, such eutectic growth does not result in anomalous eutectics in another part of the sample. Therefore, the solidification of Ag–Cu eutectic alloy at undercooling below 76 K is not investigated here. When the melt undercooling is into the range of 76–100 K, one dendrite grows from the nucleation site exclusively and covers the entire surface of the sample (Fig.1(a)). At

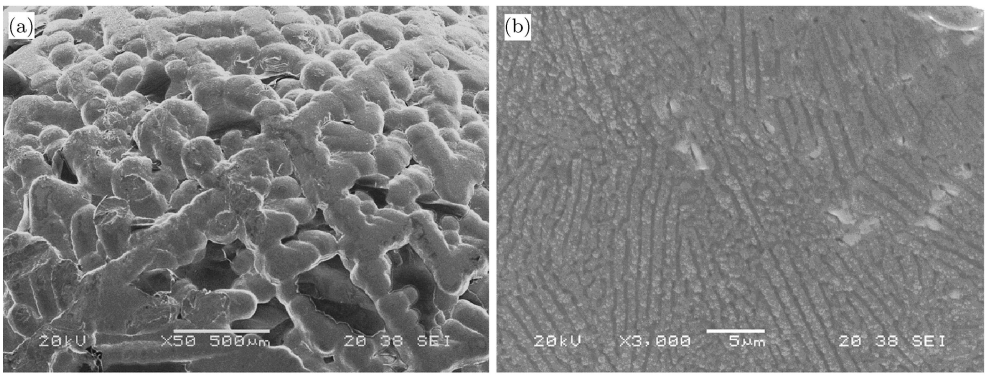
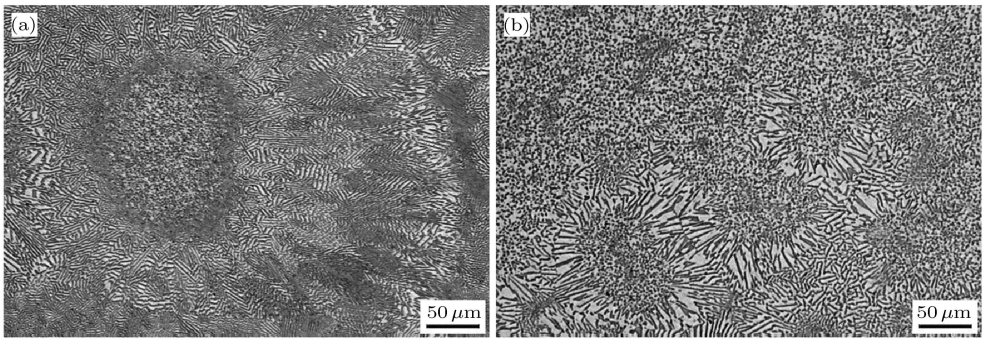


Fig.1. SEM images of the surface structure undercooled by 76 K: (a) dendritic morphology at low magnification; (b) eutectic lamellae in the dendrite arms at high magnification.

high magnification, lamellar eutectics are found in the dendrite arms (Fig.1(b)). Such solidification structures are referred to as eutectic dendrites so as to distinguish them from the dendrites consisting of a single phase. As undercooling increases, the diameters of the eutectic dendrite arms become smaller. On the section of the sample, a dendritic morphology is present in the macrostructure. At high magnification, it can be found that the anomalous eutectics occupy the centre, and around them lamellar eutectics grow outward directionally. The microstructures comprising anomalous eutectics surrounded by lamellar eutectics have been referred to as eutectic colonies in the literature.[19] The eutectic colony is very large at 76 K undercooling (Fig.2(a)). The bright phase has been determined to be rich in Ag, and the dark phase rich



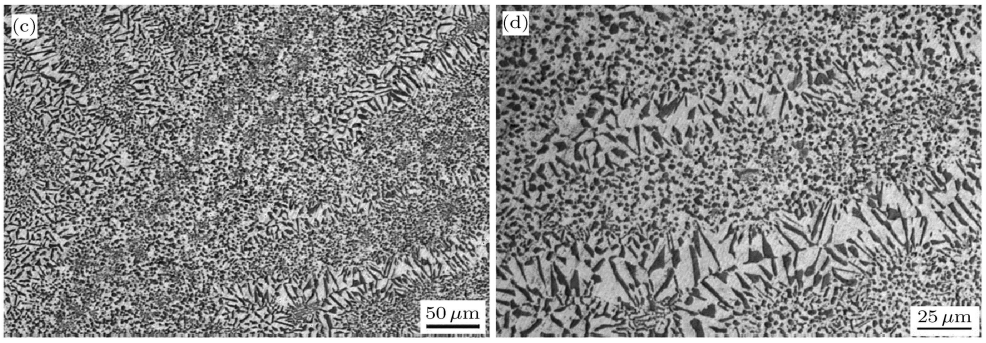


Fig.2. Optical microstructures at different undercoolings: (a) a big eutectic colony inside the sample undercooled by 76 K; (b) small eutectic colonies at an undercooling of 90 K; (c) dendritic morphology of the anomalous eutectic zone at 100 K undercooling; (d) anomalous eutectics in the dendrite arms and lamellar eutectics between the arms at high magnification.

in Cu. With the increase of undercooling, eutectic colonies become smaller (Fig.2(b)). At an undercooling of 100 K, the branching of the eutectic dendrites is so dense that a dendritic contour of the anomalous eutectic structure is present in the microimages (Fig.2(c)). A few lamellar eutectics are between the dendrite arms (Fig.2(d)).

4. Discussion

4.1. Theoretical prediction of the growth mode

During the solidification of undercooled eutectic melts, whether two eutectic phases grow in a coupled or decoupled mode depends on the relative magnitude of growth velocity between two growth modes.[16,20,21] If the velocity of eutectic growth is higher than that of dendrite growth for either of the two eutectic phases, coupled eutectic growth occurs. Otherwise, dendrite growth of a single phase will take place. Recently, a theoretical model for regular lamellar eutectic growth in undercooled melts has been established by Li and Zhou (LZ).[22] Two types of phase diagrams were treated by the LZ model: one with the same solute distribution coefficients for two eutectic phases; the other with parallel metastable solidus and liquidus. The Ag–39.9at% Cu eutectic alloy can be described approximately by the first type of phase diagram.[23] Using the physical data listed in Table 1, we calculate the eutectic growth velocity during rapid solidification of the undercooled Ag–Cu eutectic melt (Fig.3). The

Table 1. Physical parameters of the Ag–Cu eutectic alloy.[12,23]

parameters	values
latent heat of fusion for α-Ag/β-Cu/(J/mol)	11326/13027
specific heat of the liquid/(J/mol·K)	32.21
interdiffusion coefficient of solutes/(m^2/s)	$2.42\times10^{-7}\exp(-48886/8.314T)$
volume fraction of α-Ag in the eutectic	0.743
thermal diffusivity in the liquid/(m^2/s)	5.435×10^{-5}
Gibbs–Thomson parameter for α-Ag/β-Cu/(m·K)	$1.5\times10^{-7}/1.3\times10^{-7}$
eutectic composition/(at% Cu)	39.9
eutectic temperature/K	1053
liquidus slope for α-Ag/β-Cu/(K/at%)	–4.560/5.067
kinetic parameter for α-Ag/β-Cu/(m/s·K)	0.614/0.707
equilibrium solute partition coefficient	0.353

single-phase dendrite growth in undercooled alloy melts has been well described by Boettinger, Coriell, and Trivedi (BCT),[24] from which the dendrite growth velocities of α-Ag and β-Cu in the undercooled Ag–39.9 at%Cu melt were calculated, and the results are also plotted in Fig.3. It is shown that β-Cu grows faster than α-Ag. So β-Cu rather than α-Ag should grow as the primary phase once decoupled growth oc-

curs. The two curves for β-Cu and eutectic growths intersect at about 145 K undercooling, below which the eutectic dendrite grows faster than the β-Cu dendrite. This means that lamellar eutectic dendrite growth occurs when the melt undercooling is less than 145 K, i.e. at the experimental undercoolings, no single-phase dendrite growth takes place.

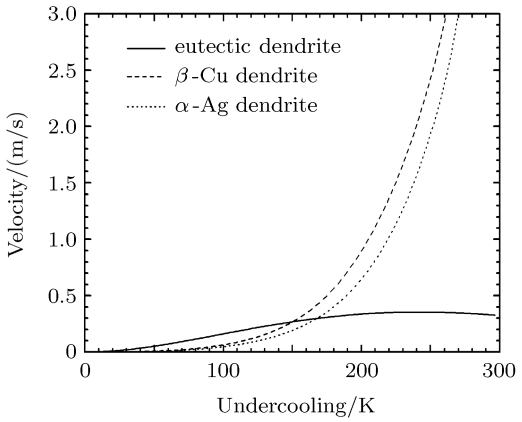


Fig.3. Calculated growth velocities in undercooled melt when eutectic dendrite, β-Cu dendrite or α-Ag dendrite is assumed to grow.

4.2. Formation mechanism of anomalous eutectic

Considering that at the Ag–Cu eutectic composition, the 76 K critical undercooling for the appearance of anomalous eutectics is in accordance with the Ag–Cu system's T_0 curve at which the free energies of liquid and solid of the given composition are equal,[25] Walder and Ryder[11] suggested that a segregation-free solid solution was formed firstly by diffusionless transformation and then was decomposed into anomalous eutectics. From the thermodynamic point of view, the temperature of the dendrite tip must fall below the T_0 temperature during rapid growth in order that a segregation-free solid solution is obtained.[26] In fact, as the latent heat is released during rapid solidification, the dendrite tip must be reheated above the T_0 temperature. Growth of the segregation-free solid solution is impossible in our experiment. This is supported by the observation that at all experimental undercoolings, the highest recalescence temperatures of the Ag–Cu eutectic alloy always exceed the T_0 temperature 978 K after rapid growth (Fig.4).

Dendritic growth of lamellar eutectics in the highly undercooled Ag–Cu eutectic alloy melt can be confirmed by that eutectic dendrites survived on the

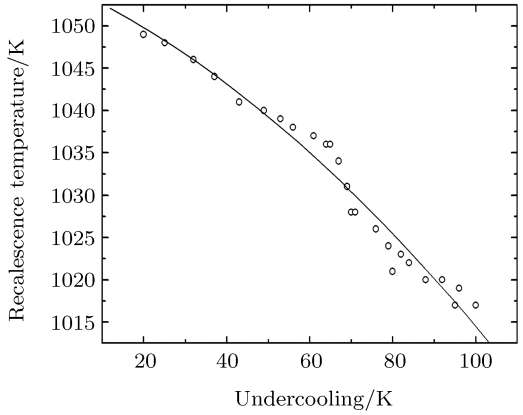


Fig.4. Highest recalescence temperature measured from the sample surface. The line is a guide for the eye.

sample surface (Fig.1). In contact with the crucible wall and glass purifier, the undercooled melt at the sample surface solidified under non-adiabatic conditions. The recalescence temperature is depressed while the local solidification time is shortened.[16] In contrast, the rapid solidification of the undercooled melt inside the sample is adiabatic, which makes the temperature recalesce close to the eutectic temperature. The superheating-induced remelting results in the disappearance of original lamellar eutectics and the formation of anomalous eutectics inside the sample (Figs.2(c) and 2(d)). Details of the explanation are given below.

During rapid solidification, the solubility extension is a very common phenomenon due to the shorter atom diffusion time. Goetzinger *et al*[15] suggested that the excess solute trapped in the primary lamellar eutectics can promote remelting of the eutectics during recalescence. After recalescence, the fragmentation process is promoted in the semi-liquid state with the reduction of the large interface energy in the fine lamellae as the driving force.[15,27,28] Li *et al*[29] recently pointed out that the supersaturation of solute in the primary eutectics induced by solute trapping was very slight. Since the composition of a growing solid is a function of the interface temperature, they proposed that the compositions of the primary eutectics deviate from the equilibrium values, because the temperature at the growing eutectic dendrite tip is lower than the equilibrium eutectic temperature.

According to the LZ model,[22] the average compositions of the liquid at the interface in front of α-

phase and β-phase can be expressed as follows:

$$\bar{C}_\alpha = C_\mathrm{E} + B_0 + \frac{2(S_\alpha + S_\beta)^2}{S_\alpha}\frac{V}{D}(1-k)\,P, \quad (1a)$$

$$\bar{C}_\beta = C_\mathrm{E} + B_0 - \frac{2(S_\alpha + S_\beta)^2}{S_\beta}\frac{V}{D}(1-k)\,P, \quad (1b)$$

where C_E is the eutectic composition, S_i is the half width of each phase, i represents α or β, V is the growth velocity, D is the solute interdiffusion coefficient in the liquid, and k is the equilibrium solute distribution coefficient. The parameters B_0 and P have been described as

$$B_0 = \frac{2(1-k)}{k}\frac{S_\alpha C_\mathrm{E} - S_\beta(1-C_\mathrm{E})}{\lambda}, \quad (2a)$$

where λ denotes the lamellar spacing.

$$P = \sum_1^\infty \frac{1}{(n\pi)^3}\left[\sin(n\pi f)\right]^2 \frac{p_n}{1+\sqrt{1+p_n^2}-1+2k}, \quad (2b)$$

where f is the volume fraction of the α phase, $p_n = 2n\pi/P_\mathrm{e}$, a function of the eutectic Pelect number $P_\mathrm{e} = V\lambda/2D$.

The average compositions of the two eutectic phases at the dendrite tip, C_α^* and C_β^*, can be deduced from the equilibrium phase diagram with $\bar{C}_\alpha$ and $\bar{C}_\beta$, since the effect of solute trapping in the lamellar eutectic growth is not remarkable.[29] Assuming that the system is reheated to a certain temperature because of recalescence, and the compositions of the liquid and solid are approximately equal to their equilibrium values at this temperature, we can estimate the average remelted fractions of the primary eutectic structures from the phase diagram:[29]

$$f^\mathrm{L} = f\frac{C_\alpha^* - C_\alpha^\mathrm{S}}{C_\alpha^\mathrm{L} - C_\alpha^\mathrm{S}} + (1-f)\frac{C_\beta^* - C_\beta^\mathrm{S}}{C_\beta^\mathrm{L} - C_\beta^\mathrm{S}}, \quad (3)$$

where C_α^L and C_β^L are the equilibrium liquid compositions of α and β phases at the recalescence temperature respectively, C_α^S and C_β^S are the corresponding equilibrium solid compositions of α and β phases. These parameters can be obtained from the extrapolation of the solidus and the liquidus through the eutectic point in the equilibrium phase diagram.

Using the recalescence temperature (measured experimentally by the two-colour infrared pyrometer for the sample surface (Fig.4) and assumed to be the eutectic temperature for the sample inner), we plot the calculated results in Fig.5. It is shown that the remelted fractions increase with the increase of undercooling, which indicates that the volume fraction of anomalous eutectics increases with the increase of undercooling (Fig.2). The remelted fraction at the sample surface is lower than that inside the sample due to the better heat dissipation conditions, which results in the appearance of eutectic dendrites on the sample surface (Fig.1) but their disappearence inside the sample.

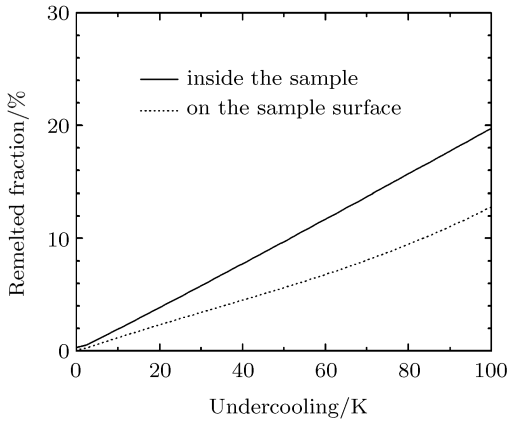


Fig.5. Remelted fractions of the primary lamellar eutectics at the sample surface or inside the sample.

5. Conclusions

(1) When the undercooling of the Ag–39.9at% Cu eutectic alloy melt is in the range from a critical undercooling of 76 K to the highest experimental undercooling 100 K, lamellar eutectics grow in a dendritic form during the rapid solidification.

(2) Due to severe deviation from equilibrium, the primarily formed lamellar eutectics are supersaturated with solute, and then partially remelted during recalescence and ripened into anomalous eutectics during the subsequent solidification.

(3) The volume fraction of the primary eutectics increases with the increase of undercooling, resulting in more anomalous eutectics in the solidification structures at higher undercoolings.

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