

Undercooling heredity of $\text{Cu}_{70}\text{Ni}_{30}$ melt solidified in non-catalytic nucleation coated mould^①

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[Abstract] A new concept of undercooling heredity is developed to evaluate the undercooling ability in a non-catalytic nucleation coated mould, where alloy melts were highly undercooled previously. Before the heredity experiment a non-catalytic nucleation composite glass-lined coating (B-F) was prepared on the inner surface of mould and the $\text{Cu}_{70}\text{Ni}_{30}$ alloy was selected to perform undercooling experiment in the B-F non-catalytic coating mould. Its ratio of undercooling heredity was 0.76. The results prove that the B-F coating is an ideal non-catalytic media for purified $\text{Cu}_{70}\text{Ni}_{30}$ alloy melts due to its small contact angle between the melt and coating layer. Considering that various microstructures form under different undercoolings, two critical undercoolings, ΔT_1 and ΔT_2 , and their corresponding microstructures of $\text{Cu}_{70}\text{Ni}_{30}$ alloy are well defined. Moreover, it is found that the manned-triggering solidification in the non-catalytic coating mould could be used to get directional undercooling dendrite structure while the melt undercooling is larger than the critical undercooling ΔT_2 .

[Key words] $\text{Cu}_{70}\text{Ni}_{30}$ alloy; non-catalytic nucleation coating; undercooling heredity

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1 INTRODUCTION

Through composite purification of physical and chemical method, a stable undercooling can be obtained in the Cu-Ni melt^[1-3]. As for the highly undercooled melt, it could stay in its state when the temperature is higher than the undercooling temperature corresponding to nucleating. If pouring the purified melt into a non-catalytic coated mould at that time, its undercooling should be partly or completely retained^[4]. The remained undercooling is called the undercooling heredity of the undercooled melt solidified in a coated mould, and the ratio of the highest undercooling obtained in the coating to the primitive undercooling after purification is defined as the heredity rate of undercooled melt in the coated mould. Under different undercoolings, rapid solidification of highly undercooled melt, which could be realized in the undercooled melt by manned-triggering, can directly prepare rapidly solidified bulk materials with excellent physical, chemical and mechanical properties^[3,5]. However, the rapid solidification process of bulk alloy melt is only limited to the basic research of microstructure evolution in a quartz glass crucible or under the condition of levitation melting. How to prepare bulk materials rapidly solidified by means of undercooling is not discussed yet up to now, there are two difficulties influencing its development: one is that the basic knowledge about undercooling heredity

is very limited, the other is that there is no effective and cheap way explored to prepare a non-catalytic nucleation coating mould^[4-6]. Here a B-F non-catalytic composite glass-lined coating mould was successfully prepared by the sol-gel, then the $\text{Cu}_{70}\text{Ni}_{30}$ melt was chosen to perform the undercooling heredity experiment in the B-F coating mould, and the microstructural evolution of the undercooled $\text{Cu}_{70}\text{Ni}_{30}$ alloy melt in the coated mould was systematically analyzed.

2 EXPERIMENTAL

2.1 Preparation of B-F coating mould

The glassdust, SiO_2 , with a granularity less than $88\ \mu\text{m}$ and a purity higher than 99.8% (mass fraction), and silicasol composed of 28% SiO_2 (mass fraction), 0.3% of Na_2O and H_2O were selected to prepare the substrate coating layer B on the investment casting mould. The composition formula was 150 g quartz glassdust and 28 mL silicasol. The substrate layer was prepared after sintering at 1173 K for 30 min.

In order to form a non-catalytic layer on the mould, another thin film coating F has to be covered on the substrate layer B. The preparation process of layer F is as follows^[1]. At first, a precursor solution which composed of 4 H_2O , 4 $\text{C}_2\text{H}_5\text{OH}$, 0.1 HCl with a purity of 37% and 1 $\text{SiCO}(\text{C}_2\text{H}_5)_4$ (mole ratio) was heat treated at 333 K for 180 min to prepare the

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F-sol by reactions of hydrolyzing-condensation. After the mould B was immersed in the F-sol solution for about 5 ~ 10 s, then the remained liquid sol from the mould was poured to leave a thin sol film on the inner surface of B-coating.

For the purpose of improving the surface property of the coated layer B, the heat treatment is also scheduled. After aging at ambient temperature for 24 h, the thin sol film was heated from ambient temperature to 333 K at a rate of 5 K/min in a furnace and kept at 333 K for 2 h. Then rose the temperature from 333 K to 673 K at a rate of 4 K/min and held at 673 K for 30 min. At last cooled it down in the furnace and formed an F-coating layer.

The above-mentioned processes were repeated for six times to get a relatively thick layer of coating. After that the mould was heat treated at 1173 K for 1 h in order to form a glass-lined coating.

A Rigaku X-ray diffraction meter with a source of CuK_α was adopted to analyze the crystalline structure of the B-F coating.

2.2 Undercooling heredity of alloy melt solidified in B-F mould

The undercooling experiments were performed in a high-frequency induction heater. The high purity nickel (99.987%) and copper (99.95%) with a mass fraction being composition of $\text{Cu}_{70}\text{Ni}_{30}$ (10 g) was melted in situ in a quartz glass crucible, and the melt was covered by the molten glass with an effort to achieve large undercooling. The purification process was given in Ref.[1].

The cooling curves of the alloy melts were measured by an infrared pyrometer with a response time 1 ms, and relatively accuracy 5 K (Fig.1). The absolute temperature was calibrated by a standard PtRh30-PtRh6 thermocouple.

During the undercooling experiment, the purification agent, glass, (granularity 2 ~ 4 mm) and alloy

particles were previously set in the crucible before the undercooling experiment. Then the vacuum chamber was evacuated to 1.33×10^{-4} Pa and the alloy was heated to 1637 K and degassed for 2 min, after that the melt was superheated to 1823 ~ 1873 K and held at the temperature for 1 min, repeated the above heating and cooling process in sequences again. Followed by two cooling-solidification-melting-superheating cycles. Then the alloy melt was dropped into the non-catalytic coated mould, which was placed at the bottom of quartz glass crucible, superheated to 1773 K and held for 30 s. At last the melt was cooled down to the ambient temperature. Various solidification structures at different undercoolings were obtained by trigger nucleation in the liquid Ga-In alloy placed at the bottom of the mould.

3 RESULTS

X-ray diffraction analysis was performed to identify the structure of the B-F coating. Its X-ray diffraction spectra are shown in Fig.2. It shows that B-F coating belongs to a quartz glass.

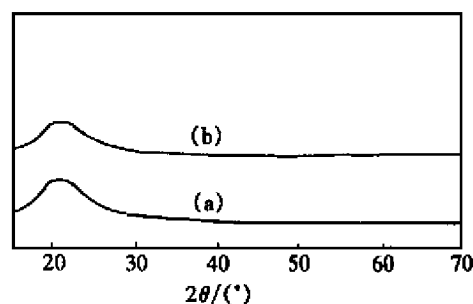


Fig.2 XRD spectra of B-F coating
(a) —B coating; (b) —F-coating

The undercooling heredity of melt in the B-F coated mould amounts to 0.76. Solidification structures at different undercoolings are shown in Fig.3.

4 DISCUSSION

4.1 Non-catalytic nucleation of B-F coating

The nucleation inhibition of alloy melt in a coated mould can be described by the wetting angle (θ) between the coating and melt according to the crystal lattice misfit model^[7]. Then the heterogeneous nucleation rate (I_s) of the alloy melt on the surface of B-F coating proposed by the classical nucleation theory^[8], could be expressed as

$$I_s = \frac{10^{21}}{\eta(T)} \exp \left[- \frac{16\pi}{3kT} \frac{f(\theta) \sigma^3}{\Delta G_v^2} \right] \quad (1)$$

where σ is the liquid/solid interfacial energy, T is the nucleation temperature, k is the Boltzmann constant, ΔG_v is Gibbs free energy difference between the solid and liquid phases, and $\eta(T)$ is the viscosity

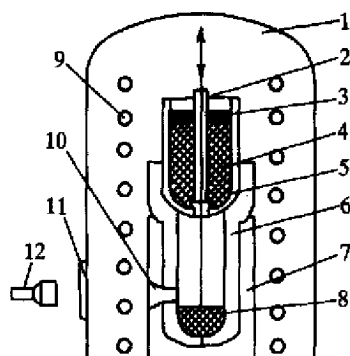


Fig.1 Schematic of undercooling heredity experimental setup

- 1 — Vacuum chamber; 2 — Quartz rod; 3 — Fused slag; 4 — Melt;
5 — Quartz crucible; 6 — Shell mold; 7 — Aluminous refractory;
8 — Fused slag; 9 — Induction coils; 10 — Quartz tube;
11 — Observing hole; 12 — Infrared pyrometry

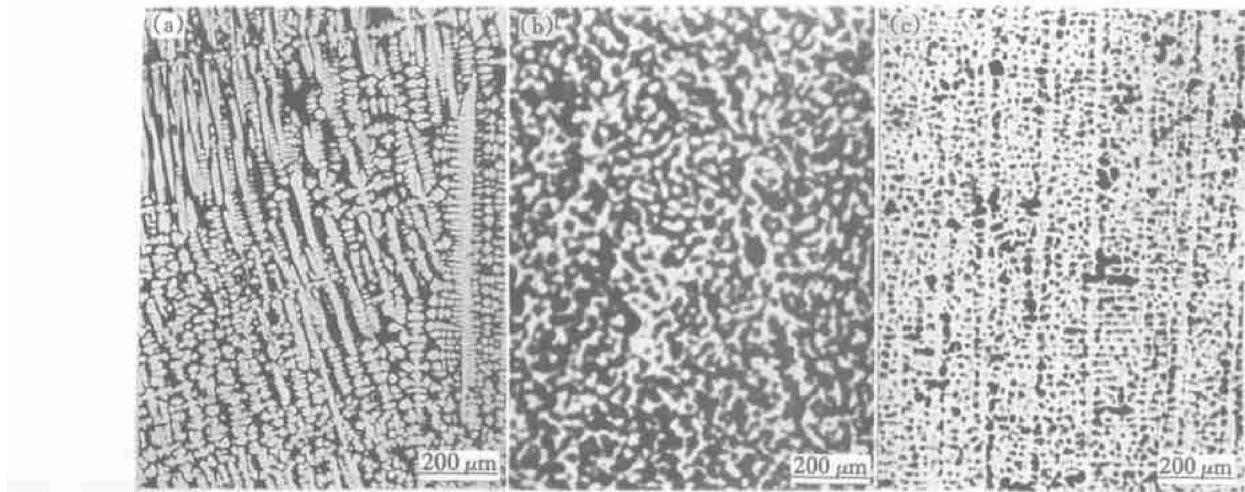


Fig.3 Microstructures of $\text{Cu}_{70}\text{Ni}_{30}$ alloy melt at different undercoolings

(a) — Dendrite, $\Delta T = 20$ K; (b) — Granular grain, $\Delta T = 71$ K; (c) — Undercooling dendrite, $\Delta T = 187$ K

of the melt^[9].

$$\eta(T) = 10^{-4.3} \exp[3.34 T_L / (T - T_g)] \quad (2)$$

where T_L is the liquidus temperature of the melt, and T_g is the glass transition temperature of the melt could be calculated from following equation^[9]:

$$T_g = 0.25[(1 - C_0) T_m(\text{Ni}) + C_0 T_m(\text{Cu})] \quad (3)$$

where C_0 is alloy composition, $T_m(\text{Ni})$, $T_m(\text{Cu})$ are melting temperatures of pure nickel and copper, respectively.

$$f(\theta) = \frac{(2 + \cos \theta)(1 - \cos \theta)^2}{4} \quad (4)$$

$$\Delta G_v = \frac{\Delta H_f \Delta T}{T_L} \quad (5)$$

where ΔH_f is the latent heat, $\Delta T = (T_L - T)$ is the nucleation undercooling.

When the B-F coating loses its effects and triggers alloy melt to nucleate, the critical condition for nucleation is

$$I_s \cdot t \cdot S = 1 \quad (6)$$

where t is nucleation time, S is the neighboring area between melt and coating.

The relationship between the wetting angle and undercooling is plotted in Fig.4 and the thermodynamics parameters of the alloy melt used for calculation are given in Table 1.

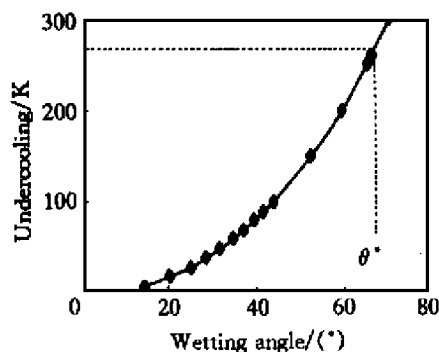


Fig.4 Relationship of wetting angel with undercooling of melts

Fig.4 shows that the corresponding wetting angle θ^* between the alloy melt and B-F coating is 66.6° for an undercooling 260 K, which was obtained by molten glass purification in Cu-Ni alloy melt^[2,3]. It is more smaller than the wetting angle θ_{G-L} between quartz glass and melt, 158° . Therefore, the B-F coating is an ideal non-catalytic coating for the purifying $\text{Cu}_{70}\text{Ni}_{30}$ alloy melts.

Table 1 Thermodynamic parameters of $\text{Cu}_{70}\text{Ni}_{30}$ alloy^[10]

σ /($\text{J} \cdot \text{m}^{-2}$)	ΔH_f /($\text{J} \cdot \text{m}^{-3}$)	θ_{G-L} /($^\circ$)	T_L /K	$T_m(\text{Ni})$ /K	$T_m(\text{Cu})$ /K	S / m^2	t /s
0.374	2.062×10^9	158	1510	1728	1357.5	0.4×10^{-3}	60

4.2 Microstructure

Within the achieved range of undercooling, solidification microstructure could be classified as three categories: highly branched dendrite structure, when $\Delta T < \Delta T_1$; granular crystal structure, when $\Delta T_1 < \Delta T < \Delta T_2$; and highly undercooled directionally solidified dendrites, when $\Delta T > \Delta T_2$ (as shown in Fig. 3). Two critical undercoolings were marked out as, $\Delta T_1 = 38$ K and $\Delta T_2 = 120$ K. The calculation result of the rapid dendritic growth model in undercooled melt proposed by Boettinger, Coriel and Trevidi^[11] shows that the dendrite tip radius lays in the minimum range (about 1.35×10^{-7} m), the recalescence superheat in rapid solidification lays in the maximum range (about 49.8 K) and the composition difference between the liquid and solute is relatively high (8.16 % Ni, mole fraction) with increasing undercooling within the range of $\Delta T_1 < \Delta T < \Delta T_2$. As a result dendrite remelting took place widely and turned to be the crowded fine dendrite structure under effects of the large composition difference and high superheat. Then it leads to the formation of the granular

crystal (Fig. 3(b)). When the undercooling is larger than ΔT_2 , thermal undercooling is higher than the solute undercooling in front of the dendrite. Solute-diffusion was replaced by heat diffusion to control the dendrite growth process. Therefore, the higher the undercooling and the higher the thermal undercooling, the more convenient for dissipating of the latent of dendrite tip in the growth process. Once a nucleus separates from the melt, dendrites will grow into the undercooled liquid rapidly, consequently leading to the formation of the fine directional dendrite. Furthermore, recalescence superheat (less than 27 K) and the composition difference with a nickel content between 7.62% ~ 3.29% (mole fraction) between liquid and solid decrease notably with increasing the undercooling. Then the fraction of dendritic remelting in recalescence decreases, which results in the formation of directionally solidified dendrite structure in rapid solidification process (as shown in Fig. 3(c)). Therefore, directionally solidified dendrite under negative temperature gradient could be obtained in a non-catalytic coated mould by means of manned-triggering solidification by the undercooling above ΔT_2 , which provides a new way for preparing high performance of new materials^[1,12]. It has been shown that the mechanical property of the material prepared by this method is several times higher than that of materials obtained under conventional solidification condition^[1,3,5].

5 CONCLUSIONS

1) A composite glass-lined B/F coating is successfully prepared and proved to be an effective non-catalytic nucleation coating mould in the undercooling experiment of Cu₇₀Ni₃₀ alloy melt.

2) A new concept of undercooling heredity is developed to evaluate the undercooling of alloy melt solidified in a B/F coated mould and that of the Cu₇₀Ni₃₀ alloy melt amounts to 0.76.

3) Microstructure evolution of the undercooled Cu₇₀Ni₃₀ alloy melt at different undercoolings is sys-

tematically studied, and a directionally solidified structure can be achieved when the melt with an undercooling larger than the critical undercooling, ΔT_2 .

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