

Non-catalytic nucleation coating for undercooled $\text{Cu}_{50}\text{Ni}_{50}$ melt*

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Abstract A non-catalytic nucleation coating (B-F_3) was prepared by the high temperature curing process of the sol-gel glass film based on the viscous flow mechanism of the coating. X-ray diffraction technology was adopted to study the crystallization behavior of the coating as a function of treating temperature. It was evident that no crystallization phenomenon happened on the coating which kept stable after the heat treatment of 60 min at 1773 K. The purified melt of $\text{Cu}_{50}\text{Ni}_{50}$ was selected to evaluate the effectiveness of undercooling heredity of the coating in the undercooling experiments. The maximum undercooling of the melt solidified in the coated mold could reach 236 K. Based on the solidified microstructural evolution at different undercoolings, a single crystal of the alloy $\text{Cu}_{50}\text{Ni}_{50}$ was achieved with no aid of the selection process of the crystal in the mold with the B-F_3 coating by means of undercooling technology.

Keywords: undercooled $\text{Cu}_{50}\text{Ni}_{50}$ melt, non-catalytic nucleation coating, single crystal.

The rapid solidification of highly undercooled melts has attracted much attention in the research activities of physics of condensed matter and materials science for its convenience to achieve the ultra-fine directional dendrites and single crystal^[1-4]. However, most of undercooling experiments were carried out through levitation melting^[4] or in quartz glass crucibles^[1, 3], which makes it impossible to prepare directly bulk single crystal due to the limitation of melt size and shape. Bulk rapidly-solidified materials can be prepared only by pouring the previously undercooled melt into a mold coated with non-catalytic nucleation layer to ensure that the undercooling is partly or completely retained. However, no effective way, up to now, has been developed for the preparation of non-catalytic nucleation coating under high temperature, which limits the advancement of bulk rapidly-solidified materials. Recent research results have shown that the undercooling heredity of melt solidified in a mold coated with non-catalytic nucleation layer depends on the structure and high temperature stability of the coating¹⁾. The high undercooling of melts could be retained in glass coated mold, which kept stable vitreous at high temperature^[5]. Therefore, the preparation of the high temperature stable glass-lined coating is a key to the preparation of bulk rapidly solidified materials. The high temperature curing method was adopted to obtain the glass-lined coating of mirror-like sol-gel $\text{SiO}_2\text{-B}_2\text{O}_3$ composite, and

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1) Guo, X. F., Amorphous coating and solidification structure selection in the coating of undercooled single phase alloy, Ph. D thesis, Northwestern Polytechnical University, Xi'an, 1999, 62.

the viscous flow characteristics of the glass at high temperature were analyzed. In this study the $\text{Cu}_{50}\text{Ni}_{50}$ melt was chosen to perform the experiments of undercooling heredity in the coated mold. A bulk single crystal was prepared directly from the undercooled melt based on the systematical analysis of microstructure evolution under different undercoolings.

1 Experimental

1.1 Preparation of coating B

The raw material of coating B consisted of SiO_2 glassdust, binder and softening agent. The binder SiO_2 sol was prepared in the hydrolysis-polymerization of $\text{Si}(\text{OC}_2\text{H}_5)_4$ (TEOS) at 333 K for 180 min. The starting solution for the sol consisted of 4 mole H_2O , 4 mole $\text{C}_2\text{H}_5\text{OH}$, 0.1 mole HCl and 1 mole $\text{Si}(\text{OC}_2\text{H}_5)_4$, and the softening agent was the H_3BO_3 . Four steps were employed to prepare the coating B. Firstly, a mixture of 98.56% SiO_2 and 1.44% B_2O_3 was prepared by adding H_3BO_3 aqueous solution to the SiO_2 glassdust. After the mixture was dried at 333 K, 110 mL SiO_2 sol was added into the mixture of 257.5g and stirred for 120 min to form a coating material of B. Then the substrate coating layer B was prepared by the same way as the investment casting process. At last, the investment mold with the substrate layer B was sintered at 1173 K for 30 min for vitrification.

1.2 Film coating F_3

In order to improve the surface quality of the coating B, the SiO_2 - B_2O_3 sol film F_3 was coated on the substrate layer B by a dip-coating and step-heating process. The dip-coating was performed by immersing the mold in the SiO_2 - B_2O_3 sol for 5—10 s and withdrawing the mold out, then a thin sol film was left on the inner surface of coating B.

The heating process was composed of four steps to vitrify the coating. Firstly, after aging at ambient temperature for 24 h, the mold was heated from room temperature to 333 at a rate of 5 K/min and then stayed at this temperature for 2 h. Secondly, the temperature was raised from 333 K to 673 K at a rate of 4 K/min and kept at 673 K for 1 h. Thirdly, the mold was cooled down to room temperature and the dip-coating and step-heating process was repeated for six times to form a seven-layer thin film. After that, the mold was heated at 1173 K for 30 min to form a B- F_3 composite glass-lined coating.

1.3 High temperature curing of the B- F_3 coating

The coated mold was also heated at 1173 K for 30 min to eliminate micropores and cracks in the coating B by the structural viscous flow of glass existing between the SiO_2 particles.

1.4 High temperature structural stability of B- F_3 coating

In order to analyze the high temperature structural stability of the F_3 coating, the SiO_2 - B_2O_3 sol was gelled on a glass plate. After aging for 24 h, the xerogel was torn off from the glass plate and underwent the same step-heating treatment as that for obtaining the F_3 coating sample. B and F_3 coatings were separately put into quartz glass crucibles and heated to 1773 K for crystallization analysis. The crystallization of the glass coatings was measured by a Rigaku X-ray diffraction meter with a fitter of

Cu-K_α at certain heating intervals. The analysis results are shown in figure 1.

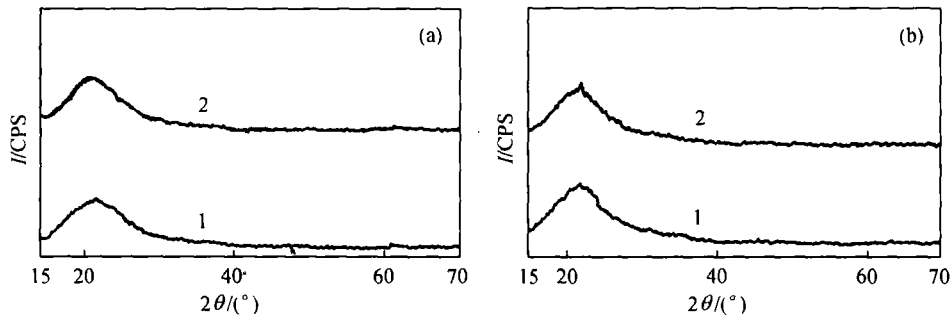


Fig. 1. XRD analyzing results of B and F_3 coatings. (a) F_3 coating. 1, 1173 ± 5 K, 30 min; 2, 1173 ± 5 K, 30 min + 1773 ± 5 K, 60 min; (b) B coating, 1, 1173 ± 5 K, 30 min; 2, 1173 ± 5 K, 30 min + 1773 ± 5 K, 90 min.

2 Undercooling heredity and single crystal preparation in the B- F_3 mold

Under the protection of purification agent consisting of 50% ($\text{Na}_2\text{B}_4\text{O}_7$) glass^[5], the high purity nickel (99.987%) and copper (99.95%) were melted *in situ* in a quartz glass crucible in a

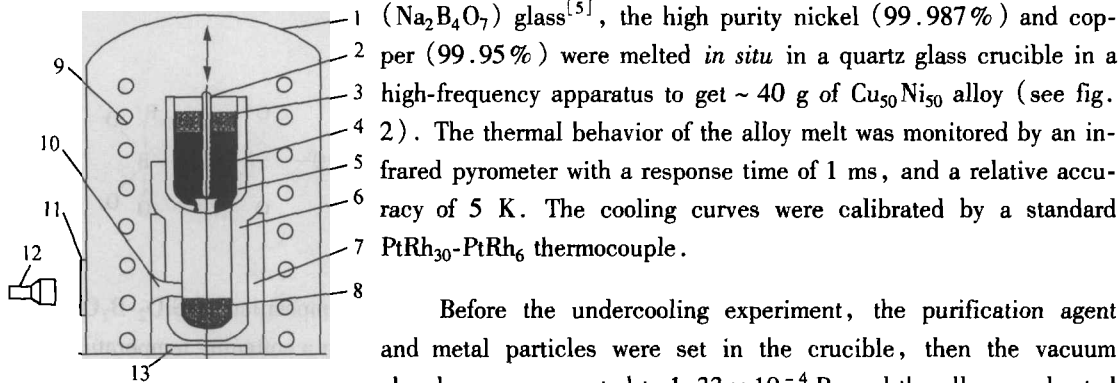


Fig. 2. Schematic diagram of undercooling heredity experimental setup. 1, vacuum chamber; 2, quartz rod; 3, fused slag; 4, quartz crucible; 5, melt; 6, shell mold; 7, aluminous refractory; 8, fused slag; 9, induction coils; 10, quartz tube; 11, observing hole; 12, infrared pyrometer; 13, Ga-In triggering source.

high-frequency apparatus to get ~ 40 g of $\text{Cu}_{50}\text{Ni}_{50}$ alloy (see fig. 2). The thermal behavior of the alloy melt was monitored by an infrared pyrometer with a response time of 1 ms, and a relative accuracy of 5 K. The cooling curves were calibrated by a standard $\text{PtRh}_{30}\text{-PtRh}_6$ thermocouple.

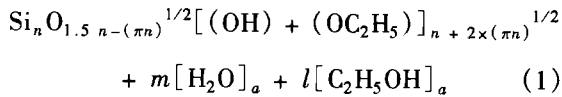
Before the undercooling experiment, the purification agent and metal particles were set in the crucible, then the vacuum chamber was evacuated to 1.33×10^{-4} Pa and the alloy was heated to 1637 K and degassed for 2 min. After that the melt was superheated to about 1837K and held for 1 min, followed by cooling. Repeating the above melting-superheating-cooling for two cycles, the alloy melt was dropped into the B- F_3 coated mold which was placed right at the bottom of quartz glass crucible, and superheated to 1773K then held for 30 s. At last the melt was cooled down.

Various solidification structures at different undercoolings were obtained by triggering the melt to nucleate by the liquid Ga-In alloy placed under the mold, and thus a directionally solidified single crystal was formed (see figure 3).

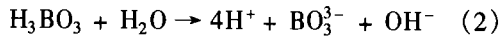
3 Analysis and discussion

3.1 $\text{SiO}_2\text{-B}_2\text{O}_3$ sol

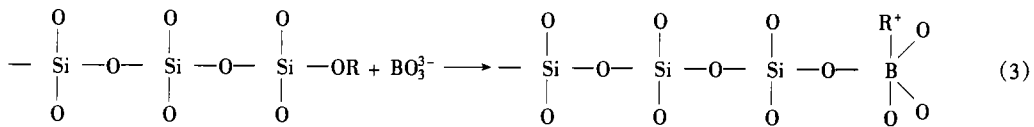
The SiO_2 sol is a kind of polymer colloid with the main skeleton of Si-O network on which -OH and $\text{-OC}_2\text{H}_5$ groups were bonded. The chemical make-up of the sol can be expressed as^[6, 7]



where n is natural number, m and l are constants dependent on the time and temperature of hydrolysis and condensation reactions. When H_3BO_3 was added to the SiO_2 sol, or the SiO_2 sol was added into SiO_2 glassdust covered by the H_3BO_3 , a reaction as follows would occur:



The rate of hydrolysis-condensation was accelerated by the existence of H^+ [8-10]. Some $-\text{OH}$ and $-\text{OC}_2\text{H}_5$ groups were substituted and some open networks in Si-O main chains were connected by $[\text{BO}_4]^-$ tetrahedral¹⁾. As a result, the connectivity increased, and the $\text{SiO}_2\text{-B}_2\text{O}_3$ sol formed. The reaction could be represented as



where R is H or C_2H_5 .

According to the amount of H_3BO_3 added in the glassdust, the composition of $\text{SiO}_2\text{-B}_2\text{O}_3$ sol in the interstices of SiO_2 glassdusts was 78.5% SiO_2 and 21.5% B_2O_3 , with a softening temperature T_r of 1315 K^[10].

3.2 Heat treatment of the B-F₃ coating

During the heat and vitrification treatments, the composite glass-lined coating B-F₃ formed (fig. 1, curves 1) by the dissociation of $-\text{OH}$ and $-\text{OC}_2\text{H}_5$ groups of the $\text{SiO}_2\text{-B}_2\text{O}_3$ gel^[9] and the structural viscous flow of the network structure^[11].

During the high temperature curing process, the glass distributed in the interstices of the SiO_2 glassdusts began to soften by the structural viscous flow when the temperature was higher than T_r . Under this circumstances cracks and micropores were cured by minimization of the surface energy driven by the capillary force. Meanwhile, those SiO_2 grains would react with the glass, and the strength of the Si-O connectivity might increase which could improve the T_r of the glass, thus the $\text{SiO}_2\text{-B}_2\text{O}_3$ composite glass-lined coating formed (figure 4).

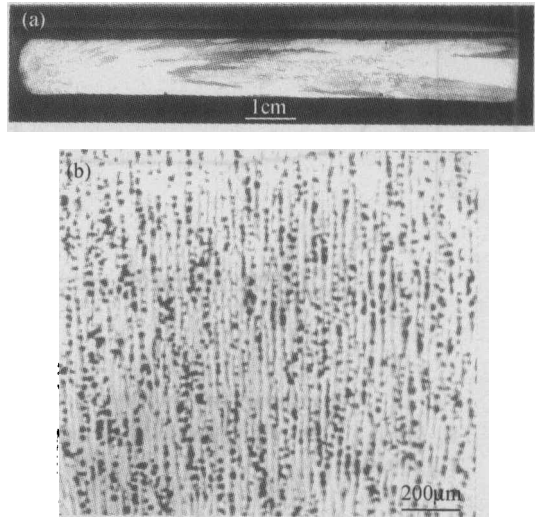


Fig. 3. Optical micrograph of the $\text{Cu}_{50}\text{Ni}_{50}$ alloy solidified at 154 K undercooling. (a) Macrostructure; (b) microstructure.

1) See footnote on page 619.

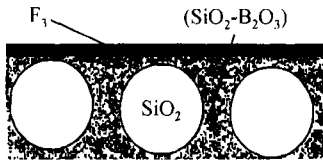


Fig. 4. Schematic diagram of (SiO₂-B₂O₃)/SiO₂ coating.

The softening temperature of coating B is not only dependent on the SiO₂-B₂O₃ glass, but also closely related to SiO₂ grains. After the curing reaction of the coating B at a higher softening temperature T_r of 1643 K, the differential temperature analysis (DTA) result (as shown in fig. 5) gave only the softening of SiO₂-B₂O₃ glass among SiO₂ grains.

Based on the hypothesis that the SiO₂-B₂O₃ glass was homogeneous, the reaction parts of SiO₂ grains with SiO₂-B₂O₃ glass could be calculated, thus the composite glass could be revealed. According to the DTA result, the composition of the glass between SiO₂ grains after heat-curing reaction can be represented as^[10]

$$96.46\% \text{SiO}_2 + 3.54\% \text{B}_2\text{O}_3 \quad (4)$$

Considering the formula of coating B, the total weight of SiO₂ and H₃BO₃ is

$$W_0 + W_0 \times 3\% (\text{H}_3\text{BO}_3) + W_2, \quad (5)$$

where W_0 is the primitive weight of SiO₂ glassdust in coating B, and W_2 the SiO₂ content in SiO₂ sol. From the reaction of



the total amount of B₂O₃ can be written as

$$W_3 = \frac{M_{\text{B}_2\text{O}_3} \times W_0 \times 3\%}{2M_{\text{H}_3\text{BO}_3}}, \quad (7)$$

$$X_3 = \frac{W_0 \times 3\%}{2M_{\text{H}_3\text{BO}_3}}, \quad (8)$$

where W_3 and X_3 are the weight and mole fraction of B₂O₃; $M_{\text{B}_2\text{O}_3}$ and $M_{\text{H}_3\text{BO}_3}$ the molar mass of B₂O₃ and H₃BO₃ respectively. Then the following expression can be deduced from eqs. (4) and (8)

$$(X_1 + X_2) = \frac{96.46}{3.54} \times \frac{W_0 \times 3\%}{2M_{\text{H}_3\text{BO}_3}}. \quad (9)$$

Therefore the reaction part of SiO₂ glassdust can be calculated by

$$W_1 = M_{\text{SiO}_2} \times \left(\frac{96.46 \times 3\%}{2 \times 3.54} \times \frac{W_0}{M_{\text{H}_3\text{BO}_3}} - \frac{W_2}{M_{\text{SiO}_2}} \right) \quad (10)$$

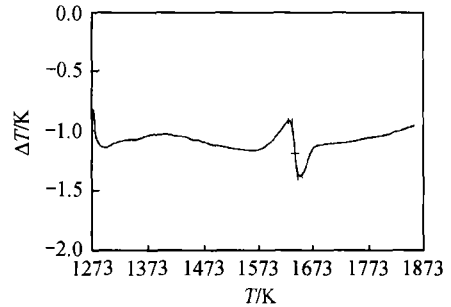


Fig. 5. DTA analyzing result of B coating.

or

$$V = \sum_{i=1}^4 n_i V_i = \sum n_i \frac{4}{3} \pi [R_i^3 - (R_i - d)^3], \quad (11)$$

with

$$n_i = \frac{3 \times 250 a_i}{4\pi R_i^3 \rho_g}, \quad (12)$$

where the M_{SiO_2} is the molar mass of SiO_2 , ρ_g the density of quartz glass, R_i the grain radius of the glassdust, V_i the volume of grain with different granularity, $\sum n_i$ the total grains involved in the heat-curing reaction (the subscript i stands for different granularities of grains), d the mean reaction depth of the SiO_2 grain.

Calculation results show that the depth reached by the curing reaction, d , on the SiO_2 glassdust surface is $3.9 \mu\text{m}$. The curing reaction between the grains takes place only on the surface of the grains. Therefore, the perfectly softening temperature of $\text{SiO}_2\text{-B}_2\text{O}_3$ coating should be higher than 1643 K due to the higher softening temperature of SiO_2 grains. Once the melt was pouring into the as-coated mold, it could tolerate the heat shock of the high temperature melt. The granularities of the SiO_2 grains are shown in table 1.

Table 1 The granularities of the SiO_2 grains

| | | | | |
|--|----|------|----|------|
| Radius of the grains $R/\mu\text{m}$ | 44 | 31.5 | 22 | 18.5 |
| Weight percent of different grains $a/\text{wt}\%$ | 12 | 67 | 16 | 5 |

It can be conjectured that the coating layer F_3 can improve the surface smoothness of the coating B because it can also undergo the structural viscous flow during the heat-curing process.

3.3 Influences of coating structure on undercooling heredity of melt

According to the classical heterogeneous nucleation theory, the nucleation inhibition of alloy melt in a coated mold can be described as the wetting angle (θ) between the coating and melt according to the crystal lattice misfit model. For Cu-Ni alloy with the fcc structure, its structure is different from the vitreous of the B- F_3 coating. Therefore, the wetting angle between the coating and the melt should be 180° . The nucleation process of the alloy in the coated mold should be homogenous. On the other hand, if the coating was crystallized at high temperature under the effect of the wetting angle of the melt, the undercooling heredity of melt in the coated mold would be dependent on the high temperature structural stability. Melt undercooling could be retained without any crystallization of coating at high temperature. XRD results showed that F_3/B layers held at 1773 K for 60/90 min was vitreous (fig. 1). Therefore the B- F_3 coating with a high devitrification resistance is an ideal non-catalytic nucleation coating for the highly undercooled $\text{Cu}_{50}\text{Ni}_{50}$ melt. The maximum undercooling of $\text{Cu}_{50}\text{Ni}_{50}$ retained in the coating amounts to 236 K.

3.4 Preparation of $\text{Cu}_{50}\text{Ni}_{50}$ single crystal

The microstructure appeared to be directional dendrites when the $\text{Cu}_{50}\text{Ni}_{50}$ melt was undercooled by 120—192 K, showing that the rapid directional solidification process (RDS) at negative temperature gradient could be observed^[3]. Compared with the conventional directional solidification technology (CDS), no crystal-selection apparatus is needed to prepare the single crystal of highly undercooled melt in the RDS, and the crystal selection zone is very short. Through the natural exclusion of primitive grains and a shorter crystal-selection zone, the crystal growth immediately enters RDS zone. The image of microstructure shows that the arm spacing of the RDS dendrite, especially the primary spacing, is much finer (figure 3).

4 Summary

(i) The mirror-like coating of B- F_3 composite was prepared by the following sol-gel principle and using the structural viscous flow characteristics of glass at high temperature.

(ii) With an addition of H_3BO_3 to SiO_2 sol, the B and F_3 coatings kept stable in an amorphous state at 1773 K for 90 and 60 min, respectively.

(iii) The undercooling heredity of $\text{Cu}_{50}\text{Ni}_{50}$ melt solidified in a B- F_3 coating was dependent on the structural stability of the coating and could reach 236 K.

(iv) The bulk RDS single crystal of $\text{Cu}_{50}\text{Ni}_{50}$ was prepared from the undercooled melt in a B- F_3 coating with no aid of the crystal-selection apparatus.

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