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Effects of static magnetic field on undercooling of a copper melt

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The effects of static magnetic field (5000 Oe) were investigated on undercooling of a copper melt in glass slag. The procedure of melting and solidifying was repeated 13 times in each sample. The thermal analysis curves for ten samples (five samples in the presence of magnetic field and five samples in the absence of magnetic field) were measured during every melting–solidifying cycle and the degree of undercooling was obtained in every cycle. The undercoolings of all samples increased in a few numbers of early cycles and after about six cycles they were almost saturated and independent of cycle number. Irregular and unexpectedly large decreases of undercooling sometimes appeared. Two remarkable effects of magnetic field on undercooling were found. One is that the maximum undercooling in the presence of a magnetic field is apparently higher than that in the absence of a magnetic field for every sample. The second is that the application of magnetic field tends to suppress the irregular and unexpectedly large decreases of undercooling. These results are discussed in respect of the thermodynamic effect (the magnetic free energy change on solidification) and the magnetohydrodynamic effect (the suppression of thermal convection).

1. Introduction

It is expected that novel metastable materials will be obtained when metal or alloys highly undercooled are solidified. For this reason, a number of studies have been reported on methods to achieve high undercooling of the melt and on the relations between the structure of solidified material and the undercooling [1–5]. Heterogeneous nucleation which could mainly dominate nucleation phenomena in the melt and tend to decrease undercooling, is well known to stem from the static or dynamic stimuli. The highly undercooled melts in most of the studies previously reported have been obtained by preventing nucleation in the static situation, for example, melting in glass slag. On the other hand, if the nucleation is suppressed by dynamic stimuli, such as vibration, convection and agitation, one can expect to produce a highly undercooled melt. According to the theory of magnetohydrodynamics, forced and/or thermal convection in a melt can be suppressed by the application of a static magnetic field. Many researchers have investigated this effect on the temperature distribution or its fluctuation in the melt [6–10]. Kishida *et al.* [10] showed the anisotropic effects of a magnetic field on the macrostructures of alloys and the thermal convection in a mercury pool. One of the industrial successes using this effect is the growth of high-quality semiconductor single crystal without defects [11]. From these results, one may induce the subsequent high undercooling in a melt by the application of a magnetic field.

In addition to the magnetohydrodynamic effect, Schieber [12] discussed the thermodynamic effect, i.e. the effective change of free energy due to the application of a magnetic field on the isothermal dissolution and the growth rates of inorganic seed crystals. Youdelis *et al.* [13] also discussed the thermodynamic effect of a magnetic field on the segregation of alloys. Although these researchers concluded that this effect was negligible because the magnitude of the magnetic free energy change was very small compared with that of specific heat change, Aoki *et al.* [14] suggested that the applied magnetic field could also be effective in promoting the thermodynamic change during solidification.

In the present work, the effects of magnetic field were investigated on undercooling of a copper melt dipped into glass slag. Because highly undercooled melts have been obtained easily and statically using the glass slag method and the mechanism of undercooling has been well discussed in many other studies, the glass slag method was favourably employed here.

2. Experimental procedure

The experimental apparatus used in this work is shown schematically in Fig. 1. The electromagnet employed had a 12 cm pole gap with 10 cm diameter pole shoes. It provided a homogeneous transverse magnetic field across the melt. The vertical furnace was placed between the poles of the electromagnet and provided with a silicon carbide double-helical heating element. The atmosphere temperature in the furnace was monitored by a Pt/Pt–13%Rh control thermocouple under a crucible connected to a PID controller.

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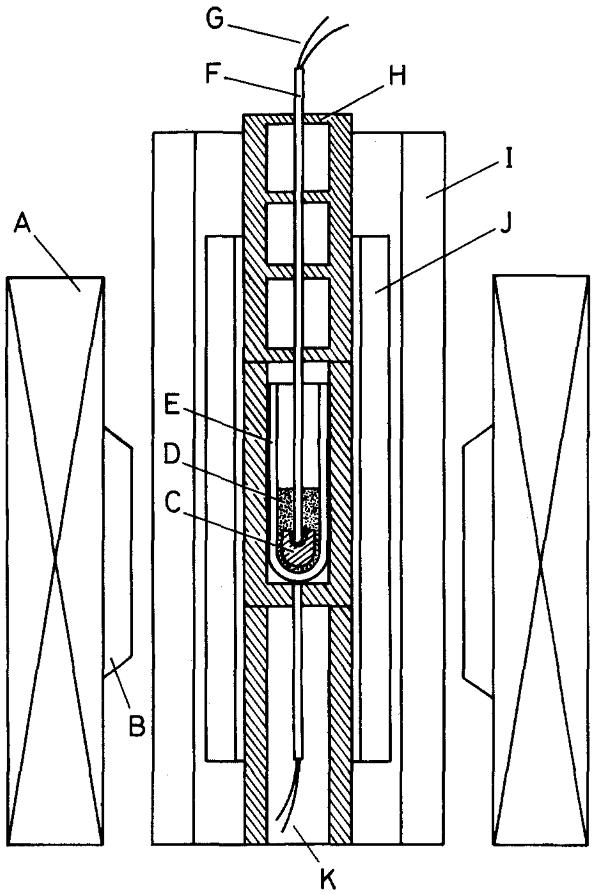

Figure 1 Schematic diagram of the experimental apparatus. A, electromagnet; B, pole shoe; C, sample; D, glass slag; E, alumina crucible; F, alumina protection tube; G, monitoring thermocouple; H, spacer; I, insulating tube; J, silicon carbide heater; K, control thermocouple.

The high-purity alumina crucible (2 cm i.d.) containing the sample was placed in a support container within the furnace. The sample was about 1.2 cm high and positioned at the same height as the centre of the pole faces. The sample temperature was measured using a Pt/Pt–13%Rh monitoring thermocouple, 0.5 mm diameter, protected by a high-purity alumina tube (4 mm i.d. and 6 mm o.d.), which was inserted from the top into the sample. Some support spacers within the furnace were employed to fix the protection tube at regular positions in every experiment. The sample was wholly surrounded by glass slag.

Every experiment was conducted on a copper melt (melting point 1357 K). Each melting stock was weighed in 20 g. The chemical compositions are shown in Table I, and the chemical compositions of the powder glass slag employed are shown in Table II. Each sample was first heated in high-purity argon gas to prevent it from being oxidized until the surrounding slag was melted. After the sample was allowed to superheat at 1580 K, it was cooled until the complete solidification without special means of heat extraction, and then heated again. The cooling rate below the melting point was about 0.35 K s^{-1}. This cycle was repeated 13 times in each run because it has been reported that the repetition of being melted and solidified encourages high undercooling of the melt in glass slag [15]. Five samples were employed for the experiments in the presence of a 5000 Oe magnetic field, which was applied during cooling until the recalescence point; the same number of samples were used in the absence of a magnetic field.

3. Results and discussion

An example of one-cycle thermal analysis results for a copper melt is shown in Fig. 2. The temperature of a sample decreased monotonically from 1580 K and then increased quickly at a temperature lower than the melting point, 1357 K. This increase indicates recalescence due to the solidification of the undercooled melt. The amount of undercooling was, therefore, defined as the difference between the recalescence temperature and the melting point 1357 K. After recalescence, the temperature increased up to 1580 K after passing through the two plateaus which indicate solidifying and melting, respectively. Every sample cooled after all 13 cycles was wholly surrounded by solid glass, and so the surface was glassy.

The dependence of melting and solidifying cycle number on undercooling is shown in Fig. 3 for all samples in the presence or absence of a magnetic field. The undercoolings in most of the samples increased with increasing cycle number in the early few cycles, and after about six cycles they were almost saturated and independent of cycle number except in the cases indicating irregular and unexpectedly large decreases. The effects of magnetic field on undercooling were noted from two points of view, i.e. the maximum value of undercooling and the number of irregular and unexpectedly large decreases in each experiment. The data related to these points are summarized in Table III. The maximum values in every experiment in the presence of a magnetic field were apparently higher than those in the absence of the magnetic field. It was found here that the application of a magnetic field was, therefore, very effective in increasing the undercooling of a copper melt. It was also noted that in most of the samples this effect appeared to occur around four cycles number, which reflects the small peak in each cycle dependence as seen in Fig. 3. The other effect was found in the numbers of irregular and unexpectedly large decreases of undercooling. Such decreases were suppressed by an applied magnetic field, as shown in Table III.

The two main aspects of magnetic field effects on undercooling are now considered: the thermodynamic effect and the magnetohydrodynamic one. The former

TABLE I Chemical composition of the copper stock

Cu	As	Pb	Bi	Fe	P	S	O	H
99.9	< 0.001	< 0.002	< 0.002	< 0.001	< 0.002	< 0.002	0.0005	0.0001

TABLE II Chemical composition of glass slag

SiO_2	Al_2O_3	Na_2O	K_2O	MgO	CaO
72.0	2.0	13.5	3.5		9.0

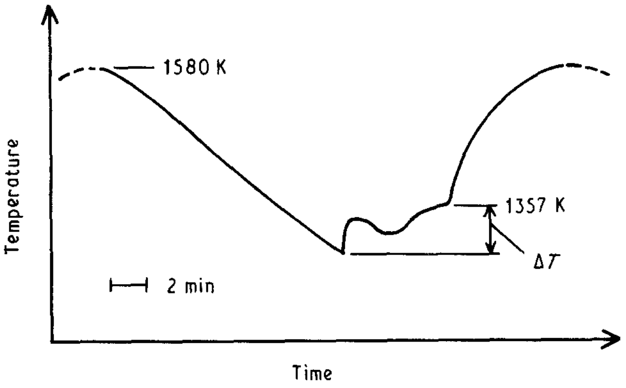

Figure 2 Thermal analysis curve over one cycle.

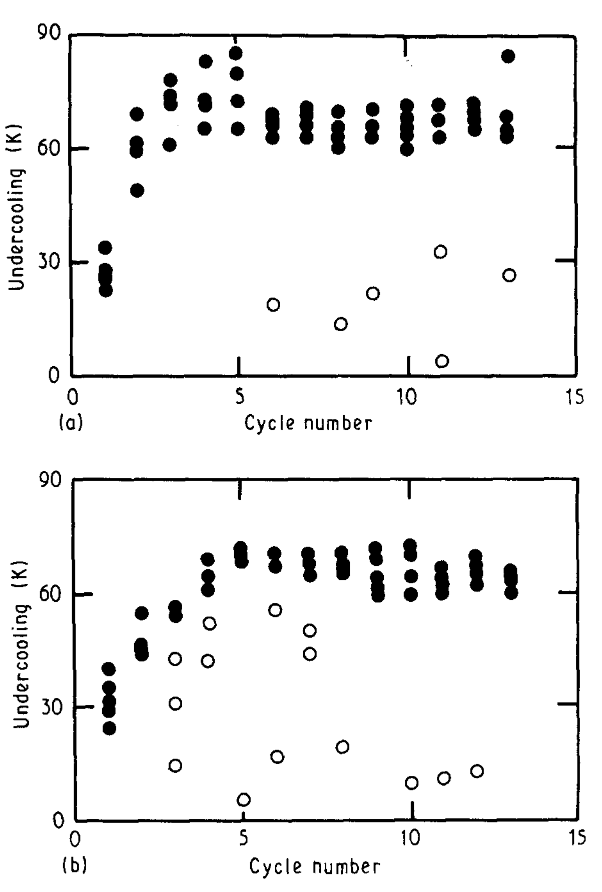

Figure 3 Dependence on melting and solidifying cycle number of the undercooling of copper melts: (a) in the presence of a magnetic field, (b) in the absence of a magnetic field. (●) Regular undercooling, (○) irregular and unexpectedly small undercooling.

results from the change in the free energy on solidification caused by the magnetic field. The latter perhaps derives from suppressing the motion in the melt by the applied magnetic field which is one of the dynamic stimuli for heterogeneous nucleation. According to the theory of thermodynamics, the change in volume free energy, ΔG_v, on solidification in the presence of a magnetic field is given by

$$\Delta G_v = L_m \Delta T / T_m + \tfrac{1}{2} H^2 \Delta\chi_v \qquad (1)$$

where L_m is the latent heat of melting, ΔT is the amount of undercooling, T_m is the melting point, H is the magnetic field, and $\Delta\chi_v$ is the change in volume magnetic susceptibility between the solid and liquid. $\Delta\chi_v$ is given by

$$\Delta\chi_v = \chi_L \rho_L - \chi_S \rho_S \qquad (2)$$

where χ_L and χ_S are the mass susceptibilities of the liquid and solid, respectively, and ρ_L and ρ_S are the respective densities. In the case of pure copper, these values are given as follows; $L_m = 1.6 \times 10^{10}$ erg cm^{-3}, $T_m = 1357$ K, $H = 5.0 \times 10^3$ Oe, $\chi_L = -9.1 \times 10^{-8}$ e.m.u. g^{-1} and $\chi_S = -8.0 \times 10^{-8}$ e.m.u. g^{-1}. ρ_L and ρ_S are taken as the values of liquid density at 1357 K, that is, $\rho_L = \rho_S = 8.0$ g cm^{-3}. ΔT is taken as 85 K, which is the maximum value of undercooling in the presence of a magnetic field in this study. Substitution for ΔG_v definition written above indicates that the second magnetic term of -1.1 erg cm^{-3} is negligible compared with the first heat term of 1.0×10^9 erg cm^{-3} under the experimental conditions. It is, therefore, impossible to consider that the magnetic field effects on undercooling in this study are attributable to the thermodynamic free energy change caused by the magnetic field on solidification.

The Hartmann number, M, of the system determines whether or not an electromagnetic force induced by the magnetic field has sufficient effect to suppress the motion in the melt. The Hartmann number, defined as

$$M = LB(\sigma/\eta)^{1/2} \qquad (3)$$

is a measure of the ratio of pondermotive force, $\sigma U B^2$, to viscous force, $\eta U / L^2$, where L is the characteristic length of the system, B is the magnetic flux density, σ is the electrical conductivity, η is the coefficient of viscosity, and U is the characteristic velocity of the system. If M is much larger than unity, the magnetic field is supposed to suppress liquid motion such as thermal convection. Substituting the following values of pure copper and the experimental conditions for

TABLE III Summary of the maximum values of undercooling and the numbers of irregular and unexpectedly large decreases of undercooling in samples S1-S10

	Magnetic field									
	Present					Absent				
	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
Maximum value (K)	74	78	72	85	83	69	71	70	70	71
Decrease number	0	2	0	1	3	3	5	3	3	0

evaluating the value of M; $\sigma = 5.0 \times 10^6 \Omega^{-1}\,\mathrm{m}^{-1}$, $\eta = 4.0 \times 10^{-3}\,\mathrm{N\,s\,m}^{-2}$, $B = 0.50\,\mathrm{T}$ and $L = 1.2 \times 10^{-2}\,\mathrm{m}$, $M = 212$ is obtained. This value is so much larger than unity that the magnetohydrodynamic effect resulting in the suppression of the thermal convection in a copper melt can definitely be expected in this study. The magnetic field effects on undercooling in this study are, therefore, likely to originate in this magnetohydrodynamic effect. Experiments will be continued to investigate this subject.

4. Conclusions

The effects of static magnetic field were investigated on the undercooling of a copper melt in glass slag when each sample was repeatedly melted and solidified 13 times. Two remarkable effects were found as follows. Firstly, the maximum undercooling values in every experiment in the presence of a magnetic field became apparently higher in comparison with those in the absence of a magnetic field. Secondly, the application of a magnetic field led to suppression of the irregular and unexpectedly large decrease of undercooling. The magnetic field effects on undercooling are considered to be attributable to the flow-suppressing function of the static magnetic field in this study.

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