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Undercooling behavior of glass-fluxed Sb melts under gradient magnetic fields

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Abstract The influence of gradient magnetic field on the undercooling behavior of glass-fluxed pure Sb melts was investigated using a superconducting magnet. It was found that under a positive gradient magnetic field, the mean undercooling of pure Sb melts increased with increasing magnetic field intensity. However, under a negative gradient magnetic field, the mean undercooling showed a decreasing tendency following an initial increase with increasing magnetic field intensity. The results were discussed by considering the Lorentz force and the magnetization force imposed by the gradient magnetic field.

Introduction

The application of a static magnetic field to solidification processing of materials has attracted much attention because of observations of a number of interesting phenomena. It has been shown that a uniform magnetic field imposes a localized force on liquid metals, known as the Lorentz force, leading to damping of natural or forced convection [1, 2] and therefore to modification of segregation patterns of castings [3–5]. In parallel, a gradient magnetic field produces a body force, known as magnetization force, enabling levitation of diamagnetic materials [6], alignment of diamagnetic or paramagnetic crystals [7], and fabrication of a graded material [8]. Recently, it has been shown that the gradient magnetic field can change the interdiffusion behavior at a solid/liquid interface [9]. In addition to liquid–solid transitions, solid-state transformations can also be influenced by imposition of a static magnetic field, leading to morphological and orientational changes of the product phases [10]. It is expected that the increased use of the magnetic field in the field of solidification processing will yield more findings of novel and interesting phenomena.

Glass fluxing has been established as a facile method for deep undercooling of bulk liquid metals since many years ago [11–13]. It is of scientific and technical interest to know if undercooling behavior of a glass-fluxed metallic melt can be influenced by imposing a static magnetic field. There have been few studies on the influence of a uniform magnetic field. Hasegawa and Asai [14] found that the application of a 0.5 T magnetic field on glass-fluxed pure Cu melts leads to suppression of irregular and abrupt reduction of undercooling through repetitive melting and solidification cycles and an increase of the maximum undercooling as well. Esin et al. [15] observed a similar influence of a uniform magnetic field, 2.0 T, on undercooling of glass-fluxed pure Sn melts. Recently, some of the present authors [16] showed that the influence of the uniform magnetic field depends on the species of liquid metals. The mean undercooling of a pure Cu melt increases with increasing magnetic field intensity, whereas that of a pure Ge melt does not show any consistent variations with increasing magnetic field intensity. So far, little has been known about the influence of a gradient magnetic field on undercooling of glass-fluxed liquid metals. The present work reported that glass fluxing experiments on a pure Sb melt under gradient magnetic fields. The choice of pure Sb was because its large entropy of fusion corresponded to a

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large temperature rise, which is desirable for determination of the nucleation temperature with a thermocouple.

Experimental

The experimental apparatus is schematically shown in Fig. 1, which consisted of a superconducting magnet of a cylindrical bore of 300 mm in diameter and a coaxially installed DC resistance heating vacuum furnace of a cylindrical geometry of 260 mm in outer diameter. The magnet provides a uniform magnetic field B of maximum 6 T at the bore center as well as a position-dependent gradient magnetic field $B\mathrm{d}B/\mathrm{d}z$ off the bore center. A 4 N purity Sb sample of 0.6 g in mass was put into an alumina crucible of 3 mm in diameter together with a small amount of B_2O_3 powder of 4 N purity. The crucible was supported by an alumina rod, and its position was adjustable within a distance of ±50 mm from the bore center of the magnet so as to keep the sample under a suitable gradient magnetic field. After the furnace chamber was evacuated to a pressure of 1.0 Pa, the sample and the B_2O_3 powder were heated to 573 K and soaked for 20 min in vacuum for dehydrating. Then, the furnace chamber was backfilled with pure argon (5 N purity) to a pressure of 7 kPa. The magnet was excited to a magnetic field intensity of 0, 0.5, 1.0, 1.5, and 2.0 T at the bore center. Accordingly, a gradient magnetic field of 0, 11.8, 23.6, 35.5, and 47.1 T^2/m was established at the location of the sample, respectively. Under the gradient magnetic field, the sample was further heated to a temperature of 1,123 K (about 150 K above the melting point of pure Sb), and soaked for 5 min. By turning off the heating power, the sample was furnace cooled and solidified in the presence of the gradient magnetic field. During heating and cooling, the sample temperature was monitored continuously with an S-type thermocouple which was installed below the bottom of the crucible, and was recorded by a computer-controlled data acquisition unit at a sampling rate of 100 Hz. In order to determine the thermal delay caused by indirect contact between the sample and the thermocouple, the recalescence of an undercooled pure Cu sample was monitored using a pyrometer. The onset temperature of recalescence was found to have a delay of about 1 s. If a cooling rate of 0.5–1 K/s was considered, such a delay was equivalent to an error of about 1 K for the thermocouple. Under each gradient magnetic field, the sample was melted and solidified several times. Through the experiments, only one sample was used in order to avoid the influence of a random impurity concentration of individual samples. The experiments were performed first under the positive gradient magnetic field in sequence of increasing intensity of the gradient magnetic field. The vacuum chamber of the furnace was opened, re-evacuated, and re-backfilled with pure argon after adding a small amount of fresh B_2O_3 powder. Then, the experiments were performed under the negative gradient magnetic field.

Results

Typical temperature–time curves of undercooled pure Sb samples are illustrated in Fig. 2. Because a large amount of latent heat was extracted to the crucible, the sample temperature did not rise to the melting temperature. However, the temperature rise was evident yet. Hence, the undercooling of the samples could be determined from the

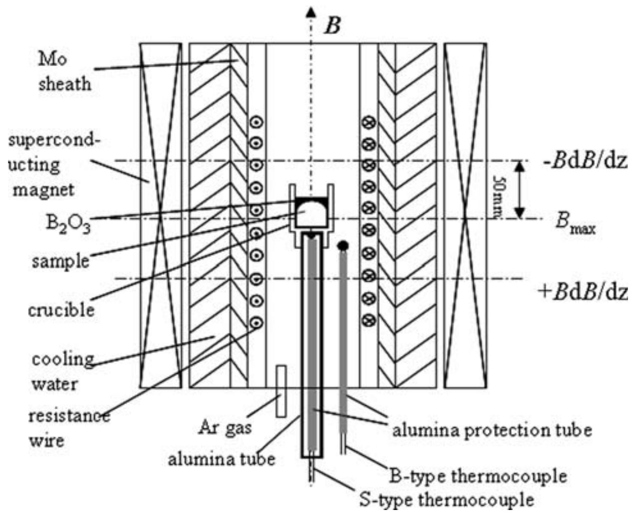

Fig. 1 Schematic illustration of the experimental setup consisting of a superconducting magnet and a resistance heating furnace

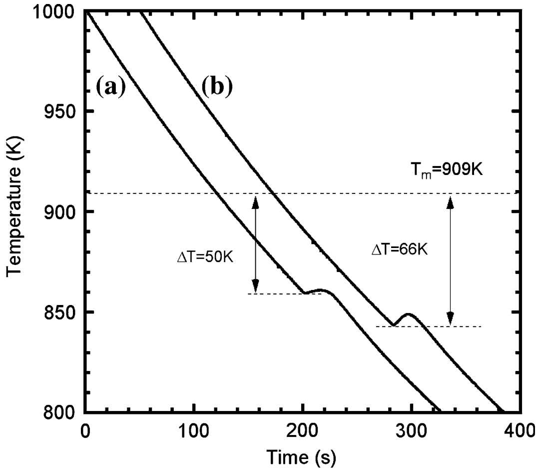

Fig. 2 Illustration of typical time–temperature curves of an undercooled Sb sample. *a* $\Delta T = 50$ K under a zero magnetic field and *b* $\Delta T = 66$ K under a gradient magnetic field of $B\mathrm{d}B/\mathrm{d}z = +47.1\ \mathrm{T}^2/\mathrm{m}^2$

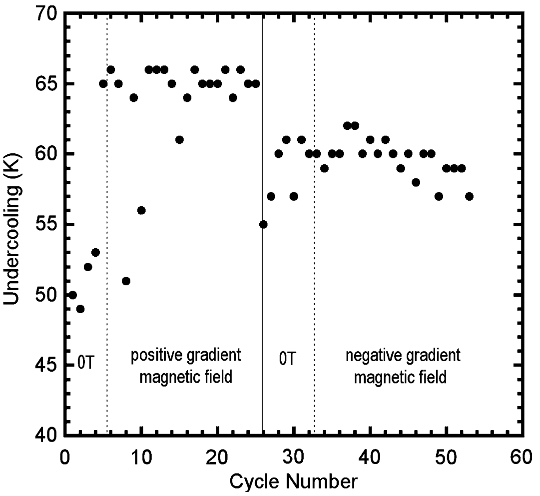

Fig. 3 Undercooling history of the glass-fluxed Sb sample under different gradient magnetic fields. Starting with a zero magnetic field, the first 25 cycles were performed under a positive magnetic field in sequence of increasing magnetic field, whereas the last 28 cycles were performed under a negative magnetic field in sequence of increasing magnetic field

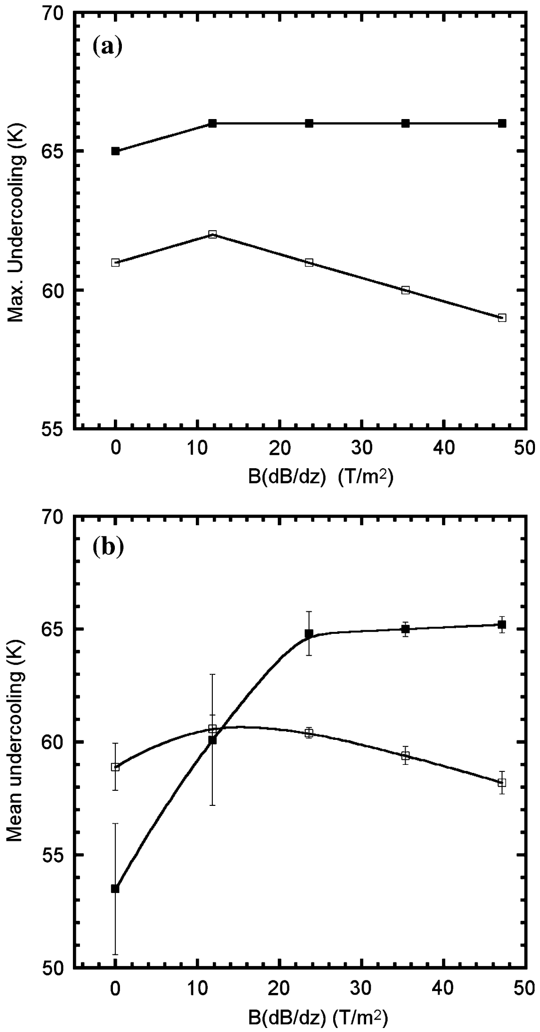

Fig. 4 Illustration of maximum undercooling (**a**) and mean undercooling (**b**) of the glass-fluxed Sb sample as a function of the gradient magnetic field. The *solid symbols* show data for the positive gradient magnetic field, whereas the *open symbols* show data for the negative gradient magnetic field

temperature–time curves. Figure 3 shows the undercooling history of the Sb sample. The first 25 cycles were carried out under the positive gradient magnetic field, whereas the following 28 cycles were carried out under the negative gradient magnetic field. During the initial cycles including those under a zero magnetic field, the undercooling of the sample increased significantly. Then, the undercooling tended to be saturated, though a sudden drop was observed in a few cycles. The sudden drop was found to cease over the last 10 cycles under the positive gradient magnetic field. When the sample was glass fluxed under the negative gradient magnetic field, the initial undercooling of the sample, which was actually attained in the zero magnetic field, showed a large drop with respect to the saturated value of the preceding cycles. The slight surface oxidation of the sample during reopening of the vacuum chamber was assumed to be responsible for this change. In the following cycles, the undercooling of the sample was progressively increased, till it was saturated again. However, the novel saturation value of the undercooling fell below that attained under the positive gradient magnetic field. More surprisingly, the undercooling of the sample showed a declining tendency after going through a short saturation period. At the end of the last cycle, the undercooling had declined by 10%. Apparently, the imposition of the negative gradient magnetic field brought about a reduction of the undercooling of the sample. In order to learn more about the influence of the gradient magnetic field, the maximum undercooling and the mean undercooling of the sample were examined. The results are shown in Fig. 4. In general, the maximum undercooling of the sample under the positive gradient magnetic field was higher than that under the negative gradient magnetic field (see Fig. 4a). Under the positive gradient magnetic field, the maximum undercooling showed an initial increase, and leveled off soon. Under the negative gradient magnetic field, the maximum undercooling increased initially. However, it began to decrease after reaching a peak value at a low gradient. As to the mean undercooling (see Fig. 4b), it increased steadily with increasing intensity of the positive gradient magnetic field, and leveled off at a medium gradient. Under the negative gradient magnetic field, the mean undercooling varied in the same way as the maximum undercooling did. With increasing intensity of the magnetic field, it showed a decreasing tendency following an initial increase. By comparison, the change in the mean undercooling was more significant for the positive gradient magnetic field. Interestingly, an identical undercooling was attained at the positive and negative gradient magnetic field of an intensity of 11.8 T/m^2. Since then, the difference in the mean undercooling between the two types of the gradient magnetic fields was progressively enlarged with increasing field intensity. Apparently, the positive gradient magnetic field tended to enlarge the mean undercooling of the glass-fluxed Sb sample, whereas the negative gradient magnetic field tended to decline the mean undercooling of the glass-fluxed Sb sample, particularly at higher magnetic fields. In the following section, the undercooling refers to the mean undercooling, unless specified.

Discussion

The present results can be explained by reference to a recent model for the glass fluxing process, which was proposed by Wilde et al. following tremendous DTA measurements on pure Au and a statistical nucleation analysis [17]. The model included four major assumptions: (1) initial precipitation of catalytic oxides at the glass/liquid metal interface and subsequent heterogeneous nucleation of solid metal on them, (2) oxygen removal by partial dissolution of the catalytic oxides into the glass melt during further cooling, (3) oxygen uptake from the atmosphere through a semi-open surface of the liquid metal during next melting cycle, and (4) establishment of a balance between removal and uptake of oxygen. The initial increase and subsequent saturation of the undercooling of the present Sb sample can be easily explained by applying the model. However, the smaller saturation value and following decreasing tendency of the undercooling under the negative gradient magnetic field remain an open question. In order to answer this question, potential influences of the gradient magnetic fields on the glass fluxing process are considered.

First of all, the species of the catalytic oxides inside the Sb samples needs to be specified. As the oxide of Sb cannot survive at the glass fluxing temperature, catalytic oxides for heterogeneous nucleation are assumed to form by a combination of oxygen with impurity elements dissolved in the liquid Sb sample, as was done by Wilde et al. for nucleation of pure Au [17]. The impurities of high purity Sb include As, Si, Cd, Pb, Zn, and Fe. The melting point and physical properties of their oxides are listed in Table 1. Note that the oxides of all impurities, except for that of As, are stable at the highest glass fluxing temperature (1,123 K), thus having a potential to act as the catalytic sites for heterogeneous nucleation of solid Sb. In order to be dissolved by the glass, the catalytic oxides should stay at the glass/liquid metal interface, which is determined by the buoyancy force and the gravity. As seen in Table 1, CdO and PbO have a larger density than that of pure liquid Sb. Hence, a particle of them cannot be kept at the glass/liquid metal interface due to an insufficient buoyancy force, but will sediment into liquid Sb under the action of the gravity. After losing the contact with the glass, they will not be dissolved. As a result, the oxygen removal mechanism is out of action, and the undercooling of the sample is not increased. This assumption is contradictory to the present results. Thus, the two oxides are dropped from the list of the potential catalytic oxides. Those left are SiO_2, ZnO, and FeO. Due to a lack of data of the wetting factor, it is difficult to identify which of them is the most catalytic species. Thus, each of them has to be considered.

Table 1 List of melting points, density, and volumetric magnetic susceptibility of pure Sb, B_2O_3 glass, argon, and oxides of impurities

Substance	Melting point (K)	Density (kg/m^3)	Volumetric magnetic susceptibility ($\times 10^{-6}$)
Sb	909	6,680	−68.2
B_2O_3	–	2,340	−16.3
Ar	–	1,780	−10.8
As_2O_3	548	3,865	−7.5
SiO_2	>1,943	2,660	−16.5
CdO	>1,773	8,150	−23.9
PbO	1,159	9,530	−22.5
ZnO	2,248	5,606	−23.6
FeO	1,642	5,780	+7200

The density and volumetric susceptibility were all for room temperature. The magnetic susceptibility data were taken from http://www-d0.fnal.gov/hardware/cal/lvps_info/engineering/elementmagn.pdf

It is known that a uniform magnetic field imposes the Lorentz force on an electrically conducting liquid, leading to suppression of fluid flow with its direction or a component vertical to the direction of the magnetic field [1, 2]. In the present work, the Lorentz force should act on the liquid Sb sample, and therefore may change the migration behavior of the catalytic particles inside. In the Wilde's model [17], the catalytic oxide particles are formed preferentially at the fluxing glass/liquid metal interface. Under the action of a downward convection of any origin, some of the particles may move away from the interface, and be trapped into the liquid metal. If this happens, the efficiency of oxygen removal by glass fluxing will decline. However, if the downward fluid flow is reduced or suppressed by the Lorentz force, the particles will rest at the fluxing glass/liquid metal interface, thus increasing their possibility of being dissolved into the fluxing glass and therefore promoting development of a large undercooling [15]. For the present Sb sample, its bulk volume can be divided into numerous small units, in which the intensity of the magnetic field is approximately constant. With such consideration, the gradient magnetic field is supposed to have a beneficial influence on the attainment of a large undercooling by suppressing local downward convection. However, consideration of the Lorentz force only does not yield a reasonable explanation of the decreasing undercooling of the Sb sample when glass fluxed under the negative gradient magnetic field of higher intensity. Therefore, a second mechanism is assumed to be co-operative.

The magnetization force acting on an object in vacuum can be written as follows:

$$F_{\mathrm{m}} = \frac{\chi_{\mathrm{V}}}{\mu_0} B \frac{\mathrm{d}B}{\mathrm{d}z} V, \tag{1}$$

where χ_{V} is the volumetric magnetic susceptibility, μ_0 is the magnetic permeability in vacuum, B is the intensity of the magnetic field, $\mathrm{d}B/\mathrm{d}z$ is the gradient of the magnetic field in the z-axis direction (namely the vertical direction here), and V is the volume of the object. The force tends to push the object with a negative χ_{V} away from the center of the magnetic field, but to pull the object with a positive χ_{V} toward the center of the magnetic field. For an object in a medium, the magnetization force acting on it is rewritten as follows [18]:

$$F_{\mathrm{m}} = \frac{(\chi_{\mathrm{p}} - \chi_{\mathrm{M}})}{\mu_0} B \frac{\mathrm{d}B}{\mathrm{d}z} V, \tag{2}$$

where χ_{p} and χ_{M} are the volumetric magnetic susceptibility of the object and the medium, respectively. The magnetization force is assumed to have two important effects on the glass fluxing process. First, it may have an effect on the catalytic oxides, of which partial volumes were immersed in the B_2O_3 flux and in the Sb sample, respectively. Second, it may have an effect on the B_2O_3 flux, which was seated on the top surface of the Sb sample under the pressure of the argon atmosphere. The details of the two effects are explained below.

As schematically shown in Fig. 5a, a catalytic oxide particle is assumed to rest at the fluxing glass/liquid metal interface initially due to a balance between the downward gravity G and the upward buoyancy force F_{b}. When a gradient magnetic field is applied, the balance will be shifted or even broken due to the action of the magnetization forces onto the particle. Depending on the magnitude and the sign of the magnetization forces, the particle is raised or lowered with respect to its original position under the zero magnetic field. For example, the position of a diamagnetic particle with a χ_{V} ranging between those of B_2O_3 and Sb is lowered under a negative gradient magnetic field, but it is raised under a positive gradient magnetic field (see Fig. 5b, c, respectively). In an extreme case, the particle is pushed away from the fluxing glass/liquid Sb interface, thus sinking in liquid Sb or being trapped into the B_2O_3 glass melt. Such changes of the particle position, if occur, will change the kinetic aspects of the glass fluxing process, and impose an influence on the undercooling of the Sb sample. By substituting the magnetic susceptibility data of Table 1 into Eq. 2, the magnetization forces acting onto the particles of each potential catalytic oxide is estimated as a function of the magnetic field gradients. Furthermore, by adding it onto the gravity or onto the buoyancy force depending on its sign, the new equilibrium position of the particle at the glass/liquid metal interface is determined. In order to evaluate the shift of the position of the particle, a new quantity termed volume ratio is defined as the ratio of the partial volume of the particle immersed in the B_2O_3 flux to the total particle volume and calculated. As shown in Fig. 6, the volume ratios for the two diamagnetic oxide species, SiO_2 and ZnO, show an increasing and a decreasing tendency for positive and negative magnetic field gradients, respectively. Due to a comparable

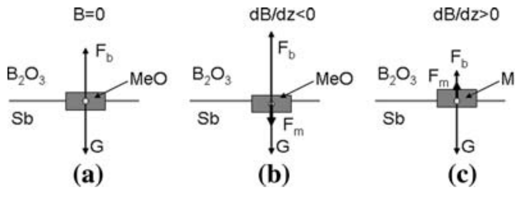

Fig. 5 Schematic illustration of the position of a catalytic MeO oxide particle rested at the glass/liquid Sb interface as well as forces acting on it. The MeO particle is assumed to be diamagnetic and have a χ_{V} in-between those of B_2O_3 and Sb_2O_3. B is the gradient magnetic field, $\mathrm{d}B/\mathrm{d}z$ is the gradient of the magnetic field, G is the gravity of the particle, F_{b} is the buoyancy force by the B_2O_3 glass, and F_{m} is the magnetization force

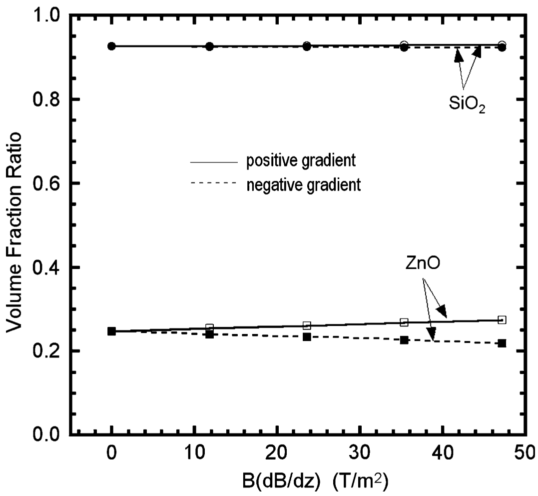

Fig. 6 Calculated volume ratio of a diamagnetic catalytic oxide particle as a function of the magnitude of the positive (*solid line*) and negative (*dashed line*) gradient magnetic field. The catalytic oxides are supposed to be SiO_2 and ZnO

density to liquid Sb, the ZnO particle shows a larger change in the volume ratio than that of the SiO_2 particle upon the imposition of the gradient magnetic field. From a kinetics point of view, the increased volume ratio promotes the dissolution kinetics of the catalytic oxide through an increased interfacial area, and therefore, is beneficial to the incremental rise of the undercooling in a single cycle. Inversely, the decreased volume ratio leads to a lower efficiency in oxygen removal, and therefore, corresponds to a smaller incremental rise of the undercooling. Consideration of the increased volume ratio of the diamagnetic oxides under the positive gradient magnetic field offers a supplementary explanation to the progressively increasing undercooling as well as a larger saturation undercooling of the Sb sample. Similarly, consideration of the decreased volume ratio of them under the negative gradient magnetic field allows us to understand the smaller saturation value and following declining tendency of the undercooling of the Sb sample at higher magnetic field intensities, because the unfavorable dissolution kinetics tends to diminish the beneficial effect of the Lorentz force. A similar analysis of the effect of the magnetization force on the position of the FeO oxide particle at the fluxing glass/liquid metal interface, however, allows us to preclude it from the list of the catalytic oxides, because the force is so large that the particle is either pushed into the B_2O_3 glass or submerged into the liquid Sb. As a result, the potential catalytic oxides are reduced to SiO_2 and ZnO. If we further consider a calculated larger change in the volume ratio under the present gradient magnetic field, ZnO is more likely to be the real catalytic oxide.

Second, the effect of the magnetization force on the fluxing reagent is considered. According to the model by Wilde et al. [17], perfect covering of a liquid sample by a fluxing glass reduces the oxygen uptake during re-melting of the sample, thus increasing the undercooling of the sample. The present Sb sample was not fully covered by the B_2O_3 flux because of imperfect wetting, as was observed by Wilde for the Au sample in a Pyrex glass [17]. Due to the capillary effect, the B_2O_3 flux was thicker at the crucible wall side than at the center of the top surface of the liquid Sb sample. The maximum thickness of the B_2O_3 flux is usually determined by a balance between surface tension and the gravity. For a given mass of the B_2O_3 glass, a larger thickness of the B_2O_3 flux at the crucible side means worse covering to the top surface of the liquid Sb sample. In the present work, the gradient magnetic field imposes a magnetization force onto the B_2O_3 flux, which will change the resultant force of gravity and the buoyancy force and hence the thickness of the B_2O_3 flux. According to Eq. 2, the magnetization force acting on the B_2O_3 flux under the argon atmosphere is estimated. It amounts to only 1% of the gravity force for the highest gradient magnetic field. Such a small value suggests that the influence of the magnetization force on the covering of the B_2O_3 flux over the liquid Sb sample can be neglected.

In summary, the gradient magnetic field imposes a Lorentz force onto the liquid Sb sample, and therefore promotes liquid undercooling on the basis of cycling treatment generally. On this ground, the positive gradient magnetic field imposes an additional upward magnetization force on the particles of the diamagnetic catalytic oxides, leading to accelerated dissolution kinetics of the particles and therefore to a large undercooling. Inversely, the negative gradient magnetic field imposes an additional downward magnetization force on the particles of the diamagnetic catalytic oxides, leading to reduced dissolution kinetics and therefore to a reduced undercooling.

Conclusions

The undercooling behavior of a glass-fluxed Sb sample under gradient magnetic field has been investigated using a superconducting magnet. It has been found that under positive gradient magnetic field, the undercooling of the sample increases with increasing magnetic field initially, and ends up with a saturation value. Under negative gradient magnetic field, the undercooling of the sample shows a decreasing tendency with increasing field intensity following an initial increase. Based on a recent nucleant refining model and consideration of the interactions between the magnetic field and the glass fluxing system, the identity of the catalytic oxides for heterogeneous nucleation as well as the mechanisms underlying the variations of the undercooling with the gradient magnetic field have been discussed. The diamagnetic SiO_2 and ZnO oxides have been suggested to be the most probable catalytic oxide. The initial increase and subsequent saturation of the undercooling of the sample has been explained by considering both the general cycling effect and a beneficial effect of the Lorentz force acting on the liquid Sb sample. Under the positive gradient magnetic field, the magnetization force acting on the catalytic oxide particles tends to speed up their dissolution kinetics, therefore making an additional contribution to the enlargement of the undercooling. However, under the negative gradient magnetic field, the magnetization force tends to slow down the dissolution kinetics of the catalytic oxides, thus leading to a lower saturation undercooling and a decreasing tendency of the undercooling at high gradient magnetic field.

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