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TOPICAL REVIEW

Texturing by cooling a metallic melt in a magnetic field

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Abstract
Processing in a magnetic field leads to the texturing of materials along an easy-magnetization axis when a minimum anisotropy energy exists at the processing temperature; the magnetic field can be applied to a particle assembly embedded into a liquid, or to a solid at a high diffusion temperature close to the melting temperature or between the liquidus and the solidus temperatures in a region of partial melting. It has been shown in many experiments that texturing is easy to achieve in congruent and noncongruent compounds by applying the field above the melting temperature $T_m$ or above the liquidus temperature of alloys. Texturing from a melt is successful when the overheating temperature is just a few degrees above $T_m$ and fails when the processing time above $T_m$ is too long or when the overheating temperature is too high; these observations indicate the presence of unmelted crystals above $T_m$ with a size depending on these two variables that act as growth nuclei. A recent model that predicts the existence of unmelted crystals above the melting temperature is used to calculate their radius in a bismuth melt.

Keywords: magnetoscience, magnetic processing, nucleation, magnetic texturing, undercooled liquids, intrinsic nuclei, magnetic susceptibility, metallic melt, crystallization

(Some figures in this article are in colour only in the electronic version)

1. Introduction
Magnetoscience is being increasingly used in many research fields. The main effect of a magnetic field applied during processing is to align the elementary crystals along their easy magnetization axis. A review of this phenomenon, which has been observed in many materials, has recently been published [1]; the surprising phenomenon of texturing from the melt indicates that the crystallization is probably governed by numerous intrinsic nuclei. We recall from experiments that texturing is successful when a metallic melt is heated above the melting temperature of congruent compounds or above the alloy-liquidus temperature [2]. These results contradict the classical nucleation model, which does not predict the presence of unmelted crystals in the melt acting as growth nuclei below $T_m$; the free-energy change due to crystal formation does not contain any contribution from conduction electrons, in spite of the fact that the energy saving is associated with the Fermi-energy equalization of a crystal and its melt [3, 4]. This unknown contribution has recently been introduced in the Gibbs free-energy change; a new critical radius and crystal-energy barrier have been calculated and used to determine this energy saving from the undercooling degree of liquid elements. This model predicts the maximum radius of unmelted crystals at $T_m$ and the temperature above $T_m$ at which these crystals completely disappear [5–8].

This energy saving per unit volume is a fraction $\varepsilon_{ls}$ of the fusion heat $\Delta H_m$ per unit volume, which is maximum at
where \( \frac{d\Delta G}{dT} = 0 \). Under this condition, the thermodynamics constraint for all radius
\[
\left[ \frac{3d(\Delta G_{\text{free}})}{4\pi R^3} \right]_{T=T_m} = \left( \frac{\Delta S_m}{V_m} \right)
\]
is satisfied. Here, \( \Delta G_{\text{free}} \) is the free energy change for crystal formation, \( R \) is the crystal radius, \( \Delta S_m \) is the fusion molar entropy and \( V_m \) is the molar volume. The coefficient \( \varepsilon_{b_k} \) is
\[
\varepsilon_{b_k} = \varepsilon_{b0} \left[ 1 - \frac{\theta^2}{\theta_0^2} + O(\theta^4) \right],
\]
where \( \theta = \frac{T-T_m}{T_m} \), in agreement with many experiments on liquid-element undercooling; it is zero for \( \theta = \theta_0 \) and \( T = T_0 \), where \( T_0 \) is the free-volume disappearance temperature and \( \varepsilon_{b0} = 0.217 \) for many liquid elements [5]. The critical radius varies as \( (\theta - \varepsilon_{b0})^{-1} \) and diverges for \( \theta = \varepsilon_{b0} \); thus, the temperature of disappearance of intrinsic nuclei must occur at \( \theta = \varepsilon_{b0} \). For many liquid elements, this disappearance is predicted at \( \theta = 0.19 \) because \( \varepsilon_{b0} = 0.217 \). This temperature may be much higher in metallic glass-forming melts. The unmelted crystals cannot grow above \( T_m \) because the energy barrier increases when \( \theta \) increases. In fact, a fraction of droplet inside crystals may reduce their size when the temperature increases.

Goetz raised the problem in 1930 by studying bismuth crystal formation from a seed; a systematic study of the conditions under which the seed-crystal transfers its orientation to a rod was performed. Goetz’s experiments on artificially distorted seeds showed that crystalline units must exist in the liquid state, and this ‘liquid crystal’ is destroyed at \( \sim 10^\circ \)C above the melting point. He also noted that crystals grown without a predetermined orientation indicated a preference for an orientation in which the direction of the smallest diamagnetic susceptibility (along the trigonal axis) was parallel to the lines of force. He concluded that although this effect is much smaller than the orienting forces of a seed, the fact that it exists, supports the assumption of a block phase slightly above the melting point [9]. The formation of oriented bismuth crystals in a magnetic field had been already observed in 1849 and in 1905 [10, 11].

In 1981, Mikelson and Karklin described how to control the crystallization process in Al–Cu and Cd–Zn alloys by a magnetic field [12]. They carefully studied magnetic texturing in the partial-melting window between solidus and liquidus temperatures. The alignment degree was measured as a function of the temperature at which the magnetic field \( B \) was switched on and as a function of the temperature at which it was switched off after applying the field to the liquid state. The temperature range in the partial-melting window, in which the dendrites can be effectively ordered by a magnetic field, lies below the liquidus line and correspond to 20% of the partial melting window. These results demonstrated for the first time that crystal alignment is only possible in this temperature interval when crystals are sufficiently large, but not too large to avoid mechanical interaction between them. The mechanical force moment causing the crystal embedded in the melt to orient in a homogeneous magnetic field \( B \) is given by
\[
K_3 = \frac{\Delta \chi B^2 v \sin(2\alpha)}{2\mu_0}.
\]
This expression is valid for an anisotropic crystal characterized by the difference \( \Delta \chi \) in magnetic susceptibility along two mutually perpendicular axes; it neglects the effect of the crystal shape, which is negligible for small susceptibility values. Here, \( v \) is the sample volume, \( \mu_0 \) is the magnetic constant and \( \alpha \) is the angle between \( B \) and the axis having the maximum value of \( |\chi| \). A paramagnetic crystal is aligned along its easy magnetization axis, and a diamagnetic crystal is aligned along the axis having the minimum value of \( |\chi| \). The effect of the shape and the field inhomogeneity on the mechanical force moment was also discussed in [12]. There was no discussion at this time about the origin of growth nuclei and no study on the detrimental effect of overheating on the orientation.

De Rango and co-workers have confirmed that the presence of a liquid is necessary to texture a material. Full melting and melt overheating were used for the first time to texture the high-temperature superconductor YBCO. These experiments convincingly showed that a magnetic field can be used to texture any material with residual magnetocrystalline anisotropy at its melting temperature [13–15].

Magnetic processing from the melt uses furnaces and crucibles containing the sample in a high magnetic field. The region where the magnetic field gradient is maximum is also used to apply a magnetic force to the sample and to the sample holder to observe the changes in magnetic susceptibility accompanying the melting, the overheating and the crystal alignment during the cooling and heating cycle [2]. Electromagnetic heating in a cold crucible was also applied to levitate a metallic melt and to observe the stability conditions of diamagnetic and paramagnetic melts in a magnetic field [16]. The cooling involving the levitation of a levitated melt is not easy to realize, because the change in susceptibility during solidification induces a change in magnetic force and moves the sample in a variable ac field and in a variable dc magnetic field gradient. Titanium has nevertheless been crystallized under levitation conditions [17, 18]. Under the effect of the magnetic force, due to the magnetic field gradient applied to the sample magnetization, a paramagnetic melt with a very high susceptibility can escape from the electromagnetic crucible [19]. The radial forces around the vertical axis of a magnetic field can also push a highly paramagnetic sample onto the cold crucible edge and prevent the fusion of a part of the sample. In general, the sample is melted, rapidly solidified and textured in a cold crucible or even by casting at the maximum field in a cold mold [19–21].

This review of the magnetic texturing of metallic materials contains five parts: congruent materials, non-congruent materials, ferromagnets having a Curie temperature near the melting temperature, improvement of magnetic texturing techniques, and the effect of time of processing in the liquid state on the unmelted-crystal radius in bismuth.
2. Congruent compounds

2.1. Bismuth

Susceptibility measurement has been used to evaluate the solidified fraction near the melting temperature as a function of temperature by varying the cooling rate [2, 22]. Bi susceptibility has been also measured as a function of temperature by heating to 331 °C, which is 60 °C above the melting temperature \( T_m = 271 °C \), followed by cooling to room temperature as shown in figure 1. The susceptibility measured at room temperature after cycling the sample in an inhomogeneous magnetic field of 5 T at high temperatures is equal to the crystal susceptibility measured along the c-axis [2]. A 100% orientation has been obtained. Note that grain-boundary motion in Bi is affected by a magnetic field and the microstructure development can be modified by selecting the mode of grain growth and the preferential orientation [23, 24].

The critical volume of the crystal necessary to achieve an orientation in a magnetic field is approximately given by

\[
\frac{\Delta \chi \nu B^2}{\mu_0 k_B T} > 1, \tag{3}
\]

where \( \nu \) corresponds to a radius equal to 16.5 nm with \( \Delta \chi = 1.6 \times 10^{-7} \) emu g\(^{-1}\) Oe\(^{-1}\); this value is far above the critical radius \( R_{\text{cr}} = 2.5 \) nm required for crystal growth at \( T_m \). Alignment is only possible during the crystal growth when the crystal is still surrounded by liquid. The time for crystal growth of 50% is long because the growth is governed by the thermal exchange of the sample with its environment. This time is equal to about 100 s for a cooling rate of 650 °C h\(^{-1}\) and 400 s for 70 °C h\(^{-1}\).

The time needed to orient a spherical particle in a magnetic field is small; it mainly depends on the liquid viscosity \( \eta \) and on the magnetic moment and is of the order of several milliseconds. For a 90° rotation, it is approximately

\[
t = \frac{3 \pi^2 \mu_0 \eta}{\Delta \chi B^2}. \tag{4}
\]

This orientation time plays no role because it is negligible as compared with the crystallization time of one 1 cm\(^3\) sample. Precise calculations of this time have been made under various assumptions [25]. Homogeneous nucleation cannot explain crystallization occurring slightly below \( T_m \); if homogeneous nucleation occurred, the nucleation time would be minimum at \( T = T_m/3! \). The crystallization is due to the presence of residual intrinsic nuclei [5].

2.2. Ce–Ni

Ce–Ni is a congruent compound having a melting temperature of 680 °C and an orthorhombic lattice. The temperature cycle is applied up to 700 °C at a rate of 20 °C s\(^{-1}\) using a cold crucible; the susceptibility is measured in an inhomogeneous magnetic field of 5 T to apply a magnetic force to the sample. The undercooling is equal to 5 °C, and a susceptibility increase of \( 2.0 \times 10^{-7} \) emu g\(^{-1}\) Oe\(^{-1}\) is directly obtained at the solidification temperature as shown in figure 2. The susceptibility anisotropy varies as T\(^{-2}\); x-ray diffraction measurements confirm that the c-axis is parallel to the applied magnetic field. The susceptibility represented in figure 2 is shown without correction of the contribution from the sample holder; only the susceptibility change at the melting temperature is an absolute value. For critical volume, the orientation corresponds to a particle radius of 18.5 nm; here, too, the crystallization time is much larger than the orientation time and the melt contains residual nuclei that cause the crystallization close to \( T_m \) [2].

2.3. Dy\(_3\)Al\(_2\)

This congruent compound has a Curie temperature of 76 K and a tetragonal lattice; it melts at \( T = 1030 °C \); the applied
heating and cooling rates are 200 °C h⁻¹ and the sample weight is 3 g. The overheating was, in successive experiments, 4.5, 8, 27 and 49 °C. The compound was textured after a small overheating as shown in figure 3, while an abrupt liquid-solid transformation occurs for the two largest values of overheating without any texturing as shown in figure 4. The susceptibility increase due to texturing at $T = 1007$ °C is $4.0 \times 10^{-7}$ emu g⁻¹ Oe⁻¹. Excess overheating produces some undercooling followed by recrystallization. The size of the residual nuclei is reduced at higher temperatures and the crystallization at the surface is probably induced by the crucible boundary [8].

2.4. Sm₂Co₁₇

This compound is congruent; it is possible to modify its composition to produce permanent magnets. The susceptibilities of Sm(Co₀₆Fe₂₅Cu₀₀₆Zr₀₂₀₂₅)₈.₃₅ and Sm(Co₀₄Fe₂₇Cu₀₀₆Zr₀₂₀₂₅)₄.₁ have been measured during a temperature cycle including melting and solidification in a 3.5 T magnetic field. The fusion is observed as a decrease of the paramagnetic susceptibility occurring in the temperature interval 1150–1250 °C as shown in figure 5. An overheating of about 15 °C is applied to the melt by an inductive heating. The susceptibility increase after solidification is large and of the order of $1.5 \times 10^{-6}$ emu g⁻¹ Oe⁻¹. It has been shown that magnetic texturing can be realized by melting and cooling the material in a cold crucible. An orientation degree of 90% was obtained by measuring the saturated magnetization in a magnetic field [19, 26].

3. Non-congruent materials

All the following studies show that the presence of a liquid is necessary to texture a material. The effect of overheating the melt was only studied in a few publications.

Figure 3. Susceptibility of Dy₃Al₅ measured in an inhomogeneous magnetic field of 2.9 T versus the temperature. The solid line corresponds to the heating of a non-oriented sample. The higher susceptibility measured after solidification (dotted line) is due to the alignment of crystallites with their easy magnetization axis parallel to the applied field. An overheating of 8 °C has been applied after the sample fusion. These results are extracted from the PhD thesis of B Legrand (1996) and from her diploma report (1992).

Figure 4. Magnetic susceptibility of Dy₃Al₅ measured in an inhomogeneous magnetic field of 2.9 T versus the temperature. The solid line corresponds to the heating of a non-oriented sample. The susceptibility measured after solidification (dotted line) is not higher because there is no alignment of crystallites in the applied field. An overheating of 27 °C has been applied after the sample fusion. These results are extracted from the PhD thesis of B Legrand (1996) and from her diploma report (1992).

Figure 5. Susceptibility of Sm₂Co₁₇ type alloy having a permanent magnet composition Sm(Co₀₆Fe₂₅Cu₀₀₆Zr₀₂₀₂₅)₈.₃₅ plotted versus temperature. The solid line corresponds to the inductive heating of a non-oriented sample. The higher susceptibility measured after solidification (dotted line) is due to the alignment of crystallites with their easy magnetization axis parallel to the applied field. An overheating of 15 °C was applied after the sample fusion. These results are extracted from the PhD thesis of B Legrand (1996).

3.1. YBa₂Cu₃O₇₋ₓ

Single-crystal grains of YBCO are aligned in liquid silver by a 5 T magnetic field [14]. Significant anisotropy still exists in the paramagnetic susceptibility at a temperature of 1020 °C close to the peritectic temperature of 1040 °C in flowing oxygen. The magnetic texturing obtained by de Rango and coworkers [13] is due to the existence of this residual anisotropy, and the alignment occurs when a crystal is free to rotate in the surrounding liquid. Annealing for two hours at $T = 1030$ °C in a 7 T field followed by cooling at a rate of 20 °C h⁻¹ leads to a weak alignment, whereas annealing at 1055 °C in the liquid state leads to a perfectly textured material. Disorientation occurs at an annealing temperature
of approximately 1070 °C. The anisotropy ratio deduced from magnetization measurements in the superconducting state plotted as a function of the annealing temperature reaches a maximum a few degrees above the peritectic temperature. These experiments demonstrated, for the first time, that at excessively high temperatures, above the peritectic temperature, the particles become too small to act as growth nuclei [15].

3.2. Bi 2223

A recent attempt to texture this ceramic in a high magnetic field and at a high temperature below the solidus temperature did not lead to a textured material because of the absence of liquid [27]. Pellets of the superconducting ceramic Bi1.8Pb0.4Sr2Ca2.5O10.34 (Bi2223) were heated in air to the partial-melting window and in a magnetic field of 8 T to a variable maximum temperature \( T_A \) for 1 h and slowly cooled at 2 °C h−1. The melting started above 855 °C. The samples were textured along the c-axis; the dispersion angle is almost 8 °. The critical current for each sample was measured at 77 K; its maximum was 1450 A cm−2 for \( T_A = 860 °C \); then, it progressively decreased as the temperature increased to 890 °C where it became very small. The nuclei disappeared owing to the decomposition of Bi 2223 in several phases far above 860 °C and to the reduction of the nucleus size above the peritectic temperature [28, 29]. In spite of this success, this technique has not been used to prepare tapes or multifilament materials at an industrial scale because it was thought that any melting would decompose the Bi 2223 phase and a long period of annealing at a lower temperature would be necessary to recover this phase; long annealing and even a partial melting of chemical precursors have been used to obtain the Bi 2223 phase. Recently, experiments have again shown that this phase can be rapidly recomposed after melting, in agreement with the previous work on magnetic texturing [30, 31]. All these results indicate the existence, above the liquidus temperature, of untextured crystals acting as crystal growth nuclei.

This work was completed using an apparatus enabling both high pressure sintering at high temperature and magnetic field processing for texturing ceramics. The melting of crystallites pellets followed by solidification leads to a lower density than that of the crystal. A high-pressure step immediately below the solidus temperature increases the density and improves the contact between grains. A much higher critical current has been obtained as compared with processing in a magnetic field without using the pressure step. Meanders have been cut to transport the current along a 21 cm length; pulsed currents of 300 A have been applied at 77 K to several meanders, having a cross-sectional area of 1 mm² and being connected in series without degradation of the superconducting properties. The mechanical properties of this ceramic are strongly enhanced by these steps of hot pressing [32–34].

3.3. Bi 2212

The Bi 2212 crystallization has been studied using pellets doped with 10% MgO [35–37]. The conditions required for full melting have been determined by measuring the magnetic susceptibility as a function of temperature for different overheating temperatures. The partial-melting window has been described as a function of temperature by susceptibility measurement cycles, each of them being characterized by an annealing temperature [6, 36]. A partial melting starts at 877 °C and full melting occurs at 892 °C. The magnetic texturing phenomenon has been observed by considering the magnetization anisotropy of bulk materials in the superconducting state at \( T = 4.2 °K \) as a function of the overheating temperature. The best crystal orientation is obtained after an overheating of about 1 °C above the temperature of complete melting. A further increase in the overheating temperature decreases the degree of orientation, thus, this melt also contains residual nuclei which are progressively melted when the overheating temperature is increased [6].

Bi 2212 bulks containing 10% Ag or Pb instead of MgO can also be textured by a magnetic field after annealing at 893 °C [38, 39]. Magnetic texturing has been applied to tapes and multifilament conductors to prepare for industrial applications [38–43]. Dip-coated monolayer Bi 2212/Ag tapes (60 μm in thickness) are textured with a 7.5 T field perpendicular to the tape and an annealing temperature of 890 °C [42]. Higher fields of up to 15 T are also applied in the magnetic melt processing of Bi 2212 bulks and Ag-sheathed tapes with a core thickness above 80 μm. The degree of texturing and the anisotropy factor upon magnetization strongly increase with the field amplitude. The critical current for transport reaches 1000 A in self-field for tapes with a core thickness of 180 μm [43].

Multifilamentary Bi 2212/AgMg wires were heat treated in a 12 T background field oriented perpendicular to the wide surface of the wires using a shorter temperature time profile than the conventional one. The wires are partially textured and have a critical current in self field increasing by 10% [44]. A dynamic process has been developed to texture long wires by continuously moving them in a perpendicular magnetic field of 5 T at a velocity adapted to the temperature profile of the furnace. The critical current increased by 40% to 630 A and the critical current density attains 190 kA cm−2 at 4.2 K [45].

3.4. SmCo5 and NdCo5

SmCo5 and NdCo5 precursor alloys have been melted in a hemispherical cold crucible and cooled by switching off the power of the induction furnace in a magnetic field of 2.5 T. Solidification occurred in a few seconds because the copper crucible was cooled by water circulation. In spite of this quenching, in the presence of various thermal gradients due to the crucible wall and in spite of the melt instability, the material is oriented by the magnetic field. The saturation magnetization along the applied magnetic field is nearly equal to the saturation magnetization of a crystal along the easy axis of the hexagonal lattice [19].

3.5. Nd5Fe14B and Dy3Fe14B

The magnetocrystalline anisotropy of Dy3Fe14B is larger than that of Nd5Fe14B at room temperature. Thus, the
high-temperature anisotropy is expected to also be larger in 
this compound. The fusion is controlled by measuring the 
magnetic force applied to the sample heated by induction. 
In the first step, Dy\textsubscript{17}Fe\textsubscript{86.5}B\textsubscript{2.5}Cu\textsubscript{1.5} is melted in a 5\,T 
inhomogeneous magnetic field by heating to 1220°C, a 
few degrees above the peritectic temperature. The partial 
alignment of crystals is achieved; this magnetic field 
amplitude is nevertheless too weak to achieve a full alignment. 
When the sample is overheated to 1350°C and cooled 
in an inhomogeneous magnetic field, the sample magnetic 
properties are isotropic. At high temperatures, the nuclei 
become too small to be active for crystal growth near $T_m = 1214$°C.

Nd\textsubscript{2}Fe\textsubscript{14}B crystals have too small anisotropy to be 
aligned in a 5\,T magnetic field at their melting temperature. 
Susceptibility has been measured during temperature cycles 
by progressively varying the overheating temperature up to 
1348°C knowing that the peritectic temperature is 1170°C. 
There is no alignment of crystals in the magnetic field 
regardless of the cycle [16]. In a first step, the overheating 
is equal to 10°C using a cooling rate of 3\,°C/h. An 
isothermal solidification transition in Nd\textsubscript{2}Fe\textsubscript{14}B is observed 
at a constant temperature as shown in figure 6. In contrast, 
an overheating of 51–98°C induces an undercooling of 36°C; 
the Nd\textsubscript{2}Fe\textsubscript{14}B nuclei are too small to act as growth nuclei; 
an abrupt transformation from the melt to the Nd\textsubscript{2}Fe\textsubscript{14}B solid 
is thus observed accompanied by recalescence as shown in 
figure 7 [46].

4. Ferromagnets having a Curie temperature near 
the melting temperature

Alloys with an approximately eutectic composition have 
melting temperatures much lower than those of elements 
that comprise these alloys; the Curie temperatures of Bi–Mn, 
Co–B and Co–Sn alloys can be larger than the melting 
temperature under specific conditions such as undercooling.

4.1. Bi–Mn

The Curie temperature $T_C = 355$°C of Bi–Mn is higher than 
the melting temperature of the alloy. The Bi–Mn phase is 
aligned by the magnetic field inside liquid Bi–Mn alloys 
during its solidification [47]. An excessively large magnetic 
field pushes the Bi–Mn needles to the periphery because a 
radial field gradient exists even when $d\mathbf{B}/dz = 0$ [48]. This 
finding is a new demonstration that the magnetic field gradient 
can separate a phase subjected to a large magnetic force 
because of its large paramagnetic susceptibility.

4.2. Nd–Fe

The same phenomenon is observed by subjecting eutectic 
Nd–Fe to a strong vertical magnetic force. The eutectic Nd–Fe 
separated into two domains: the bottom corresponds to a 
eutectic alloy of Nd and Nd\textsubscript{2}Fe\textsubscript{17}; the top corresponds to 
a eutectic alloy of Nd and Nd\textsubscript{2}Fe\textsubscript{17}; the global composition is 
the same along the direction of the applied force. In contrast, 
a sample solidified in zero field exhibits a homogeneous 
morphology in which Nd, Nd\textsubscript{5}Fe\textsubscript{17} and Nd\textsubscript{2}Fe\textsubscript{17} are randomly 
distributed. The perfect separation into two domains suggests 
that slightly above the melting point and during solidification, 
nuclei of the different phases coexist with a liquid phase. 
The migration paths of the nuclei separate according to the 
amplitude of their magnetic susceptibility, which depends on 
the nucleus size [2].

4.3. Co–B

In Co–B alloys, the eutectic temperature is about 1100°C, 
only 20°C above the Curie temperature of the Co-rich 
phase. Thus, the ferromagnetic transition can be reached by 
undercooling the melt obtained after a large overheating. 
A Faraday balance is used to measure the sample 
susceptibility along the heating-cooling cycle. From \textit{in situ} 
magnetic susceptibility measurement, it was found that the 
solidification of Co–B eutectic alloys can occur in the
ferromagnetic state, cobalt particles are then strongly coupled and form elongated needle-like stacking, despite an external magnetic force that should cause their sedimentation [49].

4.4. Co–Sn

The solidification of Co–Co3Sn2 occurs at 1112°C, slightly above the Curie temperature of about 1050°C. In situ susceptibility measurement was used to observe the phase transformations. The field-cooled Co–Sn sample exhibits long primary cobalt dendrites parallel to the magnetic field. No strong undercooling was obtained [50].

5. Improvement of magnetic texturing of alloys

Unidirectional solidification and magnetic fields are driving forces for crystal alignment; the combination of these two forces can reinforce the texture.

5.1. Dendrite orientation in a magnetic field

The alignment of crystals along the magnetic field direction at various cooling rates was first studied without applying unidirectional thermal gradients, in order to facilitate dendrite growth along the field direction. The magnetic alignment of dendrites for Al–Cu and Cd–Zn alloys has been obtained in 1981 [12]; the alignment was attributed to a difference in susceptibility between the dendrites and the melt without actually carrying out susceptibility measurements. In his PhD thesis, Rakotoarison studied the crystallization of the superalloy AM1 for various cooling rates, in a homogeneous magnetic field of 5 T and in a zero field. He used a vertical Al2O3 cylindrical crucible, an electrical furnace and samples having a diameter of 25 mm and a height of 60 mm. The weight composition of the alloy was Ni66.7Cr6.7Co9.6Mo3.4Ta2.3W1.9Ti1.2Al5.3 which was overheated to 1407–1412°C, about 15–20°C above the liquidus temperature. Upon cooling at a rate of 122°C h⁻¹, the ingot was a single grain. The solidification velocity was 34 mm h⁻¹. The dendrite lattice was oriented along a ⟨100⟩ axis, which was tilted by 12° from the vertical axis of the magnetic field. The susceptibility difference between the ⟨100⟩ and ⟨111⟩ axes at room temperature was about 1.3% of the susceptibility, while the susceptibility increase induced by melting was about 5.0 × 10⁻⁷ emu g⁻¹ Oe⁻¹ as shown in figure 8. This observation explains why the AM1 dendrites were easily oriented by a magnetic field [12]. The zero-field-cooled ingots, cooled at various cooling rates, contained several non-oriented crystals.

5.2. Unidirectional solidification parallel to the magnetic field

There have been several studies of unidirectional solidification parallel to the applied magnetic field. The most recent one was devoted to Pb-33 at.% Bi and Sn-1.0 at.% Cd alloys [51]. A magnetic field of 10 T does not affect the solid periodic structure; its length is nevertheless markedly increased in the first alloys and unchanged in the second alloy upon applying the magnetic field. The main effect of the field is to reduce the convection which changes the temperature distribution. Several references to this type of study can be found in [51].

5.3. Thermal gradients and vertical magnetic fields

Magnetic texturing appears successful when the magnetic field B is parallel to the thermal gradient and the easy growth plane is parallel to the easy magnetization axis. This condition is not always easy to realize. The magnetic texturing of YBCO by a vertical melted-zone technique does not work well because of the simultaneous presence of a large radial thermal gradient and because the easy magnetization axis is perpendicular to the easy growth plane [52]. The magnetic texturing of Terfenol-D has been studied for the composition Tb0.3Dy0.7Fe with 1.85 < y < 1.95. The texturing readily occurs when a thermal gradient is applied along the [1–10] direction while the easy-magnetization axis is parallel to the [111] direction. A unidirectional thermal gradient parallel to B improves the texture as shown by Bonino in his PhD thesis (1998) because the convection is damped but the magnetostriiction performance is not improved as compared with that obtained by unidirectional solidification without applying a magnetic field [53]. It would be more efficient to form the texture by applying a magnetic field with a thermal gradient perpendicular to B.

5.4. Rotating magnetic field and modulated rotating magnetic field

New techniques of texturing are now being used when the c-axis is not the easy magnetization axis. The c-axis of crystals can be aligned when a rotating magnetic field is applied perpendicular to the plane in which the c-axis rotates; an equivalent technique is to rotate the crucible under a static magnetic field [54, 55]. Rotation of a crucible in a static magnetic field during the slip-casting of Si3N4 powder with a hexagonal structure results in the formation of a c-axis

Figure 8. Susceptibility of superalloy AM1 is plotted versus temperature during the heating and cooling cycle; there is no correction associated with the sample holder. The susceptibilities of the solid and then of the dendrites is smaller than that of the melt. This figure is extracted from the PhD thesis of S Rakotoarison (1995).
oriented material [56]. A rotating magnetic field having a periodically modulated intensity or frequency induces three-dimensional alignment of crystals [57]; a pseudo–single crystal can be fabricated from crystalline powders [58].

6. Effect of the processing time in the liquid state on the radius of unmelted bismuth crystals

The cooling rate of bismuth melt has been varied from 25 to 650 °C h⁻¹ after an overheating of 60 °C above the melting temperature. Crystallization induced by one intrinsic nucleus having the critical size is not as abrupt as that induced by numerous heterogeneous nuclei related to the cooled surface of the crucible, which produces recalescence. The time in the liquid state decreases by an order of magnitude from about 9000 s to a few hundred seconds. When this time is larger than 3600 s, an abrupt transformation to the solid is accompanied by recalescence. These results demonstrate that the radius of residual crystals in the melt decreases with time, as expected from the time dependence of critical-size-droplet formation into the largest unmelted crystals [2, 5].

The radius of unmelted crystal can be evaluated from an undercooling of 4 °C observed after processing for 200 s below Tm = 271 °C that corresponds to a cooling rate of 72 °C h⁻¹. The radius becomes too small to induce crystallization after an undercooling of 7 °C for a processing time of 8640 s above Tm corresponding to a cooling rate of 25 °C h⁻¹. The calculation is based on the formation of unmelted crystals stabilized by the energy saving associated with the Fermi energy equalization of the particles and of the melt; the energy saving coefficient εsls has already been determined as 0.217 at Tm [5]. The change in the Gibbs free energy associated with a formation of a crystal of radius Rnm is given by the volume and surface contributions

\[ \Delta G_{nm}(\theta) = (\Delta G_v - \varepsilon_v)4\pi R_{nm}^3 + 4\pi R_{nm}^2\sigma_{2ls}, \]

where

\[ \sigma_{2ls} = \alpha_{2ls} \left( \frac{\Delta H_m}{V_m} \right) \left( \frac{V_m}{N_A} \right)^{1/3}, \quad \Delta G_v = \frac{\Delta H_m}{V_m} \theta, \]

\[ \alpha_{2ls} = \frac{12N_A k_B}{432\pi}, \quad \Delta S_{nm}^{1/3} = \left( \frac{12N_A k_B}{432\pi} \right)^{1/3} \ln(K_{ls})^{1/3}(1 + \varepsilon_{ls}) \]

\[ = 0.42 \times \ln(K_{ls})^{1/3}(1 + \varepsilon_{ls}). \]

In Kls is nearly temperature independent and equal to 90 ± 2, ΔHm is the molar fusion heat, Nᴀ is the Avogadro number, k_B is the Boltzmann constant, and εls is given by (2).

The nucleation rate J defines the steady state, first-crystallization time tₙ₀ when ln(Jνtₙ₀) = 0, where ν is the sample volume. The value of J corresponds to the probability of one growth nucleus being present in volume ν after time tₙ₀; the sample volume ν is 1 cm³ here. The nucleation time tₙ₀ is defined by

\[ \ln(J\nu t_{n0}) = \ln(K_{ls}v_{n0}) - \frac{\Delta G^*_2ls}{k_B T} + \frac{\Delta G_{nm}}{k_B T} = 0, \]

where

\[ \Delta G^*_2ls = \frac{16\pi \Delta S_{nm}\sigma_{2ls}^2}{3N_A k_B(\theta - \varepsilon_{ls})^2(1 + \theta)}, \]

ΔG^*_2ls is the critical energy barrier, ΔG_{nm} is the reduction in the energy barrier induced by an unmelted crystal, given by (4), and lnKls = 90. The nucleation time tₙ₀ is plotted in figure 9 as a function of the absolute temperature for various radii R_{nm}. The unmelted crystal radius R_{nm} producing an undercooling of 4 K is equal to 1.81 nm for tₙ₀ = 200 s and ν = 1 cm³. Our prediction of a radius 1.25 nm after an overheating of 60 K leading to an undercooling of ΔT = 41 K was based on the assumption that εls = εsl. The unmelted crystals are larger than expected and the critical radius for growth of a liquid droplet into an unmelted crystal is larger; thus, εls is much weaker than εsl because the electron transfer takes place in unclosed volumes, increases the Fermi energy of liquid droplet and strongly reduces the energy saving. Our previous assumption must be modified by considering that εsl is radius dependent [5–7].

A 3.3% reduction of the unmelted crystal radius (10% volume reduction) from 1.81 to 1.75 nm after 9000 s processing above Tm is expected to increase the undercooling from ΔT = 4 K to ΔT = 7 K. This observation shows that the unmelted crystal radius is sufficiently stable to act as a growth nucleus during the minimum duration of the magnetic texturing process.
7. Conclusion

Magnetic texturing is very successful when magnetic field is applied to a melt under the condition that sufficient residual magnetocrystalline anisotropy exists at the melting temperature $T_m$ and that the highest annealing temperature in the process corresponds to a small overheating and to a limited processing time above $T_m$. These results indicate that intrinsic crystals can survive temperatures above $T_m$ with a radius smaller than the critical value at $T_m$. Their presence in congruent materials is a strong indication that they always exist even when the melt composition is identical to the solid composition.

Acknowledgments

The authors have used several PhD theses: YBCO, P de Rango (1991); magneto-science, E Beaunignon (1992); Nd$_2$Fe$_{14}$B, P Courtois (1995); Sm-Co, B Legrand (1996); Bi 2212, S Pavard (1999); other PhD theses devoted to magnetic texturing from a melt: Bi 2223, J G Noudem; YBCO; J M Barbut (1994); X Chaud (1996); L Porcar (1997); P Gautier–Picard (1998); superalloys, S Rakotoarison; Terfenol, O Bonino (1998); ferromagnetic euctectics: F Gaucherand (2002). All these works provide convincing evidence that growth nuclei are intrinsic crystals instead of impurity nuclei.

References

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