

Dmitry G. Eskin  
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# Solidification Processing of Metallic Alloys Under External Fields

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Editors

# Solidification Processing of Metallic Alloys Under External Fields

 Springer



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# Contents

|          |                                                                                           |            |
|----------|-------------------------------------------------------------------------------------------|------------|
| <b>1</b> | <b>Basics of Solidification Processing of Metallic Alloys . . . . .</b>                   | <b>1</b>   |
|          | Dmitry G. Eskin                                                                           |            |
| <b>2</b> | <b>In Situ Studies of the Solidification Dynamics of Metal Alloys . . . . .</b>           | <b>19</b>  |
|          | Jiawei Mi                                                                                 |            |
| <b>3</b> | <b>Magnetohydrodynamics Processing and Modeling . . . . .</b>                             | <b>75</b>  |
|          | Koulis A. Pericleous, Valdis Bojarevics, and Georgi S. Djambazov                          |            |
| <b>4</b> | <b>Electromagnetic Stirring and Low-Frequency Electromagnetic<br/>Vibration . . . . .</b> | <b>119</b> |
|          | Jianzhong Cui, Haitao Zhang, Lei Li, Yubo Zuo, and Hiromi Nagaumi                         |            |
| <b>5</b> | <b>High-Frequency Vibration and Ultrasonic Processing . . . . .</b>                       | <b>153</b> |
|          | Dmitry G. Eskin and Iakovos Tzanakis                                                      |            |
| <b>6</b> | <b>High Magnetic Field Processing of Metal Alloys . . . . .</b>                           | <b>195</b> |
|          | Yves Fautrelle, Jiang Wang, Dafan Du, Xi Li, and Zhongming Ren                            |            |
| <b>7</b> | <b>Pulse External Fields Processing of Metal Alloys . . . . .</b>                         | <b>243</b> |
|          | Jiawei Mi                                                                                 |            |
| <b>8</b> | <b>Thermal Melt Processing of Metallic Alloys . . . . .</b>                               | <b>277</b> |
|          | Ulf Dahlborg, Monique Calvo-Dahlborg, Dmitry G. Eskin,<br>and Piotr S. Popel              |            |
|          | <b>Index . . . . .</b>                                                                    | <b>317</b> |

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# Chapter 1

## Basics of Solidification Processing of Metallic Alloys



Dmitry G. Eskin

### 1.1 Structure Formation Upon Casting

The micro- and macrostructure of cast metal is very important from the point of view of casting and downstream processing performance, as it determines the quality of the casting and mechanical properties of as-cast and deformed products. Fine grain structure means uniform distribution of grain size in the billet (ingot) cross-section, elimination of columnar and feathery grains, lesser macrosegregation, uniform and improved mechanical properties in the semisolid and solid states, decreased propensity to hot and cold cracks, etc. Intermetallics and other excess inclusions (oxides, carbides, nitrides, borides, etc.) should also be fine and evenly distributed in the cast matrix. These inclusions are usually intrinsic to the metallic material and result from its composition or contamination. Sometimes, however, the foreign inclusions may be intentionally added to form a composite material or for the purpose of grain refining (acting as substrates).

In this section, we will consider the main mechanisms of structure formation and outline the main means to affect or control this structure.

Structure formation on the microscopic level depends on two basic phenomena: nucleation and growth.

The fundamentals of nucleation are discussed in detail elsewhere [1, 2]. Here, we only consider some most important parameters of heterogeneous nucleation, as this type of nucleation is most relevant to real casting practice.

The solidification sites (or substrates, or heterogeneous nuclei) that ease the nucleation are specially introduced or naturally form in the melt. Heterogeneous

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nucleation is energetically advantageous over homogeneous nucleation as the undercooling (energy stimulus) required for the formation of the new solid phase from the melt is lower by the level of energy required to form the new interface. Hence, heterogeneous nucleation is stimulated by the decrease of the interfacial energy that is required to form the new solid phase. The substrate that can efficiently do the job should therefore: (1) be wettable by the liquid phase (active); (2) provide crystallographic planes that resemble the crystallographic planes of the solid phase; (3) provide chemistry required for the formation of the new phase; and (4) be of the size that matches the actual undercooling achieved upon solidification. For example, the actual undercooling required for activation of all potent heterogeneous solidification sites in liquid aluminum is less than 2 °C [2]. The type, amount, and size of the substrates determine the efficiency of heterogeneous nucleation. First, particles have to be sufficiently large to become active substrates at a given undercooling. In the case of good wetting and crystallographic match, the required undercooling is very small. The nucleation rate depends solely on the temperature (not on the time since nucleation occurs instantaneously), and this type of nucleation is sometimes called “athermal,” though this term is misleading. Then, growth occurs until the new phase reaches the size of the substrate and subsequent growth will require further undercooling. The nature of the substrate (interfacial energy) determines how efficient the nucleation is, while the size of the substrate determines the ease of subsequent growth [3].

The undercooling  $\Delta T$  for the so-called free growth is related to the size of the substrate  $d$  as

$$\Delta T = \frac{4\sigma_{sl}}{\Delta S_V d}, \quad (1.1)$$

where  $\sigma_{sl}$  is the solid–liquid interfacial energy and  $\Delta S_V$  is the volumetric entropy of fusion. In reality, there is a size distribution of potential solidification sites that become active in the melt at a specific degree of undercooling. For the substrate size of 1  $\mu\text{m}$ , the required undercooling for free growth in liquid aluminum is about 0.5 °C, whereas the real measured undercooling in aluminum alloys is about 0.2 °C which corresponds to the size range 3–5  $\mu\text{m}$  [3].

The growth of the nucleated grain is determined to a large extent by the composition of the melt ahead of the solid–liquid interface. Despite the common notion that the diffusion in liquid occurs almost instantaneously, there is always an accumulation of solute elements at the solid–liquid interface as compared to the bulk composition. This accumulation causes on the one hand the phenomenon called constitutional undercooling, and on the other hand prevents the growth of the solid phase, as the growth can only occur when the compositions of the solid and liquid phases at the solid–liquid interface are in equilibrium, according to the phase diagram. The degree of solute accumulation depends on the alloy composition (partitioning coefficients of alloying elements) and on the solidification conditions (diffusion and convection), which explains why the final structure formed in a casting depends on both the alloy composition and the casting conditions

**Fig. 1.1** Dependence of the grain size in Al–Cu alloys on the cooling rate and the composition

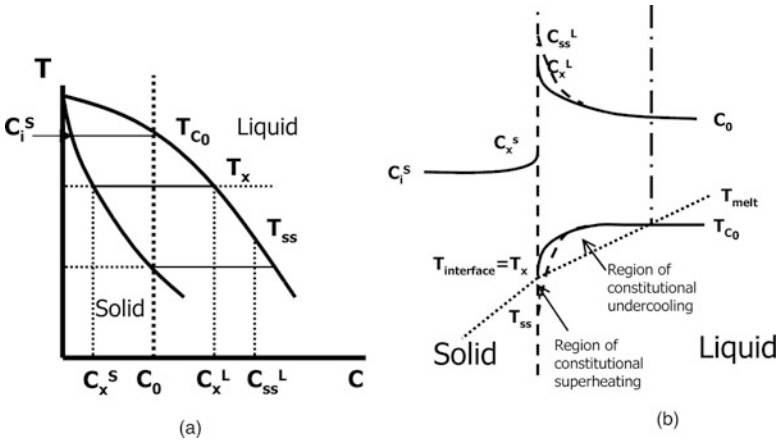
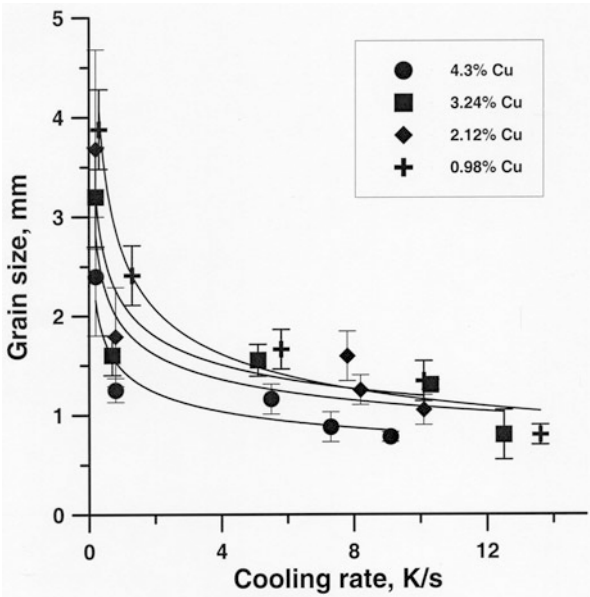


**Fig. 1.2** Characteristic points on the binary phase diagrams (a) and the variation of compositionally determined solidification temperature ( $T_c$ ) and real melt temperature ( $T_{melt}$ ) forming the regions of constitutional undercooling (or superheating) (b)

(e.g., temperature gradient). Figure 1.1 illustrates this fact for binary Al–Cu alloys and Fig. 1.2 explains the principle of constitutional undercooling. Early systematic work to examine the factors controlling the formation of the equiaxed structure was reported by Northcott who showed for copper alloys that the amount of alloying elements influenced the length of columnar crystals and the extent of the equiaxed structure [4]. He demonstrated that alloys with a wider freezing range more readily

produced the equiaxed structure. Cibula [5] and Eborall [6] reported the effect of alloy composition on grain refinement. Nowadays, the growth-restriction theory is generally accepted as one of the main mechanisms to control the grain size in castings [3, 7–11]. Let us consider it in brief.

Two parameters have been suggested for quantifying the effect of alloy composition on grain size, both parameters being proportional to the solidification range. These are the undercooling parameter:

$$P = mC_0(K - 1)/K = \Delta T_0 \quad (1.2)$$

and the growth-restriction factor:

$$Q = mC_0(K - 1) = K\Delta T_0, \quad (1.3)$$

where  $m$  is the liquidus slope at the alloy composition  $C_0$ ,  $K$  is the partition coefficient, and  $\Delta T_0$  is the equilibrium solidification range, i.e., difference between equilibrium liquidus and solidus temperatures.

The undercooling parameter represents the maximum possible undercooling and is equal to the solidification range of an alloy with composition  $C_0$ , while the growth-restriction factor reflects the solute rejection at the solid/liquid interface and potential degree of solute accumulation at the interface (see Fig. 1.2b).

The constitutional undercooling at the solid/liquid interface is proportional to the growth-restriction factor:

$$\Delta T_c = \Xi Q, \quad (1.4)$$

where  $\Xi = (C_{ss}^L - C_0)/(C_{ss}^L(1 - K))$  is the solutal supersaturation.  $C_{ss}^L$  represents the liquid constitution at the interface, which is different from the equilibrium nominal composition  $C_0$ , when undercooling is present (see Fig. 1.2).

Generally, the constitutional undercooling at the solid/liquid interface will control the growth according to the general formulation for the maximum growth velocity [12, 13]:

$$V_{\text{growth}} = A D_s \Delta T^2 / Q \Gamma, \quad (1.5)$$

where  $D_s$  is the diffusion coefficient of the solute in the melt,  $\Delta T$  is the undercooling required for the growth (can be constitutional undercooling or the total undercooling),  $Q$  is the growth-restriction factor,  $\Gamma$  as the Gibbs–Thompson coefficient reflecting the effect of the dendrite tip curvature on the tip growth velocity. ( $\Gamma = \sigma_{ls}/\Delta S_f$ , where  $\sigma_{ls}$  is the solid/liquid interfacial energy and  $\Delta S_f$  is the volumetric entropy of fusion, which corresponds to the latent heat of solidification), and  $A$  is a coefficient. We can see, at least qualitatively, that slow solute diffusion ( $D_s$ ), small undercooling ( $\Delta T_c$ ), large solidification range and partitioning ( $Q$ ), and large interfacial energy ( $\sigma_{ls}$ ) would result in limited growth of the solid phase into the liquid.

The growth of the solid phase requires that the solute supersaturation at the interface is dissipated either by diffusion (convection) or by remelting of the solid phase, which has been experimentally demonstrated [14]. There may be various



reasons for the solute accumulation or the solute influx to the solid/liquid interface. Most frequently, the growth restriction is considered in relation to grain refinement by inoculants and to the columnar-to-equiaxed transition (CET) [7–9]. In the course of grain refinement, the solute rejected by the growing grain slows down its growth and, at the same time, may create the constitutional undercooling sufficient for the nucleation of a new grain at the substrate that preexists in the melt [9].

In the case of CET, the “added” solute is the solute rejected by the columnar grain tip, but it can also come from the neighboring columnar grain or the solid phase nucleated ahead of the columnar front. The constitutional undercooling due to the solute rejection at the solid/liquid interface creates favorable conditions for heterogeneous nucleation at some distance ahead of the solidification front (see Fig. 1.2b). The nucleated grains start to grow and reject solute as well as generate the latent heat. As a result, the growth of the “parent” interface stops. The greater the solidification rate (solid fraction evolution per unit time), the more effective is this growth restriction. Martorano et al. showed that the rejection of solute by newly formed grains with a high grain density would, in fact, effectively decrease the constitutional undercooling initially created at the “parent” interface and stop its advance [15].

One can notice that the area of maximum constitutional undercooling caused by solute accumulation (or depletion in the case of  $K > 1$ , e.g., Ti in Al) is at the some distance from the solid/liquid interface, where the condition for the nucleation of a new solid crystal is the most favorable (Fig. 1.2b).

The solute can be also brought to the interface by flows during solidification that can be natural, e.g., thermo-solutal and shrinkage-driven, or forced by external fields, e.g., stirring, streaming, mixing, as well as can result from nonequilibrium solidification conditions. In all cases, the volume around the interface cannot be considered as a closed system. The extent of this solute accumulation depends on the effective diffusivity of the solute in the melt (see Eq. (1.5)). In order to maintain the local equilibrium at the interface and get the momentum for further growth (solidification), the interface should first remelt and absorb the excess of the solute. This situation is shown in Fig. 1.2b and is often a case upon fragmentation of dendrite branches [16, 17]. It is worth mentioning here that fragmentation or “grain multiplication” is considered as one of the mechanisms of grain refinement in castings, also under the action of external fields (see Chaps. 4, 5, 6, and 7). Intense convection during solidification may assist in flattening solute diffusion profiles ahead of the solid/liquid interface, which may result in a faster grain growth and, according to the solute-suppressed nucleation concept, in finer grain sizes in commercial alloys [18].

It is also suggested that the solute accumulated at the interface hinders the growth only until some values of  $Q$ , when the solid–liquid interface is relatively smooth (which is the case of globular and little-branched grains) [9, 19]. In the case of high  $Q$ , and hence high constitutional undercooling, grains start to grow faster and in a much more branched manner. As a consequence, the solute is rejected from the sharp and elongated dendrite-branch tips not only to the front but also sideways. This solute is accumulated in the liquid between the dendrite branches and is, on decreasing the temperature, absorbed by the solid phase. In such a way, the effective growth restriction is decreased and the dendrite grains get an opportunity to grow faster, even if the average concentration of solute in the melt is high.

We can summarize that the accumulation of solute (solvent in peritectic systems) that assists the nucleation at some distance ahead of the solid/liquid interface simultaneously prevents the growth of the parent particles. The latent heat released during solidification has the same effect. The larger the nucleation density of the primary grains, the sooner their thermo-solutal fields start to interact and the lesser is their dendritic development. As a result, a fine and not well-developed dendritic equiaxed structure is formed. Sometimes, the branching is so negligible that the grains are called globular or nondendritic.

One of the main means of controlling the structure is by grain refinement through the sharp increase of solidification sites for heterogeneous nucleation of the primary phase. This can be done essentially in four ways:

- By alloying with elements that will form nucleating substrates (intermetallics) during solidification prior to the primary solidification of the solid solution (e.g., Ti and Zr in aluminum and magnesium alloys, respectively);
- By adding special insoluble particles to an alloy that act as substrates either for nucleating intermetallic particles or for the solid solution (e.g.,  $\text{TiB}_2$  and  $\text{Al}_4\text{C}_3$  in aluminum and magnesium alloys, respectively);
- By activation of insoluble particles (e.g.,  $\text{Al}_2\text{O}_3$  by wetting and  $\text{Al}_4\text{C}_3$  by melt superheating in aluminum and magnesium alloys, respectively);
- By multiplication of solidification sites by fragmentation of existing solid grains or fragmentation of nucleating intermetallic particles, or de-agglomeration of nucleating insoluble particles (e.g., by cavitation melt treatment).

The first two means of grain refinement are by far the most widely used methods for producing castings with small, equiaxed, and uniformly distributed grains. The application of external fields may be useful in accelerating the dissolution of alloying additions or dispersion and de-agglomeration of added particles.

In the two other approaches, the use of external fields maybe decisive for success.

The insoluble inclusions (e.g., oxides or carbides) are usually not very wettable by the liquid metal, either due to gaseous phase being present, other contamination absorbed at the surface, or due to too high surface energy. They, therefore, are excluded from the process of solidification. If, however, they could be wetted with liquid phase and form substrates either for grain refining phases (e.g., intermetallics like  $\text{Al}_3\text{Ti}$ ) or for the solid matrix phase (aluminum or magnesium), then they would trigger efficient refinement. This process is called activation.

In aluminum, the most likely indigenous inclusions are represented by alumina or aluminum oxide. Alumina may exist in various crystal modifications, depending on the temperature range, origin, and presence of hydrogen and other alloying elements.

The transition between the lower-temperature modifications of alumina upon heating is in reality continuous and related to the dehydration (removal of hydrogen from the crystal lattice). On increasing the melt temperature,  $\delta$ -alumina (or  $\gamma$ -alumina which is sometimes considered to be the same phase) transforms to  $\chi$ -alumina (700–850 °C) and then the stable  $\alpha$ -alumina is formed at above 1000 °C [20]. During cooling from 1000 °C, the stable modification  $\alpha$ -alumina is either retained (at high cooling rates) or is transformed to  $\chi$ -alumina (at low cooling rates) without  $\delta$ -alumina forming [20].

One of the approaches to grain refinement is multiplication of available or potential solidification sites (substrates for heterogeneous nucleation). Technological approaches towards realizing this mechanism usually involve physical action upon the melt with fragmentation of growing crystals or agglomerates and dispersion of the formed solidification sites in the melt volume by forced convection.

These approaches include structure refinement through cavitation, shearing, electromagnetic stirring, and vibration [26–28] and will be considered in detail in Chaps. 3, 4, 5, and 6. For example, it was shown that the intense shearing (not covered in this book) of liquid aluminum alloys results in dispersion of oxide films and facilitates activation of fine oxide particles with respect to (Al) and  $\text{Al}_3\text{Ti}$  [21]. The activation of oxides can be also done by thermal (see Chap. 8) or other physical action upon the melt (see, e.g., Chap. 5).

The presence of magnesium in aluminum alloys changes the nature of indigenous oxides as magnesium has greater affinity for oxygen than aluminum [20]. Even small concentrations of magnesium, 0.01–1 wt%, result in the formation of mixed oxides  $\text{MgO} \cdot \text{Al}_2\text{O}_3 + \text{MgO}$ . At the magnesium content above 1%, the magnesium oxide  $\text{MgO}$  almost completely substitutes alumina.

The role of magnesium oxide in grain refining of aluminum is not reported, but there is enough evidence to suggest that it may play a significant part in grain refinement of magnesium alloys. The activation of magnesia particles can be achieved by ultrasonic cavitation treatment, which is evidenced by grain refinement of cavitation-treated magnesium melts [22, 23]. Melt shearing is also shown to be very efficient in activating magnesium oxides. The intense shearing of melt flow performed by twin screws well above the liquidus of a magnesium alloy results in efficient fragmentation of oxide films and increases the density of  $\text{MgO}$  particles by three orders of magnitude and the amount of particles that become active at the reached undercooling by a factor of 20 [24].

The formation of new solidification sites can be achieved, in some special cases, by superheating of the melt as considered in Chap. 8. For example, in Mg–Al–Mn alloys melt superheating followed by relatively rapid cooling results in the preferential formation of the refining metastable  $\tau(\text{Al}_4\text{Mn})$  phase, thus producing grain refinement [25]. Similar effect can be achieved in Al–Zr alloys when rapid cooling of the melt from high temperature produces metastable cubic  $L1_2 \text{Al}_3\text{Zr}$  phase with the crystal structure similar to that of aluminum. In both cases, the melt superheating deactivates all available substrates for heterogeneous nucleation of the solid solution and equilibrium intermetallics. As a result, a deeper undercooling can be achieved for the primary solidifying phase, deep enough to trigger the formation of a metastable phase.

Castings also have macroscopic structure features, such as zones of fine and coarse equiaxed grains, columnar and feathery grains, segregates, and porosity. All these features depend on the kinetics of solidification and can be controlled by the macroscopic and microscopic melt flow (convection and shrinkage, forced convection), heat flow (thermal gradient and positions of liquidus and solidus), and precipitation of solid and gaseous phases. The effect of flow is illustrated in the next section.

## 1.2 Effects of Flow on Structure Formation During Solidification

Over the past 50 years, many attempts have been made to design special techniques with the purpose of improvement and control of the final solidified structure by forced flow, which is the subject of Chaps. 3, 4, 5, 6, and 7.

During casting, flow generally occurs in the bulk liquid and in the semisolid regions. Some of the techniques that have been successfully used in academic research with the aim to study the fundamentals of solidification under forced-flow conditions are: gravity flow-through systems [29], mechanical stirring [30], centrifugal casting [31], controlled flow forced by an electromagnetic pump [32], application of magnetic or electromagnetic field creating the Lorenz force (see Chaps. 3, 4, and 5), etc. While the experimental research has been developing over the last 50 years, computational modeling and simulation have been widely used in the last three decades as a cost-saving tool for prediction and interpretation of the experimental results (see Chaps. 3, 4, and 7). The combination of these two approaches helps in gaining deeper understanding of the effects of melt flow on solidification phenomena in metallic alloys, that is, (1) morphology of grains and their deflection towards incoming flow; (2) columnar to equiaxed transition (CET) and grain morphology; and (3) change of segregation pattern.

Flemings' pioneering work [33] and several later studies [29, 34] where the gravity-driven system was used have reported that the columnar grain structure is formed in the casting systems where the melt flows perpendicular to the heat extraction. The grains are deflected towards the incoming flow. The tendency of growing columnar dendrites to incline into the flow under the influence of some shear forces at the solidification front is also a common phenomenon in centrifugal casting [31], electromagnetic stirring [35, 36], and directional solidification [37]. Initially, it was proposed that the driving forces leading to the preferred growth directions were due to interface kinetics and anisotropic surface energy. They were attributed to flow-induced asymmetric thermal or concentration fields around the growing crystal [33]. The solute-rich liquid is swept away from the upstream side of the dendrite tip to the downstream side, leading to a local enrichment of the solute and lowering of the liquidus temperature on the downstream side. This gives preferential growth conditions on the upstream side, thus causing the crystal tips to incline upstream [30]. Another theory suggested that the deflection of the growth direction of columnar grains could be controlled by the dendrite branching mechanism, namely by the competitive growth of primary and secondary arms [29]. The dendritic evolution of an initially small nucleus affected by an external flow was also treated using phase-field modeling [38]. It was shown that the local heat transfer at the solid/liquid interface controlled the dendrite growth and when the forced flow was increased, the main vertical stem tilted gradually towards the upstream direction.

The CET, various grain morphologies, and complex grain distribution due to melt flow are the subjects of many studies. Several theories were developed to explain the CET, including: heterogeneous nucleation in the undercooled melt [39, 40]; floating

grains [41]; and crystal multiplication due to thermomechanical fragmentation promoted by forced convection [31, 34, 42–44].

Feathery grains represent a specific growth morphology that is found in aluminum alloys [45]. In addition to high thermal gradient about  $100 \text{ K cm}^{-1}$  and growth rate about  $1 \text{ mm s}^{-1}$ , feathery grains are known to be favored by the presence of strong fluid flow.

The melt flow is found to have an influence on the microstructure of metallic alloys. The analytical solution based on asymptotic expansion method showed that in Pb–Cu and Al–Cu alloys a weak convective flow increased the eutectic lamellar spacing since the convection produced a slight shift of solute concentration profile at the interface and decreased the eutectic growth undercooling [46]. Similar results were obtained in another work [47], where the Jackson–Hunt model of eutectic growth was extended to allow for different densities of the phases. Additionally, it was experimentally found that the dendritic shape obtained under conditions of natural convection changed to a globular form when the melt flow by electromagnetic stirring was applied [42]. This was further confirmed by simulations [48]. Forced flow, applied to the bulk of the molten metal, interacts with the growing solid producing the distortion of the solid–liquid interface [29], altering the shape of the mushy zone [49] and affecting solidification parameters [50]. Depending on the nature of the flow and the initial velocity, oscillation of various magnitudes may occur at the solidification front.

Let us illustrate the effects of melt flow on the structure formed during solidification using experimental data obtained using an Al–4.5% Cu alloy and a special setup where forced controlled flow was directed along the chilled cavity [32, 51].

Figure 1.3 shows two typical macrostructures of the longitudinal section of an Al–4.5% Cu alloy obtained during solidification in the cavity under conditions of constant forced flow along the solidification front. Depending on the flow conditions, the macrostructure of samples either comprises a zone of equiaxed grains with a columnar zone on top in the central part of the sample, expanding in the direction of the downstream edge with respect to the bulk flow direction (Fig. 1.3a), or consists entirely of columnar grains deflected towards incoming flow (Fig. 1.3b). Equiaxed to columnar transition (ECT) is clearly seen at the bottom of the sample (Fig. 1.3a).

The longitudinal macrostructure of the samples obtained under forced-flow conditions can be conditionally divided into three zones. Zone 1 is the region close to upstream edge with regard to the initial flow while zone 3 is the region of downstream edge of the cavity. Therefore, zone 2 is the central part of the cavity. During experiment, zone 1 is constantly affected by the hottest melt flow and the highest thermal gradient. However, due to heat extraction from the bottom and the side wall, the solidification onset occurs after the first seconds of experiment. Similar heat extraction conditions are typical for zone 3. According to computational results, zone 2 is affected by traveling either counter or/and clockwise vortices.

The following phenomena may contribute to formation of the zone of equiaxed grains in Fig. 1.3a: (1) transport and continuous deposition of the detached dendrites along the chill wall by the forced flow and (2) detachment of the slender dendrite

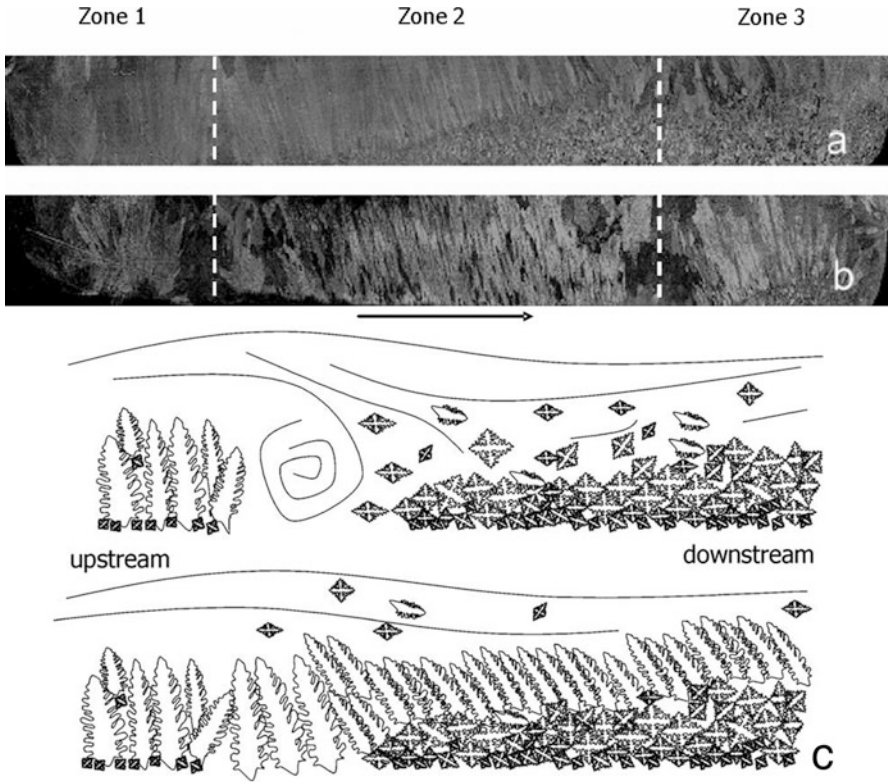


**Fig. 1.3** Macrostructures of an Al–4.5% Cu alloy solidified under forced flow (from left to right) at (a) 0.15 m/s and (b) 0.05 m/s over the 100 mm water-cooled chill. A diagram in (c) illustrates the formation of the structure shown in (a). (A.N. Turchin and D.G Eskin, 2008)

arms, and (3) their transport and deposition at the downstream edge of the cavity. The macrostructural features, such as tiny columnar dendrites, duplex (coarse and fine) internal structure, etc., observed in this zone [32] support the suggested mechanisms.

The particular phenomenon of equiaxed-to-columnar transition (ECT) (Fig. 1.3a) can be attributed to the termination of the fragmentation and settling processes with the growth of the columnar dendrites under conditions of thermal gradient. After onset of solidification, the fragments may form as results of detachment of the equiaxed and columnar dendrites at the chill surface or fragmentation of their slender dendrite arms. These fragments are either immediately removed from the chill zone by the constantly coming forced flow or continuously settled in the downstream edge of the chill. In the meantime, the columnar dendrites keep growing at the upstream edge due to the highest thermal gradient and at the same time strong heat extraction in this region (Fig. 1.3c). While the progressing solidification on the one hand facilitates fragmentation due to branching of dendrites, on the other hand it increases



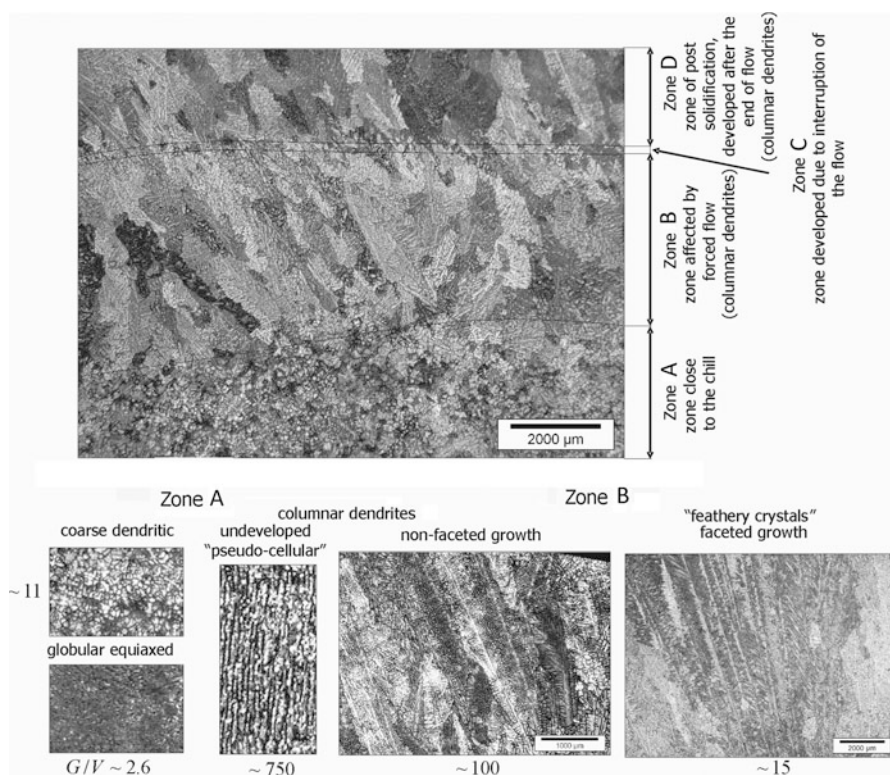


**Fig. 1.4** Typical microstructures of an Al-4.5% Cu alloy solidified under different forced-flow conditions onto a water-cooled chill. The thermal gradient to solidification rate ratio  $G/V$  is given (A.N. Turchin and D.G. Eskin, 2008)

the probability of fragments removal from the chill zone by the melt outflow due to the decreasing geometrical ratio of the chill cavity with the progressed solidification. At the same time, due to the gap between the family of columnar dendrites at the upstream corner and the settled fragments at the downstream corner, the preferable thermal conditions promote the free growth of columnar dendrites that are clearly distinguished in Fig. 1.3a.

It is also possible to separate some zones in the vertical section (Fig. 1.4). It is found that the zone close to the chill surface (zone A) may exhibit different structures, such as: (1) coarse dendritic equiaxed structure, (2) globular equiaxed structure, and (3) undeveloped columnar structure. The zone affected by forced flow (zone B) consists of columnar dendrites and in some cases of “feathery crystals” deflected towards incoming flow. The next zone (zone C) marks the solidification front. Finally, at the top of the sample there is a zone (zone D) developed after the end of experiment consisting of columnar dendrites, but with completely different, always finer, internal structure as compared with the zone B.

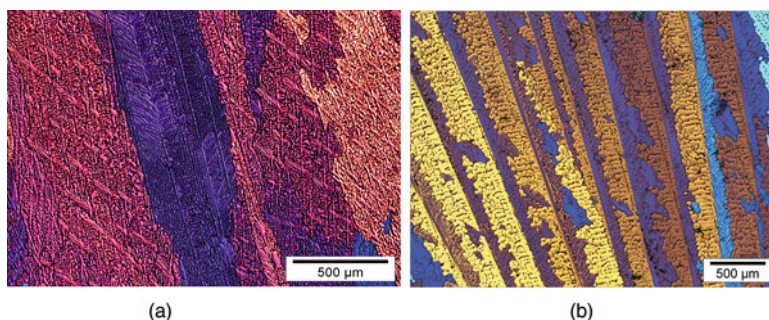


**Fig. 1.5** Feathery grain structure of an Al–4.5% Cu alloy obtained under forced-flow conditions at solidification rate of 0.6 mm/s and thermal gradient of 9 K/mm (a) and 0.7 mm/s, 15 K/mm (b); flow direction: left to right (A.N. Turchin and D.G. Eskin, 2008)

The dimensions of each zone may vary depending on the flow conditions. The grains growing in the flowing melt are generally deflected towards the incoming flow. Also, the forced flow generally promotes the columnar growth. At the same time, the increased flow velocity triggers columnar–equiaxed–columnar transitions, mostly due to the fragmentation of dendrites (Fig 1.3).

Peculiar grain morphologies form upon solidification under forced-flow conditions with a highly superheated melt ( $>55$  K) and upon slow bulk flow ( $<0.05$  m/s). Figure 1.5a shows typical feathery crystals consisting of parallel lamellae growing into the incoming flow. These lamellae are separated either by wavy or by straight boundaries. The latter is a twinned boundary. Another morphology, typical of the high thermal gradient and the solidification rate less than 1 mm/s, is presented in Fig. 1.5b. Here, the dendrite arms, growing on the upstream side at  $40^\circ$  from the primary trunk, exhibit a curved, woven-type shape and are directed to the incoming flow. This type of morphology formed under forced-flow conditions is discussed in detail elsewhere [45, 52].

The primary dendrite arm spacing ( $\lambda_1$ ) is plotted in Fig. 1.6 as a function of solidification rate for different flow velocities at a thermal gradient of 4–4.5 K/mm, superheat  $55^\circ\text{C}$ . The accelerated flow results in decreasing of primary dendrite arm spacing and, at the same time, increasing of the solidification rate decreases the distance between primary trunks. This tendency is valid for different superheats and thermal gradients.

Dependence of secondary dendrite arm spacing ( $\lambda_2$ ) on solidification time, flow velocity, and superheat is shown in Fig. 1.7. Although it has long been known that the increasing of solidification time coarsens the structure, this plot shows the pronounced effect of forced flow itself: microstructure coarsening is affected by both the increasing solidification time and the flow rate [53]. The significant change of the coarsening exponent with the increasing flow velocity has strong implications for the formation of structure and should be taken into account.



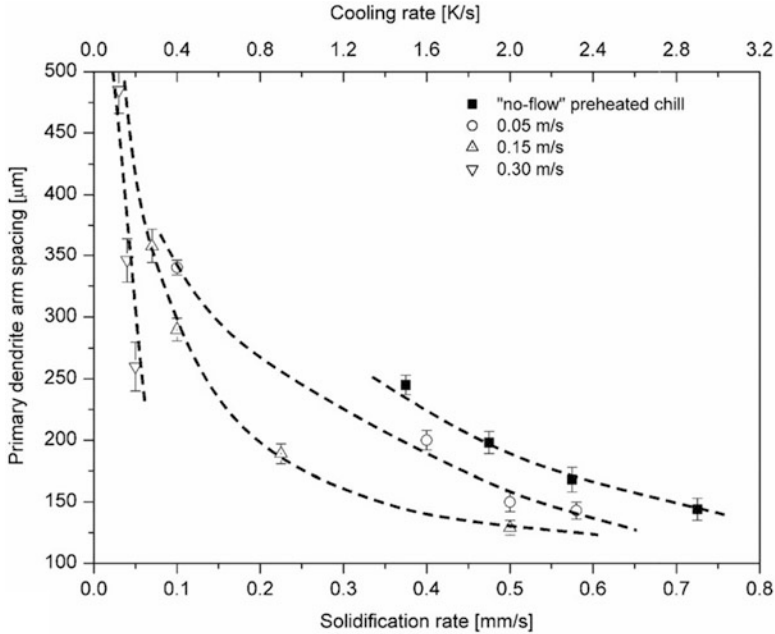


**Fig. 1.6** Primary dendrite arm spacing vs solidification rate for an Al-4.5% Cu alloy cast under different flow conditions (see the legend) and at a superheat of 55 °C (A.N. Turchin and D.G. Eskin, 2008)

### 1.3 Main Factors Affecting the Structure Formation; and Melt Processing and Casting Technologies

There are basic phenomena that can affect the structure formation and therefore the external fields are used to facilitate or suppress these phenomena. The formation of structure starts with nucleation. As it will be shown in Chaps. 5, 6, 7, and 8, improved wetting of potential substrates for heterogeneous nucleation, and their de-agglomeration and dispersion in the liquid volume (facilitated by electromagnetic stirring, high-frequency vibration, electric pulses, or high melt temperature) play an essential role in the observed structure modification. This is considered in Chaps. 3, 4, 5, 6, and 7. In addition, the change of the crystal structure of the substrates with melt superheat may make the particles either more potent or otherwise, and affect the structure formation accordingly as is shown in Chap. 8. Next comes the growth that can be affected, as is discussed in Chaps. 3, 4, 5, and 6, by the melt flow (magnetohydrodynamics, electromagnetic stirring, magnetic, acoustic, and thermal convection), solutal redistribution (stirring, magnetic forces, forced convection, and melt temperature), and thermal gradients (melt temperature, and forced convection). Forced convection and mechanical forces (e.g., pressure pulses) in combination with thermal and concentration gradients may also fragment the growing solid

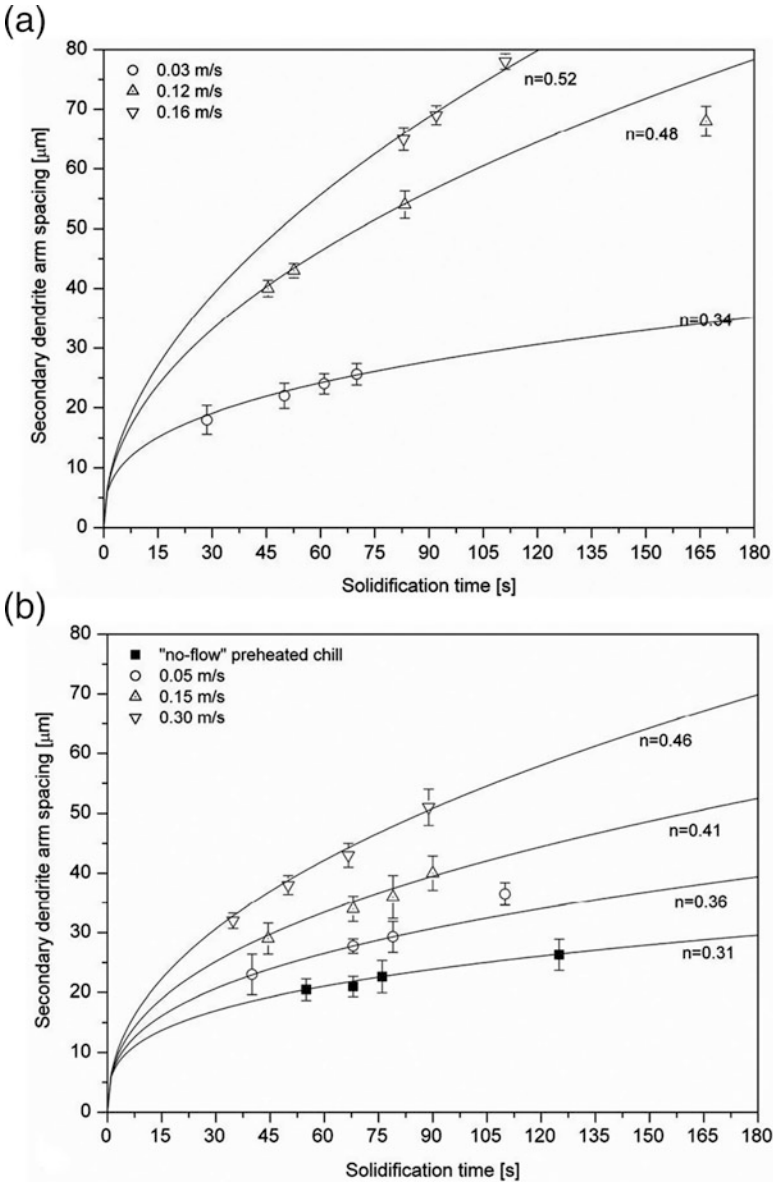


**Fig. 1.7** Secondary dendrite arm spacing vs solidification rate for an Al-4.5% Cu alloys cast under different flow conditions (see the legend) and at superheat (a) 55 °C ( $G = 4-5$  °C/mm) and (b) 75 °C ( $G = 13$  °C/mm). Coarsening exponents are given on the plot (A.N. Turchin and D.G. Eskin, 2008)

phase and therefore change its morphology and multiply the amount of individual solid crystals, effectively refining the structure. This is particularly important when applying ultrasonic cavitation, electromagnetic stirring, magnetic force, or electric pulses to the semisolid material, see Chaps. 4, 5, 6, and 7. The distribution of alloying elements and reacting substances, substrates, reinforcing particles, and crystal fragments in the bulk of the liquid as well as the control of the thermal and solutal homogeneity can be done by convection (mass and heat flow) enforced by electromagnetic, magnetic, and acoustic forces (Chaps. 3, 4, 5, and 6).

Alternating magnetic and electromagnetic fields have been used in solidification processes for quite some time, especially in the iron and steel industry and in the field of crystal growth. However, their application is still limited in the processing of other metals, e.g., aluminum, magnesium, or even copper alloys. Recent years saw an increased research and development in this area, which is due to the development of both new hardware and new applications such as control of as-cast structure, segregation, and production of gradient or composite materials.

The use of very strong continuous magnetic fields is now limited to small-scale processes. But, the rapid development of large bore magnets at a lower cost opens up prospects for their use in industrial applications.

There are special casting and melt processing methods explicitly designed to incorporate external fields such as casting under pressure (high, low, vacuum, isostatic, and centrifugal), melt processing in the presence of electromagnetic forces (electrolysis cells, electromagnetic casting, casting with electromagnetic stirring, and electromagnetic pumps), and melt processing with ultrasonic cavitation, high magnetic fields, or electro-pulse treatment. At the same time, some of these external fields can be incorporated in the conventional gravity, die, or direct-chill casting technologies, as it is demonstrated in Chaps. 4 and 5. The use of very high magnetic fields (Chap. 6), electric and magnetic pulses (Chap. 7), and very high melt temperatures (Chap. 8) is currently reserved to specialized technologies applied to relatively small melt volumes, e.g., rapid solidification or atomization.

It is worth to note that most of conventional melt processing and casting technologies use the effects of external fields as discussed in this monograph, through intrinsic features such as thermal and solutal gradients (continuous casting, direct-chill casting, suspension casting, and semisolid processing), natural thermal and solutal convection (all casting techniques during mold filling and solidification, electrolysis cells), and forced convection (low- and high-pressure die casting).

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# Chapter 2

## In Situ Studies of the Solidification Dynamics of Metal Alloys



Jiawei Mi

### 2.1 X-Rays, Their Interaction with Matter and Techniques for Materials Characterization

#### 2.1.1 A Brief Review of the Advances of X-Ray Science

In 1895, Wilhelm Conrad Röntgen, a German physicist, discovered X-rays [1] and later in 1901, he was awarded the first [Nobel Prize in Physics](#). For many years, X-rays have been also known as “Röntgen Rays” (X-ray and X-rays are used interchangeably in this chapter). In 1913, William David Coolidge from the General Electric Research Laboratories in New York invented the Coolidge tube based on the principle of thermionic emission. The patent (U.S. Patent 1,203,495, Vacuum Tube) was filed in 1913 and granted in 1916. The work principle is schematically illustrated in Fig. 2.1a. Firstly, electrons are produced by an incandescent tungsten filament (the cathode) heated by electric current; they are then accelerated by the applied voltage towards and strike a water-cooled metal target (the anode) which generates X-rays. A typical X-ray spectrum generated by this type of tube is shown in Fig. 2.1b. It contains a continuous Bremsstrahlung spectrum and characteristic X-ray lines with sharp peaks. The Coolidge tube represented a revolutionary technical advance compared to the Gas Discharge type tubes (e.g., Hittorf, Crookes, Lenard tubes) used earlier for generating X-rays. The current and voltage of the Coolidge tube can be

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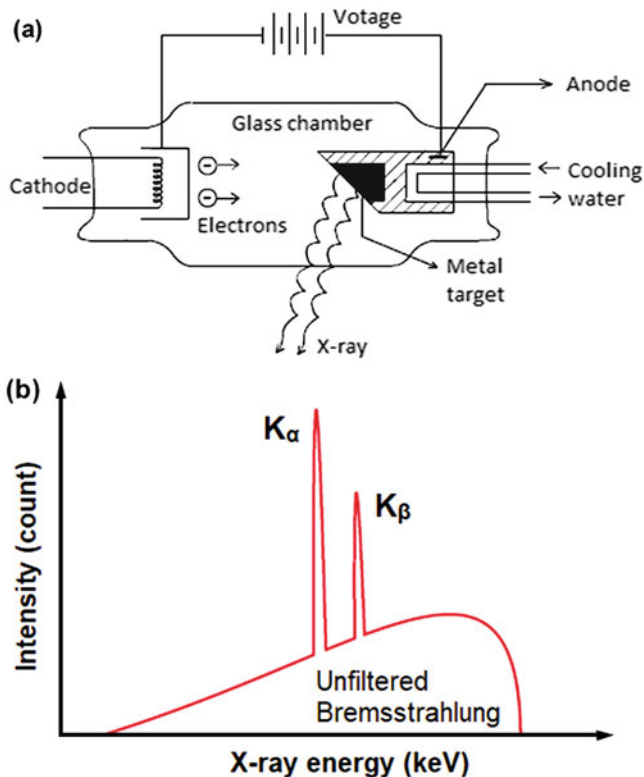


**Fig. 2.1** (a) A schematic, showing how X-ray is generated by a Coolidge X-ray tube. (b) The spectrum has two distinct components: a continuous Bremsstrahlung radiation due to deceleration of the incident electrons by the metal target, and discrete sharp peaks called characteristic X-ray lines. The  $K_\alpha$  line results from transitions between an L and K shell, whereas the  $K_\beta$  comes from an M to K shell transition [2]

varied independently to control the number of electrons produced and their energy, and therefore the intensity and energy of the X-rays produced can be controlled easily and reliably. The Coolidge tube served as standard X-ray tube for many decades with only marginal technical improvements before the age of synchrotron X-ray [2].

In 1947, Frank Elder, Anatole Gurewitsch, Robert Langmuir and Herb Pollock reported, in a letter entitled “Radiation from Electrons in a Synchrotron” [3], the observation of synchrotron radiation. It was observed in the world’s first purposely built synchrotron—the General Electric synchrotron accelerator in Schenectady, New York. Synchrotron radiation is an electromagnetic radiation emitted when charged particles are accelerated radially, i.e. when electrons are subject to an acceleration perpendicular to their velocity. Synchrotron radiation can be produced in synchrotrons or storage rings [4] using bending magnets, undulators, and/or wiggler devices [2, 5]; or can occur naturally when fast electrons move through

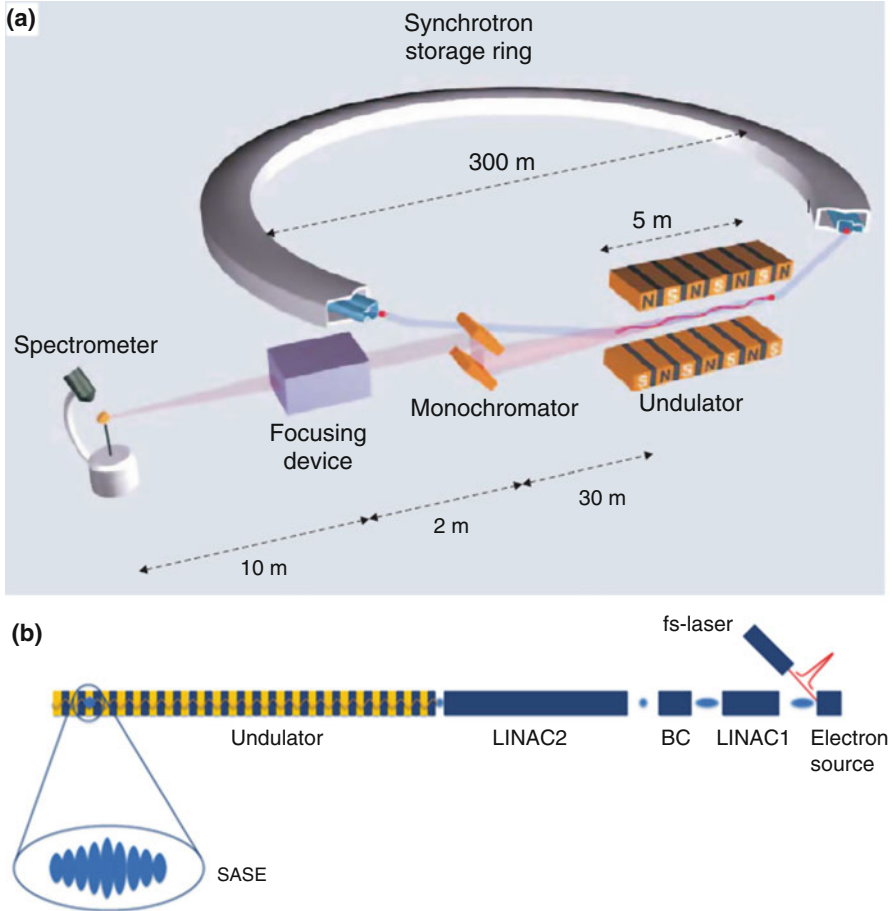


**Fig. 2.2** (a) A schematic, showing a typical third-generation synchrotron storage ring with a beamline including an undulator, monochromator, focusing device, and sample stage. (b) The layout and architecture of a free-electron laser facility, including a metallic target with a femtosecond laser, two linear accelerators, a bunch compression section, and a long undulator for producing self-amplified spontaneous emission (adapted from [2, 5])

magnetic fields. Figure 2.2a shows the work principle of how a synchrotron X-ray is generated by a third-generation synchrotron source. A bunch of charged electrons circulate in an ultrahigh vacuum storage ring (typically  $10^{-12}$  bar). The ring is designed with straight sections for “placing” an insertion device, e.g. an undulator. The lattice of magnets in an insertion device forces the electrons to execute small oscillations which produce intense beams of X-ray. This X-ray then passes through a number of X-ray optical devices, e.g. a monochromator, a focusing mirror, etc., to form a beam with the desired properties onto the sample [2]. The radiations produced in this way have characteristic properties of pulsed time structure, high intensity, high degree of polarisation and natural narrow angular collimation. The frequencies generated can span the entire electromagnetic spectrum, i.e. continuum radiation.



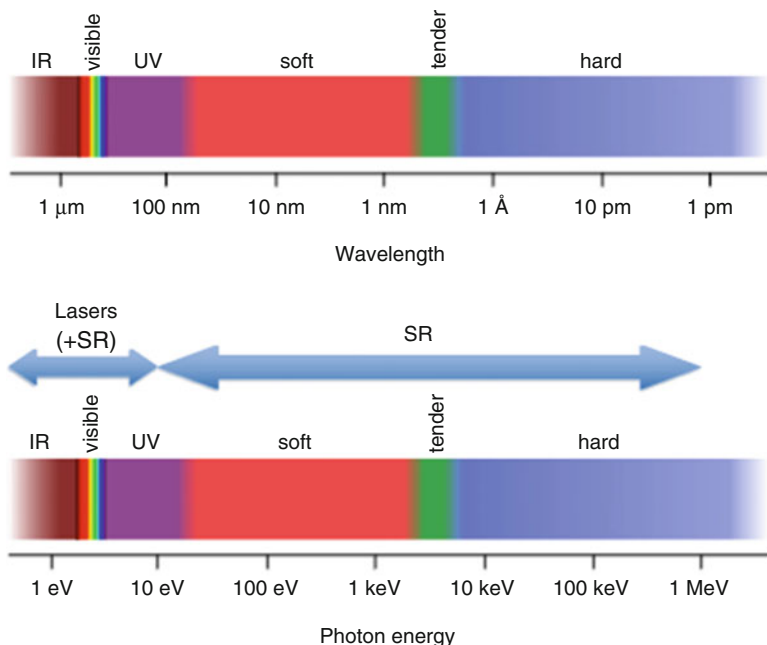


**Fig. 2.3** The wavelength and energy (in electronvolt) of lights and X-rays (adapted from [5])

The typical wavelengths (or photon energies) of the X-rays generated in a typical modern synchrotron facility are in the range from  $\sim 1 \mu\text{m}$  (in the infrared regime) to  $1 \text{ pm}$  ( $\sim$ one hundredth of a typical chemical bond length) as indicated by Fig. 2.3 [5].

Compared to the conventional X-ray beam generated from a Coolidge tube, the most important property of a synchrotron X-ray beam is the many orders of magnitude greater brilliance—a term used to describe the characteristics of an electromagnetic radiation by taking into account the combined effect of radiation intensity, divergence, source size and spectral bandwidth [4]. It is defined as:

$$\text{Brilliance} = \frac{\text{Photons/second}}{(\text{mrad})^2 \times (\text{mm}^2 \text{ source area}) \times (0.1\% \text{ bandwidth})} \quad (2.1)$$

It is the intensity (photons per second), divided by the product of horizontal and vertical beam divergences; the source size; and the relative spectral bandwidth [2, 5]. Furthermore, the term,  $(\text{mrad})^2 \times (\text{mm}^2 \text{ source area})$ , is called emittance; and the term,  $(\text{Photons/second})/(0.1\% \text{ bandwidth})$ , is actually the photon flux.

Since the first synchrotron-based experiments began in the 1950s, synchrotron X-ray beam brilliance has increased exponentially by  $\sim 13$  or  $\sim 14$  orders of magnitude over five decades, mainly due to the use of sophisticated magnet-based insertion devices called wigglers, and then undulators. X-ray brilliance has doubled every 10 months on average in the last three decades as indicated in Fig. 2.4. For comparison, when the sources' sizes, divergences, and bandwidths are all taken into account, a single synchrotron X-ray beam may have a brilliance of  $\sim 12$  orders of

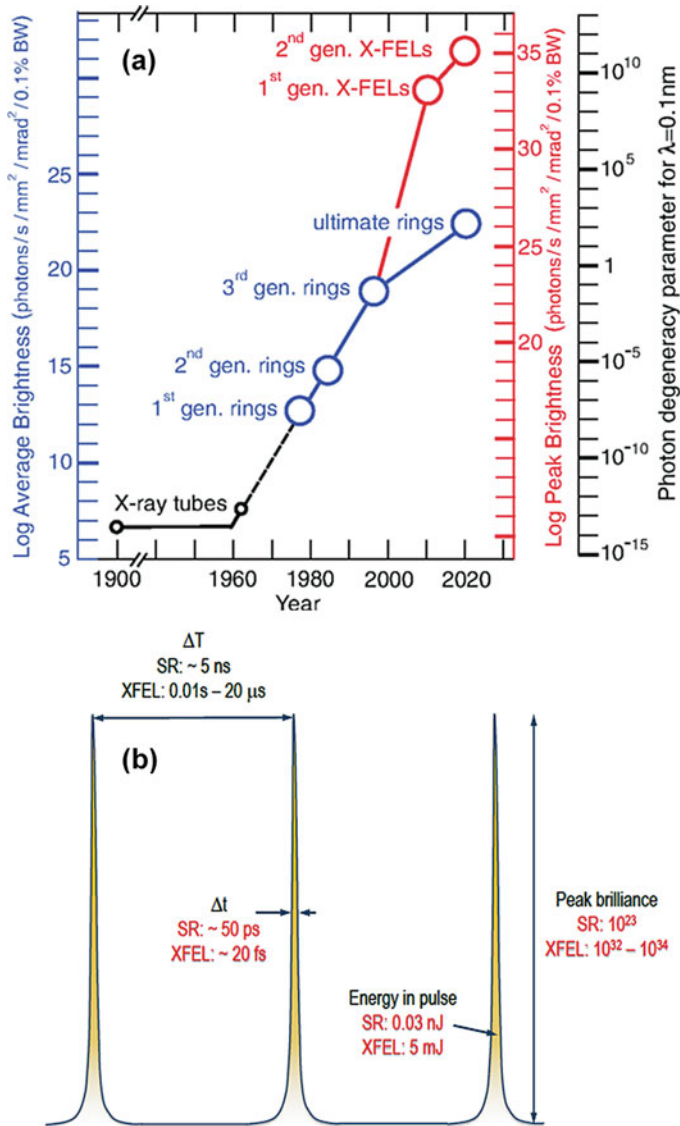


**Fig. 2.4** (a) Increase in brilliance over time for synchrotron X-ray and X-ray free electron laser (adapted from Phys. Rev. Lett. 118, 024801), and (b) comparison between synchrotron X-ray and free-electron laser in terms of beam peak brilliance, pulse length/energy, and frequency (adapted from [5])

magnitude greater than that from a conventional medical X-ray machine. However, a medical X-ray machine may generate as much as  $\sim 1$  kW X-radiation for radiography, about two orders of magnitude higher than that ( $\sim 10$  W) generated by all the beamlines combined together at a typical third-generation synchrotron facility [5].

Although firstly started and used exclusively in physics and chemistry research communities, synchrotron X-ray has, over the past two decades or so, become one of the primary research tools in all natural and biological sciences [2, 5]. Now, there are more than 50 synchrotron facilities around the world (<https://lightsources.org/lightsources-of-the-world/>). The most prominent third-generation sources are the European Synchrotron Radiation Facility (ESRF) in Grenoble (6-GeV storage ring), France the Advanced Photon Source (APS) at Argonne National Laboratory (7 GeV) in the USA, and Spring-8 (8 GeV) in Harima Science Garden City in Hyogo prefecture, Osaka, Japan.

In 2009, the first hard X-ray free-electron laser (XFEL)—the Linear Coherent Light Source began operation at the Stanford Linear Accelerator Center (SLAC) in Stanford, California. XFEL has different architecture to that of synchrotrons (Fig. 2.2b). It uses a femtosecond laser pulse to irradiate a metallic target and generate a short electron bunch. The electron bunch is accelerated in a linear accelerator (LINAC) and compressed to an even shorter pulse of  $\sim 100$  times less. The shortened electron pulse is then further accelerated along a long LINAC to several GeV energies and then enters a long magnet array—the undulator, through which the so-called self-amplified spontaneous emission (SASE) effect is induced. SASE divides the electron bunch into many microbunches, each having a duration of just a few femtoseconds. These bunches produce femtosecond X-radiation of XFEL characteristic [5]. XFEL provides X-ray beams with peak brilliances approximately ten orders of magnitude greater than those of modern synchrotrons. It is able to produce trains of pulses with durations of a few femtoseconds to a few tens of femtoseconds, which is three orders of magnitude shorter than the pulse lengths produced by synchrotrons and is sufficiently short for imaging chemical reactions in real time. XFEL has similar temporal resolution to femtosecond lasers in the visible and near-visible regime, but with similar spatial resolution to X-ray. Hence, the uses of XFEL compared to synchrotrons in an experiment are not incremental in nature, but representing a completely new technological paradigm shift [5].

In summary, for more than 100 years since its inception, X-ray has played an increasingly important role in new scientific discovery and technological advancement in human society [2, 4, 5]. It has been used in almost all scientific and academic disciplines, including physics, chemistry, materials, engineering, biology, palaeontology, art history, cultural ethnology, etc. The impact of X-ray and synchrotron X-ray on society is phenomenal. Since Röntgen, 21 Noble prizes have been awarded to scientists who had worked on matters related to X-ray science. Among them, nine are in the field of molecular biology, and the four most recent awardees (Roderick MacKinnon in 2003, Roger David Kornberg in 2006, Venkatraman Ramakrishnan in 2009, and Brian Kent Kobilka in 2012, all for chemistry) used synchrotron X-ray as a primary tool in their research. This chapter is primarily focusing on the research activities and recent advances in the field of using synchrotron X-ray based techniques to study in situ the solidification processes of advanced metal alloys.

### 2.1.2 X-Ray Interaction with Matter: Scattering and Absorption

X-ray is more conveniently characterised by its photon energy  $E$  rather than wavelength  $\lambda$ . The Planck–Einstein relationship links energy and wavelength (including wave frequency,  $\nu$ , angular frequency,  $\omega$ , and angular wavenumber,  $k$ ) together:

$$E = h (c/\lambda) = h\nu = (2\pi\hbar)(c/\lambda) = \hbar\omega = \hbar ck \quad (2.2)$$

where  $h = 2\pi\hbar = 6.626 \times 10^{-34} \text{ J}\cdot\text{s}$  is Planck's constant,  $\hbar = 1.055 \times 10^{-34} \text{ J}\cdot\text{s}$  is reduced Planck's constant, and  $c = 2.9979 \times 10^8 \text{ m/s}$  is the speed of light in vacuum. Conventionally, electronvolt is used as the unit of energy for X-ray, and it is the gain in kinetic energy of an electron when it is accelerated through an electric potential of 1 V and is equal to  $1.6022 \times 10^{-19} \text{ J}$ . When wavelength is expressed in Angstrom ( $10^{-10} \text{ m}$ ), and photon energy is in electron volts, Eq. (2.2) becomes:

$$\begin{aligned} E(\text{eV}) &= 12398.4/\lambda[\text{\AA}] \\ E(\text{keV}) &= 12.398/\lambda[\text{\AA}] \end{aligned} \quad (2.3)$$

Figure 2.3 shows the different X-ray regimes expressed in wavelength and photon energy, respectively. The vacuum ultraviolet and soft X-rays produced at synchrotrons begin at 10–20 eV and continue up to approximately 2 keV. Hard X-rays conventionally begin at 4 keV, while the tender regime spans the gap between 2 and 4 keV. Apparently, higher energy X-rays have higher penetrating capability. Hard X-rays have wavelengths comparable to or shorter than typical distances between atoms (the bond lengths). The shortest bond length at normal pressure is that of  $\text{H}_2$  molecule with  $0.74 \text{ \AA}$ . While atomic bonds of heavy elements can exceed  $\sim 3 \text{ \AA}$ , equivalent to the wavelength of 4 keV photons. The shorter wavelength of a hard X-ray is suitable for investigating atomic structures of materials, i.e. using X-ray diffraction based techniques. In addition, hard X-rays have energy similar to the bonding energies of the core electrons in atoms. The hard X-ray regime can access all elements with atomic numbers above  $Z = 20$  (Calcium). Such a property can be exploited in hard X-ray spectroscopies and in crystallography for solving structures from data recorded at specially chosen photon energies [5]. The lower energies of soft X-rays allow them to interact primarily with light atoms and the outer, or valence, electrons of heavier atoms. This can also be exploited to investigate many different properties of materials, for example, the electronic properties of metals, semiconductors, and superconductors; the chemical composition of heterogeneous systems; or imaging of magnetic domains down to nanometre scale [5].

Figure 2.5 shows all possible interaction of X-ray with matter. Nuclear and pair production only begin to dominate at photon energies above  $\sim 1 \text{ MeV}$  (see Fig. 2.6a), which is the highest end of the X-ray energy that a current synchrotron facility can produce, and therefore can be ignored for most synchrotron experiments [5].

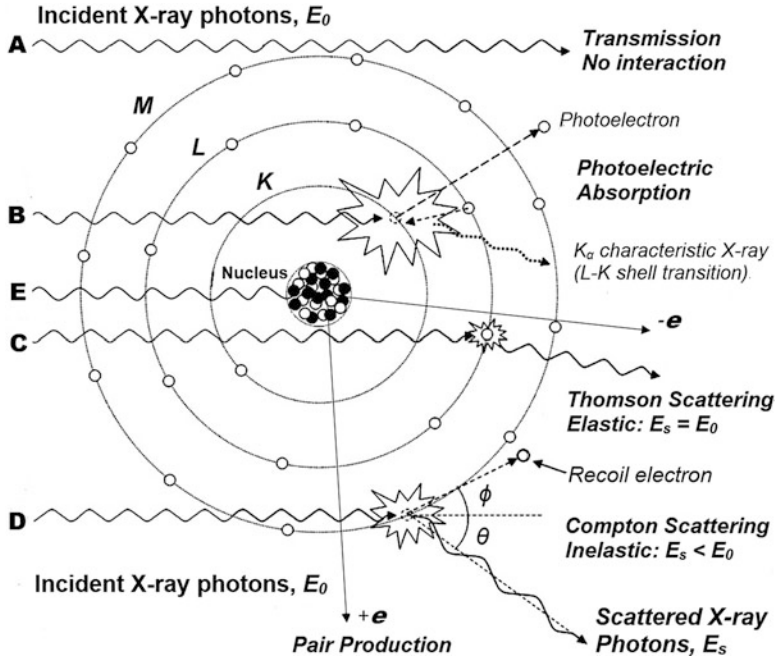


**Fig. 2.5** An illustrative description of X-ray interaction with matter: (A) Transmitted X-ray beam without any interaction. (B) Photoelectric absorption. (C) Thomson scattering. (D) Compton scattering. (E) Pair production (adapted from [6])

Hence, only Compton and Thomson scattering, and the photoabsorption process that involve the interactions of an X-ray photon and electrons are discussed here. Compton scattering is inelastic scattering of a photon by a free electron via the mechanism of photon-electron collision. It is a quantum-mechanical effect in which some of the energy and momentum of an incident photon is imparted to a free electron, which receives a change in its momentum. The energy lost by the inelastically scattered photon results in an increase in its wavelength, which depends on the scattered angle,  $\theta$ , and the initial photon energy [2, 5]:

$$\lambda - \lambda_0 = \lambda_e(1 - \cos \theta) = (2\pi\lambda_{re})(1 - \cos \theta) = \left(\frac{h}{m_e c}\right)(1 - \cos \theta) \quad (2.4)$$

where  $\lambda_0$  and  $\lambda$  are the wavelength of the incident and scattered photon, respectively.  $h$  is Planck's constant,  $m_e = 9.109 \times 10^{-31}$  Kg is the rest mass of an electron,  $c$  is the speed of light, and  $\theta$  is the scattering angle.

$\lambda_e = 2\pi\lambda_{re} = \frac{h}{m_e c} = 2.426 \times 10^{-2}$  Å is defined as the Compton wavelength of the electron, and  $\lambda_{re} = 3.86 \times 10^{-3}$  Å is the “reduced” Compton wavelength, also called the Compton scattering length [2]. It is a relative small number as the rest mass energy of an electron  $m_e c^2 = 511$  keV is a large value. Based on Eq. (2.4), the

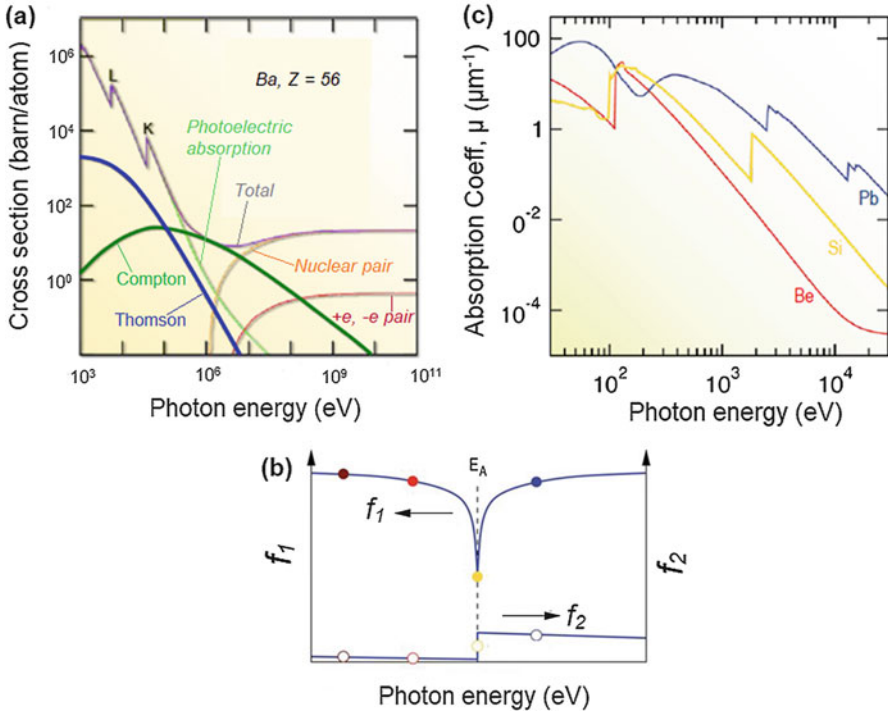


**Fig. 2.6** (a) The cross-section as a function of photon energy for Barium (Ba, atomic number  $Z = 56$ ), showing the regions of different interactions between X-ray and matter. (b) The two terms in atomic form factor,  $f_1$  and  $f_2$  as functions of photon energy, showing the abrupt change at the electron bonding energy. (c) The attenuation length of Be, Si, and Pb (adapted from [5])

relative energy loss due to Compton scattering only becomes significant above a few tens of keV (see Fig. 2.6a), and for large scattering angles, only begins to dominate above approximately 100 keV. Hence, in most synchrotron experiments, the Compton scattering is often not considered unless high-energy photon synchrotron experiments are performed [2, 5].

In contrast to the Compton scattering, Thomson scattering is elastic scattering of X-ray photons by electrons via the mechanism of electromagnetic wave-electron interactions with no loss in energy. When a monochromatic, plane wave of X-ray beam is incident on a stationary free electron with charge  $e$  and mass  $m_e$ , the oscillating electric field of the incident X-ray wave exerts a Coulombic driving force on the electron, causing it to oscillate at the same frequency as the incident radiation with oscillating acceleration. Since an accelerated charge emits electromagnetic radiation, the oscillating electron becomes a new source of X-rays that radiate spherically in all directions and have the same frequency as the incident X-rays. Effectively, the electron scatters the incident X-ray beam in all directions. Although the photon energy remains invariant, the direction, or momentum, can

change. The vector difference between the incident and scattered photon wavevectors is the wavevector transfer,  $\mathbf{Q}$ , which is called the scattering vector:

$$\Delta \mathbf{k} = \mathbf{Q} = \mathbf{k}_{\text{in}} - \mathbf{k}_{\text{out}} \quad (2.5)$$

$\mathbf{k}_{\text{in}}$  and  $\mathbf{k}_{\text{out}}$  are the wavevectors and  $|\mathbf{k}| = 2\pi/\lambda$ . For an elastic scattering of an angle of  $2\theta$ ,  $|\mathbf{k}_{\text{in}}| = |\mathbf{k}_{\text{out}}|$ , hence  $|\mathbf{Q}| = 2 |\mathbf{k}_{\text{in}}| \sin\theta = 4\pi(\sin\theta/\lambda)$ .

Joseph John Thomson, who is credited with the discovery of electron, was the first to analyse the physics of X-ray scattering by a free electron. He defined a parameter in the scattered-to-incident wave amplitude ratio to characterize how strongly an incident radiation is scattered by a free electron, which is called the Thomson scattering length,  $r_e$ :

$$r_e = \frac{1}{4\pi\epsilon_0} \times \frac{e^2}{m_e c^2} = 2.82 \times 10^{-5} [\text{\AA}] \quad (2.6)$$

Where  $\epsilon_0 = 8.85 \times 10^{-12} \text{ F m}^{-1}$  is the electric constant (permittivity of free space).  $e = -1.602 \times 10^{-19} \text{ C}$  is the electric charge of the electron. Historically, the Thomson scattering length is also called the classical electron radius. The Thomson and Compton scattering lengths are the two fundamental scattering lengths for X-ray scattering. The ratio of the two scattering lengths,  $\alpha = r_e / (\lambda_{re}) \approx 1/137$ , is called the fine structure constant which is used for characterizing the strength of the electromagnetic interaction between elementary charged particles. The Thomson scattering accounts for most X-ray scattering by electrons. The scattered X-rays have the same wavelength as the incident X-rays, which produces the interference effects responsible for diffraction of X-rays by crystals. In crystallographic X-ray diffraction measurements, the Bragg reflection peaks are due to the coherent, elastic Thomson scattering, while the diffuse and uniform background under the peaks are due to the incoherent, inelastic Compton scattering.

The scattering cross-section of a free electron is determined by integrating over all angles of the dipole radiation, and it is [5]:

$$\sigma_T = \left(\frac{8\pi}{3}\right) r_e^2 = 0.665 \times 10^{-24} \text{ cm}^2 = 0.665 \text{ barn} \quad (2.7)$$

When considering the scattering of a photon by an atom that contains  $Z$  number of electrons around it (a cloud of electrons), there are generally two scenarios. First, if the incident X-ray wavelength is significantly larger than the size of the electron cloud around the atom (a low-energy X-ray), all scattering events occur coherently, i.e. in phase, and the scattering cross-section of the electron cloud is just simply  $Z^2 \times \sigma_T$  [5], which is independent of wavelength (energy).

However, when the photon energy increases and the wavelength shortens to distances comparable or even less than the size of the electron cloud (shorter than 3 Å, i.e. higher than ~4 keV), scattering from the different elements in the electron cloud begins to interfere partially and destructively, resulting in a drop in the scattering cross-section and intensity, which is approximately proportional to the

inverse square of the incident photon energy. Such phenomena can be quantified by the atomic form factor ( $f^0$ ), also called atomic scattering factor. It describes the elastic scattering amplitude as a function of the scattering angle, wavelength, and the type of atoms. In classical theory, the atomic form factor of a free atom with a cloud of  $Z$  electrons is defined as [2, 5].

$$f^0(\mathbf{Q}) = \int \rho(\mathbf{r}) e^{i\mathbf{Q}\cdot\mathbf{r}} d\mathbf{r} \approx \sum_{i=1}^{i=4} a_i \exp(-b_i \mathbf{Q}^2) + c \quad (2.8)$$

$f^0(\mathbf{Q})$  is the atomic form factor expressed as a function of  $\mathbf{Q} = \sin\theta/\lambda$  (with a unit of  $\text{\AA}^{-1}$ ).  $\mathbf{Q}$  is a natural independent variable that takes into account both incident energy and scattered angle for the same scattered intensity.  $\rho(\mathbf{r})$  is the electron charge (number) density, i.e. the spatial density distribution of the scattering elements;  $d\mathbf{r}$  is the scattering volume at a distance  $\mathbf{r}$  from the centre of the atom. Apparently, the integral term in Eq. (2.8) is a Fourier transform operation. So, atomic form factor is mathematically a Fourier transform of the spatial electron density distribution of an atom from real space to reciprocal space [2]. In the range of scattering vectors between  $0 < |\mathbf{Q}| < 25 \text{ \AA}^{-1}$ , the atomic form factor is well approximated by a sum of the four Gaussians plus a constant shown in the right-hand side of Eq. (2.8).

The meaning of the coefficients and their values in the four Gaussians and the constant for different atoms and ions can be found in the International Tables for Crystallography [7]

In reality, the atomic form factor must be corrected to account for the fact that the electrons in a material are generally bound to the atomic nucleus, and are not entirely free to respond to an incident radiation. Hence, two dispersive correction terms are introduced for the corrections.

$$f(\mathbf{Q}, \hbar\omega) = \underbrace{f^0(\mathbf{Q}) + f'(\hbar\omega)}_{\text{dispersive}} + \underbrace{if''(\hbar\omega)}_{\text{absorptive}} = \underbrace{f_1(\mathbf{Q}, \hbar\omega)}_{\text{dispersive}} + \underbrace{if_2(\hbar\omega)}_{\text{absorptive}} \quad (2.9)$$

$f'$  is a negative term added onto  $f^0$  to account for the reduced amplitude of scattering due to damping because the electron is bound to the nucleus.  $f'$  is strongly dependent on the incident X-ray energy,  $\hbar\omega$ . When the incident energy is equal to the binding energy of the electron to the atom, i.e. at resonance,  $f'$  reaches its maximum value, i.e. the maximum damping effect (see Fig. 2.6b).  $f''$  is a positive term, accounting for the re-emission of photons due to the dissipation (absorption) of the incident X-rays. It increases abruptly at the resonance energy (Fig. 2.6b).  $f''$  lags 90 degree behind  $f'$ , so it is mathematically expressed by an imaginary term [5].

The phenomena of X-ray refraction, reflection, and absorption can be explained using atomic form factor. Firstly, considering the refraction of X-ray, the refractive index of matter for X-ray is a complex number, consisting of a real part and an imaginary component:



$$\mathbf{n} = \mathbf{n}_R + i\mathbf{n}_I = (1 - \delta) + i\beta \quad (2.10)$$

The real part is responsible for refraction of X-ray, while the imaginary part describes absorption. The correlation between refractive index  $\mathbf{n}$  and atomic form factor  $f$  can be derived by analyzing the phase difference (due to refraction) of a plane wave passing through a thin plate by the scattering approach (i.e. superposition of the scattered waves from the thin plate plus the incident wave) [2]. The analysis yields the following relation:

$$\mathbf{n} = 1 - \frac{r_e \lambda^2}{2\pi} \rho_{at} f(0) = 1 - \left[ \frac{r_e \lambda^2}{2\pi} \rho_{at} \underbrace{f_1(0)} \right] + \left[ -i \frac{r_e \lambda^2}{2\pi} \rho_{at} \overline{f_2(0)} \right] = 1 - \delta + i\beta \quad (2.11)$$

$\rho_{at}$  is the atomic number density,  $f(0)$  is the atomic form (scattering) factor in the forward direction, i.e.  $\mathbf{Q} = 0$ . Hence:

$$\delta = r_e \frac{\lambda^2}{2\pi} \rho_{at} f_1(0) = r_e \frac{2\pi}{k^2} \rho_{at} f_1(0) \Rightarrow \delta \propto (h\nu)^{-2} \quad (2.12)$$

$$\beta = -r_e \frac{\lambda^2}{2\pi} \rho_{at} f_2(0) = -r_e \frac{2\pi}{k^2} \rho_{at} f_2(0) \Rightarrow \beta \propto (h\nu)^{-4} \quad (2.13)$$

$\delta$  is the minus part of the refractive index, and  $\beta$  is the absorption index. Even for the heaviest elements,  $\delta$  is in the order of  $2 \times 10^{-5} \ll 1$ .  $\beta$  is even smaller than  $\delta$ , in most cases by up to 3–4 orders of magnitude, depending on both the element and photon energy [5]. So, the refractive index of X-rays is approximately to unity for most materials. as  $\mathbf{n}$  is less than unity, X-rays are “bent” to shallower angles when transverse from a lighter to a denser material. Hence, there exists a critical incident angle for which X-rays will be reflected entirely back to the external environment. Such characteristics allows X-ray mirrors to be constructed as described in [2], which is out of the scope of this chapter.

When an X-ray wave passes into a block of material, the wavefronts will increase their separation by a factor  $1/n_R$ . While the amplitude  $E_0$  of the electromagnetic radiation will decrease exponentially due to absorption. The propagation in time and space of a plane wave is given by the Eulerian formula [5]:

$$E(\mathbf{z}, t) = E_0 \exp [i(n k_0 \mathbf{z} - \omega t)] \quad (2.14)$$

On the spatial term,  $\mathbf{n}$  is the refractive index and  $n = 1$  in vacuum. Combining Eq. (2.10), Eq. (2.14) can be separated into a temporal or oscillatory term (Eq. 2.15), and the exponential decay of the intensity  $I$  ( $I \propto E^2$ ) versus the incident intensity  $I_0$  can be calculated as below (Eq. 2.16):

$$E(z,t) = E_0 \exp(-n_I k_0 z) \exp[i(n_R k_0 z - \omega t)] \quad (2.15)$$

$$I/I_0 = \exp(-2n_I k_0 z) = \exp(-\mu_a z) = \exp(-z/\Lambda_p) \quad (2.16)$$

where  $\mu_a = 2n_I k_0 \propto (h\nu)^{-3}$  is the linear attenuation (absorption) coefficient and  $Z$  is the distance travelled.  $\Lambda_p = 1/\mu_a = 1/(\sigma_p \rho_{at})$  is the attenuation length,  $\rho_{at}$  is the number density of atoms, and  $\sigma_p$  is the cross-section, which has a unit of area/atom. A convenient unit, “barn,” which has an area of  $10^{-28}$  square Angstroms was traditionally used as the unit for cross-section (see Fig. 2.6a) [5].

The amplitude of the X-ray wave decays when traveling through matter, and after a distance of  $(1/\mu_a)$ , it is  $1/e$  (or about 37%) of its original value. This is the absorption length. The absorption coefficient  $\mu_a$  is the reciprocal of it, and it is dependent on the electron density of the material and the photon energy. Figure 2.6c shows that the absorption length can vary from the order of 10 nm for lead at low photon energies, to centimetres for beryllium in the hard X-ray regime.

After removing an electron from the electron cloud of an atom by absorption of a photon, four main signals, namely the photoelectron itself (Fig. 2.5), fluorescence, Auger emission, and secondary electrons, can be produced. The photoelectron phenomenon is the direct product of absorption. The promoted electron may actually reside in an unoccupied orbital if the photon energy is only marginally larger than the electron’s binding energy. Such orbitals are accessed and the information used to work out both chemical and orientational information by the technique of X-ray absorption near edge structure (XANES) (also known as near edge X-ray absorption fine structure, NEXAFS). If the electron leaves the atom entirely, it can be detected, its kinetic energy determined, and from this and knowledge of the photon energy, the binding energy of the electron can be calculated. Subtle changes in this value provide invaluable chemical information in the technique of X-ray photoelectron spectroscopy (XPS) (also called Electron Spectroscopy for Chemical Analysis, ESCA), while the dependence of the yield as a function of both photon energy and exit angle of the electron in single-crystal samples yields detailed information on the sample’s electronic structure in angle-resolved photoelectron spectroscopy (or ARPES). The removal of a core electron can cause another electron from a less tightly bound orbital to relax into the “hole” left behind. The excess energy produced by this can be channelled in one of the two ways. Firstly, this energy can be removed as a photon in the form of fluorescence at characteristic photon energies, which is exploited in X-ray fluorescence techniques. Alternatively, the excess energy can cause yet another electron to be ejected. As the kinetic energy of this so-called Auger electron depends only on the energy difference between the initial hole state and that of the relaxing electron, and the binding energy of the Auger electron, its kinetic energy is independent of the incident photon energy, which distinguishes it from direct photoelectrons. Auger processes tend to dominate for low- $Z$  atoms, while fluorescence occurs more commonly for heavier elements. Finally, any ejected electron will on average collide with other electrons after a certain characteristic distance, measured in nanometres or at most tens of nanometres for most kinetic energies under consideration. This makes Auger spectroscopy and photoelectron

spectroscopy very surface sensitive. If, however, the ejected electron is generated deeper in the sample (the penetration depth of X-ray is normally significantly larger than the escape depth of electrons), then it will undergo multiple collisions, producing a cascade effect and the production of many more secondary electrons which have been thermalised and have energies measured in fractions of an electronvolt. This signal is often used as an indirect measure of absorption strength, such as in the spectromicroscopic technique of photoemission electron microscopy (PEEM).

### ***2.1.3 X-Ray Imaging-Based Characterization Techniques***

Hard X-ray imaging allows detailed information inside materials to be gathered using either full-field imaging (the whole sample is illuminated) or scanning (the beam is focused to a small spot and then is scanned across the sample). The high intensity and energy of synchrotron X-ray makes it possible to image a much larger range of materials and sample thicknesses than conventional X-ray sources, and the brilliance of the synchrotron source produces very high temporal or spatial resolution under some special imaging conditions. In addition, X-ray computed tomography can create three-dimensional reconstructions of the internal sample volume from 2D scans, making it possible to view any cross-section of the virtual image at any angle.

#### **2.1.3.1 Absorption Contrast Imaging**

Absorption contrast imaging is the most common imaging technique. An absorption contrast image is essentially a shadowgraph; the contrast is generated by the different attenuating power of different materials in a sample. The tunable beam size and high intensity of synchrotron X-rays make it possible to scan samples and provide a composite image in much finer detail than that from conventional sources. Combining absorption contrast imaging with other X-ray techniques also allows detailed complementary information to be gathered, as in diffraction enhanced imaging, or to recreate three-dimensional objects from two-dimensional scans as in tomography. The tunability of synchrotron X-ray makes it possible to compare images obtained at different X-ray energies, for example, above and below the absorption edge of a particular element. The combination of small spot size and the coherent, monochromatic radiation make very high spatial resolution possible. Reduced data acquisition times make it possible to image dynamic and transient materials processing and mechanical deformation processes in situ and in real time. Absorption contrast imaging has a wide range of applications, in biomedicine, materials science, engineering, environmental science, and nanotechnology.

### 2.1.3.2 Phase Contrast Imaging

Phase contrast imaging takes advantage of the fact that different materials have different refractive indices. This produces a phase shift in the X-ray passing through the sample. By placing the imaging detector at a specific distance from the sample, interference between waves can be used to enhance contrast in the image. While phase contrast imaging is possible using laboratory techniques, the highly coherent X-ray beams make it possible to gather data with much simpler instrumentation. In addition, it is possible to achieve higher spatial resolution, and to carry out phase contrast tomography, where 3D images are created from 2D scans. Phase contrast imaging enables the examination of crack growth and fatigue in materials under stress, which is of particular importance in the aerospace and engineering industries. It is particularly useful for enhancing the contrast of surfaces and interfaces in samples, which would not be visible using absorption contrast.

### 2.1.3.3 Photoemission Electron Microscopy

PhotoEmission Electron Microscopy (PEEM) is a non-destructive imaging technique that involves shining linearly or circularly polarised X-ray onto the surface of a sample to provide spectroscopic information on nanometre scale. This information can be used to study nanostructures significant for sensors, catalysts, magnetic materials, and nanoscale devices and phenomena such as nanomagnetism. Laboratory-based imaging techniques such as STM, AFM, and TEM are capable of resolving nanostructures but (apart from a limited capacity with STM) are unable to provide spectroscopic information. PEEM can link structure to function by providing spectroscopic data on nanometre scale. The well-defined and variable polarisation state of synchrotron radiation can also provide, via dichroism, a contrast mechanism for imaging different magnetisations in ferromagnetic and antiferromagnetic nanostructures. PEEM can be used to study the phenomenon of exchange bias, which has revolutionised the capabilities of magnetic information storage discs, but the underlying physical mechanisms are not well understood. There are also applications in study of nanoparticle catalysis, magnetic domain interactions, and characterisation of the properties of natural materials, such as chemical composition, local environment, and phase identification. The fabrication and modification of novel materials on a nanometre scale is another important area.

### 2.1.3.4 X-Ray Diffraction Imaging

Coherent X-ray diffraction is an imaging technique which overcomes some of the limitations encountered with using lenses. Instead, a series of X-ray diffraction patterns are combined to mathematically reconstruct a three-dimensional image of the structure being studied. With highly coherent synchrotron X-ray, this approach

can provide spatial resolution on a nanometre scale. In the past, this technique has been applied to model repeating crystal structures, but it is now being used to examine small, non-periodic samples. At present, this technique can only be carried out using synchrotron X-ray, as no other source is capable of producing such coherent X-ray beams. The high penetration depth that is possible with synchrotron X-ray allows the study of bulk dynamics so that a full three-dimensional analysis is possible without destroying the sample. Understanding the structure of polycrystalline materials allows information to be derived about their physical, chemical, and electronic properties. This is vital in a wide range of fields, including the development of novel materials for engineering applications, in understanding environmental processes such as the transport of pollutants through different environments, and in drug design.

### **2.1.3.5 X-Ray Tomography**

X-ray tomography is the construction of a three-dimensional image from two dimensional projections taken at different orientations (usually with phase contrast or absorption contrast imaging). The tunability of synchrotron X-ray makes it possible to provide increased contrast images, and the coherent nature and high intensity of synchrotron X-ray have led to significant developments in this field, particularly in phase tomography which in the past has required extremely complex instrumentation. High intensity, monochromatic, and highly coherent synchrotron radiation allows high spatial resolution with a good signal-to-noise ratio. High-energy synchrotron X-ray can penetrate through thicker materials, providing a tool for non-destructive examination of internal features. The parallel, monochromatic beam enhances the image quality beyond what is possible with laboratory techniques. Tomography has many applications in materials science, engineering, and biomedical fields. It can be used to characterise the internal structure of porous materials such as trabecular bone or metal foams. Tomography can be used to determine the size and shape of cracks and other defects inside components such as aircraft parts, where unexpected failures could have catastrophic results. Because it is non-destructive, X-ray tomography can be used to study the internal structure of precious and unique objects in archaeology and palaeontology—for example, studying ancient insects fossilised in amber.

### **2.1.3.6 Ptychography**

Coherent diffractive imaging (CDI) uses a coherent X-ray beam to illuminate a sample and retrieve the phase information on the sample from phase-retrieval analysis of the far-field diffraction pattern. Of the many CDI variants developed, ptychography has been shown to be the most robust and is a scanning technique where diffraction information is collected from overlapping regions and used to reconstruct the sample phase properties. The advantage of ptychography is that the spatial resolution achieved

can be higher than that achieved with conventional optics. Ptychography does not require sample isolation, and so represents an advance in CDI methods. In a ptychography experiment, the X-ray beam is focused onto a sample so that a small area is illuminated. The sample is then moved with respect to the beam to create a sequential array of overlapping illuminated areas. For each area, the light scattered by the sample is recorded as a diffraction pattern. The diffraction patterns are then processed with an iterative algorithm which retrieves the phase information. The output is a pair of images. One is a measure of the extent to which light has been absorbed by the sample. The other is a measure of the phase delay introduced to the beam as it passed through the sample. The above mentioned techniques are routinely used in materials characterisation. There are many other techniques that are used in chemistry, physics or biological disciplines for specific applications. Readers are referred to the monographs [2, 4, 5] for specific information or need.

## **2.2 In Situ Studies of Solidification Processes using X-Ray Based Technologies**

### ***2.2.1 A Brief Review on In Situ Studies of Solidification Processes***

Metal casting has been practised in human history for more than 5000 years since the end of Stone Age. In a period of approximately 4000 years from 3300 BC to 700 AD, which spans the Bronze and Iron Age, the smelting of copper and iron from ores, and the melting, casting, and making of bronze and iron goods represented major technological advances in the ancient civilisations of mankind. In contrast, solidification as a modern scientific discipline has a very short history with its inception perhaps marked by the nucleation paper of Turnbull [8] and that of the solute distribution paper of Tiller et al. [9] published in the first volume of *Acta Metallurgica* in 1953. Since then, every major scientific breakthrough in solidification has led to the successful development of applied technologies that provided step-change or innovation in manufacturing of novel alloys, materials, and products for industry and society. For example, the booming of semiconductor and computer industry was due to the development of the zone-refining technique by which ultra-pure silicon and germanium crystals could be produced and used as essential semiconductor materials. While high thrust modern aeroengines were made possible as a result of the development of directional and later single-crystal solidification and casting technique, without which the key components, i.e. single-crystal turbine blades could not have been made.

Grain nucleation and growth are the two essential steps in metal solidification. When a solid nucleus is formed in an undercooled melt, a liquid–solid (L–S) interface is created across the liquid and solid phase. Much of the early work on solidification research was devoted to analyses of the stability of L–S interface, and

the competition between heat and solute transfer at the moving L–S interface with the aims of predicting the formations of grain patterns, chemical segregation, and solidification defects [10, 11]. One of the mostly studied phenomena is the formation and evolution of dendritic structures [12, 13] because it is one of the most important structural patterns found in many materials in nature and the key microstructural feature that determines the properties of metals and other solid materials. Due to the opaqueness of metals, direct observation of dendrite formation and evolution is impossible without the use of penetrable radiation beams, e.g. X-rays or neutron beams. Hence, in the early days, transparent organic compounds were often used as the alternatives to study the growth of dendrites under visible light illumination [12, 13]. This method is still used in the present days due to the low temperature and easy experimental set-up. For example, recently, Shu et al. used succinonitrile–1% camphor to successfully study the highly dynamic phenomena of ultrasonic bubbles and their effects on the fragmentation of dendrites [14]. Historically, investigations using transparent organic compounds provided valuable visible information for understanding dendrite growth and pattern selections in different solidification conditions. However, compared to liquid metals, organic transparent compounds have huge differences in density, viscosity, surface tension, and heat/mass transfer coefficient, making it inappropriate to simply apply most of the findings from organic alloy systems to metallic systems [15]. Furthermore, in metal solidification, the viscosity, surface tension, and fraction of the liquid and solid phases are governed predominantly by changes in temperature. Therefore, it is essential to study in situ the dynamic evolutions of dendrites in real metal alloy systems [15]. Fortunately, the development and wider availability of microfocus X-ray sources and fast X-ray detector systems made such research possible. In the 1990s and early 2000s, Professor John Campbell's Casting Research Group at the University of Birmingham, UK was among the first in the world to use real-time X-ray video radiography to study liquid metal flow during mould filling processes with a focus on investigating the entrainments of air bubbles and oxide films, and the formation of casting defects [16–18]. In the late 1990s, Professor Ragnvald Mathiesen and Lar Arnborg [15] of the Norwegian University of Science and Technology began the pioneering work of using coherent and monochromatic synchrotron X-rays available at the beamlines ID22 and ID18 of ESRF to study in situ the cellular and dendritic solidification of metal alloys [15]. The spatial and temporal resolutions achieved at that time were  $\sim 2.5\text{ }\mu\text{m}$  and  $\sim 0.7\text{ s}$ , respectively, in a field of view of up to  $1\text{ mm}^2$ . Since then, worldwide research on using synchrotron X-rays to study solidification processes has grown. Systematic studies have been done to visualise directly the dynamic evolutions of dendrites and other phases in conventional solidification conditions [19, 20], under ultrasound wave [21–24], electric current [25], and pulse electromagnetic field [26, 27], and in semi-solid state [28]. These studies provided much greater insights into how dendrite morphology evolves and adapts according to the coupled physics of heat/solute transfer, fluid flow, and external fields. However, almost all such experiments were conducted using thin metal samples of 100–200  $\mu\text{m}$  thickness encapsulated inside thin cells. Hence, only 2D spatial information was obtained, which normally cannot represent

the 3D spatial environment in which dendrites experience in most practical solidification conditions. In the past 10 years or so, studies of dendritic morphology evolutions moved onto three spatial dimensions and more recently into the fourth-dimensional domain when time is included. Recently, extensive research has been carried out by Professor Peter Voorhees' research group in Northwestern University, USA on time-evolved 3D interfacial morphologies of dendrites [29]. Simultaneously, Professor Peter Lee's group at Manchester University did a systematic study on the deformation of semi-solid melt mixed with dendritic grains [30]. In parallel to these activities, Professor Jiawei Mi's group at University of Hull has concentrated on studying the dynamic evolutions of dendrites and intermetallic phases in highly dynamic solidification environments, i.e. under ultrasonic waves [21–24] and pulse electromagnetic fields [26, 27, 31]. Most of these in situ experiments have been carried out in the 3<sup>rd</sup> generation synchrotron X-ray facilities, for example, the European Synchrotron Radiation Facility (ESRF) in Grenoble, France, the Advanced Photon Source (APS) at Argonne National Laboratory, USA, the Diamond Light Source, UK, the Swiss Light Source (SLS) at the Paul Scherrer Institute, Switzerland, Synchrotron SOLEIL, France, etc. In addition to the coherent and high-brilliance X-ray sources, numerous special beamlines and dedicated instruments have also been built gradually over the years and added at these synchrotron X-ray facilities. Some of these are designed for studying structures of materials and dynamic responses to thermomechanical driving forces in a spatial and temporal resolution previously impossible. This opens a new era for solidification science. For example, it is now possible to observe directly highly dynamic phenomena in metal solidification processes, including grain nucleation, grain growth, and fragmentation of dendritic grains and intermetallic phases under forced convection, ultrasonic wave, electromagnetic field, etc.

This session gives a brief review on recent developments in this field and selected work from research groups who have been very active in research of in situ studies of the solidification processes.

### ***2.2.2 In Situ Studies of Grain Nucleation by X-Ray Diffraction***

In this section, the commonly used X-ray diffraction techniques were presented and cases are given on how to use such techniques for studying grain nucleation, growth, and phase changes in solidification process, i.e. from liquid to solid phase transformation process.

X-ray diffraction microscopy developed at synchrotron sources with high-energy X-rays is a powerful tool for probing nucleation and growth of individual grains in solid-state phase transformation in bulk materials. In 2005, Iqbal et al. were among the first to use such technique to study the crystallisation kinetics of liquid Al–Ti alloys with microscopic TiB<sub>2</sub> particles added to refine the grain size. The



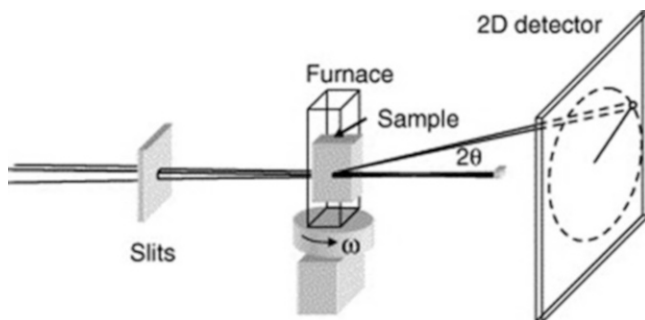


**Fig. 2.7** A schematic illustration of the experimental set-up using the 3DXRD. A monochromatic X-ray beam defined by slits was illuminating onto the sample mounted in a vacuum furnace. The diffracted intensity, scattered over an angle  $2\theta$ , was recorded by a 2D detector while the sample was rotated over an angle  $\omega$  around the vertical axis. A beam stop was used to shield the direct beam (adapted from [32])

relatively high-viscous liquid Al melt with minimal grain rotations makes it possible to monitor the complete growth of individual grains floating in the melt [32]. The experiments were performed at beamline ID11 of the ESRF using the 3D X-ray diffraction microscope (3DXRD) in transmission geometry (Fig. 2.7).

A monochromatic X-ray beam with an energy of 70 keV and a beam size of  $200 \times 200 \mu\text{m}^2$  was used to illuminate the 5 mm diameter of the sample (with a height of 10 mm). The sample was mounted in a glassy carbon container inside a vacuum furnace. A continuous sample rotation of  $1^\circ$  around the vertical axis (perpendicular to the beam) gives rise to a diffraction pattern on the 2D detector. This pattern gives direct information on both liquid and solid phases during the solidification process as shown in Figs. 2.8 and 2.9.

The study shows that, for Al alloy with Ti concentrations below 0.15 wt.%, the  $\text{TiAl}_3$  phase is metastable. The  $\text{TiAl}_3$  grains nucleate  $\sim 10$  K above the nucleation of Al grains. After formation of Al grains, the  $\text{TiAl}_3$  phase subsequently dissolves at the expense of the more stable solid Al–Ti alloy [32]. The in situ experiments reveal that the duplex nucleation theory is the mechanism responsible for the grain refinement process in these alloys. The experiments also demonstrate that nucleation and growth of individual grains in a bulk liquid metal during solidification can be studied in real time. These in situ experiments are essential for validating theoretical models and theories which, are crucially important for industry [32].

In 2010, Shuleshova et al. used synchrotron X-ray energy-dispersive diffraction technique to study in situ the phase transformations (including melting) of electromagnetically levitated ternary Ti–Al–Nb alloys [33]. The alloys were prepared from Ti, Al, and Nb elements with 4 nine (99.99%) purity in a Hukin-type cold-crucible induction melting facility under Ar atmosphere. Samples of about 1.5 g each were cut from as-cast ingots and remelted in an electromagnetic levitation apparatus [33] under 6 nine (99.9999%) He gas atmosphere to form spheres of  $\sim 8$  mm in diameter. These samples were used in a specially designed electromagnetic levitator combined

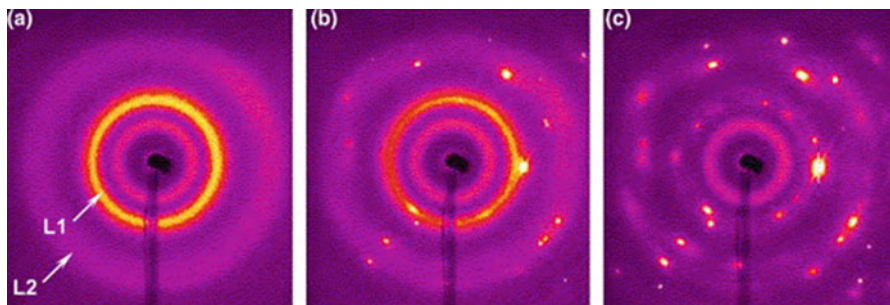


**Fig. 2.8** X-ray diffraction patterns of the Al alloy with solute Ti (0.1 wt.%) and added  $\text{TiB}_2$  particles (0.1 wt.%) at different stages of solidification. The data were collected during cooling from 973 K at a cooling rate of 1 K/min. (a) In liquid phase, the two broad outer rings (L1 and L2) are due to the first (L1) and second (L2) maximum in the liquid structure factor. (b) In mixed liquid and solid phase, the additional bright spots are Bragg reflections from the nucleated grains at the scattering angles of the Al lattice structure. (c) In solid phase, the diffraction spots have increased in number and intensity while the diffuse scattering from the liquid phase has vanished. The diffuse innermost ring arises from the quartz windows of the vacuum furnace (adapted from [32])

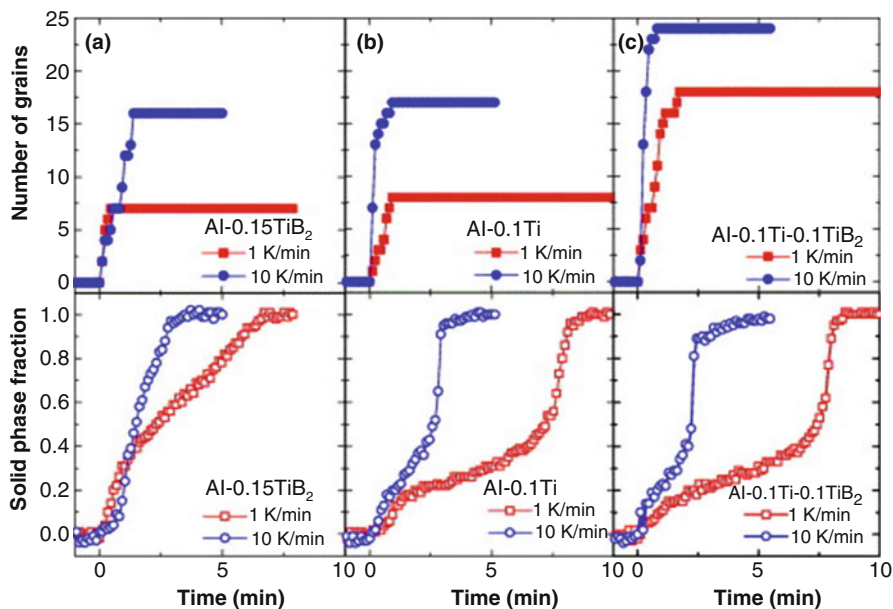


**Fig. 2.9** Grain nucleation and solid phase fraction of three Al alloys as a function of time for different cooling rates. X-ray diffraction patterns were acquired as a function of time for Al alloys with (a) added  $\text{TiB}_2$  particles (0.15 wt.%), (b) solute Ti (0.1 wt.%), and (c) both solute Ti (0.1 wt.%) and added  $\text{TiB}_2$  particles (0.1 wt.%) during cooling from 973 K with a cooling rate of 1 and 10 K/min. The top row figures show the total number of nucleated grains measured from Bragg reflection (after validation that they are nucleated in the illuminated sample volume). The bottom row figures show the corresponding solid phase fraction deduced from the scaled intensity variation in the first maximum of the liquid structure factor.  $t = 0$  corresponds to the onset of the solidification (adapted from [32])

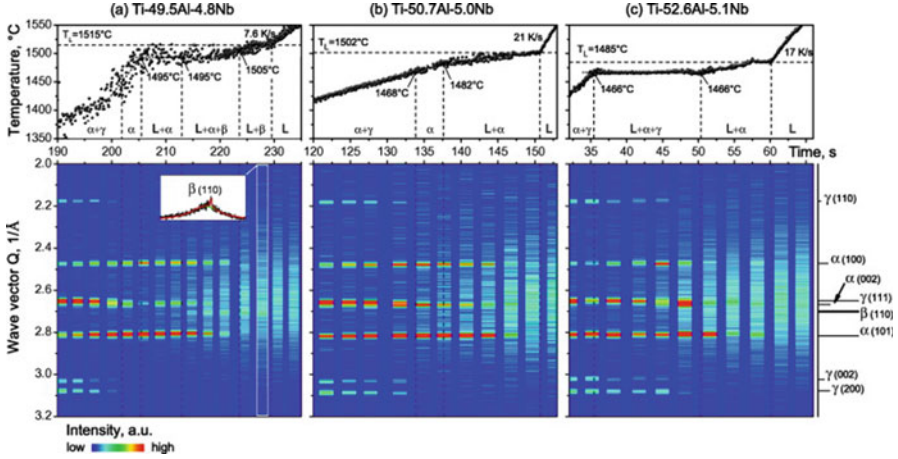


**Fig. 2.10** Time evolution of temperature and X-ray diffraction spectra during the heating of three Ti–Al–Nb alloys near the isopleth at 5 at.% Nb: (a) Ti–49.5Al–4.8Nb, (b) Ti–50.7Al–5.0Nb, and (c) Ti–52.6Al–5.1Nb. The temperature–time profiles (top) are synchronised in time with the EDXD spectra (bottom) with crystalline reflexes assigned in the right panel. Bottom: colour scale of intensities (adapted from [33])

with the high-energy white beam diffraction set-up available at beamline ID15A of the ESRF. Detailed electromagnetic levitation apparatus used is referred to [34].

The X-ray beam was collimated to a cross-section of  $0.3 \times 0.3 \text{ mm}^2$  and able to fully penetrate the bulk samples. The transmitted X-ray was collected by an energy-dispersive Ge detector at a constant scattering angle of  $2\theta = 2.5^\circ$ . Typical integration times for recording spectra of reasonable quality were 1 to 2 s. All reflections observed were explicitly indexed on the basis of the bcc lattice of  $\beta$  (Ti) (disordered A2 structure, space group Im-3 m), the hexagonal lattice of  $\alpha$  (Ti) (disordered A3 structure, space group P63/mmc), and the tetragonal lattice of  $\gamma$ -TiAl (ordered L10 structure, space group P4/mmm) phases. Figure 2.10 shows the typical time evolution of temperature and X-ray diffraction spectra during heating of three alloys.

The in situ EDXD measured boundary of the  $\alpha$  (Ti) solidification domain with respect to the neighbouring  $\beta$  (Ti) and  $\gamma$ -TiAl domains have been confirmed by conventional microstructure investigations. The experimental results agree well with the calculated liquidus and solidus boundary of the new Ti–Al–Nb phase diagram. Moreover, direct experimental information on the nature of reactions along the univariant lines has been provided, which is very difficult to obtain by other methods. It has been confirmed experimentally that the nature of the reaction along the  $L$ – $\alpha$ – $\gamma$  univariant line changes from  $L + \alpha \leftrightarrow \gamma$  peritectic type to  $L \leftrightarrow \alpha + \gamma$  eutectic type for niobium contents more than 5 at.%. Along the  $L$ – $\beta$ – $\alpha$  univariant line, the peritectic reaction is observed up to niobium levels of 10 at.%. Such in situ measured data are very valuable in reassessment of the thermodynamic database of the ternary Ti–Al–Nb system [33]. Major advantage of the experimental method is

the capability of directly identifying high-temperature phases and their evolution versus time in high-temperature environment for reactive alloys.

In 2014, Brown et al. [35] used synchrotron X-ray scattering technique to investigate in situ nucleation and early stage solidification behaviour when liquid is in contact with a specific crystal plane of a solid substrate. The material system chosen was (Al +  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) because it exhibits large nucleation undercooling, as high as 175 °C, so that the required nucleation undercooling could be easily determined [35]. The experiment was designed to investigate the orientation relationship that could form between the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> substrate and Al nucleus as orientation relationship is an important factor which influences the nucleation potency of the substrate.

Single-crystal  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> substrates were supplied by SurfaceNet GmbH and grown using the Czochralski method along [0 0 0 1] direction such that the top surface was aligned with the (0 0 0 1) basal plane of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. The top surface of the substrate was chemomechanically polished to roughness on the nanometre scale as minimal interface roughness is desirable for the measurement of surface diffraction. ~500-nm thick Al was sputtering coated onto the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> substrates [35] to ensure a sufficient quantity of material to form a liquid region when melted, but thin enough to allow the X-ray beam to transmit through the thin layer of Al. The X-ray scattering experiments were carried out on beamline I07 of Diamond Light Source, UK. The sample was mounted on a transfer plate that could be brought into contact with a small substrate heater. A thermocouple was located as close to the sample as possible for temperature measurement and control. The sample was mounted within an ultrahigh vacuum ( $\sim 6.5 \times 10^{-9}$  mbar) chamber. A 2D area detector (Pilatus 100k) was used to detect the scattered X-rays from the sample. The scattering data were recorded using a specular X-ray reflectivity geometry where X-ray of energy 15 keV was incident on the sample at an angle  $\theta$ , while the detector was set to be at an angle  $\theta$  from the sample surface. The  $\theta$ – $2\theta$  relationship required for reflectivity was maintained throughout, and the beam was focused to a size of approximately  $250 \times 200 \mu\text{m}$  [35]. X-ray scattering from the Al/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> interface was measured through reflection geometry. This arrangement renders the scattering more sensitive to interactions at buried surfaces.

Figure 2.11 shows typical measured X-ray diffraction patterns for the Al/Al<sub>2</sub>O<sub>3</sub> system during the heating and cooling cycle. The diffraction data were visualised by image concatenation to reveal the orientation relationship, and they are (0 0 0 1) <1 1 0> Al<sub>2</sub>O<sub>3</sub>// (1 1 1) <1 1 2> Al near the interface between the substrate and the nucleus.

This experiment demonstrated that the technique is feasible in providing quantitative information to relate the orientation relationship and lattice mismatch between substrate and nucleus, hence the potency of the substrate, i.e. the required undercooling for nucleation. In conclusion, the X-ray scattering approach is capable of observing in situ the orientation relationship evolution between the substrate and the nucleus [35].

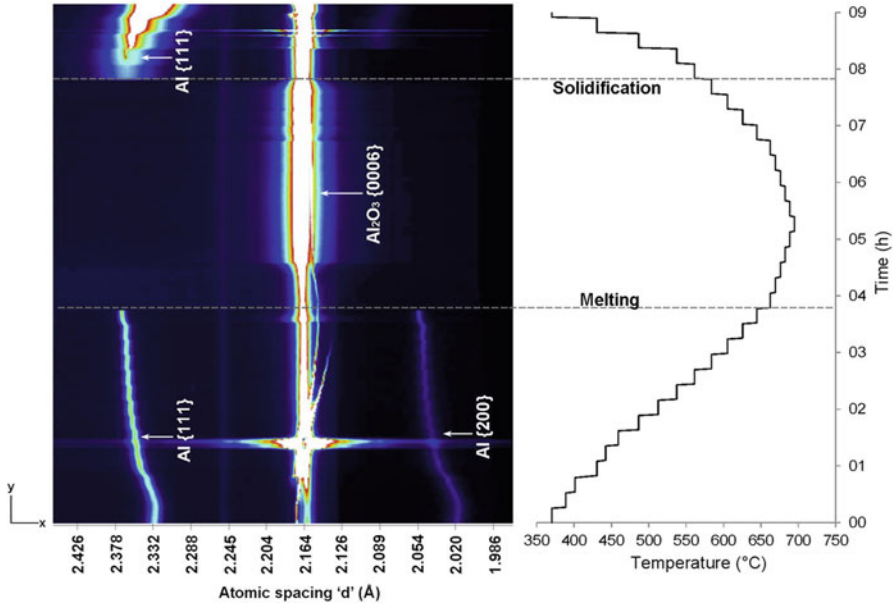


**Fig. 2.11** In situ X-ray diffraction patterns for the Al/Al<sub>2</sub>O<sub>3</sub> system. The y-axis plots diffraction patterns sequentially through the heating/cooling cycle. Heating was manually ramped to  $\sim 350$  °C prior to isothermal holds. The horizontal axis presents atomic spacing “ $d$ ”, rather than  $2\theta$ , to indicate the relation between scattering features and the planar families from which they arise (adapted from [35]).

In 2015, Zhang et al. [36] used in situ X-ray total scattering technique to study the atomic structure evolution of a Zr–Ti-based bulk metallic glass (BMG) on heating and cooling [36]. The scientific drive for such research is that, for multicomponent metallic glassy alloys, changes of atomic structures during the amorphous–crystallisation transition process is a highly complex process and much less understood, i.e. it is not well understood how the local short-range ordered structure of a amorphous phase evolves into the long-range periodic structure of a crystalline phase. This issue is highly important in designing and developing new metallic glass alloys.

One typical experimental result from Zhang’s thesis is given here to demonstrate the usefulness of the techniques. The experiments were performed at the Joint Environmental, Engineering and Processing beamline (I12) of Diamond Light Source, UK. A ZrTi-based BMG, Vit1 with a nominal composition of Zr<sub>41</sub>Ti<sub>14</sub>Cu<sub>12.5</sub>Ni<sub>10</sub>Be<sub>22.5</sub> (at.%) was used as the experimental alloy. A custom-made experimental apparatus, including a well-controlled heating and cooling unit, and a sample mounting arrangement for in situ synchrotron X-ray diffraction acquisitions was used for the experiments as detailed in [36].

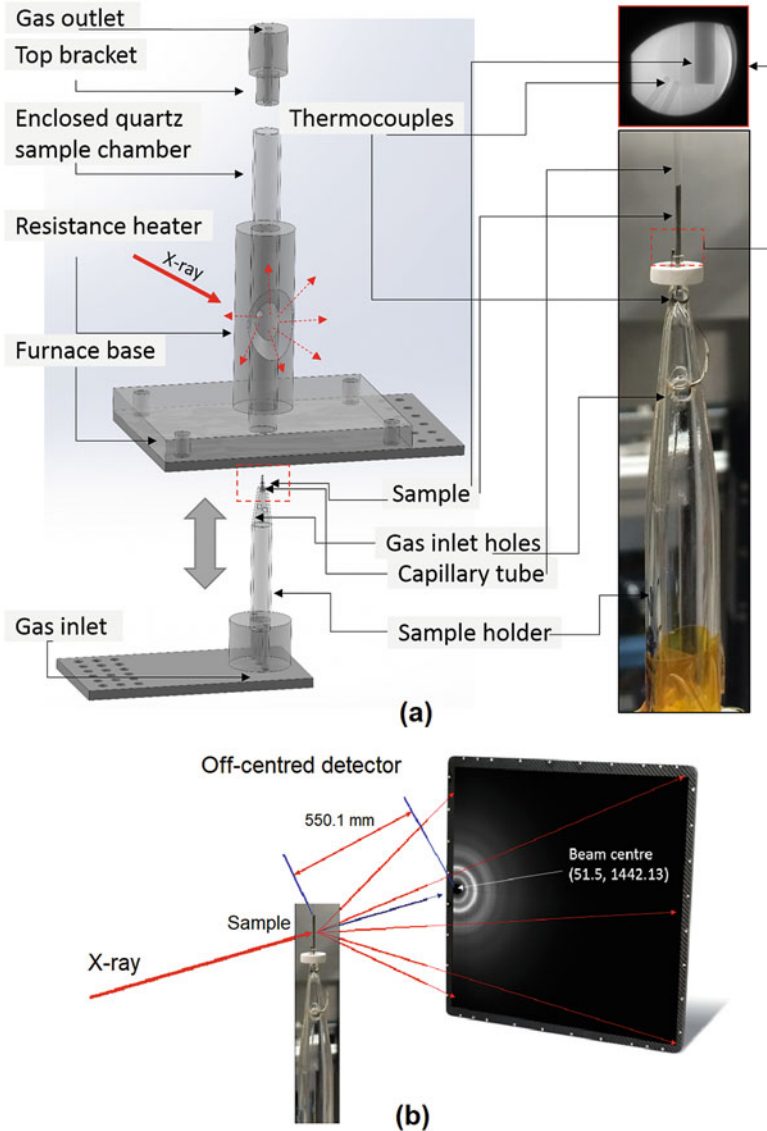


**Fig. 2.12** The purposely built experimental apparatus and the off-centre arrangement of the diffraction detector for the in situ X-ray total scattering studies of multicomponent bulk metallic glass (BMG) during heating and cooling processes (adapted from [36])

Figure 2.12a shows the purposely designed and built experimental apparatus. Figure 2.12b shows that the centre of the detector (Thales Pixium RF4343) was off-set to the X-ray beam by 205.36 mm to increase the available Q range. The X-ray beam centre and Q-calibration on the detector was determined using a cerium oxide diffraction standard.



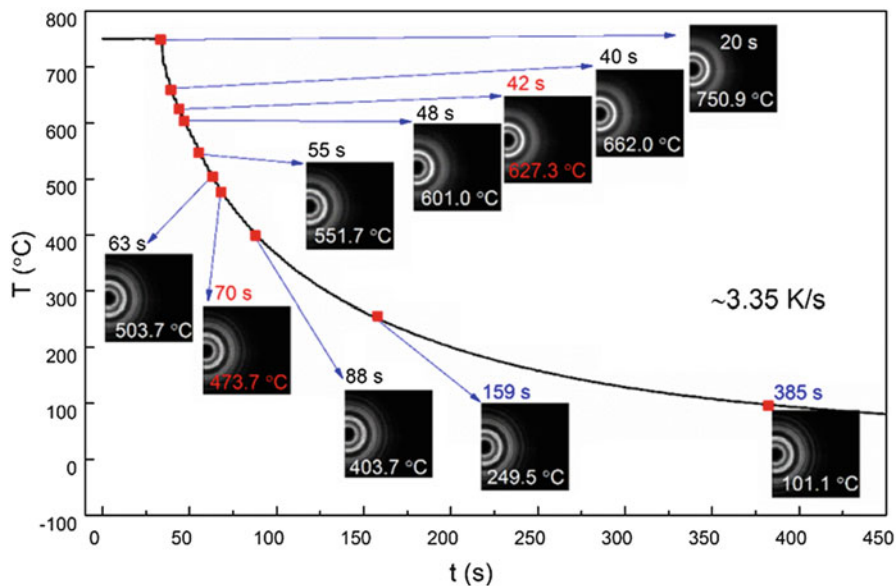


**Fig. 2.13** The temperature profile with an average cooling rate of 3.35 K/s. The diffraction patterns taken at the critical phase transformation temperature were superimposed on the curve. The temperatures marked in red denote the critical temperature during crystallisation [36]

The beam centre was at the detector coordinate of (51.5, 1438.8) pixels. The offset configuration ensured that a higher  $Q$  range up to  $\sim 20 \text{ \AA}^{-1}$  was achieved using a monochromatic X-ray beam ( $500 \times 500 \text{ \mu m}$ ) of 75.37 keV. The temperature recording from the I12 data logging system was synchronised with the diffraction pattern acquisition, and diffraction patterns were acquired in situ continually at 1 pattern per second (the exposure time was 0.5 s) during the heating and cooling processes. Hence, the temperature information was embedded into the acquired diffraction dataset simultaneously.

Figure 2.13 shows a temperature profile and the corresponding diffraction patterns taken at every second (the patterns shown in the figure are those at the critical temperatures). In this case, the average cooling rate was 3.35 K/s from the supercooled liquid. In total, there were 550 diffraction patterns. A robust procedure was developed to analyse this large dataset systematically and consistently [36]. The 2D patterns were converted into 1D scattering intensity spectra,  $I(Q)$ , and stacked together as shown in Fig. 2.14a. PDFgetX3 was used to obtain the total structural factor  $S(Q)$  and then the reduced pair distribution function (PDF),  $G(r)$  by Fourier transformation of  $S(Q)$  with  $Q_{\text{max}} = 16 \text{ \AA}^{-1}$  as the  $Q$ -cutoff value. PDFgetX3 uses an ad hoc data reduction algorithm that allows the calculations of PDFs to be executed in an automatic manner, especially suitable for batch-processing of many hundreds of PDFs with a single set of input parameters (no or very few manual inputs). It has

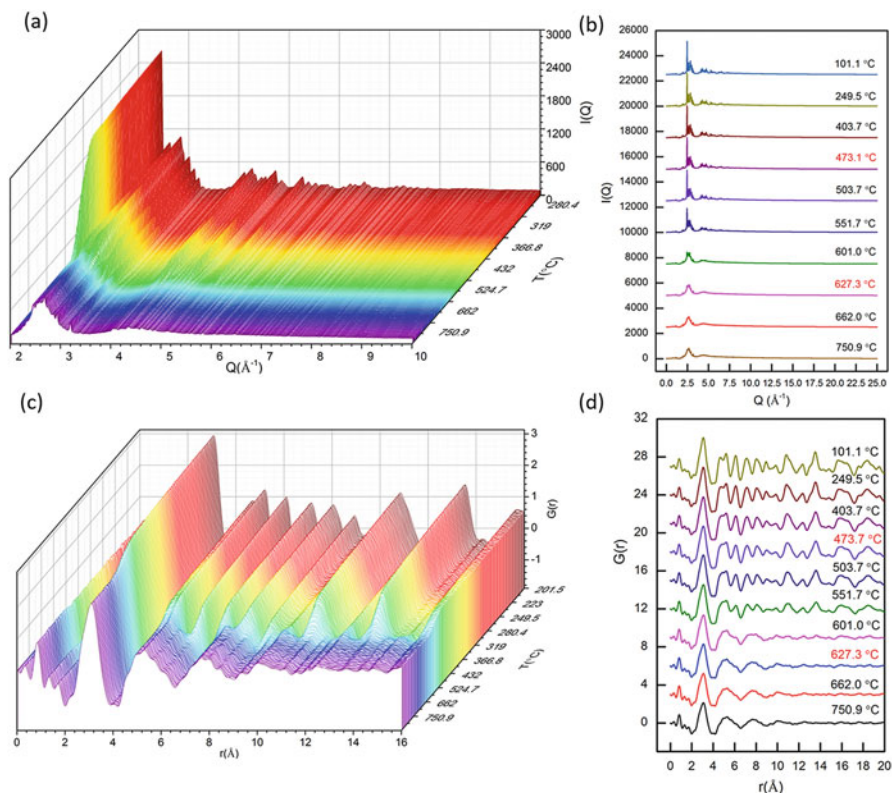


**Fig. 2.14** Evolution of (a) the diffraction spectra (Video 2.14a is included here to demonstrate the dynamics of structure evolution in the process) and (c) pair distribution functions (PDFs) as a function of temperature; (b) the diffraction spectra acquired, and (d) the corresponding PDFs for the Vit1 alloy at some critical temperatures during cooling with an average cooling rate of 3.35 K/s, the curves are stacked with an equal spacing of 2500 counts in y direction for (b), and 3 for (d) (adapted from [36])

been proven to be a useful tool for high-throughput studies and time-resolved experiments [36].

Figure 2.14a and c show that crystallisation directly from a supercooled liquid at slow cooling is different from the crystallisation induced by annealing. In the case of cooling at 3.35 K/s from the supercooled liquid, clear crystallisation events were observed, which is a rather slow process (21 s), developing over a relatively wide temperature range (from 627.3 to 473.1  $^{\circ}\text{C}$  as shown in Fig. 2.14b). The onset of crystallisation and the dynamic nature of structure evolution in the process can be seen more vividly in the accompanying video 2.14a.

Figure 2.14 also shows evolution of the PDFs and their peak intensity with decreasing temperature. Firstly, a rapid increase of PDF peak intensity was observed for all PDFs during solidification when temperature decreased from 627.3 to



503.7 °C, then the rate of increase slowed below 503.7 °C. This phenomenon indicates that the ordered crystalline structure is not stable just below 503.7 °C, and the atomic structure continues to reconfigure into an even more ordered structure during the cooling to room temperature. Detailed analyses of partial PDFs by the real space refinement method for individual atomic pairs were also made [36] to elucidate the role of different atomic pair on the amorphous–crystalline change versus temperature. Interested readers are referred to the relevant chapters in [36].

Clearly, X-ray total scattering is a powerful tool for acquiring atomic structure information, especially for amorphous materials [36].

### ***2.2.3 In Situ Studies of Liquid Metal Flow and Semi-Solid Deformation by X-Ray Radiography***

In the 1990s and early 2000s, Professor John Campbell's Casting Research Group at the University of Birmingham, UK was among the first in the world to use real-time X-ray video radiography to study liquid metal flow during mould filling processes with a focus on investigating the entrainments of air bubbles and oxide films, as well as the formation of casting defects. In his PhD project in the period of 1999–2002, Mi [16–18] studied the tilt casting process. He designed and built a computer-controlled rollover casting wheel to perform the tilt pouring of Al alloys, and later applied this practice to TiAl alloys [17]. Real-time X-ray video radiography was used to study mould filling sequences with different tilting speeds and to search for optimal parameters for achieving tranquil mould filling in casting. The liquid metal flow sequences observed and recorded by X-ray were compared with the flow sequences simulated by using the Flow-3D computational fluid dynamics code [18].

Figure 2.15 shows typical image frames selected from the X-ray videos of mould filling sequences made using a tilting speed of 14°/s and 43°/s, respectively. The real-time X-ray video sequences demonstrated that that even modest free surface turbulence involving merely contraction of the liquid metal surface appears to be capable of entraining double oxides that would act as crack initiation sites in castings, which significantly reduce the reliability of the strength properties of castings. More severe free surface turbulence entrains air and lead to bubble damage. The liquid metal flow in the mould filling process can be simulated adequately using Flow-3D. The area of free surface film that is available to be entrained into castings during filling can be calculated and used as a criterion to assess the quantity of surface film entrainment. The entrained surface films are responsible for much of the scatter in the mechanical properties and impair the reliability of castings. A mould filling free from surface turbulence and any contraction of the surface is essential for the production of reliable castings [18].

In approximately the same period of time, Lee and Hunt [37] developed a small-scale X-ray temperature-gradient stage to observe directly the evolution of hydrogen

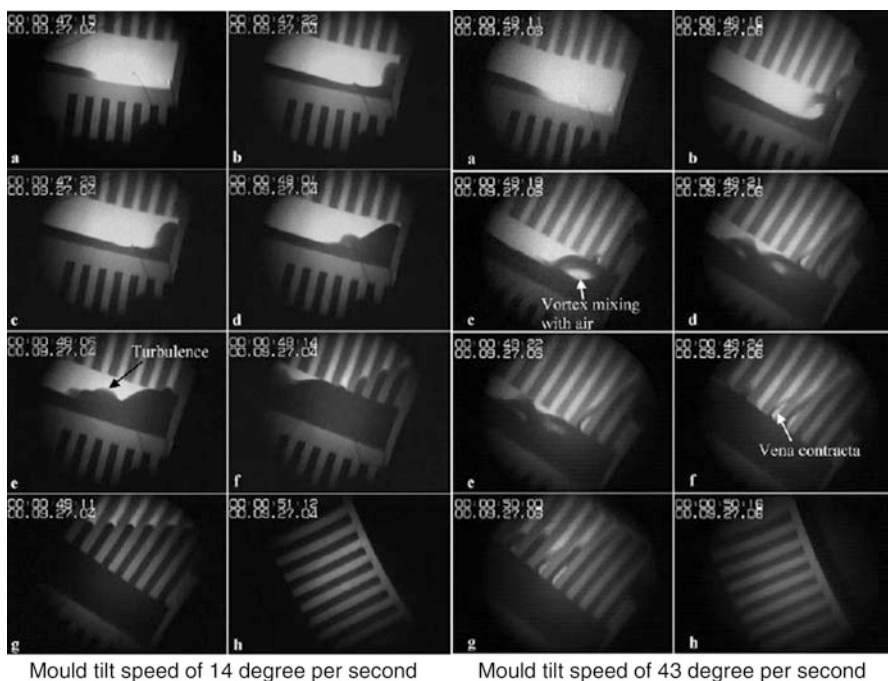


**Fig. 2.15** The typical image frames selected from the X-ray radiography videos taken during mould filling sequences of tilt pouring a liquid Al–4.5% Cu alloy into a sand mould with 10 test bar cavities (10-mm diameter cylinder type cavities for making test bars). The 8 frames on the left show the mould filling sequence of a tilt speed of 14 deg/s. Surface turbulence (showing in frame d, e) was found in the filling process in this case, but no air bubble entrainment into the test bar cavities. The 8 frames on the right show the mould filling sequence of a tilting speed of 43 deg/s. Strong flow turbulence was observed with air bubbles entrained into the test bar cavities (adapted from [18])

porosity formed in an Al–Cu alloy as a function of time during solidification. The size, distribution, and morphological evolution of hydrogen porosity and pores were observed and measured as a function of temperature and time [37]. Later in 2001, Lee developed a diffusion-controlled pore growth model to simulate the formation of porosity during solidification. The modelled results were compared with the predicted development of the porosity, including the distribution in size and morphology. The simulation agreed well with the observed experimental results [38]. The model predictions and experimental results support the hypothesis that the effect of hydrogen and its diffusion must be incorporated into any accurate model of pore formation in aluminium alloys [38].

In 2011, Phillion et al. [28] in Lee's group used a bespoke high-temperature tensile tester and synchrotron X-ray radiography (Fig. 2.16) to study the semi-solid deformation of an Al–12 wt.% Cu over a range of solid fraction from 0.35 to 0.98. Figure 2.17 shows the typical radiograph obtained in the experiments [28]. They

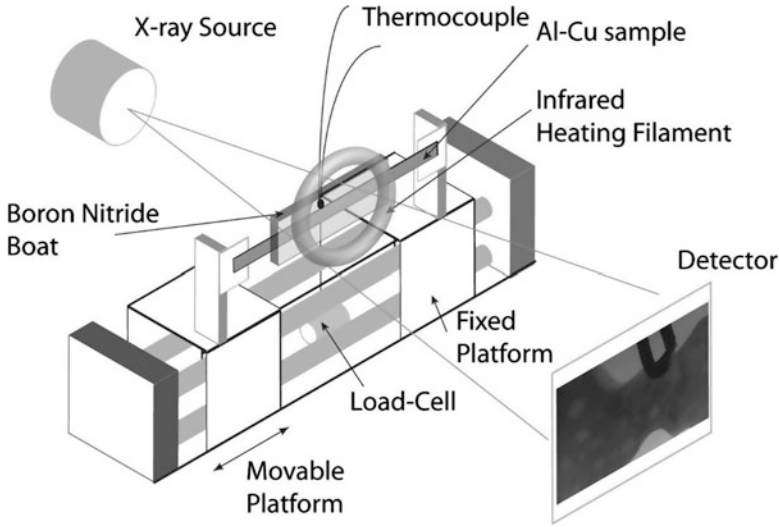


**Fig. 2.16** A schematic of the semi-solid deformation apparatus for in-situ X-ray radiography experiments

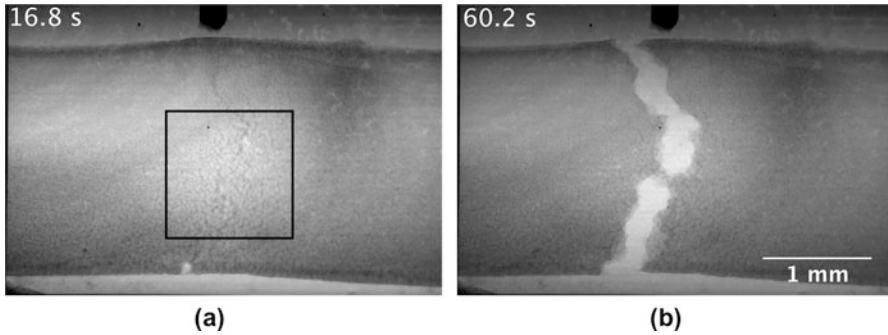


**Fig. 2.17** X-ray radiography images of the (a) initial and (b) final configurations of strain localisation and specimen failure during isothermal tensile deformation of a semi-solid Al–12 wt. % Cu at 580 °C ( $f_s \sim 0.62$ ). The scale is shown in (b), whereas the elapsed time is indicated in the upper left-hand corner of each image. The pulling direction is horizontal and towards the left (adapted from [28])

found that during deformation at low and moderate fraction solids, the X-ray radiographs indicate that there is significant feeding of interdendritic liquid in the region of strain localisation prior to crack formation. Furthermore, the measured load required to initiate localised tensile deformation was found to be similar over the range of fraction solid 0.35–0.66. At higher fraction solids, the radiographic observations are consistent with classical hot tearing behaviour: firstly, limited liquid flow due to low permeability, then void nucleation and coalescence, and finally failure.

Based on the observations, they proposed a three-stage mechanism [28] for semi-solid failure for the range of fraction solid between 0.35 and 0.66: stage (1): strain localisation and flow of liquid towards this location; stage (2): semi-solid necking in combination with damage nucleation and growth; and stage (3): formation of micronecks, and final fracture.

### ***2.2.4 In Situ Studies of Dendritic Grain Growth and Fragmentation by X-Ray Radiography***

In 1999, Mathiesen and Arnberg [15] of the Norwegian University of Science and Technology started the pioneering work of using coherent and monochromatic synchrotron X-rays available at the beamlines ID22 and ID18 of ESRF to study in situ cellular and dendritic solidification of metal alloys [15]. The spatial and temporal resolutions achieved at that time were  $\sim 2.5\ \mu\text{m}$  and  $\sim 0.7\ \text{s}$ , respectively, in a field of view of up to  $1\ \text{mm}^2$ . Figure 2.18 shows the growing columnar dendrites of Sn crystals in a Sn–10 wt.% Pb alloy, and the growing equiaxed dendrites of Pb crystals in a Sn–52 wt.% Pb alloy captured in the experiments [15]. Since then, worldwide research on using synchrotron X-rays to study the solidification processes has grown rapidly.

Later in 2005, Mathiesen and Arnberg [19] studied in situ the columnar dendritic and eutectic growth of an Al–30 wt.% Cu under directional solidification. The nominal spatial and temporal resolutions achieved in those experiments were of  $1.4\ \mu\text{m}$  and  $150\ \text{ms}$ , respectively. The images were processed to reveal spatiotemporal coordinates of the solid–liquid phase fronts for both  $\alpha$ -dendrites and the proceeding eutectic (see the images in the left column of Fig. 2.19). Also, local solute boundary layers ahead of, and in the mushy zone were extracted from image processing. In the experiments, they found that steady-state growth could not be

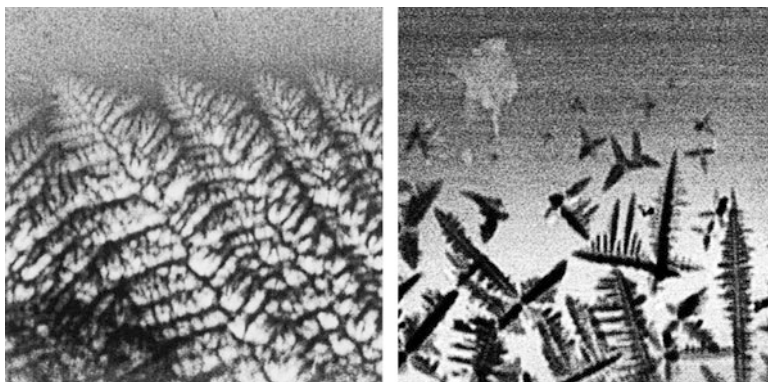


**Fig. 2.18** A typical snapshot of the growing columnar dendrites of Sn crystals in a Sn–10 wt.% Pb alloy (left); and the growing equiaxed dendrites of Pb crystals in a Sn–52 wt.% Pb alloy (adapted from [15])

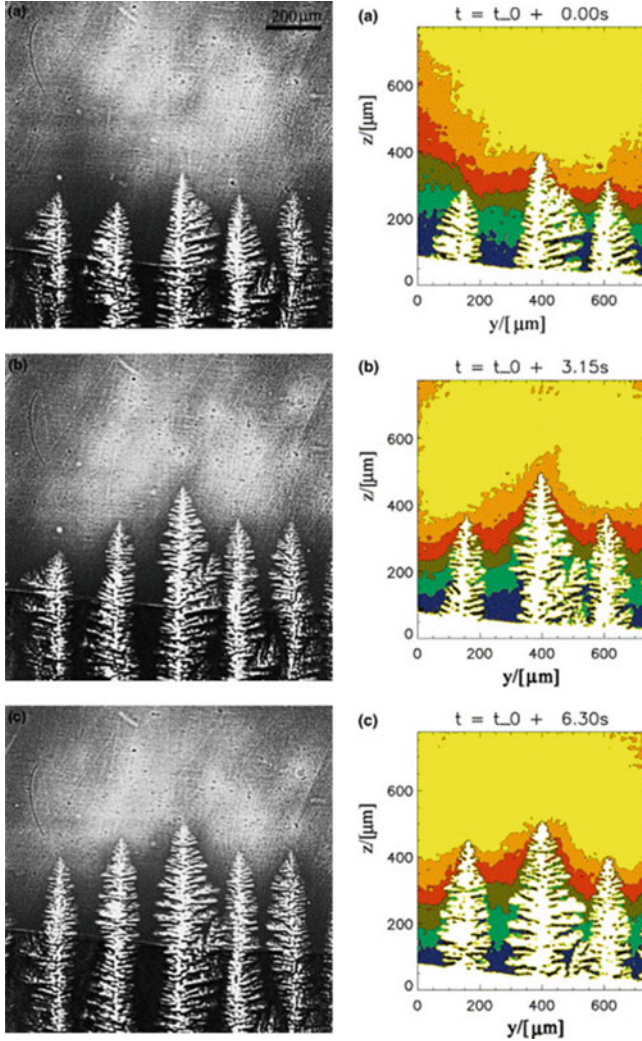


**Fig. 2.19** Left column: the growing columnar dendrites in an Al-30 wt.% Cu alloy. Right column: the mushy zone liquid constitution contour plots. Solid regions are white, liquid contours start at 33 wt.% Cu (black) with increments of 0.5 wt.% Cu (corresponding roughly to a  $2.3\sigma$  contouring) to the liquid region of 30 wt.% Cu. The primary arms shown here are the top parts of Nos. 2–4 dendrites (count from left) on the left column (adapted from [19])

realised. Possibly because of a combination of: (a) insufficient time available for initial instabilities to evolve into a steady state; (b) interaction of primary  $\alpha$ -branches through solute diffusion in the confined sample volume; (c) inevitable presence of thermo-solutal flow; and (d) a long-term sample position dependent drift in the furnace to sample heat transfers. However, the experiments at that time demonstrated that the advances in X-ray sources and detector systems make it possible to achieve



high-resolution, fast acquisition radiographic imaging of evolving solidification microstructures and local liquid constitutions in metal alloys. Subsequent image analysis is able to extract morphology and velocity of the solid–liquid interface as well as the constitutional supercooling at the tip of growing crystals. Certainly, the data collected contain information that are highly valuable for microstructure modelling of dendritic growth.

In 2017, Mathiesen and co-workers [39] studied in situ the morphology and growth of primary  $\alpha$ -Al(FeMnCr)Si intermetallics during solidification of a commercial secondary Al alloy using a lab-based X-radiography facility. The  $\alpha$ -Al(FeMnCr)Si intermetallics were found to nucleate primarily on surface oxides, and the continued growth yielded both rhombic dodecahedrons and elongated rod-like morphologies. Both morphologies were observed as hopper and massive types, where the hopper intermetallics had the higher growth rates. The growth rate, which determines the type, appears to be linked to nucleation frequency; higher nucleation frequency promoted massive types and lower nucleation frequency promoted hopper intermetallics [39].

Furthermore, in 2017, they did a comprehensive study on the heterogeneous nucleation and grain growth of Al–10 wt.% Cu alloys inoculated with Al-5Ti-1B [40]. The kinetics of heterogeneous nucleation and grain growth under the influence of cooling rate, and addition level of inoculant particles has been quantitatively studied. Figure 2.20 shows the selected grains formed during the solidification of

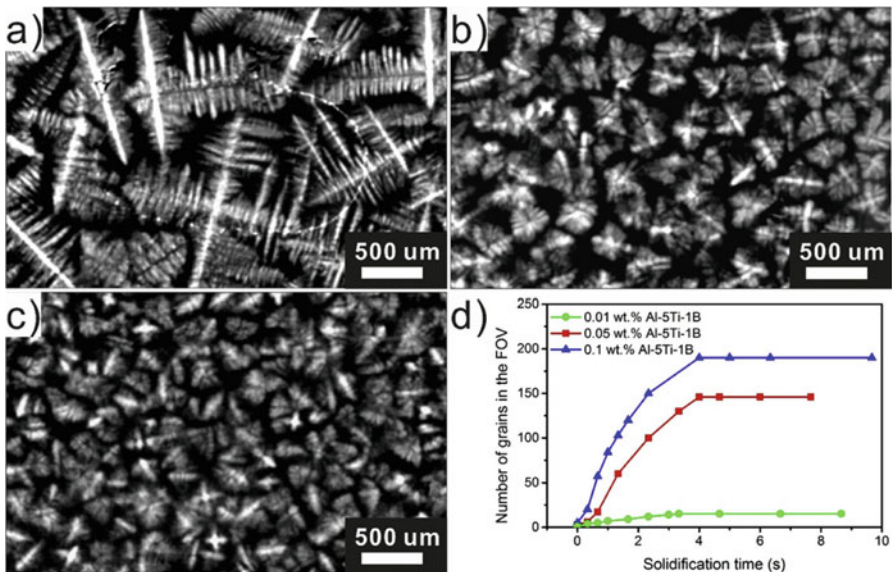


**Fig. 2.20** The selected X-radiography images collected during solidification of an Al–10 wt.% Cu alloy with different addition level of Al-5Ti-1B, (a) 0.01, (b) 0.05, and (c) 0.1 wt.% with 0.5 K/s cooling rate and (d) the corresponding evolution of the total number of grains in the FOV as a function of solidification time (adapted from [40])

Al–10 wt.% Cu alloys with different addition of Al–5Ti–1B. From the in situ X-radiography experiments, they found that high cooling rate and high inoculation level promote heterogeneous nucleation and therefore fine equiaxed grain structures. In the early stage of nucleation when undercooling in the melt is small, number density of nucleated grains is dominated by the available potent inoculant particles and undercooling in the melt. At higher undercoolings, number density of nucleated grains is dominated by the thickness of the SSN zones. The experimental results also confirm that the nucleation process of grains under recalescence-free solidification conditions stops due to the solute segregation stifling mechanism. Novel image processing and analysis approaches have been proposed and evaluated for quantitative determination of the volume fraction of grains at nucleation cessation and maximum nucleation undercooling. It shows that both the maximum nucleation undercooling and solid volume fraction at nucleation ceasing increase with increasing cooling rate but decrease with addition level of inoculation particles [40].

Researchers in Henri Nguyen-Thi group at Aix-Marseille University & CNRS, Marseille, France have also done systematic work in situ observation of solidification patterns [41, 42]. In 2011, Bogno et al. [43] used synchrotron X-ray radiography to study convection effects on the dynamic evolution of solid–liquid interface and on solute distribution during the initial transient of solidification. In situ monitoring of the initial transient of directional solidification was carried out using an Al–4 wt.% Cu alloy on beamline ID19 of the ESRF.

X-ray radiography is able to “see” solid–liquid interface evolution over time and macroscopic shape interaction with convection in the melt (Fig. 2.21). Lateral solute segregation induced by fluid flow resulted in a significant deformation of the solid–liquid interface. From the experiments, time-dependent velocity of the solidification

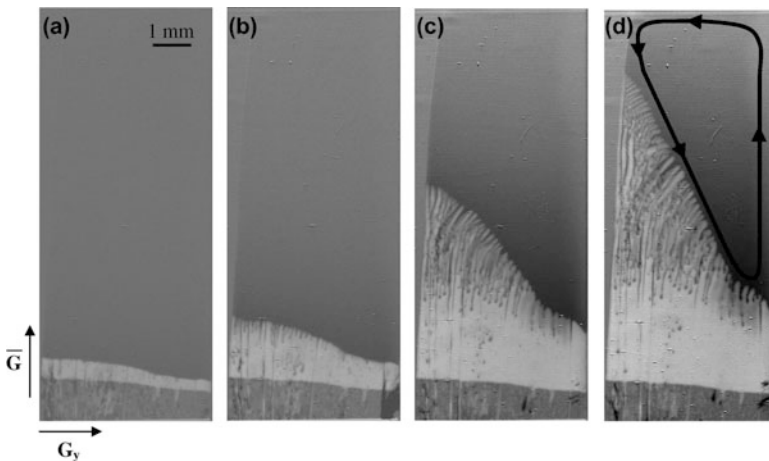


**Fig. 2.21** Four images show increasing macroscopic deformation of the solid–liquid interface during the initial transient of directional solidification of Al–4 wt.% Cu alloy ( $R_H = R_C = 0.3 \text{ K min}^{-1}$ ,  $G = 35.5 \text{ K cm}^{-1}$ ). (a)  $t \approx 17 \text{ min}$ ; (b)  $t \approx 34 \text{ min}$ ; (c)  $t \approx 70 \text{ min}$ ; and (d)  $t \approx 88 \text{ min}$  (adapted from [43])

front was determined at different abscissa values along the curved interface during the solidification process, from the growing phase with a smooth interface to the onset of morphological instability. Furthermore, using a novel quantitative image analysis technique, the longitudinal solute profiles in the melt during the initial transient were measured. Solutal length was then deduced as well as concentration in the melt, both at the interface and far away from it. Solute profiles measured in the liquid channels formed by convection are found to be linear, which suggests that the liquid tends to follow the local thermodynamic equilibrium in the channels.

In 2013, Bogno et al. studied the growth and interaction of dendritic equiaxed grains in situ [44]. Al–10 wt.% Cu alloys were used and the experiments were again at ESRF. Equiaxed solidification was achieved by cooling samples in a nearly isothermal condition, and the growth of the grains was continuously monitored from the very early stages of solidification up to a state where changes in grain structure were no longer visible to the observer's naked eye. Typical video frames extracted from the videos are shown in Figs. 2.22 and 2.23. Time evolution of the individual equiaxed grains is analysed through measurements of the lengths and tip velocities of the primary dendrite arms driving grain growth. Equiaxed dendrite propagation was found to be characterised by two growth regimes. The first regime, in which a gradual increase in the tip growth rate is observed, corresponds to free dendritic growth, where the distance between grains is large enough; and grains are considered as isolated individuals. In this regime, the far-field liquid concentration ahead of the advancing dendrite tip remains constant, equal to the initial alloy composition, and the driving force for growth is the undercooling applied by cooling of the sample, in agreement with three-dimensional models of free dendritic growth. The second regime shows a decrease in the tip velocity towards zero, and is attributed to grain interaction when the solute diffusion field in front of the advancing dendrite tip under consideration overlaps with the solute field of other nearby grains. Solute concentration profiles were measured in the liquid ahead of dendrite tips interacting with neighbouring grains, from which the far-field solute concentration and neighbour–interaction distance were deduced. These measurements confirm that impingement of the solute boundary layers is the main cause of dendrite growth slowing down and cessation. The measured solute-concentration profiles ahead of growing dendrites are characterised by the neighbour–interaction distance  $d_\infty$ , at which the minimum solute concentration  $C_\infty$  is found. The end of the accelerating regime is marked by the start of increase in  $C_\infty$  above initial solute concentration, which then drives and controls the deceleration of dendrite arm growth until cessation.

Similar research was also carried out in Japan using the Spring-8. For example, in 2011, Gourlay et al. studied the unidirectional solidification of two Pb-free solder alloys, i.e. Sn–0.7Cu and Sn–0.7Cu–0.06Ni alloys. The synchrotron X-ray radiography experiment was conducted on beamline BL20XU of the Spring-8 in Hyogo, Japan with an undulator source and X-ray energy of 18 keV [45]. They studied the morphology of growing Sn–Cu<sub>6</sub>Sn<sub>5</sub> eutectic front and its reaction to changes in growth velocity and cavity shape. They also compared the invariant and univariant



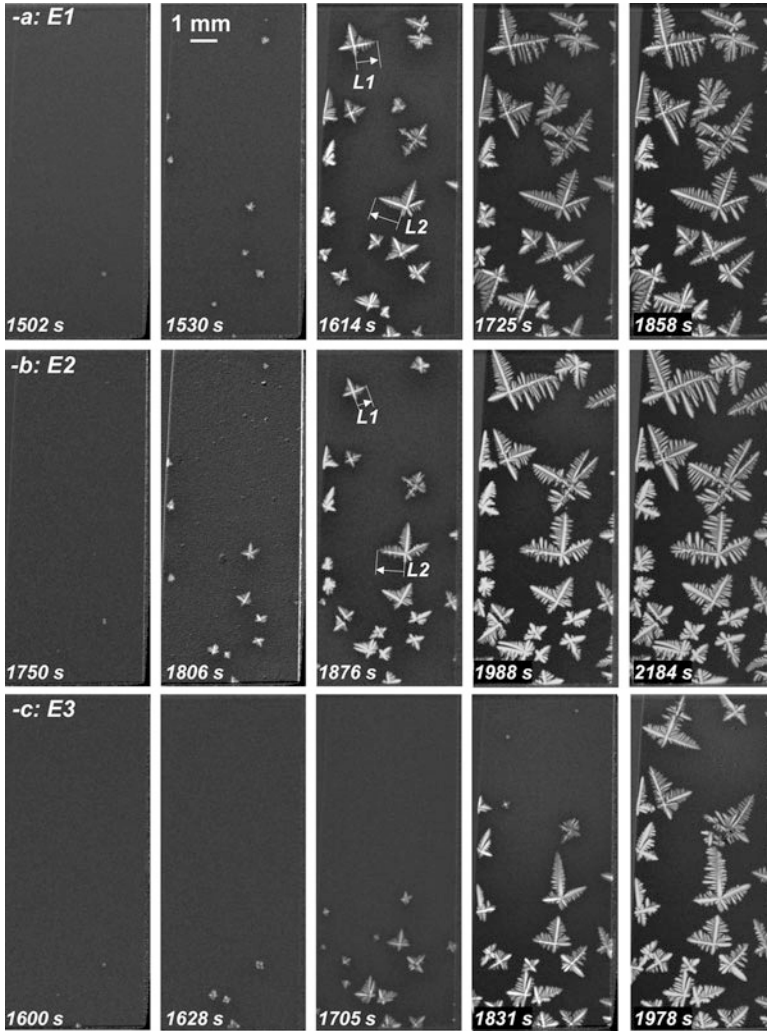


**Fig. 2.22** Sequences of in situ synchrotron X-ray radiographs, showing equiaxed microstructure formation in an Al–10 wt.% Cu in three solidification experiments: (a) E1; (b) E2; and (c) E3. Each image is tagged with the time (since cooling started) at which it was recorded (cooling rate  $R = 0.5 \text{ K min}^{-1}$ ) (adapted from [44])

eutectic growth fronts; and deduced the solidification sequence of Sn–0.7Cu–0.06Ni.

In Mi's group in the past 8 years or so, research has concentrated on studying metal solidification processes under external physical fields, e.g. ultrasonic waves and pulse magnetic fields. They [21–24] have used the ultrafast synchrotron X-ray imaging (up to 271,554 frames per second) technique available at the Advanced

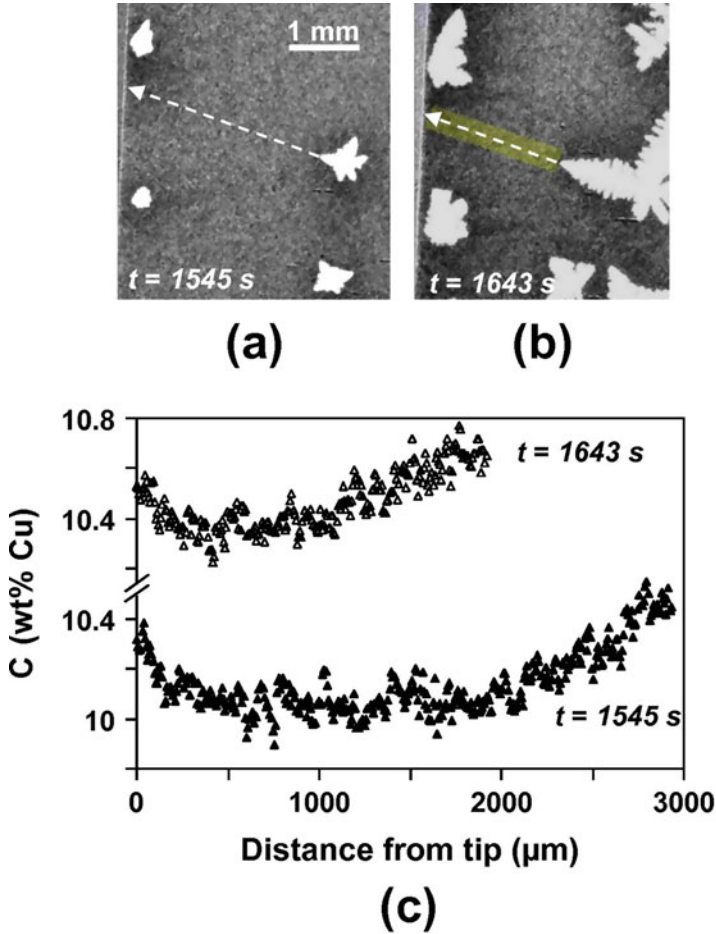


**Fig. 2.23** (a, b) Close-up on interaction of dendrite arm L2 with its neighbourhood in experiment E1. (c) Evolution with time of the solute concentration profile in the melt ahead of the tip of L2. Al-10 wt.% Cu,  $R = 0.5 \text{ K min}^{-1}$  (adapted from [44])

Photon Source, USA and the high speed imaging capabilities at Diamond Light Source, UK, ESRF and SOLEIL, France, and Swiss Light Source to investigate the dynamic interactions between ultrasonic bubbles/acoustic flow and solidifying phases in Bi-8% Zn, Sn-30wt% Cu, Al-15% Cu and Al-35% Cu alloys. The experimental apparatus is shown in Fig. 2.24. From the experiments, chaotic bubble implosion and dynamic bubble oscillations were revealed in situ for the first time in liquid metal and semi-solid metal. The fragmentation of solidifying Zn [24] and  $\text{Al}_2\text{Cu}$  [23] intermetallic phases and break up of liquid-solid interface by ultrasonic bubbles and enhanced acoustic flow [21, 22, 24] were also clearly captured. This research provides unambiguous experimental evidence and robust theoretical interpretation in elucidating the dominant mechanisms of microstructure

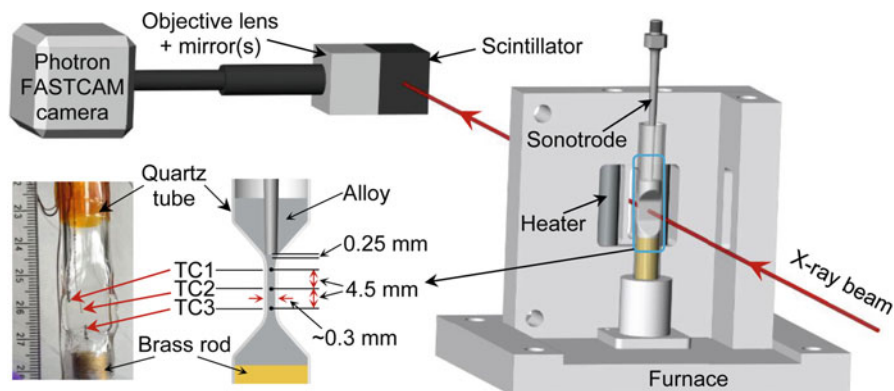


**Fig. 2.24** An illustration of the experimental set-up at the 32-ID-B of APS. A specially designed and built furnace (the front part was open to show the sample holder) was used for sample heating. A purposely made quartz tube with a thin channel of 0.3 mm thickness (bottom left) was used to contain the liquid metal where X-ray images were taken. The sonotrode tip was positioned 0.25 mm above the thin channel; three K-type thermocouples (TC1, TC2, and TC3) were positioned at the top, middle, and bottom of the thin channel to measure temperatures of the liquid metal during solidification (adapted from [24])

fragmentation and refinement in solidification under ultrasound. Figure 2.25 gives some highlighted images and the corresponding videos of the findings. The accompanying videos demonstrated more clearly and vividly the highly dynamic phenomena of chaotic bubble implosion, dynamic bubble oscillations and acoustic enhanced metal flow in the solidifying melts. Interested readers are referred to more images and videos and the theoretical interpretation in [21–24].

### 2.2.5 *In Situ Studies of Dendrites and Intermetallic Phases by X-Ray Tomography*

In recent years, extensive research has been carried out worldwide on time-evolved 3D interfacial morphologies of dendrites and intermetallic phases. The recent results and highlight are briefly described and reviewed in this section.

In 2009, Limodin et al. [46] used synchrotron fast X-ray microtomography and the experimental set-up shown in Fig. 2.26 to study in situ and in real time the microstructural evolution of an Al–Cu alloy during solidification at a constant cooling rate of  $3 \text{ K min}^{-1}$ . The evolution of dendritic microstructure with solidification time was fully characterised in a volume of  $0.3 \text{ mm}^3$  with a spatial resolution of  $2.8 \text{ }\mu\text{m}$ . The solid fraction, specific surface area of the solid–liquid interface, and distribution of local curvature were measured and analysed as typically shown in Fig. 2.27. In addition to solidification growth, at least two coarsening mechanisms were observed to act upon the dendrite arms. The first mechanism involves remelting

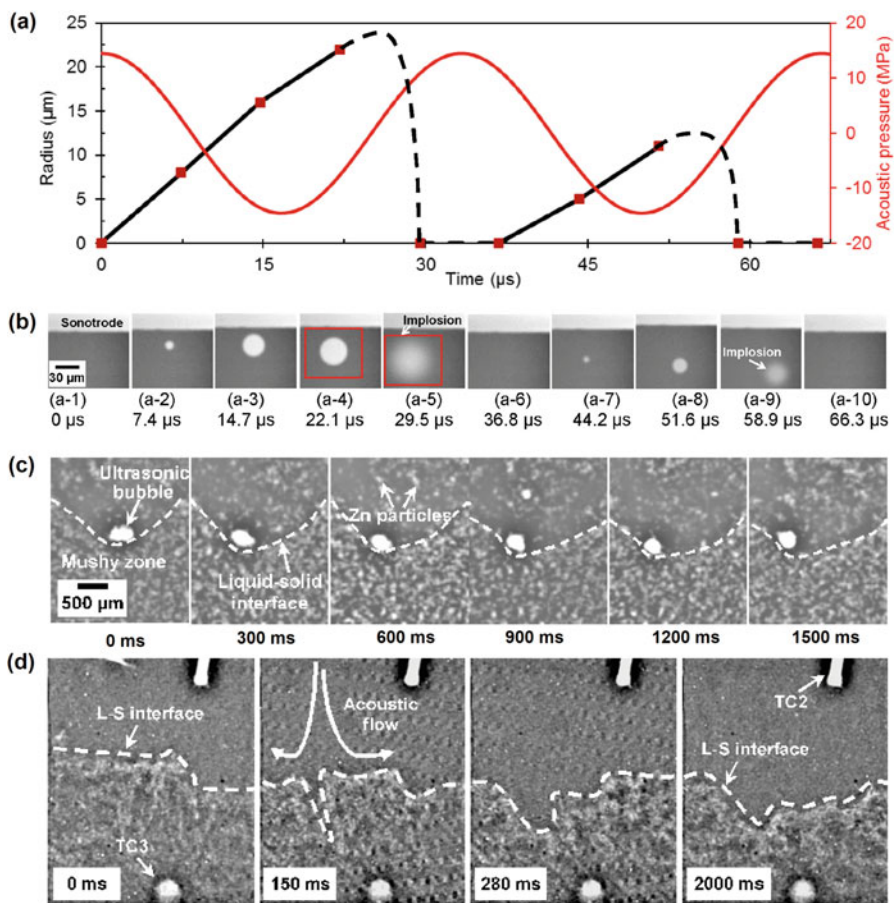


**Fig. 2.25** Selections of the typical X-ray video frames from [24], demonstrating (a) the ultrasound pressure wave of 30 kHz, (b) bubble radius evolution, implosion and shock wave emission driven by the ultrasonic pressure wave shown in Fig. 2.25a (see video 2.25b), (c) a single bubble pulsating at the liquid-solid interface (see video 2.25c), and (d) the impact of an acoustic enhanced metal flow on a liquid-solid interface (see video 2.25d)

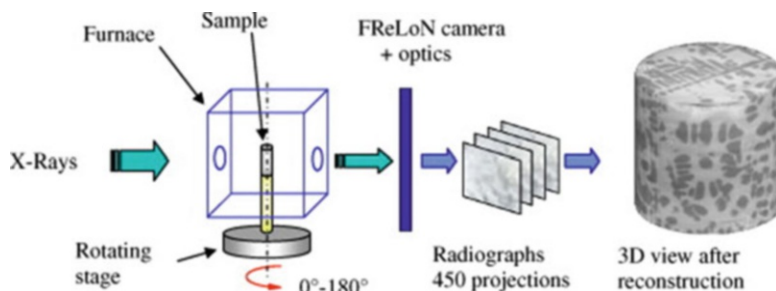


**Fig. 2.26** A schematic diagram of the set-up for in-situ synchrotron X-ray tomography experiments (adapted from [46])

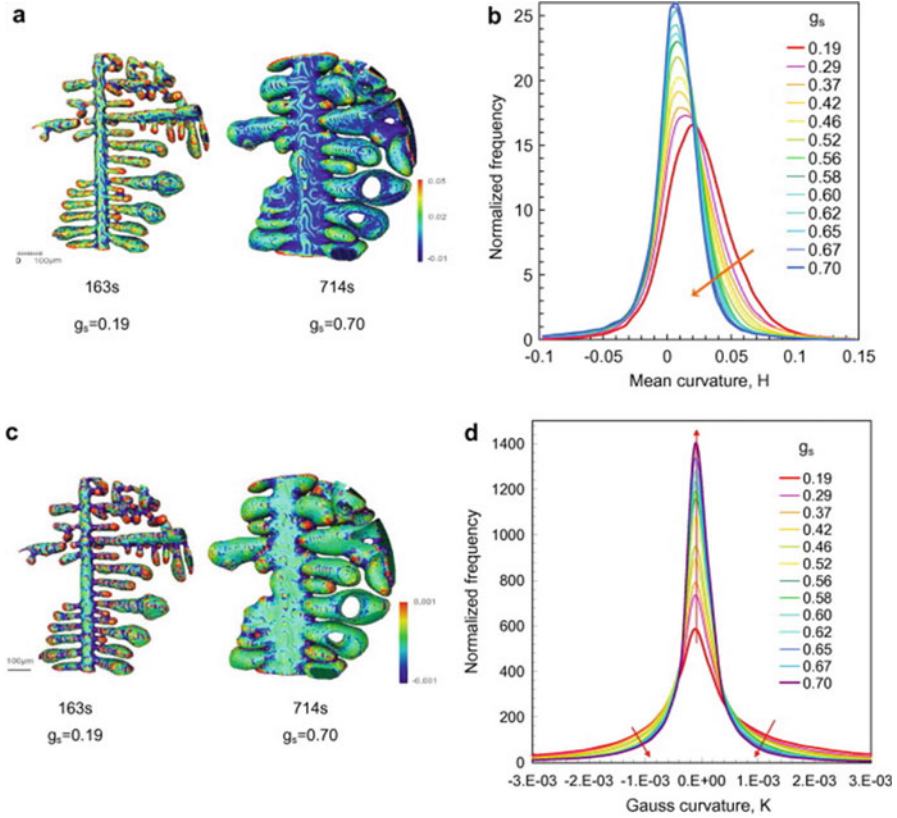


**Fig. 2.27** Mean (a, b) and Gauss curvature (c, d) of the dendrite and their distributions with increasing solid fraction (adapted from [46])

of small secondary dendrite arms to the benefit of bigger adjacent arms. The second is the coalescence of adjacent secondary arms, with progressive filling of the inter-arm spacing and coalescence at the tips. Although this mechanism preferentially occurs at high solid fractions, these results show that the evolution of the dendritic microstructure during solidification is complex and involves various mechanisms operating concurrently. In situ X-ray tomography thus allows the various models which have been proposed to account for dendrite coarsening during solidification to be revisited and further clarified [46].

However, the observations reported in this study were carried out at a cooling rate of  $3 \text{ K min}^{-1}$ . It might be interesting to conduct the same solidification experiment at different cooling rates to study the influence of this parameter on the coarsening mechanisms observed. At higher cooling rates, coarsening mechanisms probably have less influence on the dendrite morphology. However, it would be necessary to further reduce the acquisition time of a tomographic scan in order to carry out in situ observations of dendritic solidification at higher cooling rates.



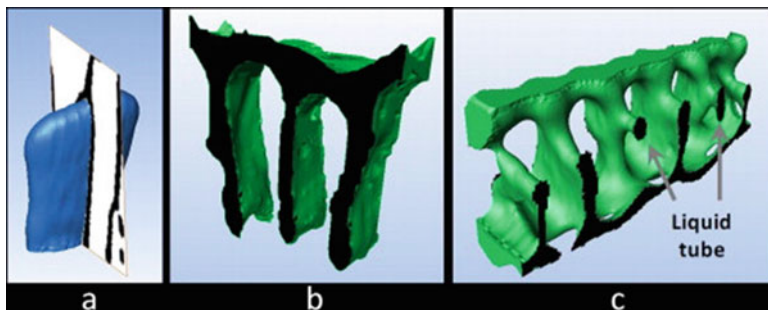


**Fig. 2.28** 3D images showing the detailed geometry considered for different coarsening mechanisms: (a) SAM (3D image of the dendrite arm); (b) IGA (3D image of the liquid); (c) CGA (3D image of the liquid) (adapted from [47])

In 2010, Terzi et al. also investigated the coarsening of dendrites in an Al–10 wt. % Cu alloy at 570 °C by fast in situ X-ray tomography [47]. They found that changes of the specific solid–liquid interface area as a function of time follow a power-law relation with an exponent close to  $-1/4$ . Three coarsening mechanisms (Fig. 2.28) operate in the alloy: (a) melting of small dendrite arms to the benefit of the adjacent arms (small arm melting), similar to Ostwald ripening; (b) gradual movement of the base of the interdendritic grooves towards the tips (interdendritic groove advancement); (c) coalescence of dendrites near the tips leading to the entrapment of liquid tubes or droplets (coalescence and groove advancement). The coarsening models proposed in literatures do not adequately resemble or predict the behaviour observed in the experiments. New models were developed for the first two coarsening mechanisms and predict the coarsening rate with very good agreement [47].

In 2016, Cai et al. [48] investigated the formation of cellular structures, growth, the cellular-to-dendrite transition, and then the established columnar dendrites. The imaging of the cellular growth showed much greater complexity than in prior organic analogue and radiographic studies (Fig. 2.29), where growth is constrained to effectively two dimensions inside a thin channel. Here, the cellular growth structures undulate both vertically and horizontally. The onset of Mullins–Sekerka morphological instabilities were then quantified as the cellular front degenerated, with protrusions forming across the front as the first stage of the transition to dendritic growth.

This transition was both rapid and relatively uniform across the whole front. Interestingly, these protrusions formed both traditional dendrites and seaweed-like structures, with the latter being overgrowth. Through competitive selection, dendrites with favourable orientations aligned with the heat flow direction formed well-developed structures. They also found dendrite fragmentation which was due to the combination of stress induced by buoyancy and the Gibbs–Thomson effect, and the failure accelerated by a transgranular liquation cracking mechanism. The results demonstrate that 4D imaging can provide new data to both inform and validate solidification models.

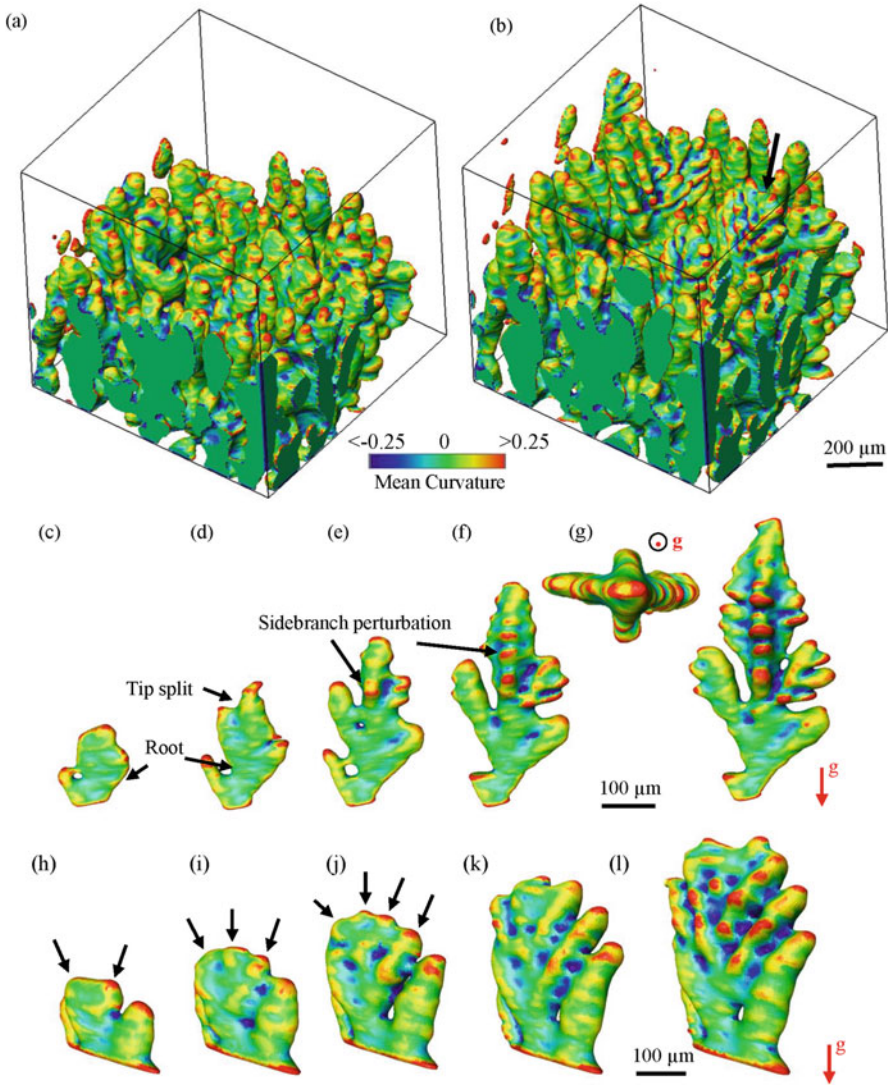


**Fig. 2.29** (a, b) 3D interface morphology evolution coloured by its mean curvature at  $t = 153$  and  $198$  s, respectively; initial growth of (c–g) dendritic structure and (h, i) coralline-like morphology: (h)  $t = 153$  s; (e) and (i)  $t = 162$  s; (d) and (j)  $t = 171$  s; (e) and (k)  $t = 180$  s; (f) and (l)  $t = 189$  s; and (g)  $t = 198$  s (adapted from [48])

In 2016, Shuai et al. [49] also studied the evolution of dendritic microstructures during the solidification (at two cooling rates,  $3$  and  $12$   $^{\circ}\text{C}/\text{min}$ ) of an  $\text{Mg}-15 \text{ wt.}\%$   $\text{Sn}$  alloy in situ via fast synchrotron X-ray microtomography. To enable these in situ observations, a novel encapsulation method was developed and integrated into a fast, pink beam, imaging beamline at Diamond Light Source.

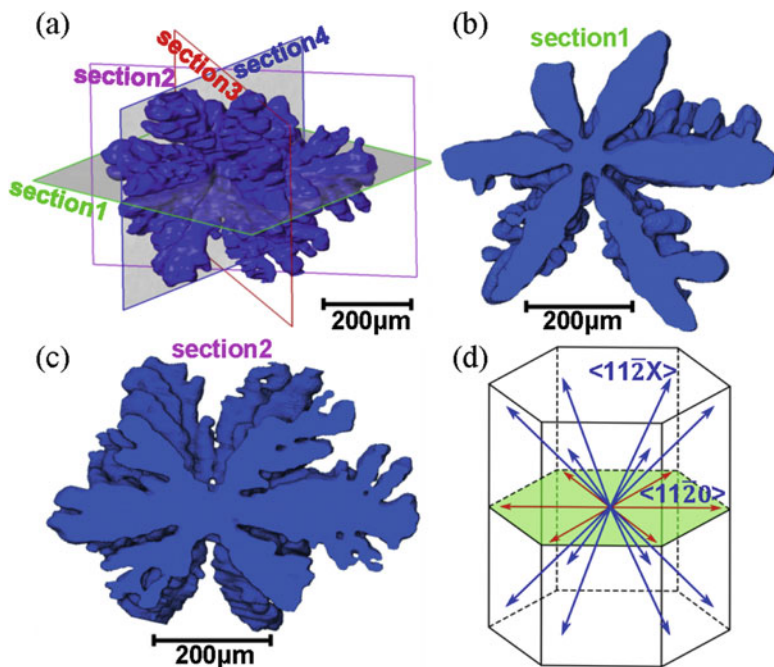


**Fig. 2.30** (a) Morphology and branching structure of an  $\alpha$ -Mg dendrite in a MgSn alloy. Eighteen-branch arm growth pattern with (b) six dendrite arms shown on the basal plane (see cut-plane “section 1” in (a) and red arrows in (d)), and (c) six of the twelve arms at approximately  $48^\circ$  from the basal plane. The twelve arms shown schematically in (d) are hypothesised to grow along a direction of  $\langle 11\bar{2} \rangle$  (between  $\langle 110 \rangle$  and  $\langle 0001 \rangle$ ) (adapted from [49])

These first 4D (3D plus time) observations of a solidifying HCP Mg alloy were quantified in terms of solid fraction, dendrite tip growth velocity, and specific surface area. The measured solid fraction versus temperature was found to correlate well with the Scheil equation. Coarsening accompanied dendritic growth. The specific surface area as a function of fraction solid compared well to the model proposed by Cahn and Rath et al. during the late stage of coarsening, but less well in the initial growth stage, suggesting that a more accurate model is needed to describe the evolution of complicated dendritic structures during the solidification/coarsening process [50].

In 2017, Azeem et al. [51] developed a novel methodology that enables in situ quantification of the microstructures formed during solidification of high-temperature alloys via synchrotron tomography. A bespoke high-temperature environment cell and high X-ray contrast alloys with a novel environmental encapsulation system were also developed. This methodology was demonstrated on Ni, Fe, and Co alloy systems, revealing dendritic pattern formation. The detailed quantification of microstructural pattern evolution in a novel high attenuation contrast Co–Hf alloy is shown in Fig. 2.31, including microstructural patterning and dendrite tip velocity. The images were quantified to provide 4D experimental data of growth and



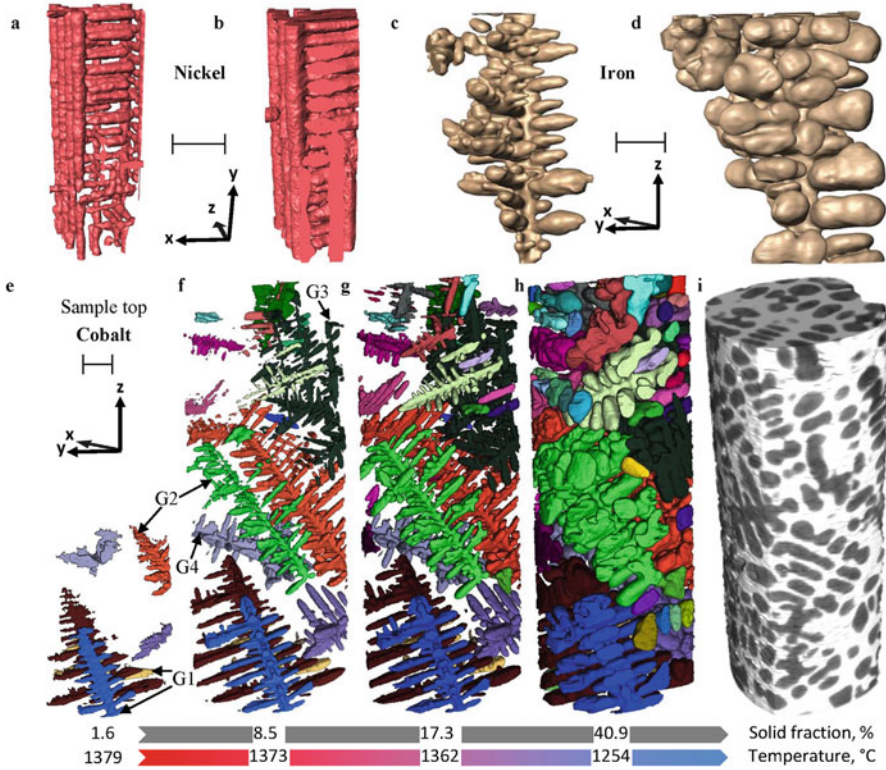


**Fig. 2.31** The 3D evolution of dendritic patterns in Ni-14 wt. % Hf, Fe-11 wt. % Hf, and Co-18 wt. % Hf alloys during solidification at a cooling rate of  $0.05\text{ }^{\circ}\text{C s}^{-1}$ . The interlocking FCC  $\alpha$ -Ni dendritic patterns at 495 and 1496 s after the start of solidification are shown in (a, b), respectively. The development of a single  $\delta$ -Fe pattern during solidification via thickening, coarsening, and coalescence mechanisms captured at 396 and 3960 s is shown in (c, d), respectively. The development of  $\alpha$ -Co patterns during solidification of the Co alloy is shown in (e–h). The corresponding volume fractions and temperatures are provided below each subfigure. (e) is captured at  $\sim 3\text{ }^{\circ}\text{C}$  below the equilibrium liquidus temperature of the alloy and (h) at  $\sim 24\text{ }^{\circ}\text{C}$  above the reported equilibrium eutectic temperature. Raw data of the reconstructed volume corresponding to (h) is shown in (i). Scale bar =  $200\text{ }\mu\text{m}$  (adapted from [51])

coarsening mechanisms in Co alloys, which are used for a range of applications in energy and aerospace industry.

In 2010, Terzi et al. [52] studied in situ the nucleation and growth of irregular  $\beta$ -Al<sub>15</sub>FeSi intermetallic plates during solidification of an Al-8% Si-4% Cu-0.8% Fe alloy. The experiment results show that, after formation of aluminium dendrites, the  $\beta$  phases form as an irregular eutectic together with eutectic  $\alpha$ -Al. Four individual plates were observed to nucleate at a very early stage of the eutectic reaction and subsequently developed into complex connected three-dimensional plates (Fig. 2.32). There is a strong indication that aluminium oxide acted as a nucleant. No heterogeneous nucleation of  $\beta$  phase occurred in the interior of the samples.

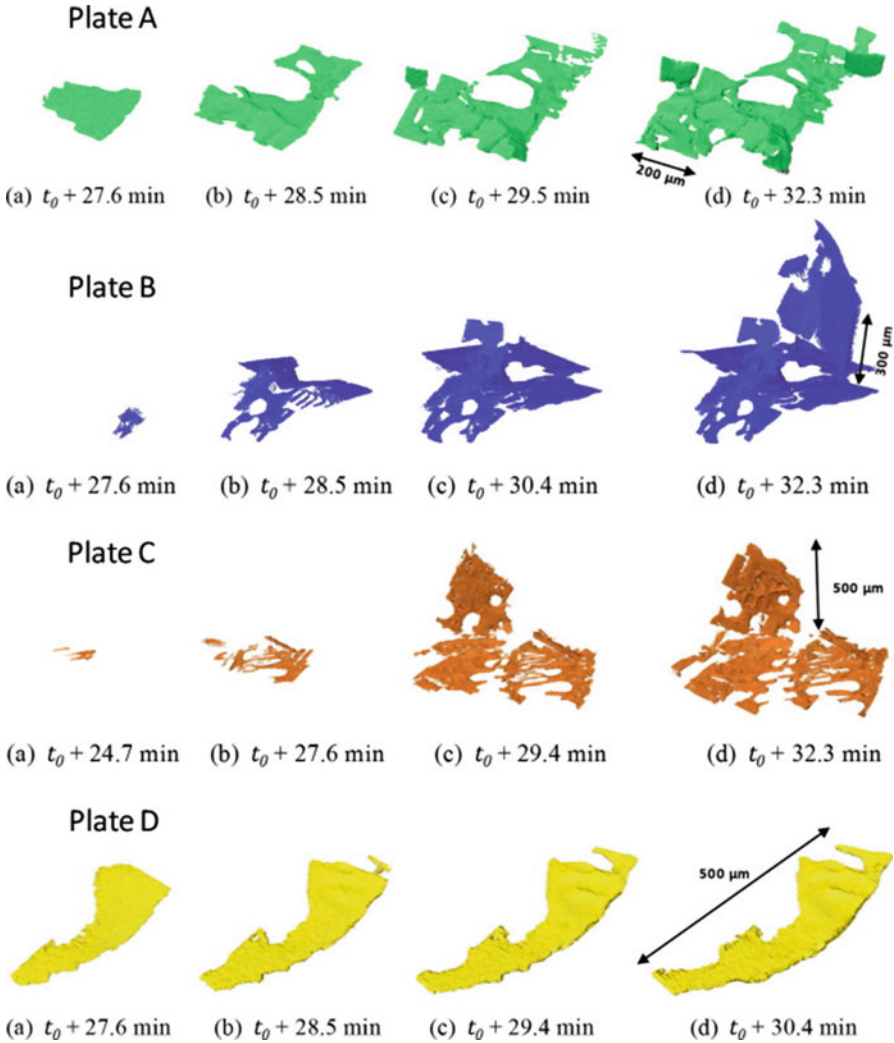


**Fig. 2.32** A series of reconstructed images from the four independently nucleated complex  $\beta$  plates, taken at several time steps during their growth (adapted from [52])

The plates initially grew rapidly in the lateral direction but had a much slower thickening rate. The thickening of the plates is a strong indication that coupling of the eutectic phases is weak, which is further evidenced by the observations of imprints of dendrites and ridges on the surface of  $\beta$  plates. The plates showed complex branching which does not appear to be crystallographically related since a range of branching angles was observed, resulting in very complex interconnected plates. Observations of the growth dynamics in this system suggests that this eutectic is not well represented by the existing models for irregular eutectic growth.

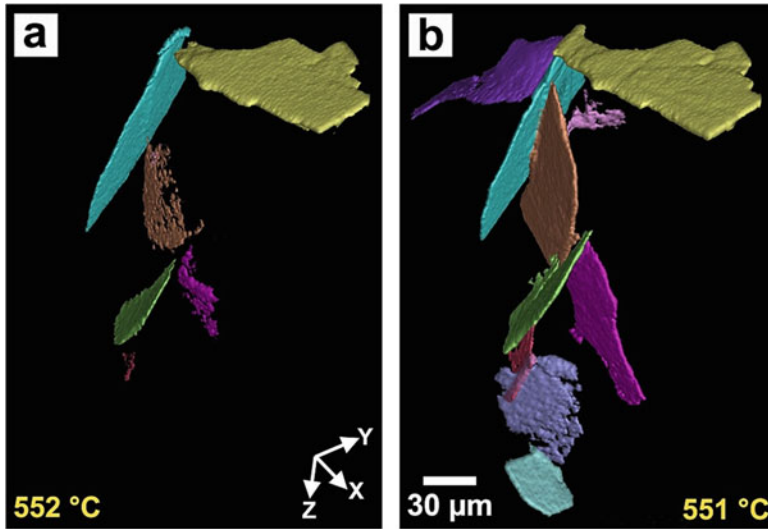


**Fig. 2.33** Formation and growth of independent  $\delta$  plates: (a) Six non-connected plates are visible at 552 °C, (b) at 551 °C four new plates have been added. All plates are interconnected. Each colour corresponds to an individually nucleated plate (adapted from [53])

In 2017, Yu et al [53], investigated formation and evolution of intermetallic  $\delta$  phase in an Al–10Si–0.3Fe alloy in situ by 4D X-ray synchrotron tomography. They found that the nucleation and growth of the  $\delta$  phase is via a “cell” formation mechanism during solidification. Small liquid areas (“cells”) gradually undergo solidification during which  $\delta$  plates nucleate on the cell walls and then grow towards their centre.

At each stage of solidification, new  $\delta$  plates may nucleate and grow. This process repeats itself and is eventually either blocked by another  $\delta$  plate or by newly formed eutectic Al–Si phases. Branched  $\delta$  plates are always observed, but branches are generated only by impingement of plates rather than via a nucleation mechanism in which new  $\delta$  plates nucleate on existing  $\delta$  plates (Fig. 2.33). The critical solute concentration is the key factor for the nucleation of the  $\delta$  phase rather than the potency of the substrate. Nucleation on the eutectic Si is the main cause for growth of the  $\delta$  phase since the solute concentration is fixed in this alloy. Since the formation of the  $\delta$  phase mainly occurs during the eutectic Al–Si reaction, interaction among the eutectic and the  $\delta$  phase is another key factor influencing the formation of the  $\delta$  phase [53].

The knowledge from this work suggests a promising processing route for improving the mechanical properties of such alloys: the intermetallic  $\delta$  phase can be largely refined and fragmented by accelerating the formation of the fine Al–Si eutectic and thus enhancing their density.

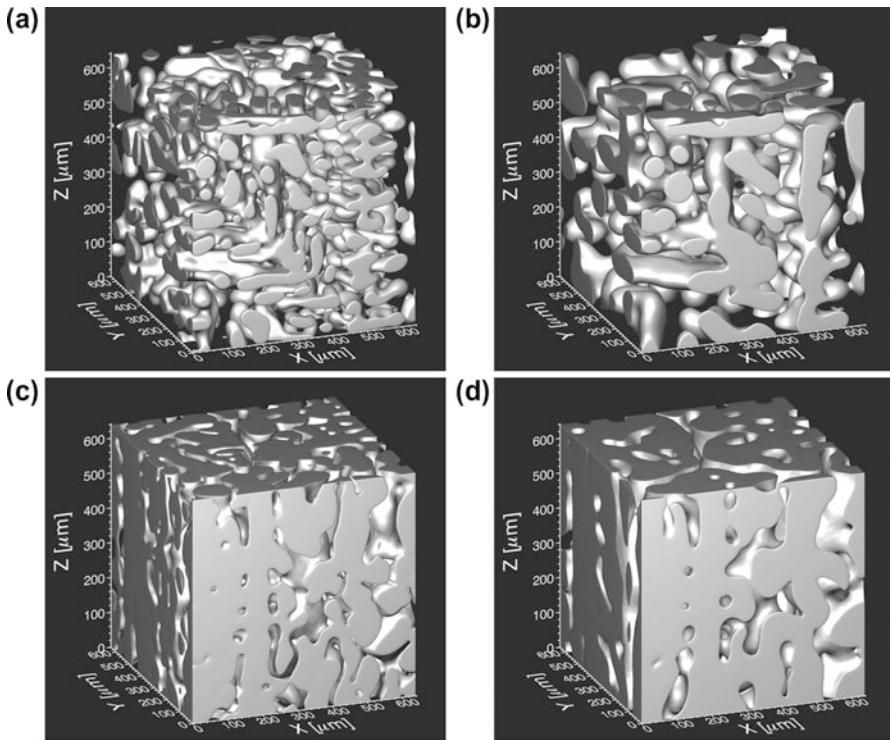


**Fig. 2.34** Representative 3-D volumes of the initial experimental microstructures examined for low and high solid volume fractions at early (a, c) and later (b, d) times during coarsening. The solid phase is shown in each reconstruction, and the liquid phase is transparent (adapted from [54])

In 2014, Fife et al. [54] reported a systematic study on the isothermal coarsening of dendritic Al–Cu microstructures using time-resolved, in situ synchrotron X-ray tomographic microscopy. The relationship between interface curvature and velocity across different solid volume fractions and at various coarsening times in Al–Cu binary mixtures has been examined. They found that, while there is a correlation between velocity and mean curvature of the interface, there is significant dispersion in the velocities for a given value of mean curvature. In addition, the Gaussian curvature plays a role in determining the interface velocity even though it has no effect on the chemical potential at the interface. They also found that there are many interface patches of various morphologies and size scales that are not evolving during the coarsening process. At higher solid volume fractions and longer coarsening times, more of the structure is active in the coarsening process, and there is an increase in localised diffusional interactions.

In 2017, Cool et al. also reported the process of fragmentation of dendrite arms during coarsening, the details of which can be found in [55].



In Mi's group, the recent work is focusing on studying 3D structures of intermetallic phases in different alloy systems. Zhang et al. [36, 56] studied systematically the 3D structures and morphologies of a metallic glass composite (a DH3 alloy with composition of  $\text{Zr}_{39.6}\text{Ti}_{33.9}\text{Nb}_{7.6}\text{Cu}_{6.4}\text{Be}_{12.5}$ ) at nano- and micrometre scale. X-ray microtomography plus FIB-SEM nanotomography were used to reveal the morphologies, volume fractions, and thermal stabilities of the nano- and microstructures. Figure 2.35 shows a view of the amorphous primary  $\beta$ -Zr dendrites in as-cast condition (Fig. 2.35a, b, c, see Video 2.35a), and the complex eutectic phases formed by nanoscale intermetallic compound of  $\text{ZrBe}_2$  and  $\text{ZrCu}_2$  after a thermal shock

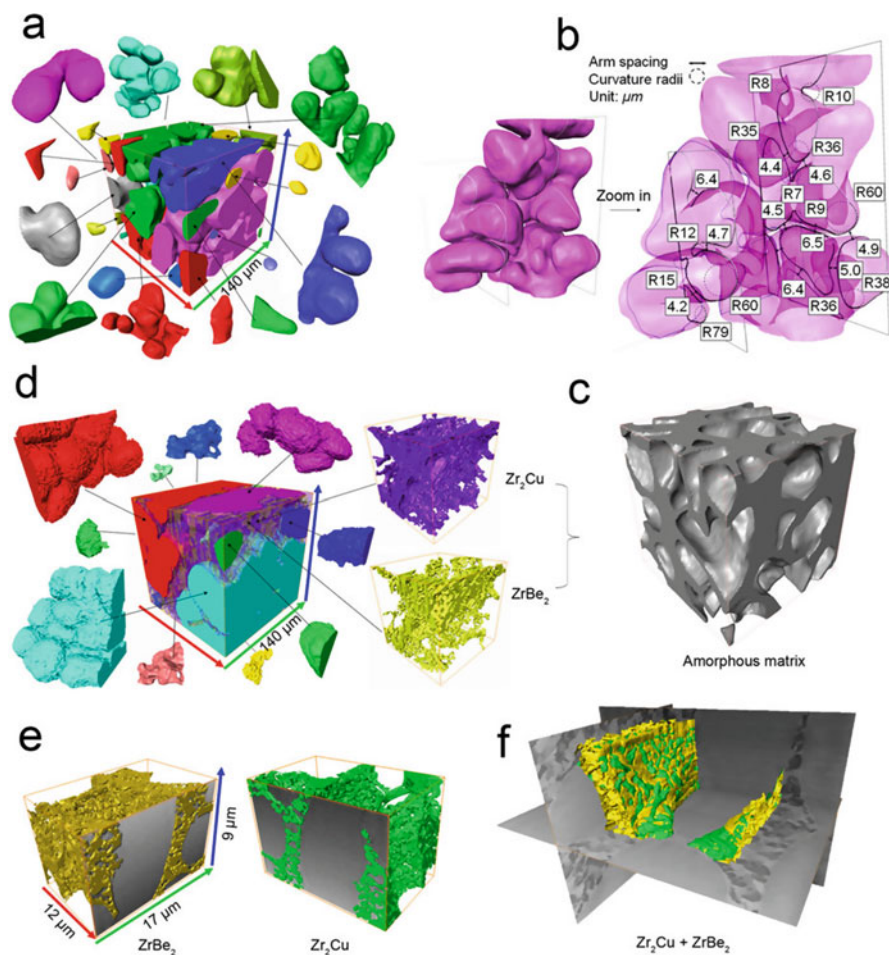


**Fig. 2.35** (a) Primary  $\beta$ -Zr dendrites in the as-cast sample, with the amorphous matrix hidden for easy visualisation; (b) a typical dendrite and measurement of arm spacing and curvature radii; (c) amorphous matrix within the as-cast sample; (d) secondary  $\text{ZrBe}_2$  (yellow),  $\text{Zr}_2\text{Cu}$  (purple) intermetallics, and primary  $\beta$ -Zr dendrites (other colours) of the 650 °C thermally shocked sample; (e, f) FIB-SEM sectioning nanotomography of the 650 °C thermally shocked sample (adapted from [56])

treatment (Fig. 2.35d, e, f, see Video2.35d). Such complex 3D structures need to be presented in different view angles for a complete understanding, hence, two accompanying videos are given here: (1) Video2.35a for the dendrites and (2) Video2.35d for the eutectic phases. Clearly, conventional 2D characterization techniques cannot fully quantify such complex 3D structures. X-ray microtomography plus FIB+ SEM nanotomography allow us to fully characterise such multiscale structures.

Understanding of these multiscale structures is essential for optimising the composition design of the composites and developing viable manufacturing methods [56].

Zhao et al. characterized the true 3D network structures and morphologies of the Fe-rich intermetallic phases in recycled Al–5.0%Cu–0.6%Mn alloys with 0.5% and 1.0% Fe using synchrotron X-ray microtomography and skeletonisation method [57]. The complex 3D networks with well-developed branches in these Fe phases were quantified for the first time [57]. Du et al. did a systematic real-time study on the dynamic evolution of primary  $\text{Al}_3\text{Ni}$  intermetallic phases in an Al-15%wtNi alloy solidified under pulse electromagnetic fields. Using the combined methods of synchrotron X-ray imaging and tomography, Du et al were able to visualise in situ the growth, fragmentation and 3D morphology of the  $\text{Al}_3\text{Ni}$  phases. Using the rich datasets acquired from tomography, the number, orientation, and surface morphology distribution of the  $\text{Al}_3\text{Ni}$  phases formed with different pulse magnetic fluxes were quantified for the first time using skeletonization function. The research provided much more quantitative insight into understanding of the dynamic evolution of intermetallic phases under the influence of pulse magnetic fields. The highlight of this work is presented in Sect. 7.3.2 of Chap. 7 of this book, so do not repeat there. Interested readers are referred Du's PhD thesis for more information [27].

## 2.3 The Challenge for In Situ Studies and Future Trend

### 2.3.1 Temporal and Spatial Resolution Issues

The challenge in this aspect is to study in situ dynamic events in metal solidification at nanometre and even atomic length scale on the nanosecond or shorter time scale. Currently, the photon flux of existing synchrotron X-ray sources and detector systems only allows materials structures of 1  $\mu\text{m}$  and above to be resolved with temporal resolution normally in milliseconds for 2D imaging and seconds for tomography. The current upgrading of ESRF will increase the performance by 100 times in terms of brilliance and coherence. Revolutionary advance has been made possible by the free-electron laser technologies. Time-resolved studies of structural dynamics with spatial resolution from nanometre to atomic length scales or with temporal resolution of 10 fs or less are possible, but not simultaneously, i.e. compromising either on spatial or temporal resolution. In addition, more advanced and robust algorithms, codes, software, and machining learning strategies for processing big data are currently under development for accelerating scientific discovery from mining big 4D datasets.

### 2.3.2 Linking Modelling with Experiments

Another trend is to link advanced modelling approaches together with in situ experiments so as to fill in the gap in time and space domains where experiments are not capable of. For example, Guo et al. have developed an ultrafast Phase Field model [58–62], which now is capable simulating the complex 3D multiple dendrites and comparing with experimental results from 3D tomography datasets. Figure 2.36 shows an example of using a newly developed anisotropy growth function to describe the growth of an 18-branch  $\alpha$ -Mg dendrite. The 3D phase field simulations agreed well with the experimental results [61], including dendrite morphology and side-branching patterns. Now, this phase field model has been used to simulate the growth and coarsening of multi-dendrites. The most recent results are shown in

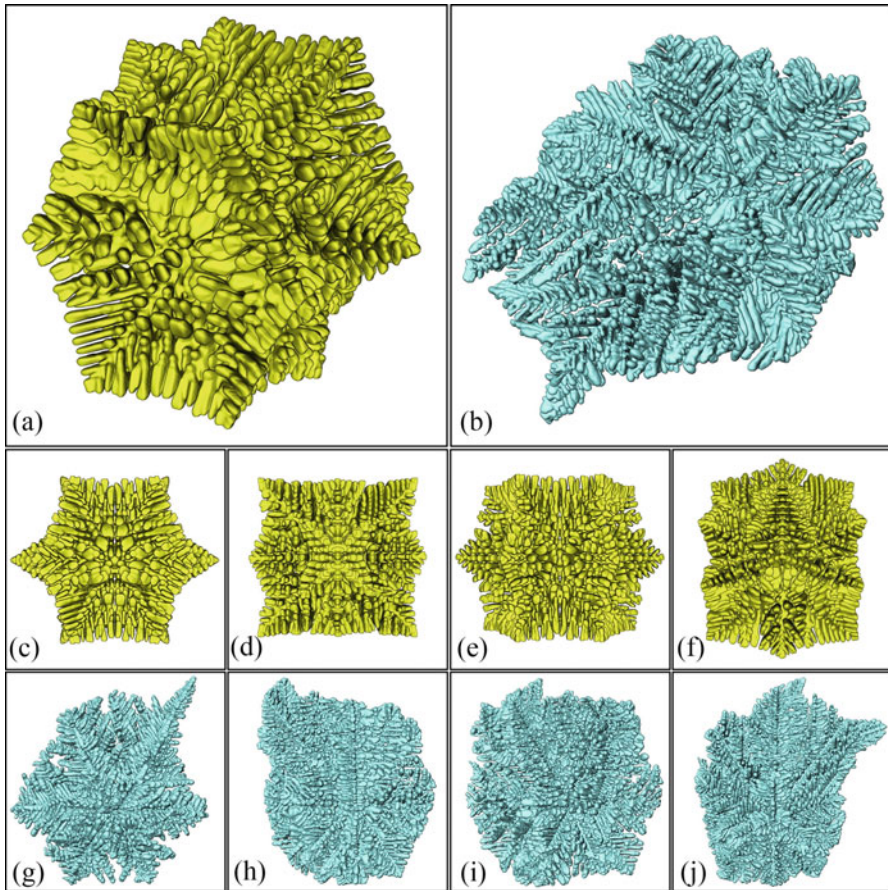


**Fig. 2.36** Comparison of the dendrite morphology between (a) phase field simulation and (b) X-tomography experiment. Dendrite morphologies with respect to four different view directions were shown in (c–f) for simulation and (g–j) for experiment, respectively (adapted from [61])



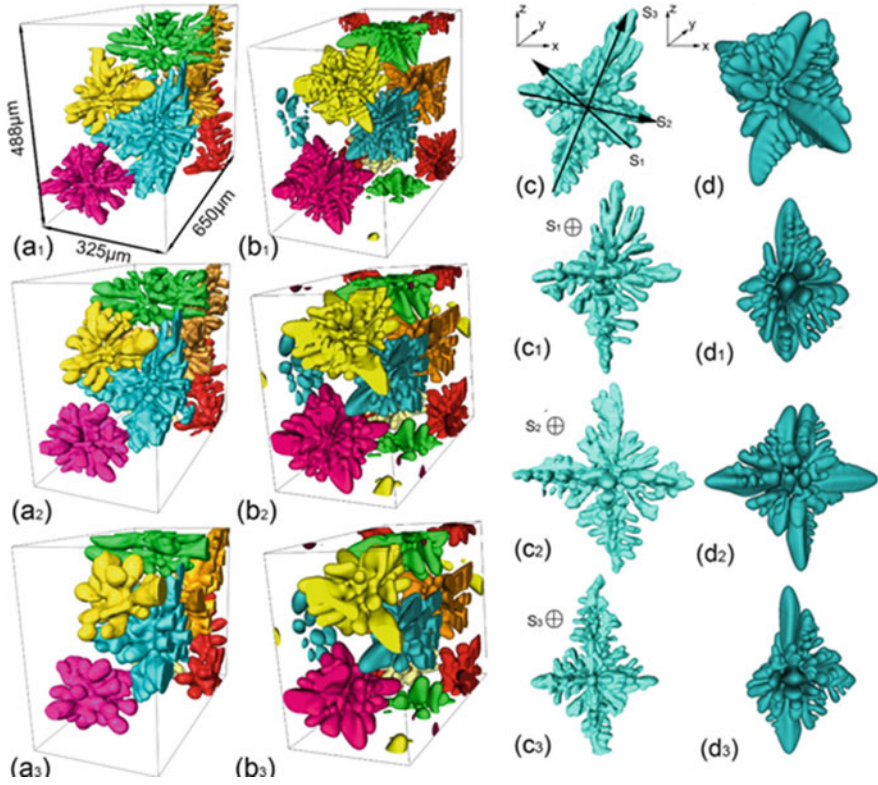


**Fig. 2.37** Comparison of multi-dendrites morphology during growth and coarsening. **(a1–a3)** Multidendrites obtained from Synchrotron X-ray tomography experiments with the growth time of 30, 60 and 110s; **(b1–b2)** The corresponding multidendrites simulated using the ultrafast Phase Field model (Video 2.37b shows more vividly the evolution of the simulated multidendrites). **(c1–c3)** one typical single dendrite in growth and coarsening; and **(d1–d3)** the corresponding dendrite simulated using the ultrafast phase field model

Fig. 2.37 (also see Video 2.37b for detailed morphology evolution over time). The agreement between modelling and experiment results is remarkable [62].

### 2.3.3 Simultaneous Acquisition of Multidimensional Datasets

Furthermore, the development of advanced detector systems to measure and obtain multidimensional datasets simultaneously is another area of rapid progress. For example, Zhao et al. reported high-speed synchrotron hard X-ray imaging and diffraction techniques to monitor the laser powder bed fusion process of Ti-6Al-4 V in situ and in real time (Fig. 2.38). They demonstrated that many scientifically and

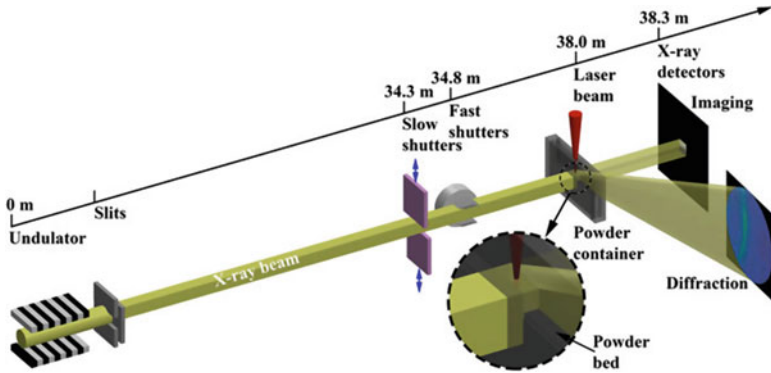


**Fig. 2.38** A schematic of high-speed X-ray imaging and diffraction experiments on the laser powder bed fusion process at the 32-ID-B beamline of the Advanced Photon Source. A short-period undulator generates a pseudo pink beam with the first harmonic energy of 24.4 keV ( $\lambda = 0.508 \text{ \AA}$ ). The laser impinges on the miniature powder bed sample from the top, and the X-rays penetrate the sample from the side. The imaging and diffraction detectors are placed downstream, about 300 mm away from the sample. The inset surrounded by the dashed circle enlarges the view of the laser-sample and X-ray-sample interaction. The distance of each component from the source is labelled on top (adapted from [63])

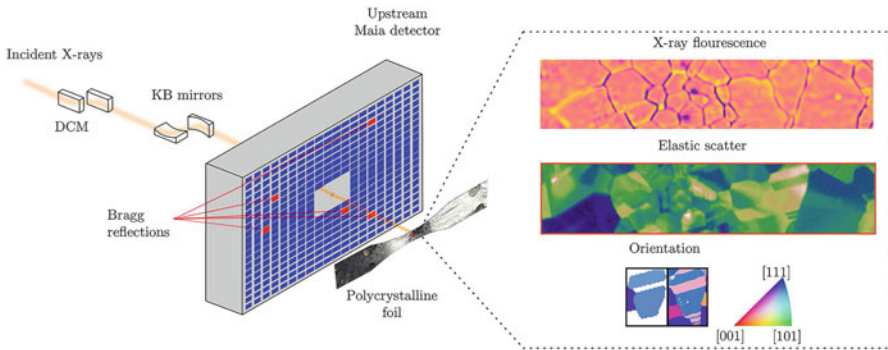


**Fig. 2.39** An illustration of using X-ray and the Maia detectors to simultaneously map the crystallographic and chemical properties of a sample (adapted from [64])

technologically significant phenomena in the process, including melt pool dynamics, powder ejection, rapid solidification, and phase transformation, can be probed with unprecedented spatial and temporal resolutions [63]. The high-speed diffraction enables a reasonable estimation of the cooling rate and phase transformation rate, and the diffusionless transformation from  $\beta$  to  $\alpha$  phase is evident. The experiment platform established will undoubtedly become a new paradigm for future research and development of metal additive manufacturing [63].

Another good example is the pixelated energy-dispersive X-ray area detector (Maia detector reported in [64]) that is able to simultaneously measure X-ray fluorescence and diffraction information in order to determine grain orientation and estimate lattice strain (Fig. 2.39). The results in [64] demonstrate the potential

of the next generation of X-ray area detectors for materials characterisation. These detectors can be used to provide a complete solution for simultaneously mapping the crystallographic and chemical properties of the sample. The extension of these techniques to broadband X-ray sources and other areas such as solidification science will offer the capability of acquiring multidimensional datasets simultaneously, greatly accelerating scientific and technological advancement.

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# Chapter 3

## Magnetohydrodynamics Processing and Modeling



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### 3.1 Physical Principles

Electro-magnetohydrodynamics (EMHD) or more commonly magnetohydrodynamics (MHD) is the scientific field devoted to studying the interaction between electric or magnetic fields and fluid flow in electrically conducting liquids. This covers a very wide range of phenomena, from astrophysics to plasma research in fusion reactors, and from the dynamo effect in geophysics to electromagnetic levitation.

Electromagnetic interaction phenomena appear in a wide range of metal processing applications, either as an unintended consequence of the presence of electric currents during processing or by the deliberate application of external magnetic fields or currents to a process. Historically, the concept of induction stems from the pioneering experiments of Faraday, who first established the connection between the time-varying magnetic field and the current generation in a conductor. The first landmark industrial applications led to the production of aluminum by electrolysis (the Hall–Héroult process [1, 2]) as a continuous process, and to the large-scale use of arc and induction furnaces in steel production in the late nineteenth century [3]. The existence of electric current leads to several interactions with conductive materials; the generation of heat due to resistive dissipation (Joule heating), the stirring of liquid melts due to the cross product of magnetic field and current (the Lorentz force), and the shaping of liquid-free surfaces or the levitation of metals against gravity due to the mutual repulsion by the field. In the case of static magnetic fields, flow damping and reduction of turbulence have been observed, see, e.g., [4, 5]. Other effects include the expulsion of impurities to the free surface of the melt [6–8] and the reshaping or realignment of crystals during solidification [9]. We

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will study examples of such phenomena through applications investigated by the authors in the following pages.

Since the processing of metallic alloys almost always starts from the liquid state, we are invariably dealing with high temperatures, ranging from ca. 700 °C for aluminum, to ca. 1700 °C for titanium. Furthermore, as at these temperatures many metals are highly reactive, the use of induction as a process tool, being contactless, offers distinct advantages over other processing methods, such as mechanical stirring, especially where contamination is a concern. For this reason among others, “Electromagnetic Processing of Materials” (EPM) as it has been termed [9] is an expanding field, with an ever-growing number of applications.

In terms of modeling and simulation, EPM remains a difficult task to master, since in addition to the usual flow, heat transfer, and solidification, one has to address the coupled electric and magnetic fields, often in a dynamic fashion. The effects mentioned above are characterized by the coupling of the equations of fluid motion and Maxwell’s equations of electrodynamics. Applications range from melting, flow control, melt cleaning, stirring, arc processes (welding, AM, vacuum arc remelting (VAR), and ESR), and electrolytic processes to, more recently, the field of liquid metal batteries. Applications of EPM to casting are considered in Chap. 4.

The governing equations of MHD in metals processing are summarized below, starting with the reduced form of Maxwell’s equations:

$$\nabla \times \mathbf{B} = \mu \mathbf{J}; \quad \nabla \cdot \mathbf{J} = 0 \quad (3.1)$$

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}; \quad \nabla \cdot \mathbf{B} = 0, \quad (3.2)$$

where  $\mathbf{B}$  is the magnetic field flux density (Tesla),  $\mathbf{J}$  the current density (A/m<sup>2</sup>),  $\mathbf{E}$  the electric field (V/m), and  $\mu$  the magnetic permeability constant (Henry/m).

Ohm’s law for a moving conductor,

$$\mathbf{J} = \sigma(\mathbf{E} + \mathbf{u} \times \mathbf{B}) \quad (3.3)$$

where  $\sigma$  is the electrical conductivity (Ohm/m). The second term on the right-hand side (RHS) of Eq. (3.3) represents the current generated by the moving conductor, in the case of liquid metals due to the convective motion of the melt at velocity  $\mathbf{u}$  (m/s). The body force  $\mathbf{F}$  (N/m<sup>3</sup>) by the interaction of the electromagnetic field, called the Lorentz force, is given by the cross product of current and magnetic field,

$$\mathbf{F} = \mathbf{J} \times \mathbf{B}. \quad (3.4)$$

Fluid flow in liquid metals is represented by the Navier–Stokes (NS) and continuity equations, given here in Reynolds-averaged (RANS) incompressible form:

$$\rho \frac{D\mathbf{u}}{Dt} = -\nabla p + \nabla(\mu_{\text{eff}} \nabla \mathbf{u}) + \rho \mathbf{g} + \mathbf{J} \times \mathbf{B}; \quad \nabla \cdot \mathbf{u} = 0, \quad (3.5)$$

where  $p$  is the pressure,  $\mu_{\text{eff}}$  the *effective* viscosity (sum of laminar and turbulent contributions), and  $\mathbf{g}$  the gravity constant. Equations (3.1)–(3.5) together with

appropriate boundary conditions represent the complete statement of the problem. As can be seen, the electromagnetic interaction appears on the RHS of Eq. (3.5) as an additional body force. Since the velocity vector  $\mathbf{u}$  also enters Eq. (3.3), the electromagnetic and flow equations are coupled, which may cause considerable difficulties in simulations where fluid velocities and magnetic flux density are very strong, for example, in fusion reactor cooling duct applications.

For such situations, Eqs. (3.1)–(3.3) can be more conveniently recast as follows:

$$\frac{\partial \mathbf{B}}{\partial t} = \sigma \nabla \times (\mathbf{u} \times \mathbf{B}) + \eta \nabla^2 \mathbf{B} \quad (3.6)$$

This is the magnetic induction equation, which contains convection and diffusion terms, respectively, on the RHS. This means that the velocity under certain conditions can distort the magnetic field. Therefore, Eq. (3.6) can be viewed as the transport equation for the magnetic flux density. The variable  $\eta$  multiplying the diffusion term in Eq. (3.6) is called the magnetic diffusivity, given by:

$$\eta = 1/\sigma\mu \quad (3.7)$$

In analogy to the Reynolds number in fluid flow, one can declare  $\text{Re}_m = U_o L_o / \eta$ , the *magnetic Reynolds number*, representing the ratio magnetic convection/magnetic diffusion. When the magnetic Reynolds number is small—typically  $\text{Re}_m < 1$  in metals processing applications, the convective part in Eq. (3.6) can be neglected and it may be simplified to:

$$\frac{\partial \mathbf{B}}{\partial t} = \eta \nabla^2 \mathbf{B} \quad (3.8)$$

The flow and electromagnetic fields are no longer coupled, and the computational task becomes much simpler to solve. However, there are other points of concern that need to be flagged. The RANS form of the NS equations relies on closure using one of the many turbulence models available in the literature and indeed in all commercial CFD codes, to determine the value of the effective viscosity  $\mu_{\text{eff}}$ . However, the Lorentz force also affects turbulence. Velocity damping takes place *across* magnetic field lines, and so, by continuity, velocity is enhanced *along* field lines. Vortices are stretched and consequently, the vorticity component along field lines is preferentially increased [4, 5, 10]. These effects are not captured by standard isotropic RANS models, which are invariably used by the metals community. Higher fidelity, direct numerical simulation (DNS), and large eddy simulation (LES) models can address these issues, but due to cost and complexity remain the domain of specialist research (e.g., see [11]). We shall see later on that when considering industrial size AC induction furnaces, due to the skin effect, the magnetic field penetration into the bulk of the melt is small and therefore uncertainties due to turbulence models are mitigated.

In terms of application, we may divide processes into two groups: those employing DC currents or static magnetic fields and those that require AC currents. In the first group, we include the aluminum electrolysis process and the various

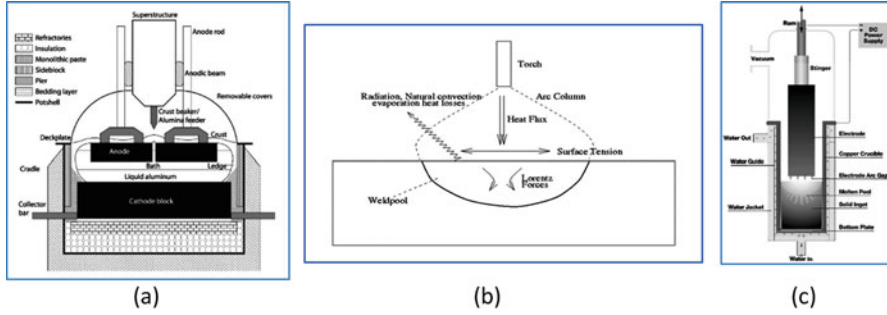


**Fig. 3.1** DC current applications in electrometallurgy, (a) the aluminum electrolysis cell, (b) physics of the arc welding process, and (c) the vacuum arc remelting process (or VAR)

arc-dependent processes, i.e., arc furnaces, arc welding, VAR, electroslag refining, and flow control devices in continuous casting [12]. Static magnetic fields are also making an appearance as flow damping devices in the measurement of thermophysical properties [13] and in basic research into microstructure morphology in solidifying alloys [14]. Some examples are given in Fig. 3.1.

In each application, the start of analysis is the numerical solution of Eqs. (3.1)–(3.8). With such a wide range of problems, specialized techniques have been developed for industry, which we will briefly touch upon in this chapter. These include shallow-layer methods for aluminum electrolysis, finite volume, or finite element methods for 3D problems and spectral collocation methods for axisymmetric applications with time-varying geometry.

Low- and high-frequency AC current coils are used as induction sources in furnaces for melting, levitation melting, and stirring. Then,  $J = J_0 e^{i\omega t}$  and it is usual to refer to the root mean square (RMS) value of current  $J_{\text{RMS}} = 0.7J_0$  in induction applications, since that is the value effective in the Lorentz force and Joule heating calculations. The current frequency  $\omega$  (rad/s) also has a very important role to play in the process, as it determines the amount of penetration of the magnetic field into a conductor. This so-called *skin depth*, is related to the diffusion rate of the magnetic field into a conductor as given by Eq. (3.8) and is defined by the following equation:

$$\delta = \left( \frac{2\eta}{\omega} \right)^{\frac{1}{2}} = \left( \frac{2}{\sigma\mu\omega} \right)^{\frac{1}{2}} \quad (3.9)$$

Examining Eq. (3.9), we can see that as the frequency  $\omega$  or the conductivity  $\sigma$  of the material increases, the skin depth will decrease. This means that there will be a concentration of force or heat into a smaller volume of material, close to its surface. It is for this reason that large volume ladle stirring is usually conducted at low frequencies (50 Hz), while liquid metal droplet electromagnetic levitation used to determine the surface tension of melts uses frequencies in the kHz range. The skin effect phenomenon is illustrated in Fig. 3.2 for the case of a sphere surrounded by a single-turn AC coil.

Figure 3.3 displays schematically a range of applications using AC induction, which we will examine in detail later on in this chapter.

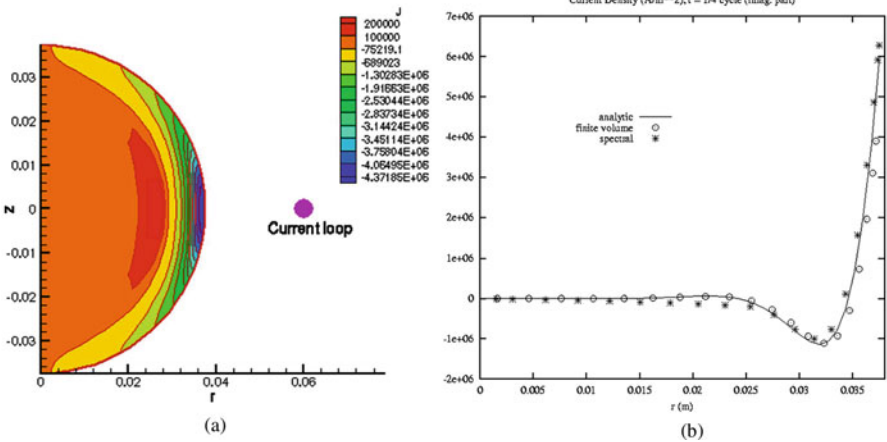


**Fig. 3.2** (a) Current induced in a conductive sphere by a single-turn coil carrying 1000 A at 6 kHz, illustrating the skin effect. The graph in (b) compares the analytic solution of this problem against spectral and finite volume numerical solutions

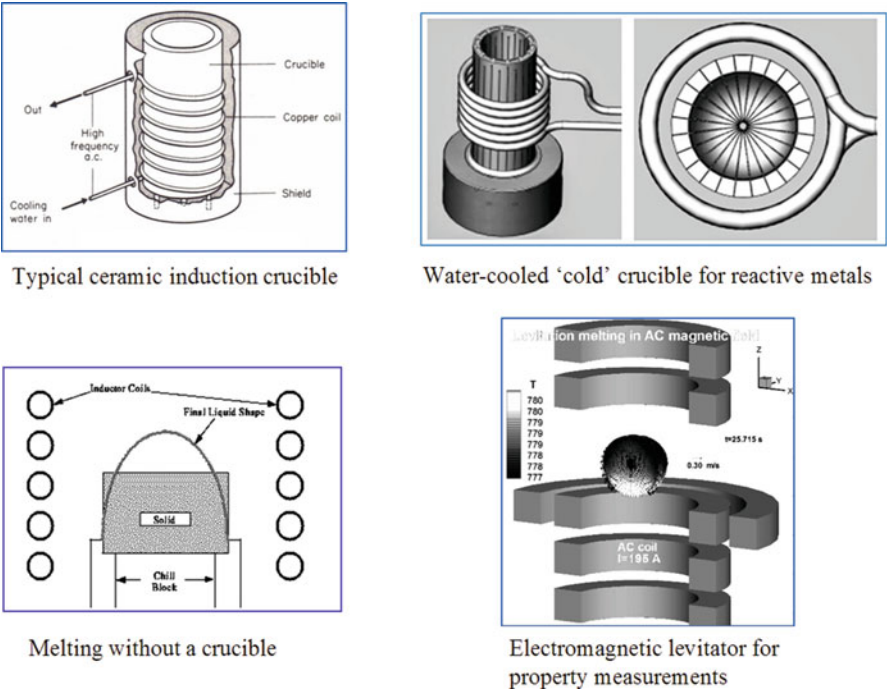


**Fig. 3.3** AC induction applications in metal processing

One of the principal applications of electromagnetic fields or current in metals processing concerns the production of heat through the thermal dissipation of current in the metal charge. The relevant transport equation for heat transfer (accounting also for phase change) is given below:

$$\rho \frac{D(C_p T)}{Dt} \nabla \cdot (k_{\text{eff}} \nabla(T)) + q_e + q_L \quad (3.10)$$

where  $T$  is the temperature,  $C_p$  the specific heat of the metal, and  $k_{\text{eff}}$  the effective conductivity containing both laminar and turbulent contributions. The RHS source terms represent the Joule heating due to current  $J$  :  $q_e = \frac{J^2}{\sigma}$  and the latent heat release  $q_L = -\frac{\partial}{\partial t}(\rho f_L L) - \nabla \cdot (\rho u f_L L)$ , respectively, where  $L$  (J/kg) is the latent heat of fusion and  $f_L$  the fraction liquid in the melt. Various models are used by the community to represent the transition from liquid to solid state and references can be found elsewhere, e.g., [15, 16].

## 3.2 DC Current Applications

### 3.2.1 The Aluminum Smelter

It is proper to start this section with the aluminum smelter as the application that pioneered the use of electric current in metals processing. Modern aluminum electrolytic production cells are extremely sophisticated devices of considerable size (up to 20–30 m in length), arranged in series of several hundred units and carrying electric current of up to 500–600 kA. The design of the cells requires good understanding of the fluid flow and heat transfer to make them economically viable, working without interruption for years of service. The presence of high electric current and the magnetic field created by the surrounding current network of neighboring cells, modified by various ferromagnetic construction elements, leads to a very complex magnetohydrodynamic flow, wavy interfaces, and complicated thermal balance. The thermal balance is an important parameter, since a frozen layer of the liquid bath needs to be preserved at all times to protect the walls from erosion by the reactive electrolyte and liquid aluminum. The electrochemical reaction takes place mostly at the top part of a thin electrolyte layer, composed of molten cryolite  $\text{NaF/AlF}_3$  and dissolved aluminum oxide  $\text{Al}_2\text{O}_3$ , where carbon anodes are immersed to produce the overall reaction  $\text{Al}_2\text{O}_3 + 3/2 \text{C} \rightarrow 2 \text{Al} + 3/2 \text{CO}_2$ . The aluminum forms a “mist” of tiny droplets that sediment towards the bottom of the cell. Although the liquid aluminum is heavier than the electrolyte, the density difference is very small. In the presence of large electric current and resulting magnetic field, this interface is subject to a quasi-stationary dome shape deformation and various wave instabilities [17]. Of particular importance are instabilities that lead to voltage fluctuations or, in extreme cases, short circuits between metal and anodes. Lossman [18] started a widespread practice of measuring such instabilities, examining

fluctuations in anode current, cell voltage, and magnetic field. These results are used to validate mathematical models intended to study MHD instabilities [19, 20]. Principal results from the modeling are the growth rates and oscillation periods of the MHD instabilities. It has been observed that the instability decreases with increasing the anode–cathode distance (ACD), i.e., the average electrolyte depth below the anodes. This result fully conforms to the known analytical criteria for the cell stability [21] and numerical models that account for realistic magnetic fields [6]. The fluctuation frequency shift due to the magnetic field was observed experimentally, and confirmed by the linear theory [22].

The design of modern aluminum cells requires knowledge of the stability and thermal balance conditions while attempting to reduce the ACD as much as possible due to the growing electricity cost. About 30% of the production costs are due to the electricity. A typical ACD of about 4–5 cm reduced by few millimeters would bring savings of millions USD at a typical plant. Nonlinear dynamically coupled mathematical theory and software based on the MHD model of the electrolysis cell have been successfully used to optimize several commercial installations [20, 22–24]. A full model needs to compute time-dependent currents, voltages, magnetic fields, bath–metal interface shape, and turbulent magnetically driven flow in the bath and liquid metal. Figure 3.4a is a model-based representation of the 500-kA potline, showing a view to the end of line and all the conductors that are part of the simulation. The temperatures of the bus bars are adjusted according to the computed Joule heating and losses to the air. The electric current in the individual anodes is computed, following at all times the wave development on the interface between liquid layers. The dome-shaped time-averaged deformation of the metal surface is projected to the bottom of the whole anode block to account for anode *bottom burnout* effect while self-adjusting to a constant ACD, except in the case of a disturbance such as during an anode change operation. The electric current distribution in the liquid zone is computed from all bus bar network connected to the anodes and cathode collectors, coupled with the cell interior details like the ledge profile, bottom (cathode) shape, collector connections, electrolyte channels, and the electrochemical voltage drop. Figure 3.5 shows the resulting magnetic field (a) above the

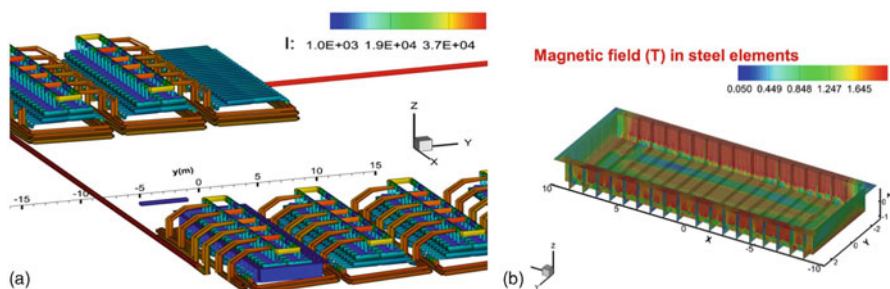


**Fig. 3.4** The model of electric current distribution for the aluminum electrolysis cells at the end of line and the computed magnetic field in the steel construction surrounding each cell

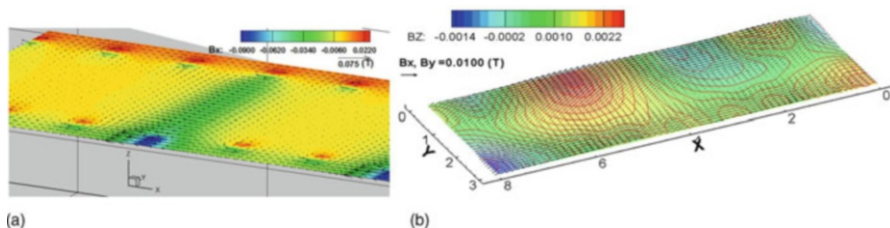


**Fig. 3.5** Magnetic field distribution at (a) the top above the cell (the magnetic field “coils” around the individual anode rods) and (b) in the middle of the liquid aluminum layer where the Bz component is highly optimized for wave stability

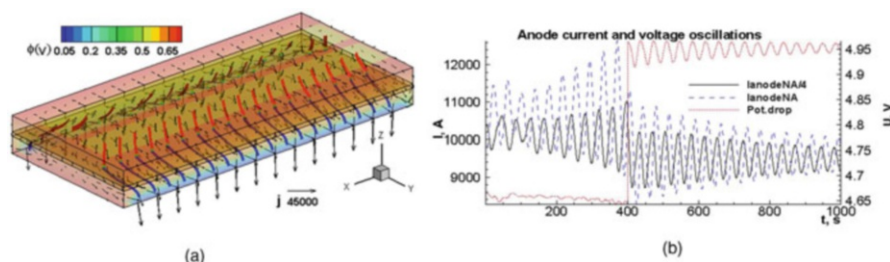


**Fig. 3.6** The 3D current distribution in the cell interior (a). (b) example numerical solution of MHD waves that initially lead to cell destabilization, followed by recovery after preventative measures, are taken by raising the ACD

cell, and (b) at the electrolyte/aluminum interface. Figure 3.6 shows the 3D current distribution in the cell interior. The magnetic field is computed at all times in order to follow the full magnetohydrodynamic wave and flow development. The detailed representation of the cell steel elements adds nonlinearity to the overall magnetic field properties (Fig. 3.4b). The MHD response of different commercial cells is quite variable, depending on their design (side-to-side, end-to-end, Soderberg, etc.), the line amperage, operational practices (metal tapping, anode change, bottom erosion, and alumina feeding), and many other factors. The numerical models, once validated against various operating cells and arrangements, serve as the easiest and most cost-effective tool to investigate the possible operational scenarios, help to design completely new potlines, or retrofit older ones. An example numerical experiment, predicting instability during anode #1 replacement, is shown in Fig. 3.6. After the oscillation frequency and rising amplitudes are detected, the whole anode block was raised so that the ACD increased (from 0.045 m) by 8 mm at the time 400 s from the anode change start. The raised ACD clearly stabilizes the magnetically excited wave. The MHD excited wave is not oscillating relative to a flat constant aluminum level, as it is often assumed. Actually, it is well documented that the metal surface forms a dome-like shape due to the variation in the electromagnetic pinching effect between the liquid electrolyte and the liquid metal layers. The typical shape of the stationary deformed interface is shown in Fig. 3.7, for a 500-kA cell. This means that the waves



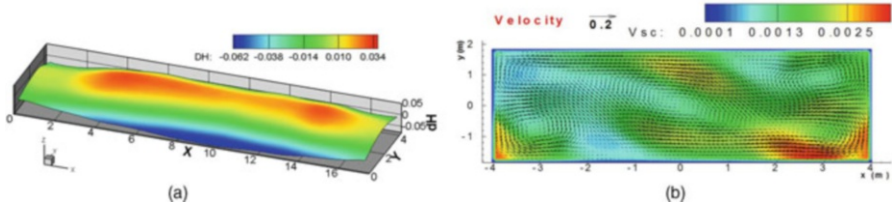


**Fig. 3.7** (a) The typical shape of stationary deformed interface between the liquid layers for a 500-kA cell and (b) the associated turbulent fluid flow in the liquid metal characterized by large-scale horizontal vortices

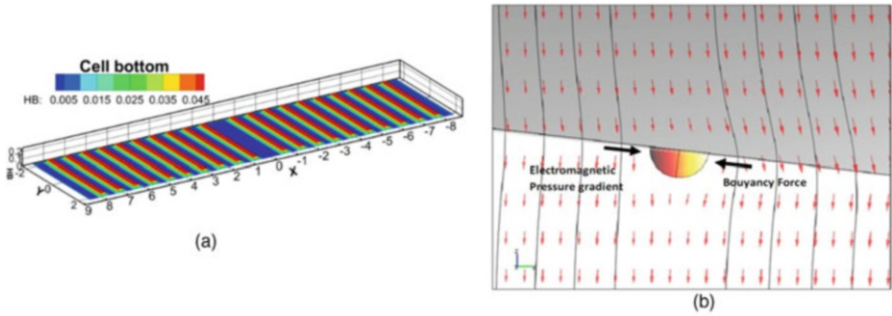


**Fig. 3.8** The bottom unevenness model for one of the cathode types (a). The electromagnetic force action on a bubble via the MHD pressure gradient in the surrounding fluid (b)

are oscillating relative to this reference shape. This affects the results obtained from simple linear theories and can be properly described using full dynamic models for the cell. The liquid layers in the cell are in a state of turbulent mixing, creating large-scale structures in the form of horizontal vortices, as shown in Fig. 3.7b. The turbulent nature of the flow ensures good mixing of the aluminum oxide as it is periodically added during the production cycle. Large horizontal vortices affect the interface deformation by contributing to the dynamic pressure distribution difference between the layers, while small-scale turbulent vortices affect the dissipation of produced heat and momentum. The latter effect has a significant influence on the wave damping which needs to be properly accounted in the modeling [22]. Since turbulent damping is recognized as the important factor in wave stability, new designs are proposed in attempts to raise bottom friction in the liquid metal by introducing ridges on the surface of cathode [24]. This bottom unevenness is not always desirable, and appropriate modeling helps to clarify the optimum construction (Fig. 3.8 demonstrates a model setup for one of the cathode types).

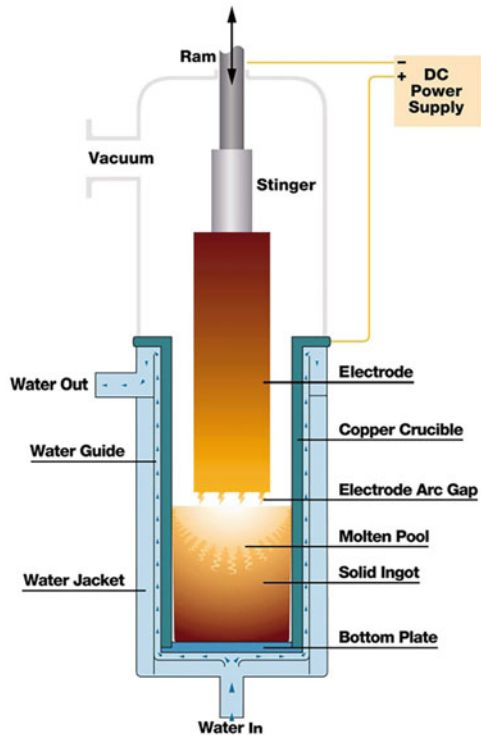
Gas bubbles are inherently present when the electrochemical reaction occurs. About  $2.5 \text{ m}^3$  of  $\text{CO}_2$  gas is released per kg of produced aluminum. The detached bubbles during the aluminum reduction are typically 3–5 mm in size, growing in volume due to collisions and coalescence. The presence of bubbles contributes to about 0.25 V of the total 4–4.5 V voltage loss in an individual cell. The bubbles at

the bottom of the anode are driven by buoyancy when they escape into the side channels between the anodes. In addition to this, the electromagnetically driven convection exerts a drag force on the bubbles. A significant contribution to the force balance arises from the so-called electro-magneto-phoretic forces [25], which are well known for a variety of MHD applications, such as removal of inclusions from steel melt, concentrating electrically insulating bubbles, and for many other purposes. The electromagnetic force action on the bubbles is explained in Fig. 3.8b. According to estimates in [26], this force becomes important for bubbles exceeding 2 mm in size. It is sufficient to overcome the drag force due to the electrolyte flow, and it could prevent translational displacement of the bubble along the base of the anode. The accumulation of gas under the anodes is controlled in modern technology by introducing deep slits at the bottom of the anodes. The modeling of bubble flow and its MHD effects on the flow and waves is an ongoing subject of investigation.

### 3.2.2 Vacuum Arc Remelting Furnace

Vacuum arc remelting (VAR) (Fig. 3.9) is a refining metallurgical process where a long cylindrical electrode is being melted by the heat of direct current (DC) electrical

Fig. 3.9 The VAR furnace



arcs in a vacuum furnace fitted with water-cooled copper crucible where the remelted metal solidifies. Its aim is high cleanliness, homogeneity, fatigue, and fracture toughness of the processed special alloys. Those can be achieved under specific solidification conditions, which lead to the desired microstructure of the newly formed ingot. Common defects in VAR ingots are “freckles” and “white spots.” Their occurrence has been studied in detail and it can be reduced with the help of computational modeling [27]. The intense heat generated by the electric arc melts the tip of the electrode and a new ingot is progressively formed in the water-cooled mold. High vacuum is maintained throughout the remelting process. The required properties of the final material can only be obtained if the inevitable segregation of the alloy components during solidification is kept to a minimum. This can be achieved when a sufficient temperature gradient at the solidification front is maintained during the entire remelting process and the depth of the molten pool at the top of the ingot is kept within optimal limits. The depth of the pool influences its profile, which determines the direction of dendrite growth whose angle relative to the ingot axis needs to be within an optimal range in order to achieve the desired microstructure. The pool shape is also affected by the melt flow behavior that in turn depends on the balance of electromagnetic and buoyancy forces acting on the liquid metal.

Two distinct stages of the computational modeling of the VAR process can be identified by size scale: (a) macroscopic (“macro”) model and (b) microscopic (“micro”) model. Data from the macro-model are supplied to the micro-model [27] to predict the likelihood of defects appearing in the cast ingot due to microstructure changes.

A multi-physics approach in the modeling allows simultaneous solution of coupled differential equations belonging to different classes as shown schematically in Fig. 3.10.

This is necessary in order to represent correctly interacting physical phenomena in a given industrial process. Figure 3.10 illustrates the feedback mechanisms in the liquid pool at the top of a VAR ingot. Undoubtedly, the electric arc is the driving force of the process. It provides the heat source that melts the electrode and sustains a liquid pool at the top of the ingot, while cooling water on the periphery of the crucible maintains the solid contact region. The other very important influence of the arc electric current is the Lorentz force, which creates recirculating flow in the melt

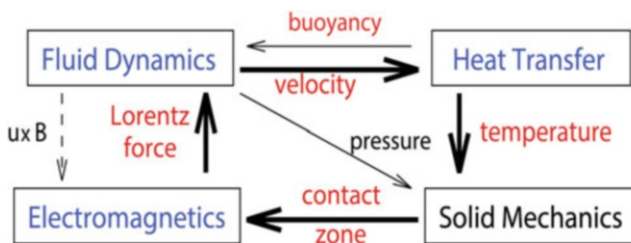


**Fig. 3.10** Relations between physical phenomena at the top of the VAR ingot

pool. In turn, the flow influences the heat transfer to the solid part of the ingot, hence the solidification profile. The resulting fluid temperature variations affect the flow through buoyancy (density variations due to the release of solute also contribute). At a certain distance below the edge of the liquid pool, the newly solidified ingot is strong enough to resist the static pressure of the liquid part and to shrink away (due to decrease in temperature) from the water-cooled crucible wall, so forming a narrow gap which breaks the electrical connection between the lower part of the ingot and the crucible. This limited “contact zone” can change the electric current paths in the ingot and affect the Lorentz force closing the feedback loop shown with thick solid lines in Fig. 3.10. For this reason, the VAR process should be modeled as a fully coupled multi-physics problem.

The DC electromagnetic field is calculated using the fact that direct current produces a static magnetic field (without electromagnetic induction) and assuming that the processed alloy is not ferromagnetic (true above the Curie point for all metals), a scalar electric potential  $\varphi$  can be defined and solved for with mixed Dirichlet and Neumann boundary conditions. Then, it can be used to calculate the electric current density  $\mathbf{J}$  with the help of the electrical conductivity  $\sigma$ :

$$\mathbf{J} = -\sigma \text{grad}\varphi, \text{div } \mathbf{J} = 0. \quad (3.11)$$

VAR geometry is axisymmetric and most of the modeling carried out to represent it takes into account this fact, to simplify the problem and reduce computational costs [28]. However, on occasion the electric arc was found to wander [29] and to vary its location over the surface of the liquid pool. Extraneous magnetic field measurements for the particular example presented here indicate the motion to be periodic (period 20–30 s) but slow enough for electromagnetic induction effects to be negligible. Because the arc can be off-center and change position in time, axial symmetry cannot be used and this then becomes a 3D problem. The 3D Biot–Savart integral has to be evaluated at each time step in order to calculate the 3D magnetic field:

$$\mathbf{B} = \frac{\mu}{4\pi} \iiint \frac{\mathbf{J} \times \mathbf{r}}{r^3} dV \quad (3.12)$$

where the volume integral is taken over all current segments  $\mathbf{J} dV$  that can possibly influence the local value of the magnetic induction  $\mathbf{B}$ ;  $\mu$  is the magnetic permeability and  $\mathbf{r}$  is the vector connecting the source point with the evaluation point. This calculation has then to be repeated in time for every computational cell in the liquid region (where the Lorentz force  $\mathbf{J} \times \mathbf{B}$  has any effect).

The contact zone at the top edge of the melt pool is electrically conducting, so a certain amount of current bypasses the ingot. The boundary conditions needed to address this situation are then as summarized in Fig. 3.11. Assuming that the contact zone is axisymmetric and cylindrical, the only parameter that remains to control it is its height. In practice, this is not known (exactly) in advance, but it is possible to *prescribe* it so that the temperature at its lower end is below the critical value for the shrinkage gap to occur. In this way, the main feedback loop from Fig. 3.10 may be

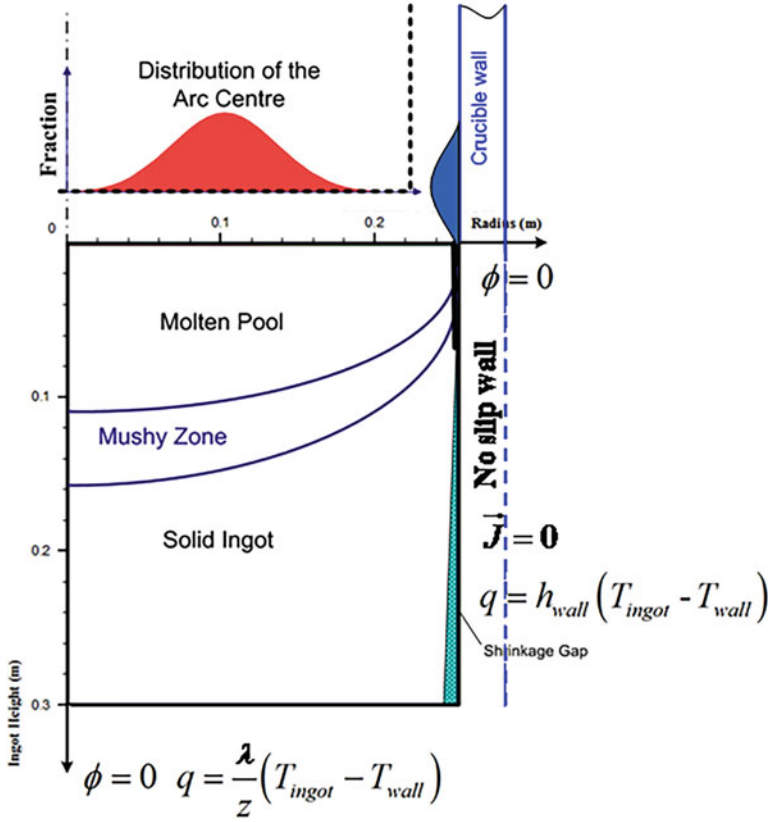


Fig. 3.11 Boundary conditions used in a macroscale VAR model

severed and a much simpler algorithm is obtained (Fig. 3.12), by neglecting the very weak magnetohydrodynamic effect  $\mathbf{u} \times \mathbf{B}$ .

With the electromagnetic field calculated once per time step (to reflect the changing position of the arc and of the contact zone), the remaining equations of fluid flow, heat transfer (see Sect. 3.1) plus turbulence can be solved in the usual for computational fluid dynamics (CFD) coupled way which allows the close interactions between these phenomena to be taken into account.

The boundary conditions shown in Fig. 3.11 are varied in time to prescribe rotational movement of the arc between the electrode and the ingot, which occupy separate computational domains with matching mesh cells. Rotation of the main arc current center is prescribed based on observations of an actual VAR furnace [29]. A Gaussian distribution of the instantaneous current is then assumed. These current densities form the Neumann boundary conditions for the electric potential equation with Dirichlet conditions defined at the top parts of the ingot and the crucible. In addition to the main arc, the peripheral arc current and the period of rotation are set to reproduce external magnetic field measurements [30].

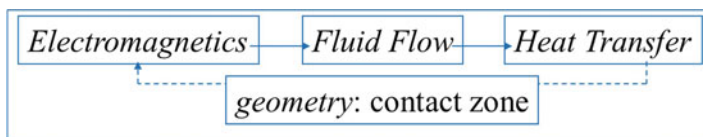


**Fig. 3.12** Modified coupling scheme for the top of the VAR ingot

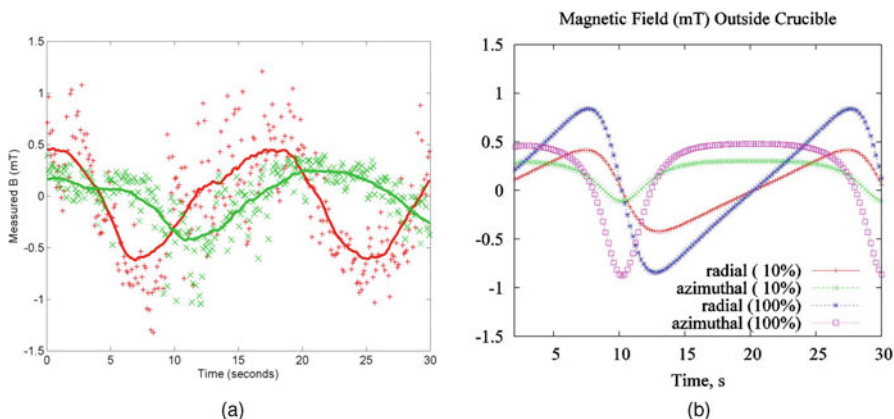


**Fig. 3.13** Experimental measurements (a) and numerical simulation (b) of magnetic field, measured outside the VAR water jacket

A comparison between measurements and numerical results is shown in Fig. 3.13. Observations indicate that the variations of both azimuthal and radial B-fields are periodic with a period of  $\sim 24$  s, a value adopted in the model.

For the fluid flow, heat transfer, and turbulence, the computational domain is restricted to contain only the upper part of the ingot (Fig. 3.11). The pool receives heat energy in two forms: radiation from the main arc and hot droplets from the melting electrode. The radiation input on the surface is assumed to follow the same “moving” Gaussian distribution as the arc current. The heat received from the droplets is calculated with a given melting rate and superheat, and it is assumed to be uniformly distributed in a volume with a prescribed depth below the surface, and with a diameter equal to the electrode diameter. Since the ingot is wider than the electrode, part of its top liquid surface does not lie directly under the electrode tip—this annular boundary can both receive (from the arc) and emit (to the cold crucible wall) radiation energy. The liquid metal free surface is assumed flat and even. (The expected local elevation of the liquid metal surface due to the pinching effect of the Lorentz force may be estimated from the balance of pressure and hydrostatic force. In a typical industrial application, it rarely exceeds 0.5 mm; being insignificant compared to the size of the liquid pool, it may be safely ignored.) In the shrinkage gap, heat is taken away by radiation and an emissivity factor needs to be specified. The lower boundary of the ingot domain is assigned a different heat transfer

coefficient, which takes into account the length of the lower solid part of the ingot and the crucible base which are outside the meshed domain.

Numerical simulations carried out with a time-dependent 3D macro-model need to run long enough in order to reach quasi-steady conditions with the prescribed period of arc center rotation. The sequence in Fig. 3.14 presents typical results obtained by the model. It shows the changes in the liquid pool profile resulting from the arc center passing the vertical monitoring plane. It can be seen that the

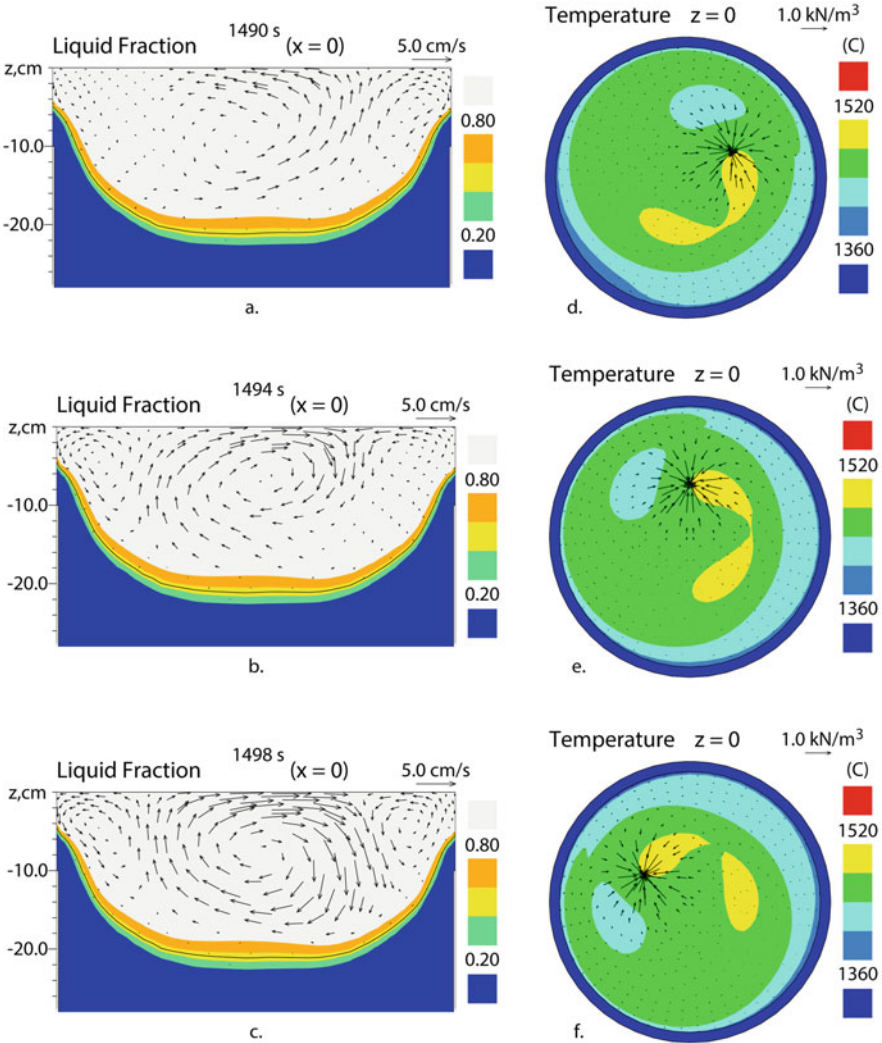


**Fig. 3.14** Time sequence of calculated results: (a, b, c) show contours of solid fraction and velocity vectors in a vertical cross section; (d, e, f) show the corresponding temperature contours and the pinching Lorentz force vectors in a horizontal plane at the top of the liquid pool



velocity field in the molten pool also changes significantly with the motion of the averaged arc center. This is evidence that for the examined case the Lorentz forces are much stronger than the buoyancy force or the inertial force. The velocity vectors in the vertical plane (left side of figure) show that the flow reverses direction as the arc rotates. The shaded area indicates the predicted shape of the melt pool, with the mushy (semi-solid) zone being thickest around the ingot axis. The change in mushy zone thickness is caused by the localized Lorentz force-driven flow under the arc, which lags in phase and only reaches the solidification region (see Fig. 3.14c) after the arc has moved 1/3 of the circumference on. The strong advection takes hot metal down to the mushy zone, causing localized remelting, as will be seen below in the microstructure subsection. The right column in Fig. 3.14 shows temperature contours on the pool surface and the corresponding volumetric Lorentz force vectors as the arc rotates. The “pinching force” generated as the arc enters the pool is evident by the incoming vectors surrounding the arc position. The Joule heat generated by the arc appears as a hot spot at the same location, with a trailing hot plume following it. The instantaneous temperature at the pool surface is also shown. Again, there is an obvious deviation from axisymmetry, with contours disturbed by the location of the arc.

The macro-model results can then be fed into two further sub-models to address defect prediction: (1) particle tracking for inclusion (“white spot”) defects, and (2) microstructure model for freckle defects. The source of white spot defects has been variously attributed to solidified crust breaking off the wall of a crucible during low-power conditions, or alternatively due to condensed material in electrode macroporosity cavities [31]. In either case, a particle tracking model can identify the eventual location of the particles within the melt pool once they are released. Solid particles falling from the electrode that are large enough to traverse the liquid pool without fully melting will end up as inclusions at the solidification front. Their trajectories were calculated by an addition of a Lagrangian *particle tracking* model, solving Newton’s second law of motion for particles where fluid drag and gravity are the main forces. Electromagnetic forces that might be affecting the particles’ motion were neglected, since the electrical conductivity of most particles is of the same order as the molten metal. If particles of foreign matter, such as oxides, need to be tracked, these forces could be included (see Sect. 3.3.3). The thermal balance between heat flux into the particle and specific heat (both particle temperature and latent heat are considered) is used to calculate the time-dependent diameter of the melting particle. This Lagrangian model uses the local time-dependent values of fluid velocity and temperature in the calculation of the particle trajectories and their melting behavior. The velocity of a particle  $\mathbf{u}_p$  is computed from the momentum equation:

$$m_p \frac{d\mathbf{u}_p}{dt} = C_d \rho (\mathbf{u} - \mathbf{u}_p) |\mathbf{u} - \mathbf{u}_p| \frac{S_p}{2} + m_p \mathbf{g} \quad (3.13)$$

where  $m_p$  and  $S_p$  are the particle mass and cross section,  $\rho$  and  $\mathbf{u}$  are the liquid density and velocity,  $\mathbf{g}$  is the gravity vector, and the drag coefficient  $C_d$  for spheres is given by:

$$C_d = \frac{24}{\text{Re}} \cdot (1 + 0.15\text{Re}^{0.687}) + \frac{0.42}{1 + \frac{42500}{\text{Re}^{1.16}}}. \quad (3.14)$$

Particle temperature  $T_p$  is governed by the enthalpy equation:

$$m_p c_p \frac{dT_p}{dt} = \alpha (T - T_p) + L \frac{dm_p}{dt}, \quad (3.15)$$

where  $T$  is the local melt pool temperature,  $L$  is the latent heat of solidification, and  $c_p$  is the particle specific heat. The heat transfer coefficient between liquid and particles  $\alpha$  is given by:

$$\alpha = \pi d_p k \text{Nu} \quad (3.16)$$

in which  $k$  is the fluid thermal conductivity,  $d_p$  the particle diameter, and Nu is provided by:

$$\text{Nu} = 2(1 + 0.3\text{Re}^{0.5}\text{Pr}^{0.33}). \quad (3.17)$$

Particles with initial diameters 4, 6, and 8 mm were modeled as falling of the electrode near the center of the melt pool. Their specific heat ( $620 \text{ J kg}^{-1} \text{ K}^{-1}$ ), latent heat ( $272 \text{ kJ/kg}$ ), solidus ( $1260^\circ \text{C}$ ), and liquidus ( $1336^\circ \text{C}$ ) temperatures were assumed to be the same as those of the investigated alloy. The initial temperature of the solid particles was prescribed at  $800^\circ \text{C}$ , which corresponded to density of  $7884 \text{ kg/m}^3$  while the liquid density was  $7490 \text{ kg/m}^3$ .

Results shown in Fig. 3.15 correlate well with predictions in reference [31] and indicate that the smallest particles fully melt, medium-sized particles are influenced

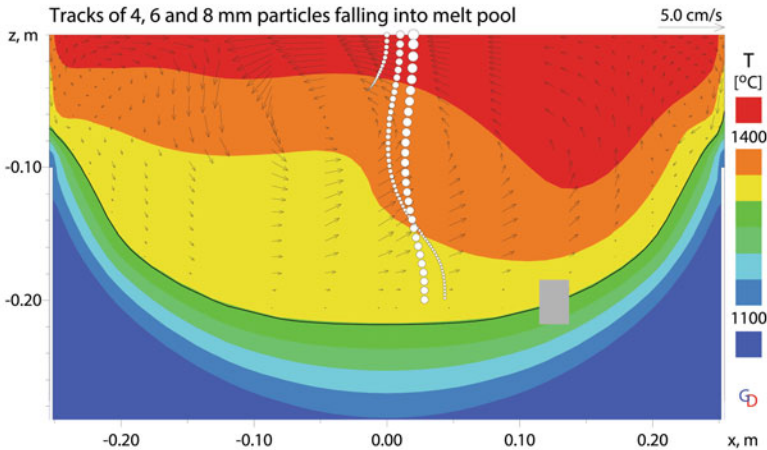


**Fig. 3.15** Temperature contours, liquid metal velocity vectors, solidification front (solid line), and melting alloy particles (shown as white circles) in the pool at top of a VAR ingot. The gray rectangle at half-radius shows the selected region for modeling freckle formation with the micro-model

by the flow near the mushy zone, and larger inclusions do not have time to melt before being trapped into the solidification front forming “white spots.” The particle size range and release position used are arbitrary in this implementation, chosen simply illustrate the likely state of inclusions as they traverse the pool, plus allow comparison to Ref. [31]. Since there is no significant interaction between such particles and the flow field, this can be a post-processing calculation from stored velocity and temperature fields that can be performed very quickly with a large number of such tracks.

### 3.2.2.1 Linking with a Microstructure Model

The scale of the macro-mesh is not fine enough to resolve the development of the dendritic microstructure during solidification and so establish a relationship between operational parameters and microstructure defects. In this example, a weakly coupled linkage was developed with a micro-model operating at selected positions within the mushy zone of the macroscale VAR model. For this one-way coupling, 3D time-dependent temperature and composition data for a selected region of the mushy zone need to be imported into the microscale model.

Figure 3.15 identifies as a gray rectangle a mid-radius location in the mushy zone, chosen for microstructure simulations. Many such positions were sampled, but the one selected is associated with the location where most commonly freckle defects are observed.

A model of both equiaxed and columnar dendritic growth was used, developed in [32–34], which incorporates thermal, solutal, and fluid flow effects in either two or three dimensions. Because the temperature profiles from the VAR model have incorporated the fluid flow effect due to both the Lorentz force and the buoyancy force, a version of the microscale solidification model without solving the Navier–Stokes equation was used in this study. This allows a much larger sample domain to be simulated with less computational cost. The governing equation for solute diffusion is given by:

$$\frac{\partial C_e}{\partial t} + \nabla \cdot (\mathbf{u} C_l) = \nabla \cdot (D_e \nabla C_l) \quad (3.18)$$

where  $\mathbf{u}$  is the velocity vector in the liquid (directly interpreted from the macroscale VAR model);  $C_e$ , the equivalent concentration, and  $D_e$ , the equivalent solute diffusion coefficient, are defined as:

$$C_e = C_l f_l + C_s f_s; \quad (3.19)$$

$$D_e = D_l f_l + k \cdot D_s f_s, \quad (3.20)$$

where  $f_l$  and  $f_s$  are the liquid and solid fraction,  $C_s$  and  $C_l$  are the average solute concentrations of the solid and liquid,  $k$  is the partition coefficient, and  $D_s$  and  $D_l$  are the solute diffusion coefficients in solid and liquid, respectively. In the solid,  $f_l = 0$

and  $f_s = 1$  then Eq. (3.18) becomes:  $\frac{\partial C_s}{\partial t} = \nabla \cdot (D_s \nabla C_s)$  and in the liquid,  $f_l = 1$  and  $f_s = 0$ , giving  $\frac{\partial C_l}{\partial t} + \nabla \cdot (\mathbf{u} C_l) = \nabla \cdot (D_l \nabla C_l)$ . At the solid/liquid interface, the growth of a dendrite is determined by local equilibrium partitioning of the solute:  $C_s = k C_l$  and  $C_l$  at the interface can be calculated from a linearized equilibrium phase relation:

$$C_l = C_0 - \frac{T_l^0 - \Gamma \kappa - T}{m_l}, \quad (3.21)$$

where  $C_0$  is the initial concentration,  $\Gamma$  is the Gibbs–Thompson coefficient,  $\kappa$  is the average curvature of the solid/liquid interface,  $m_l$  is the liquidus slope, and  $T$  is the local temperature, which is interpolated from the VAR model.

The diffusion equation is solved on the same regular spatial grid using a finite difference method. To satisfy the preferred misorientation for each grain, an imposed anisotropy algorithm was developed in [32], allowing a relatively coarse mesh to be used improving computational efficiency compared to other numerical techniques, such as phase field and level set methods. It was found that 3D simulations were required to correctly predict unconstrained solidification microstructures with the presence of fluid flow [33].

Since both finer temporal and spatial steps were required in the micro-model, the temperature and velocity fields coming from the macro-model were interpolated onto the finer mesh in the domain indicated by the shaded region in Fig. 3.15. Then, in succession, the following four algorithmic stages were executed: *nucleation*, *solute diffusion calculation*, *fraction solid update*, and *growth of dendrites calculation* before advancing to the next time step. Results from the dendrite growth simulation with the temperature history of the selected region over two cycles of the assumed arc spot rotation are presented in Fig. 3.16. It can be seen that columnar dendrites were formed in the selected domain with an approximate primary dendrite arm spacing (PDAS) of 500  $\mu\text{m}$ , consistent with experimental observations [35].

### 3.2.2.2 Freckle Defect Prediction

Here, we attempt to demonstrate the potential of freckle formation in terms of the microstructure variation in the VAR process. Due to the extreme computational cost and lack of high temperature data, direct numerical solutions of the full conservation equations modeling the freckle channel formation are not practical to be applied in industrial cases. Instead, an empirical criterion may be used, based on a Rayleigh number [36]:

$$\text{Ra}_h = \frac{g \bar{K} h}{\alpha \nu} \left( \frac{\Delta \rho}{\rho_0} \right), \quad (3.22)$$

where  $h$  is a length scale,  $g$  is the acceleration due to gravity,  $\bar{K}$  is the mean permeability of the mushy zone,  $\alpha$  and  $\nu$  are the thermal diffusivity and kinematic

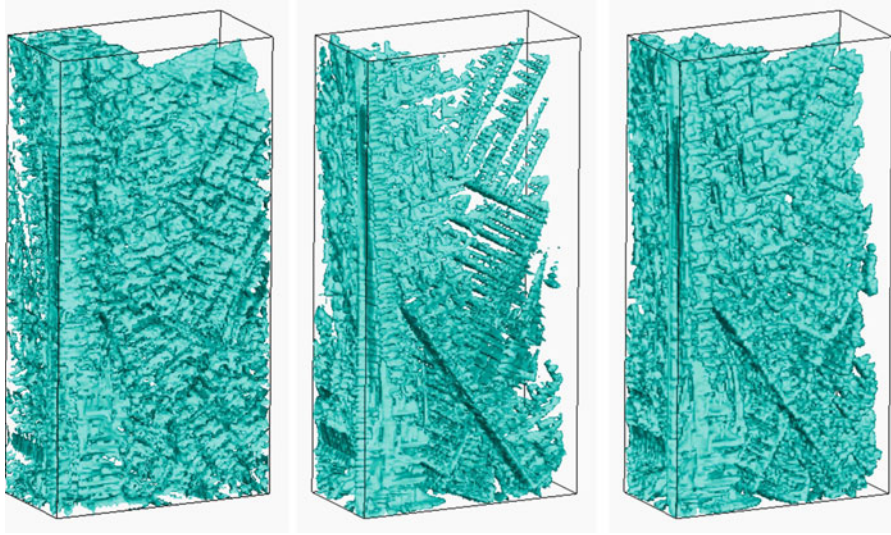


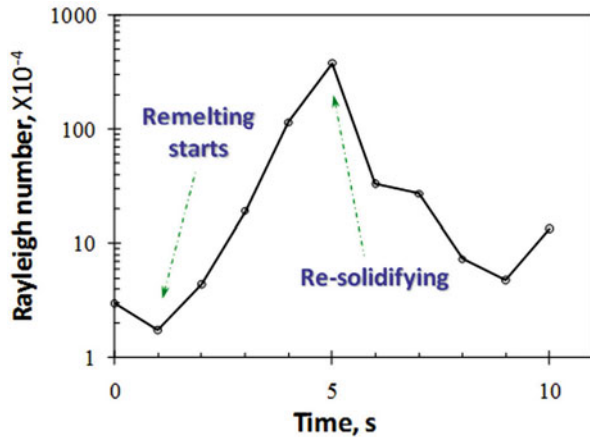
**Fig. 3.16** Dendritic microstructure for: growing (left), remelting (center), and regrowing (right)

viscosity, respectively, and  $\Delta\rho/\rho_0$  is the relative density inversion due to thermal and/or compositional variation.

The permeability in the direction normal to the temperature gradient was calculated via Darcy's law by solving the Stokes equations within the simulated dendritic structure at different time steps [26]. Permeability increased by a factor of 300 during remelting (Fig. 3.16), occurring as the temperature varies with arc passage. The increased permeability allows the flow to pass through the porous medium easily. The Rayleigh number is directly proportional to permeability, hence also increases by this amount within the mushy zone. For the case depicted in Figs. 3.14 and 3.16, the corresponding Rayleigh number changes are shown in Fig. 3.17, which clearly indicates the cyclic position of the remelting/solidification front as the arc traverses the affected region. The higher the Rayleigh number, the easier the formation of freckles [36, 37]. Such predictions were only possible by simulating the process with a 3D, transient, multiscale model.

Concluding, a 3D, transient, multi-scale computational model of the VAR process was shown in this section. This was developed and validated via comparison to experimental measurements of pool shape, surface flow velocities, and microstructural measurements. The model demonstrated its usefulness in predicting the occurrence of two key defects which can reduce the quality of VAR ingots, specifically "freckles" and "white spots." The simulation results show the crucial influence of the transient arc position on the flow and thermal fields in the melt pool and its resultant shape. Unsteady fluid flow caused by Lorentz forces due to arc motion was found to cause significant thermal perturbation within the mushy zone leading to local remelting. The associated localized transient changes in the Rayleigh number as

**Fig. 3.17** Rayleigh number variation for the case depicted in Figs. 3.14 and 3.16



the microstructure remelts provide an indicator of when fluid flow channels (i.e., freckles) will initiate in the mushy zone. By examining the simulated microstructures, it was found that the Rayleigh number increased by a factor of 300 during the arc traverse, strongly suggesting that thermal perturbation could be responsible for the breakup of columnar dendrites and the onset of freckle channel formation.

### 3.3 AC and Combined AC/DC Applications

#### 3.3.1 Levitation Principles

Magnetic levitation is often associated with magnetically levitated superfast trains or small toys of magnetically suspended objects. However, it is far less known that liquid droplets or even 20 kg of liquid metal can be levitated in molten condition without a direct contact to any solid surface. The research on small droplets melted and suspended in vacuum or inert gas is advanced for the purpose to investigate the material properties of reactive metals [38–41]. There are a growing number of applications where an electrically conducting fluid is confined, or even levitated, using a high-frequency AC magnetic field. The lifting force is commonly provided using a medium to high-frequency AC current, feeding a coaxial conically shaped coil (Fig. 3.18). An opposing eddy current develops within the sample, which in this case needs to be electrically conducting; the interaction of coil and induced currents leads to the repelling Lorentz force. It is also possible to levitate nonconducting liquid materials in a gradient DC field as has been demonstrated experimentally in many high-field laboratories, see, e.g., [42, 43].

The conditions within a levitated liquid material are largely controlled by the electromagnetic force distribution. It is important to understand how various approximations to this force field can be obtained. The general expression for

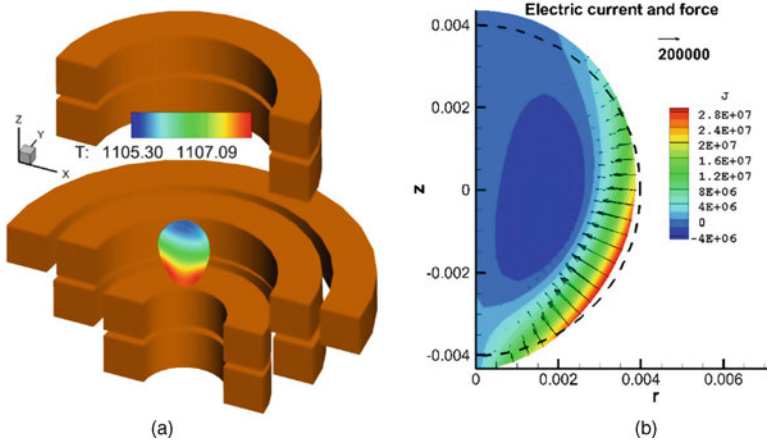


**Fig. 3.18** Copper droplet levitated in AC magnetic field. (a) 3D view of the experiment showing the temperature and the shape of droplet. (b) the distribution of induced electric current and the time-averaged force density

an electromagnetic force acting on a levitated fluid volume is rather complex, if one accounts for variable electrical conductivity and magnetic properties. For uniform material properties, the commonly used expression for the force is:

$$\mathbf{f} = \mathbf{J} \times \mathbf{B} + \chi \nabla (BDC^2/2\mu_0), \quad (3.23)$$

where the cross product of AC electric current density  $\mathbf{J}$  and the magnetic field  $\mathbf{B}$  (AC and DC) are responsible for the first term contribution, while the gradient and magnitude of the DC magnetic field  $\mathbf{B}_{DC}$  act on materials owing to their volumetric magnetic susceptibility (e.g.,  $\chi = -9.04 \times 10^{-6}$  for water and  $\chi = -4.2 \times 10^{-6}$  for silicon, which are diamagnetic). The constant  $\mu_0$  is the vacuum magnetic permeability in SI units. The relative magnetic permeability  $\mu = 1 + \chi$  is alternatively used for ferromagnetic materials. In some cases, a combination of high-frequency AC and DC magnetic fields will be considered. Time average of the force over the field oscillation period  $\tau$  ( $\sim 10^{-4}$ – $10^{-6}$  s) is often sufficient because the time scale for typical levitated droplet oscillations is  $1$ – $10^{-2}$  s. However, in addition to the time-averaged force, the oscillating part of the high-frequency AC field is still present within the fluid, adding a time-dependent vibrating force at double the frequency of the applied AC [12]. When the force is restricted to the skin layer at the liquid metal surface, the oscillating part of the force can create effects comparable to the ultrasound application via external transducer (see Sect. 3.3.4 for more details).

The electric current  $\mathbf{J}$  distribution in a moving droplet is composed of three parts. First, the magnetic induction (Eq. (3.2)) represented by the magnetic vector potential  $\mathbf{A}$  (related to the magnetic field  $\mathbf{B} = \nabla \times \mathbf{A}$ ), second, the gradient of electric potential  $\varphi$  (to ensure the continuity of induced  $\mathbf{J}$  or to add an external power source), and, third, the fluid flow-induced part  $\mathbf{u} \times \mathbf{B}$ :



$$\mathbf{J} = \sigma(-\partial_t \mathbf{A} - \nabla \varphi + \mathbf{u} \times \mathbf{B}) = \mathbf{J}_{AC} + \mathbf{J}_v. \quad (3.24)$$

Fluid dynamics and heat transfer are based on the numerical solution of the turbulent momentum and heat transfer equations for an incompressible fluid, Eq. (3.5). Despite the small size of droplets, the typical flow Reynolds number is of the order  $10^3$ – $10^4$  in the AC field levitation. For the turbulent flow, the effective viscosity  $\mu_e = \rho(\nu_T + \nu)$  is computed from the time-dependent two-equation  $k$ – $\omega$  model [44] that includes the effect of the magnetic field (see the various auxiliary functions in [45]):

$$\begin{aligned} \partial_t k + \mathbf{u} \cdot \nabla k &= \nabla \cdot [(\nu + \sigma_k \nu_T) \nabla k] + G - \beta^* \omega k - \frac{2\alpha_m k}{\rho/(\sigma B^2)} \\ \partial_t \omega + \mathbf{u} \cdot \nabla \omega &= \nabla \cdot [(\nu + \sigma_\omega \nu_T) \nabla \omega] + \alpha \frac{\omega}{k} G - \beta \omega^2 - \frac{\alpha_m \omega}{\rho/(\sigma B^2)} \end{aligned} \quad (3.25)$$

with the natural “no flux” boundary conditions at the free surface:

$$\partial_n k = 0, \quad \partial_n \omega = 0. \quad (3.26)$$

The flow boundary conditions at the external free surface are for the hydrodynamic stress tensor  $\mathbf{\Pi}$  component projections:

$$\Pi_{nn} = \gamma G, \quad \Pi_{n\tau} = \gamma_T \nabla T \cdot \mathbf{e}_\tau, \quad (3.27)$$

where  $\gamma(T) = \gamma(T_m) + \gamma_T \cdot (T - T_m)$  is the temperature-dependent surface tension coefficient above the melting temperature  $T_m$ ;  $G$  is the local mean curvature of the surface, and the subscripts  $n, \tau$  correspond to projections onto  $\mathbf{e}_n$  and  $\mathbf{e}_\tau$ —the normal and tangent unit vectors at the free surface, respectively. In addition to the dynamic conditions, Eq. (3.27), the calculated material fluid velocity  $\mathbf{u}(t)$  moves continuously the interface position  $\mathbf{R}(t)$ :

$$\mathbf{e}_n \cdot \mathbf{v} = \mathbf{e}_n \cdot \partial_t \mathbf{R}, \quad (3.28)$$

to determine the instantaneous droplet shape (kinematic condition). The thermal boundary conditions to solve the heat balance Eq. (3.10) state that radiation loss on the surface of the levitated droplet is

$$-\mathbf{e}_n \cdot (-k \nabla T) = \varepsilon \sigma (T_{\text{amb}}^4 - T^4). \quad (3.29)$$

The described theory is implemented in the numerical software SPHINX used to solve various cases of the droplet levitation dynamics [40, 41, 46]. Figure 3.18 illustrates the AC levitation of molten copper droplet in terrestrial conditions. The coil current effective value is 420 A at 400 kHz, leading to the melting and full levitation of the liquid metal in just few seconds. The initially solid sphere is of 4-mm radius where the induced current and the electromagnetic force are concentrated in thin skin layer as shown in Fig. 3.18b. After melting, the droplet surface

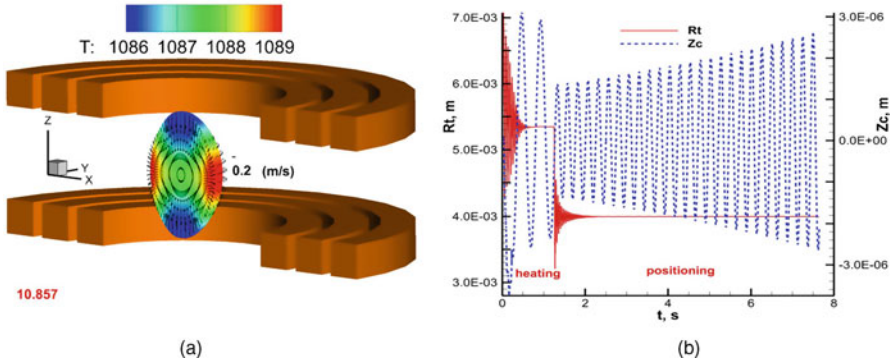


**Fig. 3.19** The MSL-EML coil system for melting at microgravity conditions (a). The droplet oscillation response (b)  $R_t$  for the top position on the surface, and  $Z_c$  for the center of mass

oscillates at frequencies similar to theoretically predicted by Rayleigh [47] taking into account the surface tension restoring force (Eq. (3.27)). However, in the full gravity conditions, the levitating force distribution leads to the generation of intense internal turbulent flow, which affects the oscillation nature by effective turbulent viscosity damping. The adjustment of the droplet surface deformation initiates the center of mass oscillation in addition to the surface motion. As a result, the determination of the material properties requires correction functions [38] and makes the result less reliable.

The experiments in space with zero gravity conditions successfully extend the technique as described in [41, 46]. The velocity field in the liquid copper droplet shortly after melting at microgravity conditions in the MSL-EML coil system is shown in Fig. 3.19. Modeling permits the prediction of the surface oscillation response after melting under the combined action of the positioning (146 kHz) and heating (370 kHz) currents in the coil system, followed by switching off the heating while retaining the positioning current. The surface oscillation at the top position on the surface  $R_t$  is still subject to significant damping due to the turbulence generated, and the center of mass motion indicates a very small rise in the amplitude, possibly leading to an unstable positioning of the sample.

Alternative magnetic levitation techniques are attempted using DC magnetic field either in combination with the AC [39] or on their own [48]. It was hoped that the AC field-driven turbulent flow will be damped in the presence of a sufficiently strong DC magnetic field. This would permit the conditions similar to laminar viscous damping, and allows the heat conduction in almost quiescent liquid material without any contact to solid walls. The experiment with the purpose of measuring the material properties of molten silicon proved the validity of this assumption at a relatively high magnetic field of 4–5 Tesla [39]. The combined AC and DC action levitation was modeled in [41] to gain a further insight on how this technique worked. At a high value of the magnetic field of 5 T, the turbulence is completely damped, and the velocities are very low and predominantly oriented along the  $B_z$ .

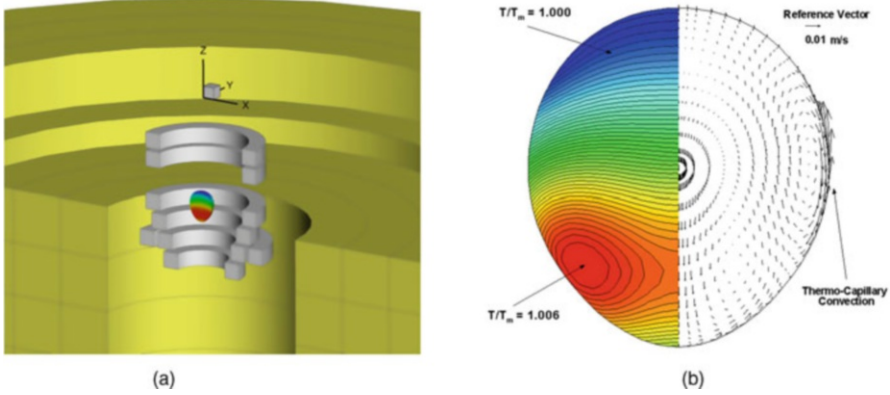


**Fig. 3.20** (a) Model of combined AC and DC levitation. Enlarged view (b) shows the velocity and normalized temperature field at  $B_{DC} = 5$  T,  $T_m = 1414$  °C

The temperature field in this case corresponds to the ideal heat conduction—the conditions required for the successful measurement of the material properties (Fig. 3.20). Unexpectedly, the weak Marangoni convection at the nearly vertical part of the side surface dominates the velocity field. This effect can be used in further experiments to investigate this type of flow, which otherwise is concealed when the magnetic damping is absent. In contrast, when the DC magnetic field is absent ( $B_{DC} = 0$ ), the turbulent flow is dominating the temperature field in the droplet, as shown in Fig. 3.21a. Adding a moderate magnetic field of 1 T leads to the situation presented in Fig. 3.21b. The velocity field increases in magnitude because the effective viscosity is reduced by damping out the small-scale turbulence in the presence of 1 T field. The surface oscillations, however, demonstrate different behavior presented in Fig. 3.21c. The surface tension dominated Rayleigh-type oscillations are present at  $B_{DC} = 0$  with a moderate damping rate determined by the turbulent effective viscosity. At the relatively low  $B_{DC} = 1$  T, the oscillations are damped at even faster rate due to the effect of flow-induced electric current proportional to  $\mathbf{u} \times \mathbf{B}$ . At high magnetic field  $B_{DC} = 5$  T, the oscillation is resumed at different frequency and a low damping rate as predicted theoretically in [42]. This result serves as an additional validation of the numerical code SPHINX used to obtain the described results [49].

As mentioned above, the liquid droplet levitation is possible in purely DC magnetic field, using para- and diamagnetic properties of the materials. In modern superconducting magnets, sufficiently high magnetic field can be easily created in a substantial volume. Potentially, this type of levitation can be used for advanced material research without the drawbacks related to the intense recirculating turbulent flow vortices appearing when the AC magnetic field is used. The diamagnetic levitation is possible at the upper part of the magnet where the negative gradient of the magnetic field counteracts the gravitational force on the diamagnetic material droplet according to Eq. (3.23). The schematic view of the magnet from the numerical model [43] is shown in Fig. 3.22. The magnetic force supporting the

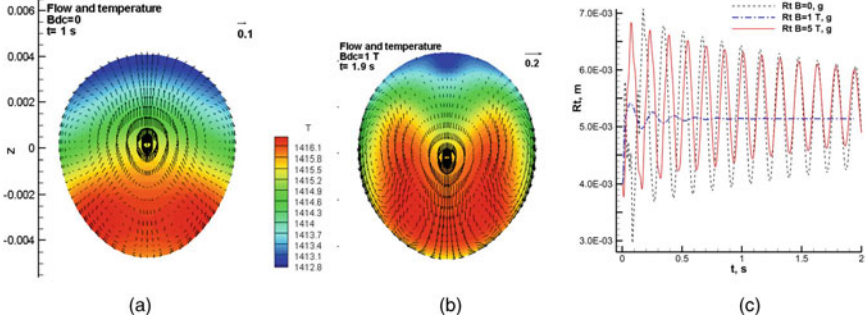


**Fig. 3.21** The velocity and temperature fields in molten silicon, computed under AC and DC levitation when  $B_{DC} = 0$  T (a) and 1 T (b) plus (c) the surface oscillation response at various values of DC magnetic field

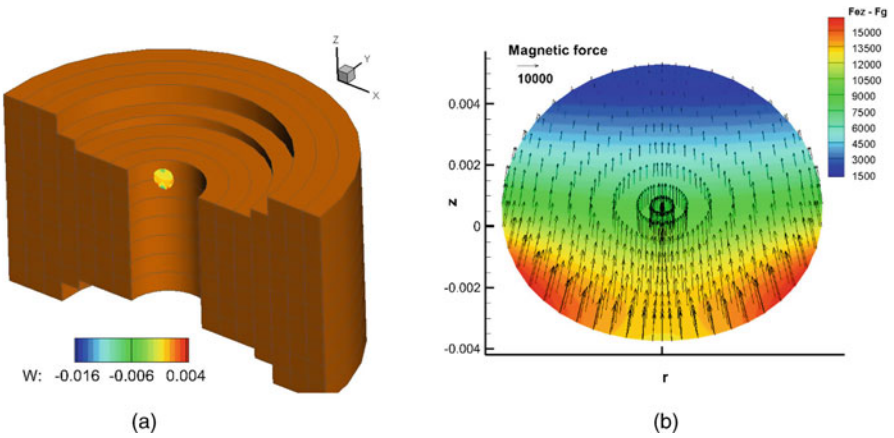


**Fig. 3.22** Model of water droplet levitation in 16.5 T DC magnetic field (a). (b) Vector distribution of the total magnetic force density and the force difference to gravity (color contours) in the droplet volume

droplet is nonuniformly distributed within the droplet volume as shown in Fig. 3.22b. This force will not generate any fluid flow in a stationary droplet because  $\text{curl}(\chi \nabla(BDC^2/2\mu_0)) = 0$  if the magnetic properties are uniform. However, a small perturbation of the suspended droplet surface will start the surface tension-controlled oscillation, which is very similar to the Rayleigh solution with a small correction due to the center of mass oscillation in the nonuniform magnetic field.

The experimental observation of a water droplet and the numerically solved velocity field in a 16.5 T field are shown in Fig. 3.23. The velocity is purely laminar, subject to the material viscosity to determine the damping rate of the oscillation. The oscillation consists of a superposition of capillary modes and the center of mass motion as shown in Fig. 3.23c. Relatively large droplets can be used to levitate, up to 3–4 cm in the experiment described in [43]. The larger volumes are more prone to

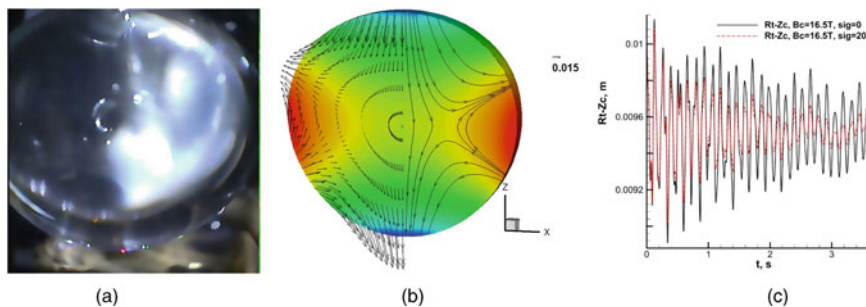


**Fig. 3.23** The water droplet in situ levitated in a 16.5-T field (a), the computed instantaneous internal velocity field, and shape of the droplet (b). (c) The droplet oscillation response: “Rt-Zc” for the top position on the surface corrected by the center of mass position

instabilities, which however are easily controlled if the liquid is weakly electrically conducting. By adding a small amount of NaCl to the pure water, the weak electrolyte is electrically conducting ( $\sigma = 20 \, \Omega^{-1} \, \text{m}^{-1}$ ) and the  $\sigma \mathbf{u} \times \mathbf{B}$  term in (3.6) ensures additional damping of the velocities in the liquid. All these effects are accurately predicted using the numerical modeling and can be used efficiently to interpret the measurements. This opens a new method to determine material properties of liquids, even molten metallic alloys, in terrestrial conditions without resorting to extraordinary expensive space missions.

### 3.3.2 Cold Crucible Examples

On a larger scale than typical magnetic levitation of droplets, there is a demand for melting reactive materials without contamination, e.g., titanium alloys for aerospace-quality castings. Titanium alloys are the light structural metals attractive for aerospace and automotive applications that offer high mechanical properties at a significant weight saving. A major barrier to manufacturing these components is melting and subsequent casting alloys free of contamination and severe segregation, which may lead to undesirable properties. The forced stirring of the melt by electromagnetic forces can significantly promote the detachment of dendrite arms and transporting the crystal fragments in a disperse fashion due to the presence of high turbulence (see also Chap. 4).

Despite attempts to achieve full levitation of large liquid volumes [50–53], different types of the so-called semi-levitation melting remain the most practical technical implementations of the magnetically confined melting using either segmented copper wall crucibles (cold crucibles) or some kind of bottom support to help with the magnetic confinement. The latter is known as semi-levitation melting [54], Fig. 3.24. The electromagnetic field induces a strong turbulent flow in the molten pool, which is beneficial for producing a homogeneous melt with uniform

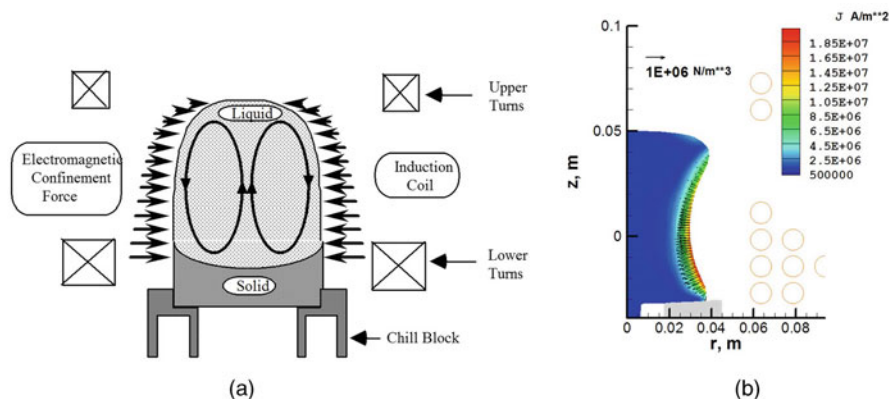


**Fig. 3.24** (a) The semi-levitation process schematic [54] and (b) the numerical solution giving insight to the force field required to suspend the liquid metal

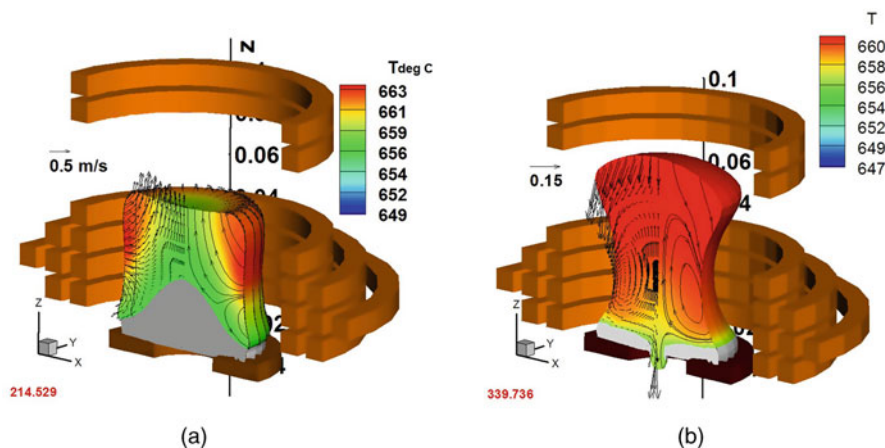


**Fig. 3.25** Semi-levitation melting stages, computed dynamically; (a) melting is from top to bottom, as the induction coil moves downwards. (b) Casting is by pouring through the hole in the bottom support into the mold below

temperature [55]. The process combines induction melting and casting into a single self-controlling operation. The charge melts from top to bottom while the induction coil moves downwards as illustrated in Fig. 3.25. Pouring of the charge through the hole in the bottom support into the mold below occurs when the liquid melting front reaches the base of the metal charge. The melt superheat is minimal, meaning that the mushy zone containing dispersed crystal fragments directly enters the mold below.

More control of the melting rate and added safety features of the crucible are obtained by enclosing the charge with a segmented copper wall, as shown in Fig. 3.26. The copper segments are electrically insulated by gaps between them, and they need to be cooled by pressurized water-based coolant circulated internally.



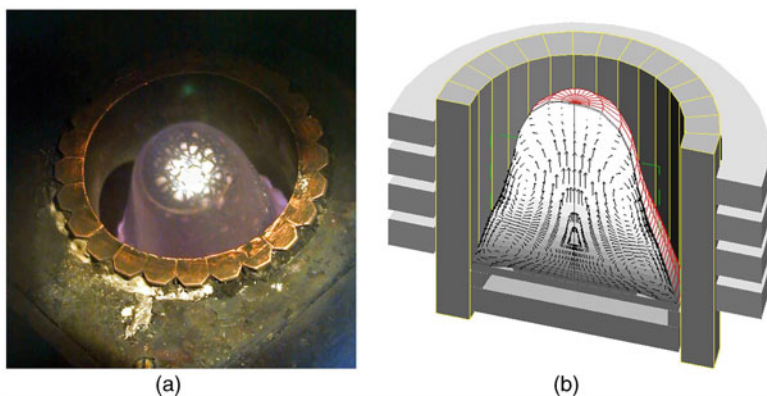


**Fig. 3.26** Comparison of the experimental aluminum alloy melt in a cylindrical cold crucible (a) and the final stage of melting obtained from the model (b)

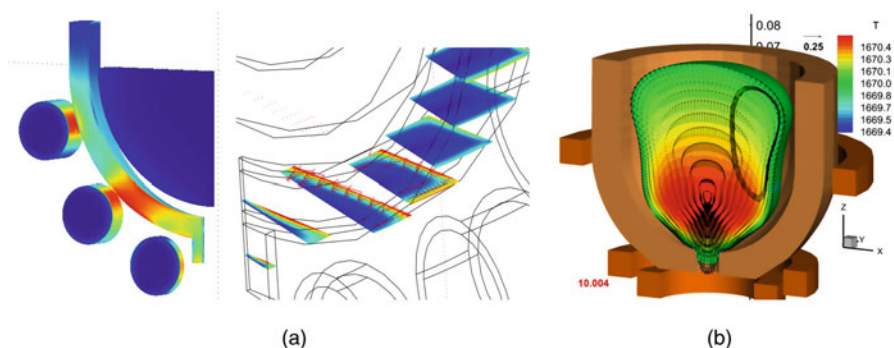


**Fig. 3.27** (a) The AC electric current distribution in the coils and in the copper segments by mutual induction plus the current path in the symmetric half of a copper segment. (b) Controlled outflow of molten titanium in a cold crucible with hemispherical bottom

The liquid metal is confined away from the copper segments due to the induced electric current mutual repulsion as illustrated in Fig. 3.27. The molten titanium is contacting the cold crucible at a very limited bottom part, which is covered by a thin frozen titanium layer. This region is relatively large in the cylindrical crucible (Fig. 3.26), which leads to a relatively low final melt superheat [56]. The situation is just marginally improved for the hemispherical bottom because the melt is oscillating periodically touching the copper bottom (Fig. 3.27). The electromagnetic force acting on the fluid volume adjusts, approaching in an oscillating way the value of the total weight of the liquid metal.

A new method to increase the superheat was discovered when applying an additional DC magnetic field of a moderate 1 T magnitude [57]. The magnetic damping of small-scale turbulence helps to reduce the level of effective thermal



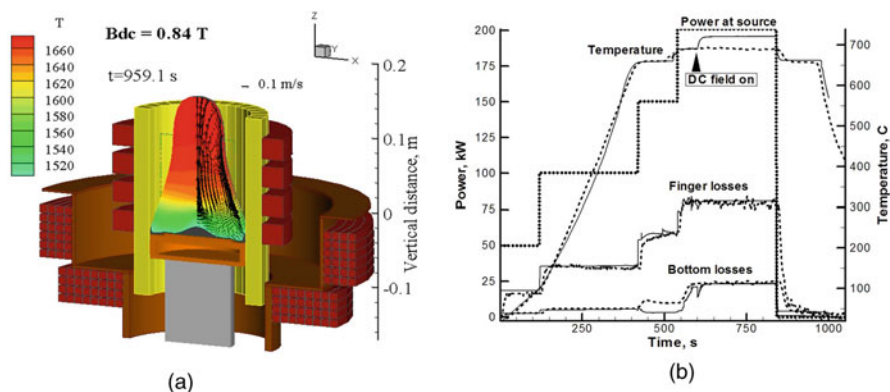


**Fig. 3.28** (a) A new type of cold crucible combining AC and DC magnetic fields. (b) Comparison of the measured and numerically predicted temperatures and power in the crucible during the melting process. Note the temperature rise after DC field activation

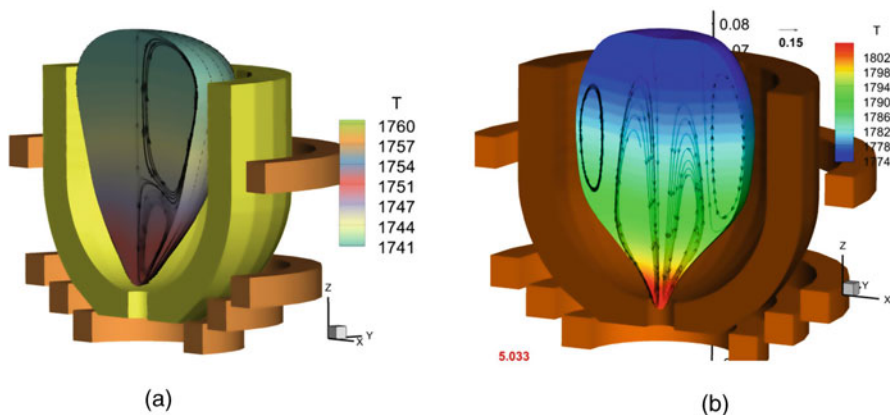


**Fig. 3.29** The increase of molten titanium superheat during the fully levitated stage (a) and further rise of maximum temperature from 1760 °C to 1802 °C when DC magnetic field is added (b)

diffusion and the related heat transfer rate. This results in the significantly increased melt superheat, as shown in Fig. 3.28.

If the contact between the copper wall and liquid metal can be avoided, the thermal losses will be limited only to radiation and possible evaporation. During the surface and flow adjustment, the liquid surface performs oscillations. With the coil design optimized, the fluid is pushed up, it detaches from the crucible, and after several oscillations it assumes a quasi-steady levitated position (Fig. 3.29). The mechanism of the levitation, and particularly the local magnetic support at the bottom, appears to be dynamic in nature. The electromagnetic force is zero at the bottom tip position and the surface tension effect is clearly not sufficient to support 1 kg of liquid titanium above the finite curvature radius. The explanation for the fact

that the liquid at the bottom is not leaking is related to the particular velocity field in this region. The bottom vortex in Fig. 3.29 is maintained by the rotational nature of the electromagnetic force ( $\text{curl} \mathbf{f}_e \neq 0$ ), which drives the fluid tangentially upwards at the side surface of the liquid, away from the tip stagnation point. Due to the continuity ( $\text{div} \mathbf{v} = 0$ ), the outflow at the bottom is redirected to the intense flow upwards along the side surface.

In levitated conditions, the liquid metal temperature rises relative to the case when there is a contact to the water-cooled copper crucible. The superheat relative to the titanium melting temperature (1667 °C) is reaching 100 °C in the situation shown in Fig. 3.29a. The further rise of the melt superheat can be achieved by adding the DC magnetic field, as shown in Fig. 3.29b. The effect of controlled stable levitation produces a higher superheat and permits investigation of materials at extreme temperatures, allows large volumes of metal to be evaporated for coating purposes [53], or to supply superheated melt without contamination for metal powder production.

### 3.3.3 Silicon Kerf Recycling

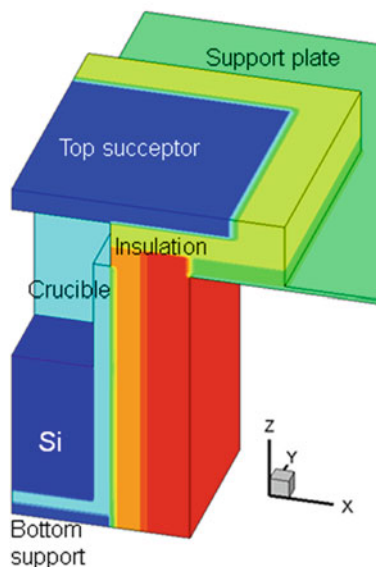
Silicon panels for solar power applications can be produced from metallurgical-grade silicon by complex and relatively expensive purifying processes [58], which also use large amounts of energy and can be harmful to the environment. The production process includes slicing of the purified silicon ingots into thin wafers by sawing with diamond-coated wires. A significant fraction of the ingot material (up to 50%) is lost into sawdust (kerf loss) during the wafering [59]. It is therefore highly desirable to recycle the sawdust but the recycling process must remove all impurities from the remelted material and restore the solar-grade quality of the new silicon ingots.

Crystallization of solar silicon ingots is normally done by directional solidification [58]. Since in the liquid state, silicon is electrically conductive like a liquid metal, induction furnaces can also be used as they provide some advantages over other types of heating for the steering of the solidification process [60]. However, before melting the silicon feedstock is not sufficiently conducting for the induction of currents strong enough to be able to melt it. Therefore, graphite susceptor plates have to be installed in suitable locations in the hot zone of the furnace—the induced currents in these susceptors produce sufficient heat to melt the charge.

Another advantage of the induction heating in the case of remelted silicon kerf is the possibility of simultaneous separation of nonconducting inclusion particles (e.g., carbon, SiC, and SiN) by the action of electromagnetic forces whose effect is to drive the particles to the sides of the solidifying ingot [59]. The contaminated thin layers on the sides can be removed by sawing and disposed of before the slicing of the solar panels.

Where graphite susceptors surround the square crucible holding the molten silicon on all sides, shielding of the magnetic field occurs, reducing the extraction force on the particles and the efficiency of their separation. A dual-frequency power

**Fig. 3.30** Furnace layout and materials



supply [61] can solve this problem as predicted by detailed numerical modeling [62]: the higher frequency has a small penetration depth, while the lower frequency easily penetrates the graphite shield. Both frequencies complement each other in retaining the particles on the sidewalls and in stirring the melt, thus allowing all particles to reach the walls of the vessel.

Even with a single frequency, the furnace can be designed with only top and bottom graphite susceptors and no shielding plates on the sides of the crucible [59]. Instead of graphite walls, the quartz crucible is supported by nonconducting insulation material (Fig. 3.30). The strong magnetic field that now easily reaches the silicon melt is produced by three set of induction coils each consisting of four turns and surrounding the insulation box (Fig. 3.31). The performance of this design can be investigated by numerical computational modeling. From all parts made of different materials that are shown in Fig. 3.30, only those parts which are essential for capturing the silicon solidification and nonconducting particles separation and retention are included in the model: the Si volume, the bottom of the crucible, and the graphite plate supporting the crucible. The model simulation is started when the silicon has been fully melted by the heat of the top and bottom susceptors.

Comparisons of the calculated electromagnetic fields with the full three-dimensional geometrical model of the charge and surrounding coils (Figs. 3.30 and 3.31) and with just a quarter of the geometry and symmetrical, square representation of all coils give practically identical results (due to the magnetic field canceling in the parallel leads). Therefore, all further detailed calculations can be done on the quarter symmetrical geometry (Fig. 3.32).

The computational model includes: electromagnetic field calculation taking into account the difference in electrical conductivities of liquid and solid silicon;

**Fig. 3.31** Induction coil  
(1 of 3 sets)

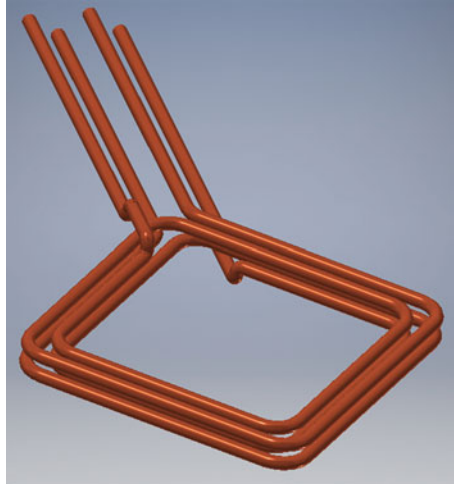
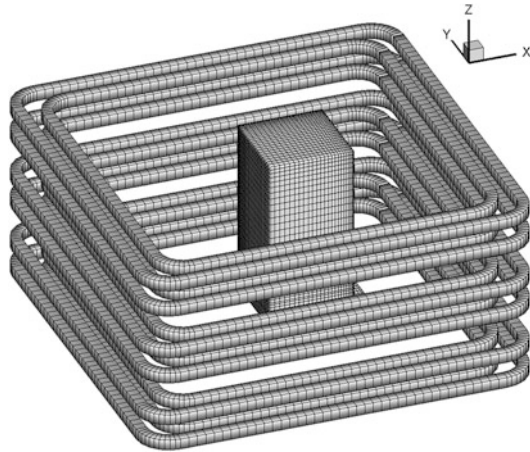


**Fig. 3.32** Computational  
3D geometry and mesh



prediction of turbulent liquid flow driven by the electromagnetic Lorentz force; calculation of heat transfer with Joule heating, radiative heat outflow, and under the liquid convection conditions; solidification simulation based on a mushy zone model with latent heat release including shape of the progressing solidification front; particle tracking under the simultaneous action of the fluid drag, the gravity, and the Leenov–Kolin force on nonconducting particles.

All numerical experiments are based on a set sample of 50- $\mu\text{m}$  SiC particles with assumed starting positions as shown in Fig. 3.33: eight layers with five rows and four columns, equally spaced in the liquid silicon volume.

After analyzing the results of a large number of model simulations, the following optimal values were found to offer best compromise between particle capturing and

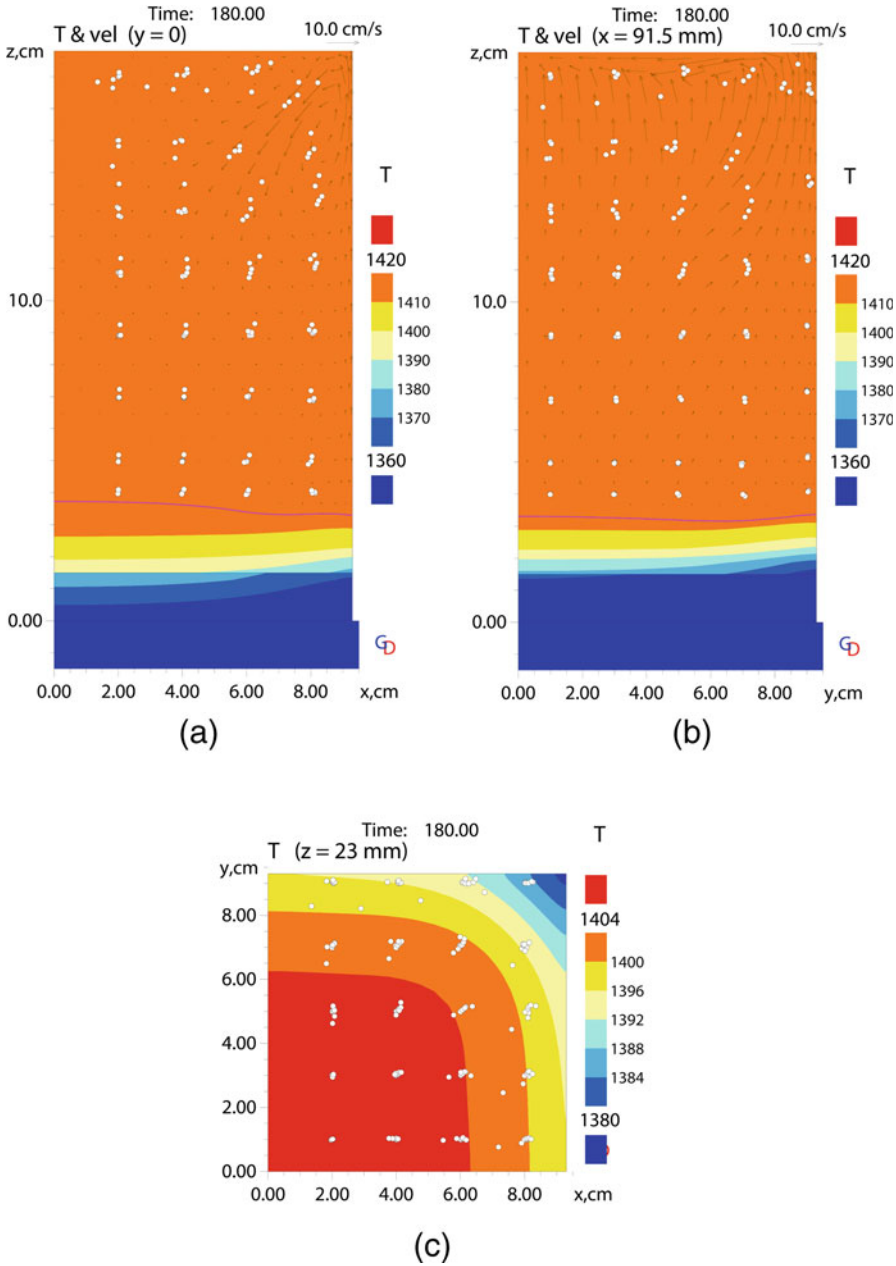
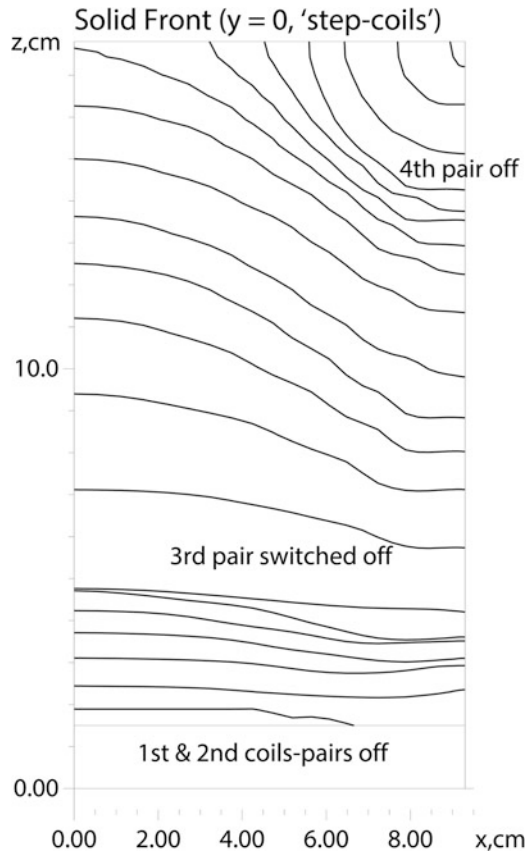


**Fig. 3.33** Initial 3-dimesional positions and first few movements of test particles for the case of 500 A at 3140 Hz. Solid front is indicated at 50% liquid fraction. The labels (a-b) correspond to side-view elevations and (c) the top view of the quarter crucible

desired shape of the solid front: coil current 1000 A, and frequency 3250 Hz. After the whole charge is fully melted, the bottom coil of the furnace and the lowest set of side coils are switched off allowing directional solidification to start from the bottom of the crucible. When the solid front reaches about 1/5th to 1/4th of the expected height of the new ingot, the lower pair of the middle set of coils is also turned off—this reduces the induced Joule heat and allows the solidification to progress upwards, see Fig. 3.34.

For the last 1/5th of the height of the ingot, the remaining two turns of the middle set of coils are also switched off leaving only the top set powered. All simulated particles are retained on the sides as required but the shape of the solid front deviates significantly from horizontal towards the end of the process, which is against the quality recommendations. This is likely to make the top of the ingot defected; it can be cut off and discarded while using the main body that is successfully recycled.

**Fig. 3.34** Progression of the solidification front in an induction silicon furnace with stepwise switching-off of the side coils



### 3.3.4 *Contactless Sonotrode*

Ultrasonic treatment (UST) improves the mechanical properties of light alloys, leading to finer microstructure, degassing, or dispersion of strengthening particles [63] (see Chap. 5 for details). The main mechanism for the observed improvements is thought to be cavitation in the melt, caused by pressure fluctuations. An immersed sonotrode probe, vibrating at ultrasonic frequency ( $\sim 20$  kHz), is commonly used to create the required pressure field. Intense pressure waves then trigger cavitation to assist nucleation [64], the breaking up of emerging dendrites [65] and to disperse particle clusters. But, even considering low-temperature melts (Al, Mg) where the process is mainly applied, there are problems preventing widespread use by industry: the probe is eroded and dissolved at varying rates contaminating the melt; the treated mass is restricted to a small volume surrounding the sonotrode (horn) and additional mechanical stirring is then necessary to spread the effect. For large process volumes, multiple sonotrodes need to be employed making scalability complex and expensive.

A contactless UST process based on electromagnetic principles has been suggested [66], which eliminates the risk of melt contamination plus the associated cost of exotic probe materials. The potential benefits of UST can then be applied to a wider range of alloys, covering high temperature and reactive melts. In contrast to the immersed sonotrode, the contactless EM device has to rely on acoustic resonance to achieve the necessary pressure amplitudes for cavitation [67], coupled to induced stirring to ensure multiple passages of the melt through active zones. Theoretically, it is then possible to scale up the process to larger volumes by means of a larger coil and current/frequency adjustments to match the acoustic resonance characteristics of the treatment volume.

As mentioned in the literature [67–69], the idea of applied static or AC magnetic fields to induce cavitation in liquid metals is not new, but the implementation described here remains unique.

One implementation of the contactless sonotrode idea is the “top-coil” sonotrode concept. A conical induction coil is inserted into the melt in the crucible, as shown in Fig. 3.35. Using the principles of levitation discussed in Sect. 3.3.1, the water-cooled coil has sufficient current running through it to prevent contact between the liquid metal and its surface. A protective ceramic coating may be used to eliminate spark erosion.

The Lorentz force due to the interaction between the coil current and the opposing current induced in the melt repels the free surface but also drives bulk stirring as shown in Fig. 3.35a. The AC component of the force operates at twice the supply frequency (see Eq. (3.33)) and induces vibrations in the melt. Although the applied force is concentrated in the thin skin layer close to the free surface, its effect is transmitted into the bulk through sound-frequency waves as pressure fluctuations. Provided that these fluctuations are strong enough, gas-filled bubbles oscillate and under certain conditions implode in analogy to the cavitation effects from the immersed sonotrode technique. To reach the necessary pressure threshold, the coil



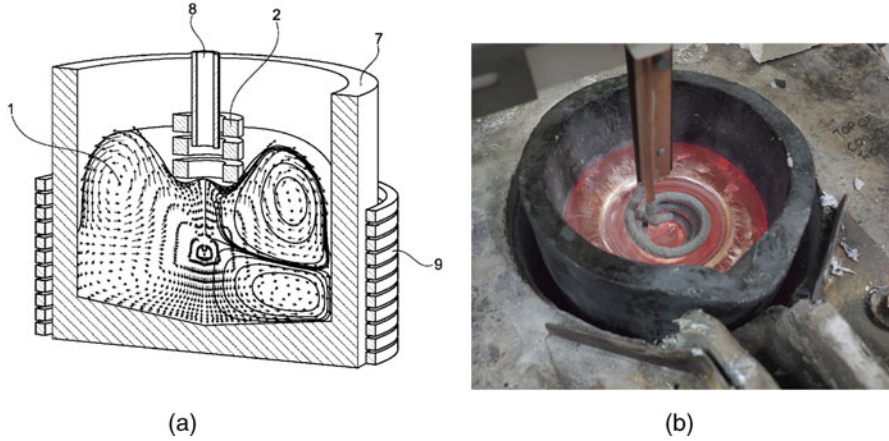


**Fig. 3.35** (a) The sonotrode concept [7], (b) shown in prototype form

frequency has to be tuned to produce resonant nodes in the treatment vessel, a condition that needs to account for the vessel geometry, free surface shape, and crucible sound absorption characteristics. In contrast to the immersed sonotrode where the cavitation energy is concentrated around the probe, in this case most activity lies in resonant nodes deep in the melt. Induced flow then ensures that gas-filled bubbles can have multiple passes through these nodes, improving cavitation efficiency.

In the first implementation of this concept in the University of Birmingham, an external high-frequency microphone was used to capture sound emitted from the crucible to detect cavitation activity, and the tracks of radioactive particles were used to determine the extent of induced stirring (see [70]).

From the mathematical point of view, this implementation covers a combination of traditional engineering fields. The set of equations representing fluid dynamics and heat transfer are solved using a spectral collocation scheme [71], on a dynamically varying solution grid [72]. Sound propagation is treated by solving the wave equations in the time domain, using a fourth-order staggered variable scheme on a regular Cartesian grid [73] and cavitation is handled using a multi-scale approach (in time and space) based on an extension of the Rayleigh–Plesset equations [74].

The AC magnetic field due to the coil,  $\mathbf{B}$ , and the induced current,  $\mathbf{J}$ , can be split into real and imaginary components:

$$\mathbf{B} = B_R \cos \omega t + B_I \sin \omega t ; \quad (3.30)$$

$$\mathbf{J} = J_R \cos \omega t + J_I \sin \omega t , \quad (3.31)$$

where

$$J_R = \sigma \frac{\omega}{2} \delta (B_R + B_I); J_I = \sigma \frac{\omega}{2} \delta (-B_R + B_I) \quad (3.32)$$

The skin depth  $\delta$  indicating current penetration into the liquid bulk was given earlier in Eq. (3.9).

The Lorentz force being the cross product of magnetic field and current can be split into mean and sinusoidal components:

$$\begin{aligned} \mathbf{F} &= \mathbf{J} \times \mathbf{B} = \bar{\mathbf{F}} + \tilde{\mathbf{F}}, \quad \bar{\mathbf{F}} = \frac{1}{2}(J_R B_R + J_I B_I) = \frac{1}{2\mu\delta} B_o^2 e^{-2\frac{x}{\delta}} \tilde{\mathbf{F}} \\ &= \frac{1}{2\mu\delta} B_o^2 e^{-2\frac{x}{\delta}} \sqrt{2} \cos\left(2\omega t - 2\frac{x}{\delta} + \frac{\pi}{4}\right) \end{aligned} \quad (3.33)$$

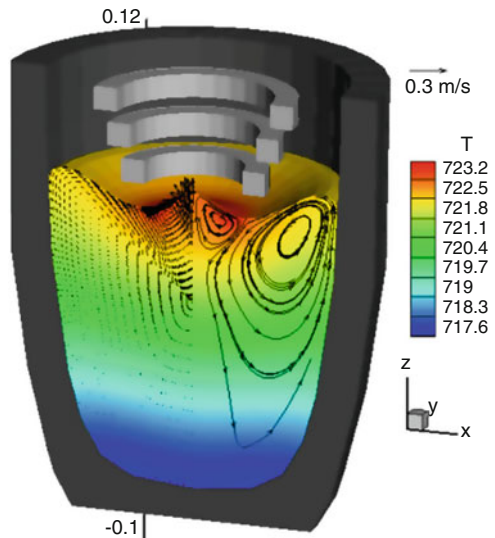
The mean component  $\bar{\mathbf{F}}$  is responsible for bulk stirring. The pressure waves generated by the time-dependent component of the Lorentz force are computed by solving the Euler form of the momentum equations, generating a perturbation velocity field  $\tilde{\mathbf{v}}$ :

$$\frac{\partial p}{\partial t} + \rho c^2 \frac{\partial \tilde{v}}{\partial x} = 0; \quad \rho \frac{\partial \tilde{v}}{\partial t} + \frac{\partial p}{\partial x} = \tilde{\mathbf{F}} \quad (3.34)$$

Zero-velocity boundary conditions are imposed on the solid walls of the vessel while at the free surface, zero-pressure boundary conditions are assumed.

Figure 3.36 is a simulation of an experimental setup, showing the predicted velocity and temperature fields in a 125-mm diameter crucible containing an A357 aluminum alloy, with the top-coil inductor immersed in the melt. The free surface is depressed by the Lorentz force, so that contact with the top coil is prevented. At the axis of the coil, the force vanishes, hence the conical elevation of the free surface. Strong stirring is observed, with a dominant toroidal vortex pushing the liquid down

**Fig. 3.36** Simulated flow and heat transfer in a small 125-mm experimental crucible, containing A357 aluminum alloy



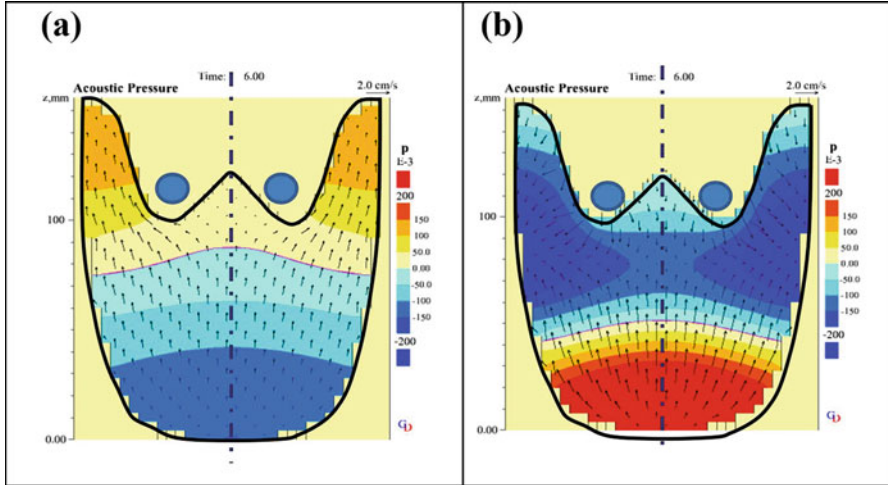


**Fig. 3.37** Sound field (instantaneous pressure) obtained at two different coil frequencies, (a) 8.8 kHz, dominated by vertical waves and (b) 15.25 kHz, dominated by radial waves

close to the axis and returning near the periphery. The induction current also contributes significantly to the heat released to the melt and for this reason the furnace induction-melting coil has to be switched off during the top-coil operation to maintain temperatures conducive to cavitation.

The sound field computed for this configuration is shown in Fig. 3.37, for an assumed speed of sound  $c = 4600$  m/s. The sound waves at two natural frequencies are seen to be quite different, highlighting the importance of accurate frequency control in the process.

This is also demonstrated in Fig. 3.38, which shows sound spectrograms obtained using a high-frequency microphone placed above the crucible free surface. With time on the horizontal axis and frequency on the vertical, they indicate cavitation activity as broadband noise (vertical lines), while the continuous horizontal line denotes the driving frequency, which as expected is twice the AC current frequency in the coil. In this case, we are looking at a larger 230-mm crucible, containing commercially pure aluminum. FFT analysis revealed a natural frequency peak at 18.06 kHz (or 9.03 kHz electrical) which was close to the 8.89 kHz (Exp 6 in Fig. 3.38) which results in almost continuous cavitation in the experiment. Increasing the frequency to 9.28 kHz reduces the effect slightly. The sensitivity to frequency is evident by the third trace, “Exp 7,” where reducing the frequency to 8.49 kHz, all but eliminates cavitation activity.

The ability of the top coil to disperse particles in the melt is clearly demonstrated in Fig. 3.39. The numerical result shows 1-mm particle tracks obtained using the Lagrangian technique, accounting for the effects of turbulence and electro-magnetophoretic Kolin–Leenov forces. The crucible is quickly filled with particles, which were seeded near the geometric center of the liquid. The corresponding

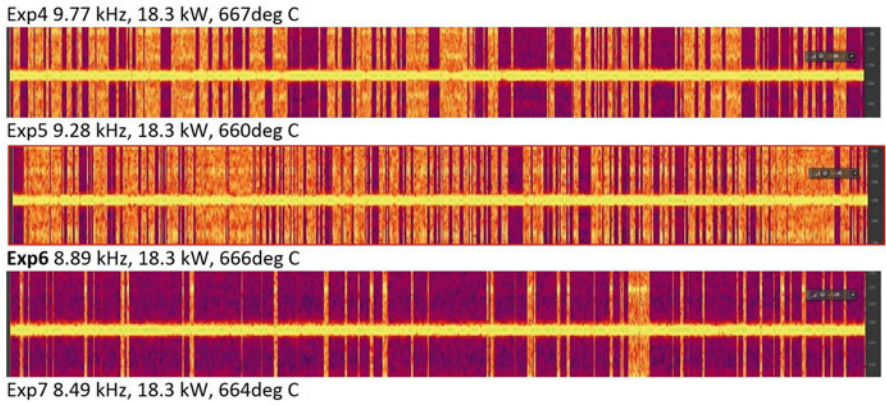


**Fig. 3.38** Spectrograms from top-coil experiments at three different AC frequencies showing the evolution of the spectrum of the recorded signals in liquid aluminum: horizontal axis—time; vertical axis—frequency; and light color—sound intensity. The continuous horizontal trace denotes the driving frequency and broad-spectrum bursts indicate cavitation activity. Highest cavitation activity observed at 8.89 kHz AC, translating to 17.78 kHz vibration

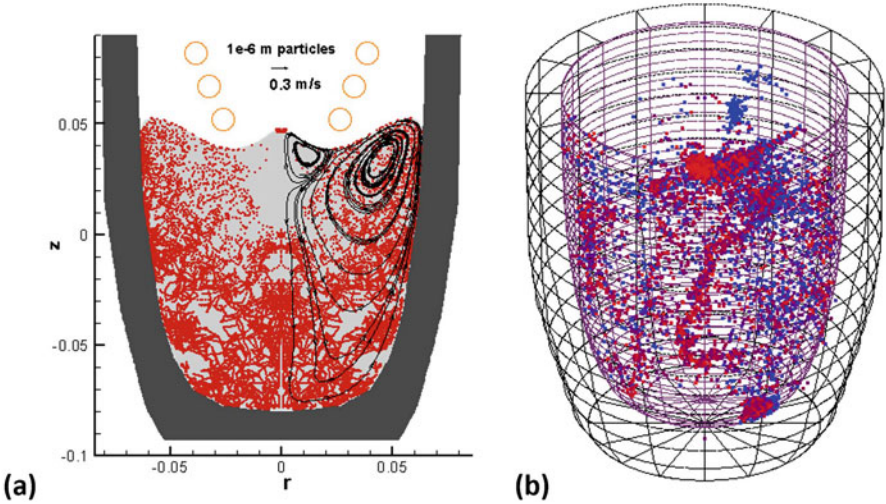


**Fig. 3.39** Comparison of (a) numerical result showing dispersion of 1-mm particles due to induction stirring against (b) experimental Positron emission particle tracking (PEPT) traces

experimental result shows a similar extent of dispersion obtained by tracking 200- $\mu$ m radioactive particles using the positron emission particle tracking (PEPT) technique.

Scaling up of the process will be necessary for adoption by industry. Numerical simulations can guide the design of the induction coil, which can be either the

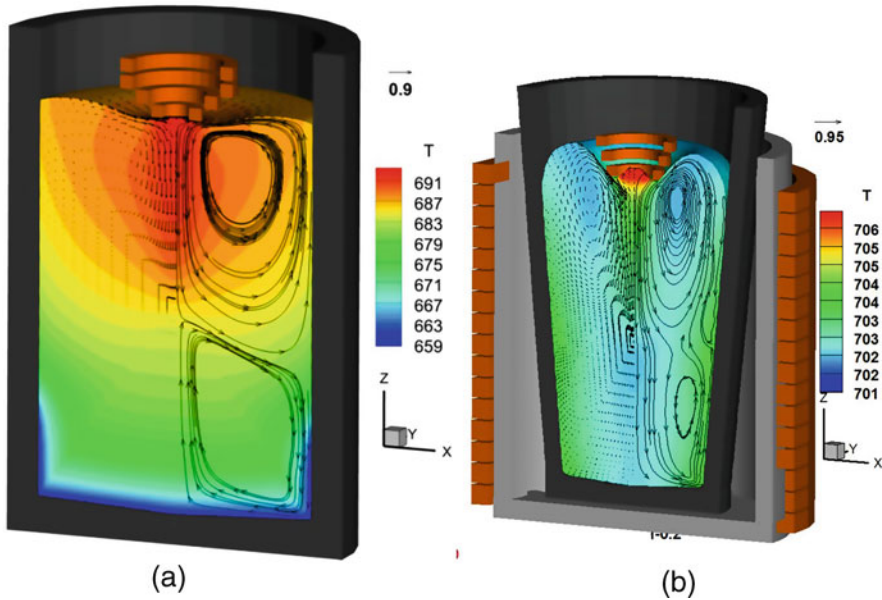


**Fig. 3.40** Numerical models for scale-up of the EM sonotrode. A 40-cm commercial size crucible is shown together with a 23-cm large experimental crucible

immersed type shown here or simply a suitably tuned melting coil. The actual configuration will depend on the application. Example simulations are shown in Fig. 3.40, for two different crucible sizes.

In conclusion, it has been shown that ultrasonic waves strong enough to produce cavitation in a crucible containing liquid metal can be generated using a contactless electromagnetic technique. This technique, originally based on a theoretical concept, was proven experimentally in the treatment of liquid aluminum. The experiments provide validation for a computational model that couples fluid flow, heat transfer, electromagnetic interaction, and sound-field simulations. It was found that resonant conditions are necessary to produce soundwaves of sufficient strength for cavitation, which means process geometrical details become important for a successful implementation. Although the experiments so far have been conducted in aluminum, since the technique is contactless, it can be in future applied to steels, nickel, and titanium alloys.

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# Chapter 4

## Electromagnetic Stirring and Low-Frequency Electromagnetic Vibration



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As the key parts of Electromagnetic Processing of Materials (EPM), electromagnetic stirring and low-frequency electromagnetic vibration processes have been developed to cause melt motion or vibration. In this chapter, we will firstly give a brief description of the physical principles of electromagnetic melt processing and solidification. Though partially repeating Chap. 3, it is still useful to recall them here. Next, the effects of electromagnetic stirring with a single set of induction coil and low-frequency electromagnetic vibration on heat/mass transfer and solidification structures are introduced. The last portion of this chapter deals with the casting technologies based on electromagnetic stirring and low-frequency electromagnetic vibration.

### 4.1 Physical Principles of Electromagnetic Melt Processing and Solidification

In metal industry, electromagnetic field has been used for many years in solidification processing. The physical principles of electromagnetic melt processing and solidification are based on the fluid dynamics with the fundamental contributions of Navier and Stokes, and the electric and magnetic science established by Maxwell in the 1880s.

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The technologies, such as electromagnetic stirring and vibration, were developed well after the scientific foundation and understanding had been established. It is known that when imposing an alternating magnetic field on a molten metal, an electromagnetic force can be induced to drive the molten metal. The phenomenon of the molten metal driven by an imposed magnetic field is well known and indicates the interaction of the electric and magnetic fields. The scientific theory that encompasses the phenomena coupling fluid dynamics and electric and magnetic science is called magnetohydrodynamics (MHD) [1], which has been used in such fields of science and engineering as plasma physics, geophysics, astronomy, nuclear fusion, and nuclear power. See also Chap. 3 for other applications.

In this chapter, when we consider problems concerning a flow of highly conductive fluids such as molten metals under an electric and/or magnetic field, an induced electromagnetic force term appears as a force source term in the equation of motion. Therefore, it is necessary to know the directions and magnitudes of the existing electric and magnetic fields. On the other hand, to obtain those parameters by solving Maxwell's equation, we have to know the fluid velocity in a generalized Ohm law. In this way, MHD couples the problems of the electric and magnetic fields with the velocity field. In most cases of EPM, it is generally considered that the electric and magnetic fields affect the velocity field, while the velocity field scarcely influences the electric and magnetic fields. Therefore, we firstly solve the equation of electric and magnetic fields without considering the influence of the velocity field, and then get the velocity field by substituting the obtained electric and magnetic fields into the driving force term in the equation of motion. That is, the coupling will be one-sided in many cases. The electric and magnetic fields are described by Maxwell's equations [2]:

$$\text{Faraday's law: } \nabla \times E = -\frac{\partial B}{\partial t}; \quad (4.1)$$

$$\text{Ampere's law: } \nabla \times B = \mu J; \quad (4.2)$$

$$\text{Gauss's law of electric field: } \nabla \cdot E = \frac{\rho_e}{\epsilon_e}; \quad (4.3)$$

$$\text{Gauss's law of magnetic field: } \nabla \cdot B = 0; \quad (4.4)$$

where  $\nabla$  is the Hamilton operator and is expressed as  $\nabla = \frac{d}{dx} \vec{i} + \frac{d}{dy} \vec{j} + \frac{d}{dz} \vec{k}$ ,  $E$  is the electric field strength,  $B$  is the magnetic flux density,  $J$  is the current density,  $\mu$  is the magnetic permeability,  $\rho_e$  is the net charge density, and  $\epsilon_e$  is the dielectric constant, respectively.

To solve the above equations, the conduction current density  $J$  in Eq. (4.2) should be expressed with Ohm's law:

$$J = \sigma(E + U \times B) \quad (4.5)$$

where  $U$  is the flow velocity of melt, and  $\sigma$  is the electric conductivity.

As the variation in the fluid field has negligible effect on the distribution of the magnetic field and the magnetic Reynolds number  $Re_m = \mu\sigma U_0 L_0$  (where  $U_0$  and  $L_0$  are the characteristic velocity and length in the system, respectively) is much smaller than 1 in melt processing, the second term ( $U \times B$ ) of the right-hand side of Eq. (4.5) can be ignored.

The electromagnetic force induced by electric and magnetic fields is called Lorentz force  $f_{em}$ , which can be given as [1]:

$$f_{em} = J \times B. \quad (4.6)$$

Substituting Eq. (4.2) into Eq. (4.6) yields:

$$f_{em} = J \times B = (1/\mu)(\nabla \times B) \times B = \underbrace{(1/\mu)(B \cdot \nabla)B}_{\text{rotational component}} - \underbrace{\nabla(B^2/2\mu)}_{\text{rotational component}} \quad (4.7)$$

From Eq. (4.7), the fluid motion is caused not by the force acting on the fluid but by its gradient, namely the rotation of the force. So, by taking the rotation of the Lorentz force  $f_{em}$ , we can find out which component of the Lorentz force is contributing to the fluid motion.

$$\nabla \times f_{em} = \nabla \times (1/\mu)(B \cdot \nabla)B - \nabla \times \nabla(B^2/2\mu) = (1/\mu)\nabla \times (B \cdot \nabla)B. \quad (4.8)$$

Equation (4.8) clearly shows the origin of the rotational and irrotational components.

In summary, the physical principles of electromagnetic melt processing and solidification are as follows: an electromagnetic force with gradient is induced in the melt by electric and magnetic fields, which results in melt flowing.

## 4.2 Mathematic Description of Heat/Mass Transfer During the Solidification of Metals Under Electromagnetic Fields

The equations of MHD describe the flow in the melt subjected to an alternating electromagnetic field. These equations couple Maxwell's electromagnetic equations to the equations of fluid flow, the Navier–Stokes equations for fluid momentum, and the mass continuity equations. The following text explains the governing equations and show how they can be simplified for the case of metal solidification in the presence of electromagnetic field.

Here, a single volume-average model is used to describe the metal solidification in the presence of electromagnetic field. Single domain models are based on the governing equations that apply to all regions of a solidification system. The model equations can be integrated across the entire domain without the need to explicitly subdivide the domain into solid, liquid, and mushy regions. Instead, these regions

are implicitly defined within the system by the distributions of energy determined from the solutions of the model equations. Therefore, the conservation equations are written as [3]:

Conservation equation of mass:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho U) = 0. \quad (4.9)$$

Conservation equation of momentum:

$$\frac{\partial (\rho U)}{\partial t} + \nabla \cdot (\rho U U) = \nabla \cdot (\mu_{\text{eff}} \nabla U) - \nabla P + S_m. \quad (4.10)$$

Conservation equation of energy:

$$\frac{\partial (\rho H)}{\partial t} + \nabla \cdot (\rho U H) = \nabla \cdot (k \nabla T) + S_{th}. \quad (4.11)$$

where  $\rho$  is the density of melt.  $\mu_{\text{eff}}$  and  $S_m$  are effective viscosity and momentum source, respectively.  $\mu_{\text{eff}}$  is given by  $\mu_{\text{eff}} = \mu_l + \mu_t$ , where  $\mu_l$  is laminar viscosity in the liquid and  $\mu_t$  turbulent viscosity. The momentum source  $S_m$  includes thermal buoyancy, Darcy source term, and electromagnetic volume force, etc.  $S_{th}$  is thermal source, which includes Joule heat and latent heat of solidification.

In the case of metal solidification in the presence of electromagnetic field, the standard  $k$ - $\varepsilon$  model, which is a semiempirical model, is used to simulate the transport of turbulence kinetic energy ( $k$ ) and its dissipation rate ( $\varepsilon$ ). The first form of this model was proposed by Harlow and Nagayama [4] who suggested:

$$\mu_t = \rho C_\mu \frac{k^2}{\varepsilon}, \quad (4.12)$$

where  $C_\mu$  is a function of the turbulent Reynolds number which is a constant value.  $k$  and  $\varepsilon$  are obtained from the following transport equations:

$$\frac{\partial (\rho k)}{\partial t} + \nabla \cdot (\rho U k) = \nabla \cdot \left[ \left( \mu_l + \frac{\mu_t}{\sigma_k} \right) \nabla k \right] + G_k - \rho \varepsilon + S_k; \quad (4.13)$$

$$\frac{\partial (\rho \varepsilon)}{\partial t} + \nabla \cdot (\rho U \varepsilon) = \nabla \cdot \left[ \left( \mu_l + \frac{\mu_t}{\sigma_\varepsilon} \right) \nabla \varepsilon \right] + C_1 \frac{\varepsilon}{k} G_k - C_2 \rho \frac{\varepsilon^2}{k} + S_\varepsilon; \quad (4.14)$$

where  $G_k$  represents the generation of turbulence kinetic energy due to the mean velocity gradients;  $C_1$  and  $C_2$  are constants;  $\sigma_k$  and  $\sigma_\varepsilon$  are the turbulent Prandtl numbers for  $k$  and  $\varepsilon$ , respectively; and  $S_k$  and  $S_\varepsilon$  are source terms for  $k$  and  $\varepsilon$ , respectively. All constants used in the model are listed in Table 4.1.

As solidification of any alloy occurs over a temperature range, the whole region in the solidification process of a multicomponent alloy can be divided into three regions, namely liquid, solid, and mushy region. At present, two methods are used

**Table 4.1** Constants used in  $k$ - $\varepsilon$  model [3].

| $C_1$ | $C_2$ | $\sigma_k$ | $\sigma_\varepsilon$ | $C_\mu$ |
|-------|-------|------------|----------------------|---------|
| 1.44  | 1.92  | 1.0        | 1.3                  | 0.09    |

frequently to model the solidification process of the alloys—single and multiple domain methods. As we have already mentioned, we will be using a single domain volume-average model, based on the governing equations that apply in all regions of the solidification system. The Scheil–Gulliver rule should preferentially be applied to describe the relationship between the liquid fraction and the local temperature for the type of solidification considered here. The Scheil–Gulliver model is formulated as [5, 6]:

$$f_L = \begin{cases} 1 & \text{when } T \geq T_L \\ \left( \frac{T_f - T}{T_f - T_L} \right)^{1/(k_p - 1)} & \text{when } T_L > T > T_S \\ 0 & \text{when } T \leq T_S \end{cases} \quad (4.15)$$

and

$$f_S = 1 - f_L, \quad (4.16)$$

where  $k_p$  is the solute partition coefficient and  $T_f$  the melting temperature of the pure base metal;  $T_L$  and  $T_S$  are the liquidus and solidus temperatures of the alloy, respectively.

In terms of treatment of the latent heat, there are two main methods used at present, i.e., the equivalent specific heat and enthalpy methods. In general, the enthalpy method is used to accurately model the energy transport during the solidification process of metals. So, the source  $S_{th}$  in Eq. (4.11) is

$$S_{th} = Q_J - \nabla \cdot [(\rho(H_l - H)(\vec{U} - \vec{U}_S))], \quad (4.17)$$

where  $H$  is the enthalpy and  $U$  is the velocity.

The first term  $Q_J$  of the right-hand side of Eq. (4.17) is the Joule heat induced by alternating electromagnetic field. Usually, the Joule heat is ignored in the presence of electromagnetic stirring because it is quite small compared to the enthalpy inflow of the liquid metals with respect to room temperature. The second term of the right-hand side of Eq. (4.17) is the latent heat released during the solidification of the metals, where:

$$\begin{aligned} H &= f_s H_s + f_l H_l; \\ c_p &= f_s c_{ps} + f_l c_{pl}; \\ H_s &= \int_{T_{\text{ref}}}^T c_{ps} dT + H_{\text{ref}}; \end{aligned}$$

$$H_l = \int_{T_{\text{ref}}}^T c_{ps} dT + \int_{T_s}^T (c_{pl} - c_{ps}) dT + L + H_{\text{ref}};$$

where  $c_{ps}$  and  $c_{pl}$  are the specific heats of solid and liquid, respectively;  $L$  is the latent heat of solidification; and  $H_{\text{ref}}$  the enthalpy at the reference temperature  $T_{\text{ref}}$ .

Thus, the energy equation (Eq. (4.11)) is changed to:

$$\frac{\partial(\rho H)}{\partial t} + \nabla \cdot (\rho \vec{U} H) = \nabla \cdot (k \nabla T) - \nabla \cdot [(\rho(H_l - H)(\vec{U} - \vec{U}_s))] \quad (4.18)$$

Furthermore, modeling of fluid flow in the mushy region and the treatment of the conservation equations in the solid region are carried out using different viscosity and permeability in different regions. Usually, the Darcy model is used to simulate solidification process. However, when electromagnetic field is imposed, some solid particles suspend in the liquid metal at the early stage of solidification. As the solid fraction is small at this stage, the solid particles move freely within the liquid metal. In such a case, Darcy flow is not important. With the increase of the solid fraction, dendrite coherency occurs. When a rigid dendrite skeleton is established, Darcy flow becomes significant. Therefore, the computation region is divided into four stages and the viscosity and the permeability of each stage must satisfy the conditions as summarized in Table 4.2 [3].

In Table 4.2,  $f_s^*$  is the solid fraction when a rigid dendrite skeleton is established. The permeability  $K$  is given as a function of solid fraction  $f_s$ . As  $K$  decreases in the solidification process ( $f_s \rightarrow 1$ ), the magnitude of the Darcy term increases. Finally, the Darcy term becomes dominant in the conservation equations. For the limit case of  $f_s = 1$ , the very small positive number  $\chi$  is used to avoid diverging the conservation equations due to the Darcy term. In addition,  $K_0$  is named the initial permeability and may be related to a structural parameter like the secondary dendrite arm spacing (DAS) [7]:

$$K_0 = \frac{(DAS)^2}{180}. \quad (4.19)$$

**Table 4.2** Viscosity and permeability in different stages of solidification [3]

| Stage                                     | Solid fraction $f_s$ | Viscosity $\mu_l$             | Permeability $K$                | Darcy term $f_{\text{Darcy}}$       |
|-------------------------------------------|----------------------|-------------------------------|---------------------------------|-------------------------------------|
| Liquid                                    | 0                    |                               | $\infty$                        | 0                                   |
| Before dendrite coherence in mushy region | $0 < f_s \leq f_s^*$ | $\mu_{l0} \times 10^{10 f_s}$ | $\infty$                        | 0                                   |
| After dendrite coherence in mushy region  | $f_s^* \leq f_s < 1$ | $\mu_{l0}$                    | $K_0 \frac{(1 - f_s)^3}{f_s^2}$ | $-\frac{\mu_l}{K + \chi} (X - X_s)$ |
| Solid                                     | 1                    | $\mu_{l0}$                    | $K_0 \frac{(1 - f_s)^3}{f_s^2}$ | $-\frac{\mu_l}{K + \chi} (X - X_s)$ |



$X$  in Table 4.2 denotes a variable that will be solved, such as velocity ( $U$ ), turbulence kinetic energy ( $k$ ), and its dissipation rate ( $\epsilon$ ).  $X_s$  denotes velocity vector ( $U$ ), turbulence kinetic energy ( $k$ ), and its dissipation rate ( $\epsilon$ ) in the solid region.

Therefore,  $S_m$  in Eq. (4.10) is written as:

$$S_m = f_{\text{Darcy}} + f_{\text{buoyancy}} + f_{em}, \quad (4.20)$$

where  $f_{\text{Darcy}}$  is the Darcy term and listed in Table 4.2,  $f_{\text{buoyancy}}$  the thermal and solute buoyancy, and  $f_{em}$  the electromagnetic force. Thus, Eq. (4.10) can be written as:

$$\frac{\partial(\rho U)}{\partial t} + \nabla \cdot (\rho U U) = \nabla \cdot (\mu_{\text{eff}} \nabla U) - \nabla P + f_{\text{Darcy}} + f_{\text{buoyancy}} + f_{em}. \quad (4.21)$$

### 4.3 Effects of Electromagnetic Stirring on Heat/Mass Transfer and Solidification Structures

In metal industry, electromagnetic stirring is widely used in melting and solidifying processes. The principle of electromagnetic stirring refers to the creation of a forced convection in the liquid metal by the electromagnetic force (Lorentz force) resulting from the interaction of the induced currents ( $J$ ) and the alternating magnetic fields ( $B$ ). In this section, the effects of electromagnetic stirring on mass/heat transport and solidification structure due to the induced Lorentz force will be introduced.

#### 4.3.1 Decoupling Due to Small Magnetic Reynolds Number

An important measure of the effect of the velocity field on the magnetic field is the magnetic Reynolds number [1]:

$$\text{Re}_m = \mu \sigma U L = UL/\eta, \quad (4.22)$$

where  $L$  is characteristic length.  $\sigma$  is the electrical conductivity of the fluid and  $\eta = (\mu \sigma)^{-1}$  its magnetic diffusivity. In the electromagnetic stirring process, this number is very small [3]:

$$\text{Re}_m \ll 1. \quad (4.23)$$

This means that the Lorentz force may be calculated by neglecting the fact that the fluid is in a motion (i.e., as if the fluid was a solid conductor). This is a very considerable simplification, which effectively decouples the electromagnetic problem from the fluid-mechanical problem.

### 4.3.2 Skin Depth for Alternating Magnetic Fields

There is a second magnetic Reynolds number based on the magnetic field frequency  $\omega$  [1]:

$$\text{Re}_\omega = \omega L^2 / \eta = 2(L/\delta)^2, \quad (4.24)$$

where

$$\delta = (2\eta/\omega)^{1/2}. \quad (4.25)$$

Here,  $\delta$  is the familiar “skin depth” of electromagnetism, i.e., the order of magnitude of the penetration depth of the alternating magnetic field into the conductor. If  $\delta < L$  (i.e.,  $\text{Re}_\omega > 1$ ), the alternating magnetic field, hence the induced current, and thus the Lorentz force  $f_{em}$  are confined to a layer of thickness  $\delta$  near the liquid surface. If  $\delta \geq L$  (i.e.,  $\text{Re}_\omega \leq 1$ ), the conductor is effectively transparent to the alternating magnetic field, and the stirring action is much more uniformly distributed throughout the interior of the conductor. When  $\text{Re}_\omega \rightarrow 0$ , however (or equivalently  $\sigma \rightarrow 0$ ), we have the limit of a nonconducting fluid in which no current is induced and the stirring force tends to be zero.

If the frequency  $\omega$  is increased from zero to infinity (keeping all other parameters constant), the stirring efficiency (measured, for example, in terms of the kinetic-energy of the stirred fluid) varies, as shown qualitatively in Fig. 4.1, with a maximum at some value of  $\text{Re}_\omega$  at the order of unity. By assuming a plausible pattern of stirring and adopting a global balance of forces, Tir [9] obtained a curve of this kind with a

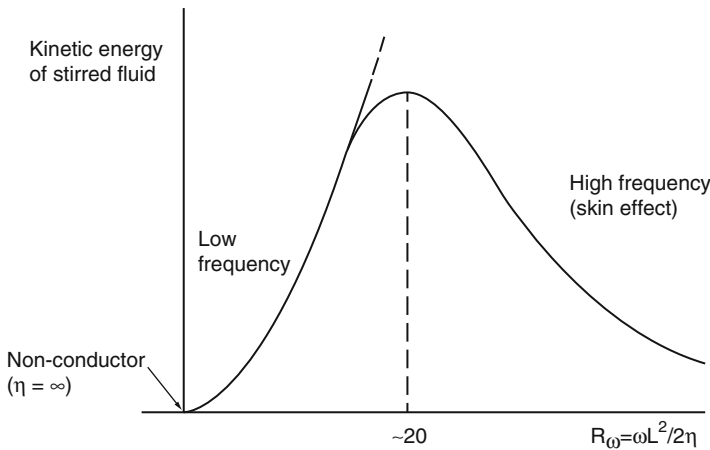


**Fig. 4.1** A qualitative sketch of the variation of kinetic energy of electromagnetically stirred fluid, as a function of the dimensionless frequency parameter  $\text{Re}_\omega$ . Regular perturbation theory is applicable in the low-frequency regime, and skin-effect analysis is applicable in the high-frequency regime (adapted from [8])

maximum at  $Re_\omega \sim 20$ . For values of  $Re_\omega$  greater than this, a skin-effect analysis may be expected to provide a reasonable description of the stirring effect. For small values of  $Re_\omega$ , a regular perturbation procedure is available. For a typical liquid metal (aluminum), it may be helpful to note that  $\delta \approx 20$  mm when  $\omega = 50$  Hz, and  $\delta \approx 140$  mm when  $\omega = 1$  Hz. If the scale  $L$  of the domain considered is much larger than  $\delta$ , obviously the high-frequency approach is appropriate.

### 4.3.3 Time-Average Value of Lorentz Force

The impact of the frequency  $\omega$  of the external alternating magnetic field on melt is related to how fast the melt can respond. There is a consideration associated with two time scales. This consideration compares the viscous time scale to a component of the external alternating time scale. When time is averaged, the body force associated with an alternating magnetic field has both a net averaged component and a negligible oscillatory component, the latter switches direction before it can impact the flow field. During the electromagnetic stirring process, Lorentz force may change much faster than flow can respond due to  $\omega L \gg U$ ; that is, the electromagnetic field period is much shorter than the momentum response time of the melt, so the time-average value of this volume force should be used to impose on the liquid metal. Therefore, at any point within a metallic conductor where the time harmonic current density is  $J$  and the magnetic flux density is  $B$ , the time-average electromagnetic volume force density (i.e.,  $f_{em}$  in Eq. (4.20)) is [3]:

$$f_{em} = \frac{1}{2} \text{Re}(J \times B^*) \quad (4.26)$$

where  $\text{Re}$  is the real part of a complex quantity.

### 4.3.4 Effects of Electromagnetic Stirring on Heat/Mass Transfer

#### 4.3.4.1 Effects of Electromagnetic Stirring on Heat Transfer

Casting of metals is closely related to heat release and heat removal during the solidification. The rate of heat removal is of importance as it determines the solidification time of the casting and the temperature distribution in the metals during solidification. When the electromagnetic stirring is applied, forced convection is created that affects the heat transport, by rapidly dissipating the superheat and homogenizing the temperature in the bulk liquid [10–13]. In this section, DC casting of an Al–10 wt% Zn–2.3 wt% Mg–2.4 wt% Cu aluminum alloy is chosen as an

example to describe the effects of the electromagnetic stirring on the heat transfer in detail [3, 14].

Figure 4.2a–c shows the velocity vectors, velocity contours, and temperature profiles in the absence/presence of the electromagnetic stirring, respectively. In each plot, the left and right parts correspond to the predicted results without and with the electromagnetic stirring, respectively.

As can be observed in Fig. 4.2a, b, both the velocity vectors and profiles are remarkably modified by the electromagnetic stirring. When the electromagnetic

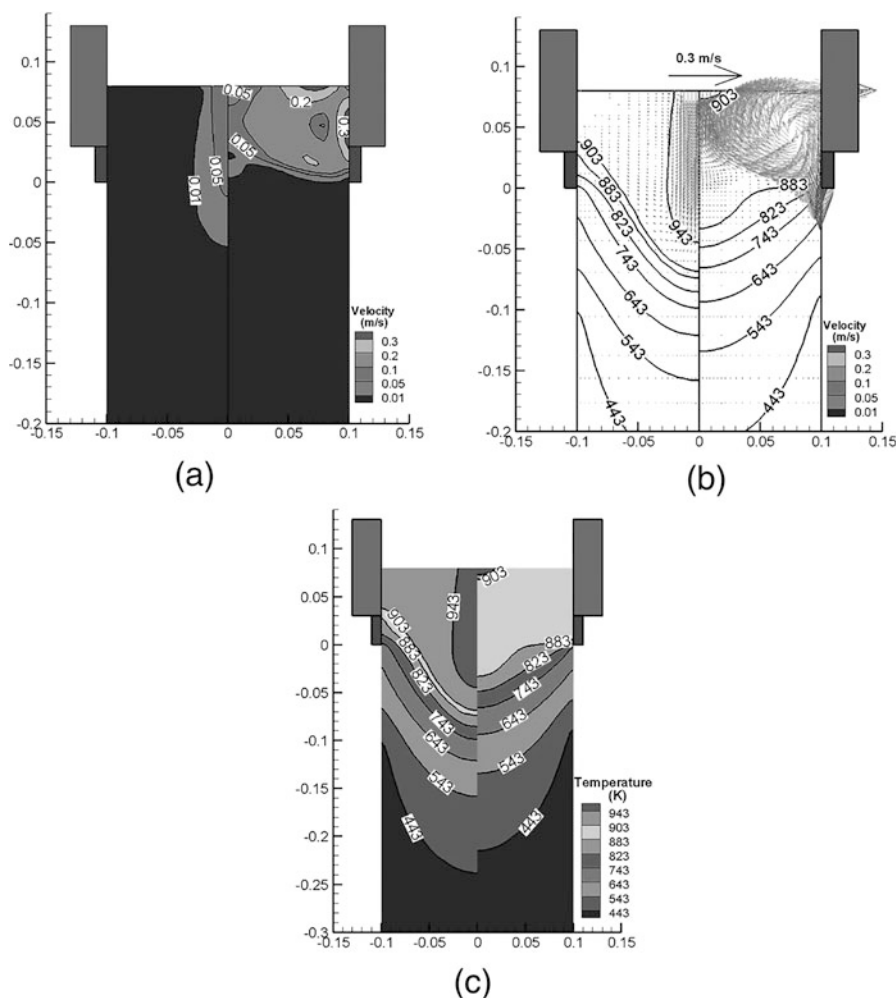


**Fig. 4.2** Comparison of the calculated results during the DC casting processes in the absence/presence of electromagnetic stirring: (a) velocity patterns; (b) velocity vectors with temperature profiles, and (c) temperature profiles. Left half is without EMS, right half is with EMS (adapted from [3])

stirring is applied, the flow direction in the melt pool is reversed and one small circulation is produced near the solidification front at the center of the billet. Furthermore, as compared to the conventional DC casting, the maximum velocity is increased about five times and its location moves from the inlet region to the contact position between the melt and the mold. These phenomena are commonly accounted for by the forced convection resulting from the rotational component of the electromagnetic force. Accordingly, this fluid flow also affects the temperature profiles, as shown in Fig. 4.2c. Firstly, the temperature contours in the right part are uplifted compared to the left part, which results in the reduction of the sump depth. In addition, the temperature in the bulk liquid is decreased and becomes more uniform when the electromagnetic field is applied. And, the heat flux along the longitudinal direction is greatly increased due to the vigorous forced convection at the solidification front. During conventional DC casting with the central pouring system, high-temperature melt poured into the melt pool from the inlet region firstly reaches the solidification front and then flows to the contact region between the melt and the mold due to the thermal buoyancy, as a result of which the sump depth is increased. Although the hot melt increases the depth of the sump, the direction of melt flow is still downwards along the sides and upwards in the center. The latter is partially suppressed by the central hot flow from the spout. Furthermore, as the flow velocity in the sump pool is very small, the heat transport of the melt within the sump mainly depends on conduction, which results in uneven temperature distribution in the melt pool. However, during the DC casting process in the presence of the electromagnetic stirring, the high-temperature melt firstly reaches the contact region between the melt and the mold along the free surface due to the forced convection. In this case, the melt temperature is decreased as soon as it is poured into the melt pool. Subsequently, the melt cooled by the mold reaches the solidification front, and then leads to a decrease in the temperature and thus a shallower sump. In addition, the heat transport in the melt pool is dominated by both conduction and convection, which promotes a uniform temperature distribution within the sump, as shown in Fig. 4.2c.

In the electromagnetic stirring technology, two technologically adjustable parameters, i.e., frequency  $f$  and electric current peak intensity  $I$ , have a profound effect on the actions of electromagnetic field. In general, an increase in the coil current peak intensity enhances the stirring effects of the electromagnetic field. However, determination of an optimal frequency is difficult as it is greatly influenced by the actual distribution of the magnetic flux densities in conductive media. The characteristic length that specifies how the magnitude of magnetic field decreases as a function of distance into the melt is, as we have already mentioned, the skin depth [1]:

$$\delta = \sqrt{\frac{1}{\sigma\mu\pi f}}, \quad (4.27)$$

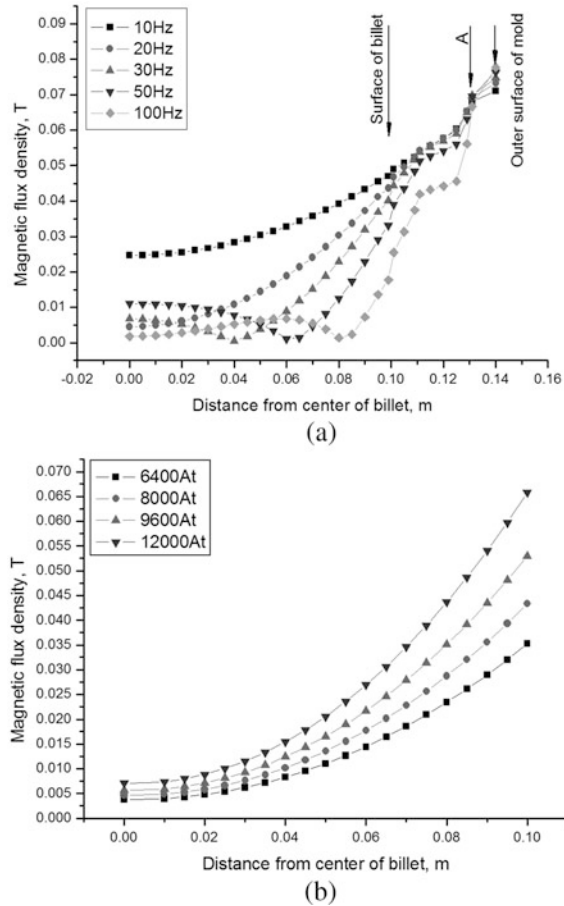
where  $\sigma$  and  $\mu$  are the electric conductivity and magnetic permeability of the liquid metal, respectively.

When the frequency is relatively high (50 Hz or more), the skin depth in DC casting process in the presence of electromagnetic stirring is extremely small and the force density is mainly concentrated near the surface of the metal. A rapid change in the magnetic flux density across a small skin depth means a large contribution of the potential component of the Lorentz force density in the narrow billet surface layer, which reduces the contact zone pressure between the melt and the mold and then decreases the primary cooling intensity. But, on the other hand, due to the small gradient of the magnetic flux density in the casting direction, the stirring effect in the liquid bulk is weak. When the frequency is decreased, the Lorentz force density throughout the bulk of the liquid metal is increased. Correspondingly, the force density component in the casting direction is enhanced, while the potential force component is reduced. Numerical results for the magnetic flux density magnitude in the DC casting process in the presence of electromagnetic stirring are shown in Fig. 4.3. To obtain the best electromagnetic stirring effects, choosing an optimal frequency is of great importance. When the frequency is at its optimum, the electromagnetic stirring is present throughout the metal melt bulk. If the frequency is above the optimal value, stirring (due to Lorentz forces) will be increased in the periphery region of the melt, but significantly decreased in other regions. On the other hand, if frequency is under the optimal value, the Lorentz forces are present in all of the melt, but are very weak because of the low magnetic field gradients.

In addition, when the electromagnetic stirring is applied, the heat exchange between the melt and the external environment is also modified remarkably. Figure 4.4 shows the temperature fluctuations of the graphite ring when the electromagnetic stirring is turned off during the DC casting process. In the presence of electromagnetic stirring, the temperatures of the graphite rings are stable—the upper thermocouple (5 mm below the mold/hot-top junction) and the lower thermocouple (10 mm below the mold/hot-top junction) are about 525 °C and 330 °C during the hot-top DC casting process with EMS, respectively. When the EMS is turned off, the temperatures of graphite ring firstly decrease and then rise. Finally, a newly steady-state hot-top DC casting process is reached—the upper and lower thermocouples are about 615 °C and 313 °C, respectively.

In order to compare the heat transport without and with the electromagnetic stirring, Fig. 4.5 shows the cooling curves and the length derivatives of the temperatures at the periphery (3 mm from the billet surface) of the billet during the hot-top DC casting process. With the application of the electromagnetic stirring, the forced convection in the sump enhances the heat transfer rate of the melt. The solidus temperature at the billet surface is closer to the mold/hot-top junction during the EMS hot-top DC casting process than that during the conventional hot-top DC casting process. This phenomenon can also be demonstrated by the temperature fluctuations of the upper thermocouple (5 mm below the mold/hot-top junction) in Fig. 4.4. When the electromagnetic stirring is turned off, the forced convection is replaced by natural convection, which reduces the heat transfer between the graphite ring and the melt. As a result, the initial solidification point of the billet at the graphite ring moves down so that the length of the contact zone with the graphite ring becomes longer. Thus, the upper thermocouple becomes closer to the melt or

**Fig. 4.3** Examples of numerical models of magnetic flux densities from the center of the billet to the outer surface of the mold on a certain path under (a) different electromagnetic frequencies with 8000 At (Amper turn) and (b) different current intensities with 20 Hz. Adapted from [14]



even immersed in the melt. This accounts for the rise of the temperature of the upper thermocouple. About 2 min later, the steady state of conventional hot-top casting is established.

#### 4.3.4.2 Effects of Electromagnetic Stirring on Mass Transfer

Other than the heat transfer, the forced convection induced by electromagnetic stirring also affects the mass transfer significantly. The changes of mass transfer during solidification are characterized by the distribution of solutes in the billets, commonly referred to as “segregation.” There are two types of segregation—macrosegregation and microsegregation, which represent the distribution of solutes on macro- and microscales, respectively. Indeed, it has been repeatedly shown on macroscale that the solute profiles within the solidified casting vary greatly, depending on the types of electromagnetic fields, such as stationary [16, 17], rotating



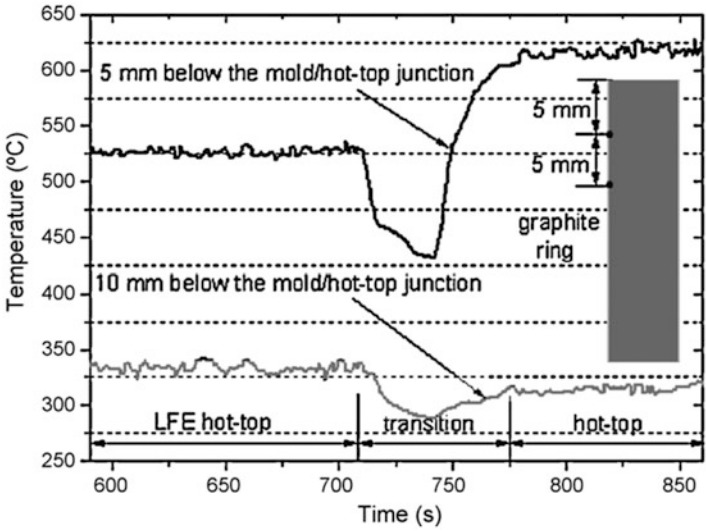


**Fig. 4.4** Temperature fluctuations of the graphite ring (adapted from [15]), where ‘hot-top’ is the conventional hot-top DC casting and ‘LFE hot-top’ is the hot-top DC casting in the presence of electromagnetic stirring

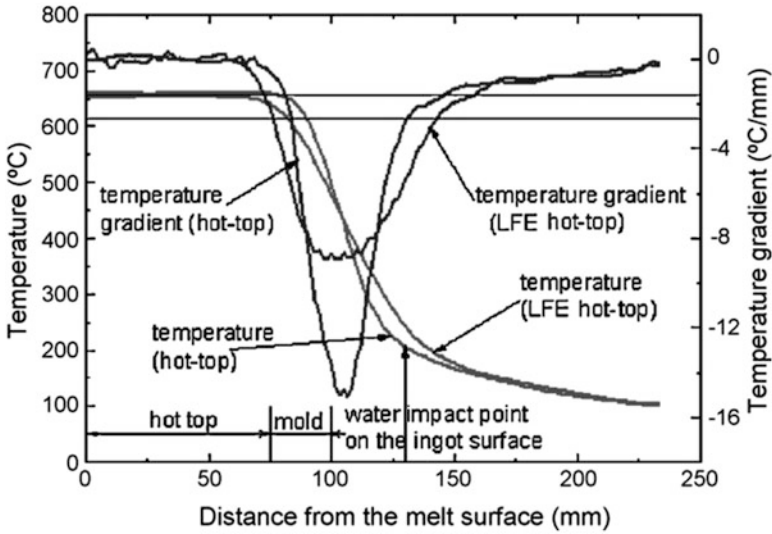


**Fig. 4.5** Cooling curves and length derivative of temperature at the periphery of the billet (adapted from [15]), where ‘hot-top’ is the conventional hot-top DC casting and ‘LFE hot-top’ is the hot-top DC casting in the presence of electromagnetic stirring

[18], and traveling magnetic fields [19]. On the microscale, the flows in the melt modify the extent of solute rejection at the solidification front, which is represented by the partition coefficient [20]. In this section, we will demonstrate the effects of electromagnetic stirring on the segregation during DC casting.

In conventional DC casting of aluminum alloys, the main mechanism behind macrosegregation is well understood: the transport of segregated alloying elements at the scale of the casting by the relative movement of the liquid and solid phase in the solidification range (i.e., slurry and mushy zones). Mechanisms leading to the relative motion are [21]:

- Thermo-solutal convection in the liquid sump caused by temperature and concentration gradients, and the penetration of this convective flow into the slurry and mushy zones of a billet;
- Transport of solid grains within the slurry zone by gravity and buoyancy forces, convective or forced flows;
- Melt flow in the mushy zone that feeds solidification shrinkage during solidification;
- Melt flow in the mushy zone caused by metallostatic pressure;
- Melt flow in the mushy zone caused by deformation (e.g., thermal contraction) of the solid network;
- Forced melt flow caused by pouring, gas evolution, stirring, vibration, cavitation, rotation, etc., which penetrates into the slurry and mushy zones of a billet or changes the direction of convective flows.

In addition, solute concentration at the ingot surface is pronouncedly higher than the average value [22–26]. As the initial solidified shell is detached from the mold because of the solidification shrinkage and thermal contraction of the billet, the formed air gap greatly reduces the heat transfer [27]; therefore, the solidified shell is reheated by the melt, and the metallostatic head forces the interdendritic liquid through the shell, forming the exudation layer. As a result, the solute concentration at the ingot surface is further increased. The parameters, such as casting temperature, casting speed, and cooling intensity, greatly affect the solute concentration over the cross-section of the ingot. The transport of heat and mass occurs in the melt and the slurry and mushy zones; the solute distribution therefore is intimately related to the shape of sump [21]. The existence of the sump in the DC casting process leads to large-scale inhomogeneity of the alloying elements over the cross-section of the ingot [24, 25, 27]. Surface exudation is determined by primary cooling intensity and the height of solidified shell, which mainly affect the solute concentration near the ingot surface. Due to the mass balance, the immediate subsurface region is depleted of alloying elements when exudation occurs [23, 25, 27]. Figure 4.6a shows the distribution of Zn along the radius of an AA7075 aluminum alloy billet in the absence of electromagnetic field. Zn highly enriches the billet surface, which greatly reduces the surface quality. Solute concentration in the central region of the billet is much lower than the average value, which is often ascribed to the sedimentation of floating dendrite fragments to the bottom of the sump [22, 25, 28].

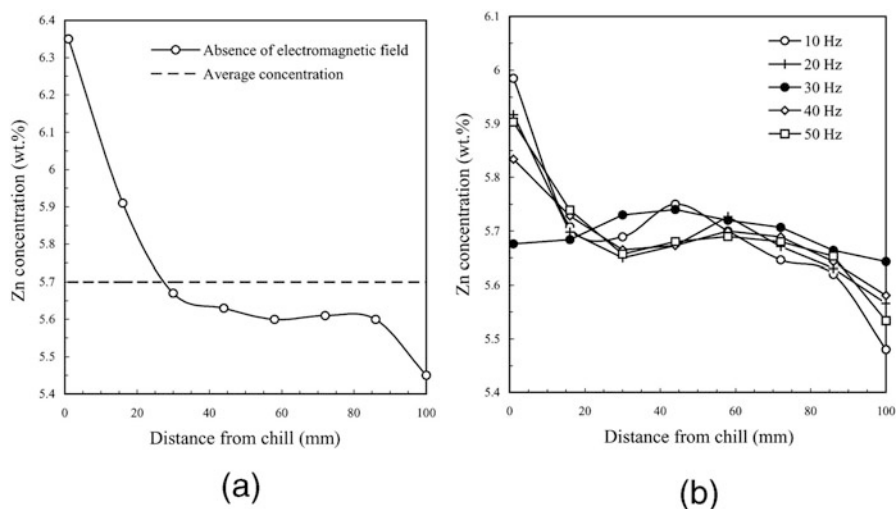


**Fig. 4.6** Zn concentration profiles in an AA7075 billet (a) in the absence of electromagnetic field and (b) under electromagnetic fields with different frequencies (adapted from [29])

Under the effect of periodic current, the inductor generates a variable magnetic field in the melt, which, in turn, gives rise to an induced current, so the melt is subject to electromagnetic body force caused by the interaction of the eddy current and the magnetic field. The Lorentz force density is expressed as Eq. (4.7). The force consists of two parts: the horizontal component is a potential force balanced by the static pressure of the melt, which results in the formation of a convex surface meniscus and reduces the height of contact line between the melt and the mold, decreasing the primary cooling intensity; the vertical component is a rotational force derived from the inclination of the magnetic field lines toward the axis of the ingot symmetry, which results in forced convection in the melt. Therefore, the ideal flow pattern in the melt will be achieved when the superheated melt is driven from the center region of the melt to the periphery (opposite to the natural convection), and the depth of sump is decreased. All the effects that can effectively refine the microstructure and broaden the equiaxed zone—for instance, the dendrites remelted, detached, and carried away by convection from the shell to the inner region of the melt, promoting heterogeneous nucleation—are helpful in the elimination of positive segregation of alloying elements [25, 30–32].

As a principal parameter, frequency greatly influences the distribution of magnetic flux density in the conductive media. In the process of electromagnetic casting, the flow pattern and temperature field of the melt can be modified by means of frequency modulation, and optimized conditions of solidification can be obtained. The characteristic length, which specifies how the magnitude of magnetic field decreases as a function of distance into the liquid metal, is the skin depth shown by Eq. (4.27). When the operating frequency is relatively high (50 Hz or more), the skin depth is extremely small and the force density is significantly concentrated near

the surface of the metal. The rapid change in magnetic flux density across a small skin depth means a high gradient of force density which forms a stronger confined pressure. The height of contact line between the melt and the mold decreased. But, at the same time, stirring effect is also weakened. With the decrease of frequency, the magnetic field, induced currents, and hence Lorentz force density are increased throughout the bulk of the liquid metal; the rotational part becomes dominant and the forced convection is enhanced. With further decrease of frequency (less than 20 Hz), the magnetic flux density and phase angle are relatively uniform throughout the melt; the rotational force is weakened again.

Therefore, under a fixed magnetic intensity, the optimum flow pattern and temperature field can be obtained by application of a proper frequency of electromagnetic field, which, in turn, reduces the macrosegregation to the best effect. Figure 4.6b shows the distribution of Zn along the billet radius under electromagnetic fields of different frequencies while the intensity is held constant at 400 A. As can be found, the large-scale centerline segregation and surface segregation are reduced in various degrees. The best effect is obtained at a medium frequency of 30 Hz.

In the case of the DC casting of an Al–Zn–Mg–Cu alloy in the presence of electromagnetic stirring [33], micro segregation is greatly suppressed by the electromagnetic stirring and decreases with decreasing electromagnetic frequency. The alloy melt is a system consisting of atomic nuclei surrounded by negatively charged electrons. The atomic nuclei make irregular thermal motion with a velocity ( $v$ ). Under the static electromagnetic field, they will perform revolution motion around the lines of the magnetic field. The revolution radius and angular velocity are [1]:

$$r_c = \frac{mv_{\perp}}{|q|B}, \quad (4.28)$$

$$\omega_c = \frac{|q|B}{m}, \quad (4.29)$$

where  $r_c$  is the revolution radius of the atomic nuclei in the magnetic field,  $q$  the quantity of charge of atomic nuclei,  $v_{\perp}$  the velocity in the vertical direction of the line of magnetic field,  $m$  the mass of atomic nuclei, and  $\omega_c$  the revolution angular velocity. The Al, Cu, Mg, and Zn ions are  $\text{Al}^{+3}$ ,  $\text{Cu}^+$ ,  $\text{Mg}^{+2}$ , and  $\text{Zn}^{+2}$ . Their revolution radius and angular velocity are different because of the difference in  $m$  and  $q$ . For instance,  $m_{\text{Al}^{+3}} < m_{\text{Cu}^+}$  and  $q_{\text{Al}^{+3}} > q_{\text{Cu}^+}$  lead to  $r_{\text{Al}^{+3}} < r_{\text{Cu}^+}$ . Thus, a relative movement among  $\text{Al}^{+3}$ ,  $\text{Cu}^+$ ,  $\text{Mg}^{+2}$ , and  $\text{Zn}^{+2}$  will occur. It is this relative movement of the different atomic nuclei that forms the entropy of the melt in front of the solid–liquid interface. In order to reduce the free energy, the solute elements automatically diffuse throughout the melt. However, when the electromagnetic field intensity increases, a large number of crystals nucleate and the distance that solute elements need to travel decreases. Therefore, the concentration of solute elements along grain boundaries becomes lower, accompanied by increase of the content of alloying elements within grains.

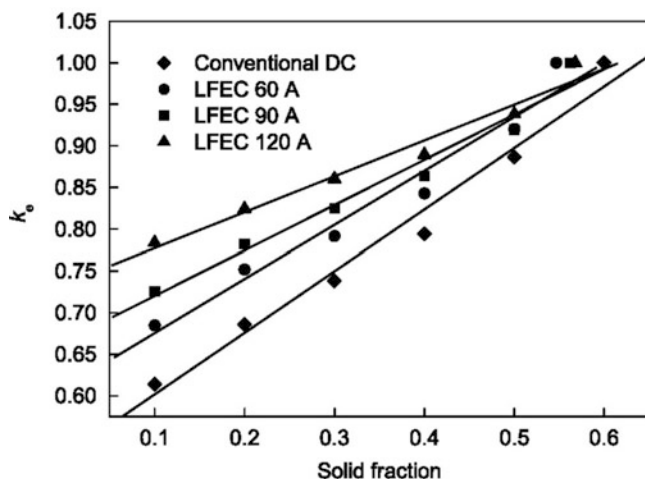


**Fig. 4.7** Effective partition coefficient vs the solid fraction in an Al-Cu alloy under different casting conditions (adapted from [34])

In addition, the purpose of electromagnetic stirring is also the introduction of a convective flow across the solid–liquid interface and into the mushy zone during solidification of an alloy. This convective flow induces changes in the thermal and solute profiles in front of the solid–liquid interface. These changes affect the composition variation throughout the solidified metal on different length scales. Chen et al. [34] studied DC casting of an Al–4.5% Cu alloy in the presence of electromagnetic stirring. The results showed that the concentration of Cu in the Al phase increased and the area fraction and dimensions of eutectic decreased markedly because of the increase in the solidification rate induced by the electromagnetic stirring. Moreover, the forced convection induced by the electromagnetic stirring made the effective partition coefficient  $k_e$  larger, and its value increased with the increasing stirring intensity, as shown in Fig. 4.7, which resulted in the increasing concentration of Cu in Al during the initial transient region and decreasing in the final transient region. Therefore, the microsegregation of Cu in the ingot was alleviated by the electromagnetic stirring.

#### 4.3.5 Effects of Electromagnetic Stirring on Solidification Structure

Equiaxed grains in castings originate from either active nucleation substrates and/or dendrite fragments. In the absence of efficient nucleation substrates, dendrite fragments are the major source of the equiaxed grain formation [35]. It is well known that convection promotes the fragmentation of dendrites [36–43]. However, different mechanisms have been put forward for the mechanisms of convection in dendrite

fragmentation. In this section, the refining mechanisms of grains will be discussed, and the effects of electromagnetic stirring on solidification structures presented.

#### 4.3.5.1 Refining Mechanism in the Presence of Electromagnetic Stirring

Figure 4.8 shows the microstructures of  $\varnothing$  200-mm Al–Zn–Mg–Cu billets prepared by DC casting technology in the absence and presence of electromagnetic stirring, respectively. In the conventional DC cast billet, the structure consists of coarse equiaxed dendrites. When the electromagnetic stirring is applied, the structure is transformed to fine and uniform globular equiaxed grains. The average grain size is decreased from about 125  $\mu\text{m}$  to 31  $\mu\text{m}$  by the electromagnetic stirring.

The fragmentation whether by breaking dendrite arms or remelting dendrite arm roots has been widely accepted to account for the grain-refining effect of electromagnetic field [36–43]. However, in terms of the grain refinement of an Al–Zn–Mg–Cu alloy by the DC casting with electromagnetic stirring, there are still some challenges in understanding the fragmentation. First of all, the mechanical breaking or bending of dendrite arms is considered unlikely. This is because the flow velocity (about 0.2–0.3 m/s) under forced convection is not large enough to break or bend the dendrite arms [46]. Calculations and direct observations of solidification under melt stirring also support the view that the mechanical destruction of the dendrites by forced convection is quite unlikely [35, 45, 46]. The most possible way of fragments formation is remelting of the roots of dendrite arms during solidification, which has been accepted and experimentally proven [47]. This mechanism perhaps makes some contribution to the transformation of microstructure from dendrite to fine spherical equiaxed structure at the beginning of switching on the electromagnetic field. However, fragmentation by remelting dendrite arms might be quite difficult at the steady stage of DC casting in the presence of electromagnetic stirring. As shown in Fig. 4.8b, the grains have a spherical equiaxed shape as a result of the forced convection. Therefore, there should also be some other mechanism of grain refinement. For metallic alloys, it is well accepted that its nucleation is heterogeneous rather than homogeneous. Any particles, such as oxides, intermetallics, and other

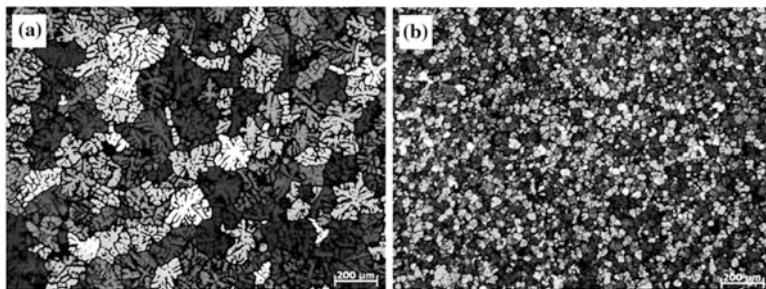


**Fig. 4.8** Microstructures of  $\varnothing$  200-mm Al–Zn–Mg–Cu billets prepared by the DC casting technology (a) in the absence and (b) presence of electromagnetic stirring (adapted from [44])

inclusions, can act as effective nucleation sites. However, the possibility of these particles acting as effective nuclei depends on the particle size and the undercooling. A free growth model proposed by Greer et al. [48] describes the correlation between the particle size and the undercooling for the free growth:

$$\Delta T_{fg} = \frac{4\sigma_{\text{interface}}}{\Delta S_V d} \quad (4.30)$$

where  $\Delta T_{fg}$  is the free growth undercooling,  $\sigma_{\text{interface}}$  the interfacial energy between the liquid and the nucleating solid phase,  $\Delta S_V$  the volumetric entropy of fusion, and  $d$  the nucleating particle size. It is clear that the free growth undercooling  $\Delta T_{fg}$  is inversely proportional to the nucleating particle size  $d$ . This means that nucleation will start firstly on the large particles and then on the smaller ones. Furthermore, a larger initial undercooling can activate smaller and more particles to act as effective nucleation sites. Based on the temperature measurements, Fig. 4.9 shows the schematic of cooling curves during DC casting in the absence and presence of electromagnetic stirring. There are four stages in the cooling curves. The first stage is the melt temperature drop from the furnace to the end of a launder. The measured melt temperature near the end of the launder is around 690 °C. The second stage is rapid cooling when the melt enters the sump because of the fast convective heat transfer between the newly poured melt and the melt in the sump. The third stage is a slow cooling in the sump from the top to the bottom. The fourth stage is a rapid cooling of the melt to the complete solidification in the mold region due to the effect of cooling water. The calculated cooling rates based on the measured temperature curves are listed in Table 4.3. EMS does not affect the cooling rates in stages 1 and 4. However, the significant differences of cooling rates appear in stages 2 and 3. During conventional DC casting process, the melt undergoes fast cooling (40 °C/s) from 690 °C to about 670 °C in stage 2. However, when the hot melt enters the sump, the cooling

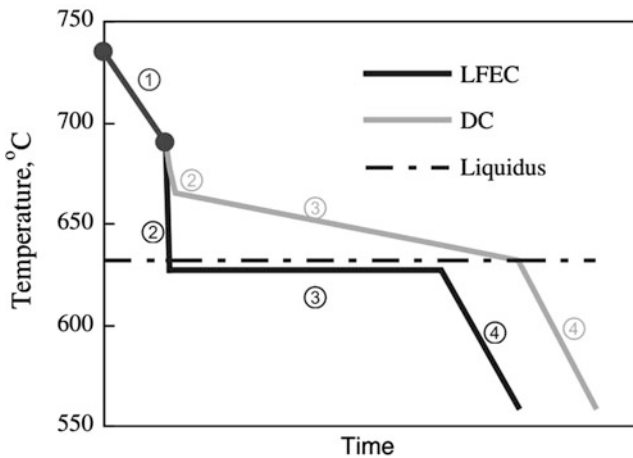


**Fig. 4.9** Schematic of cooling curves in DC casting in the absence (DC) and presence of electromagnetic stirring (LFEC) based on the measured thermal history of the melt (adapted from [44])



**Table 4.3** Variation of the cooling rates during DC casting in the absence and presence of electromagnetic stirring ( $^{\circ}\text{C/s}$ )

| DC casting process | Stage 1 | Stage 2 | Stage 3 | Stage 4 |
|--------------------|---------|---------|---------|---------|
| With EMS           | 12.5    | 126     | 0       | 8.2     |
| Without EMS        | 12.5    | 40      | 0.3     | 8.4     |

slows down ( $0.3\text{ }^{\circ}\text{C/s}$ ) in stage 3. During DC casting with the electromagnetic stirring, melt entering the hot top is subjected to very strong electromagnetic agitation. There is a much faster cooling ( $126\text{ }^{\circ}\text{C/s}$ ) from around  $690\text{ }^{\circ}\text{C}$  directly to around  $627\text{ }^{\circ}\text{C}$  ( $5\text{ }^{\circ}\text{C}$  below the liquidus) in stage 2, and then the melt is almost isothermal in stage 3. Indeed, the electromagnetic stirring plays a key role in the heterogeneous nucleation in DC casting. On the one hand, the forced convection disperses the inclusions and distributes them uniformly in the melt, which provides sufficient nucleation substrates. In addition, in stage 2, the melt is cooled down directly below the liquidus. This high cooling rate results in large undercooling and activates more particles in the melt to become sites for the heterogeneous nucleation. The nucleation rate is therefore significantly increased.

It should be noted that, based on the “separation theory” [49], the nucleation on the mold wall and the detachment of the nuclei also play an important role in increasing the nucleation rate. During conventional DC casting process, the melt temperature in the sump is higher than the liquidus. Therefore, most of the formed nuclei from the mold wall or elsewhere will disappear because of remelting and only a small amount of the nuclei can survive to act as effective nucleation sites. This is the main cause of the coarse microstructure by the conventional DC casting, unless special grain refining additions are used. However, during DC casting with electromagnetic stirring, the temperature field in the entire melt becomes quite uniform, and the melt temperature is  $3\text{--}6\text{ }^{\circ}\text{C}$  below the liquidus. This phenomenon was also confirmed in other aluminum alloys [15]. Therefore, the remelting of the formed nuclei was significantly reduced, and most of the nuclei can survive and act as effective nucleation agent, resulting in remarkable increase of effective nuclei. The microstructure of the billet made by DC casting with electromagnetic stirring is therefore much finer and uniform.

#### 4.3.5.2 Grain Growth in the Presence of Electromagnetic Stirring

The final microstructure, especially the morphology of the final grains, is not only related to the nucleation but also the growth conditions. After the formation of nuclei, they initially grow in a spherical shape and then transform to dendritic manner when the grains reach a certain size [50].

During DC casting with electromagnetic stirring, the growing grains move with the liquid flow and spin due to the forced convection. This should delay the transformation from spherical to dendritic growth. Furthermore, due to the forced

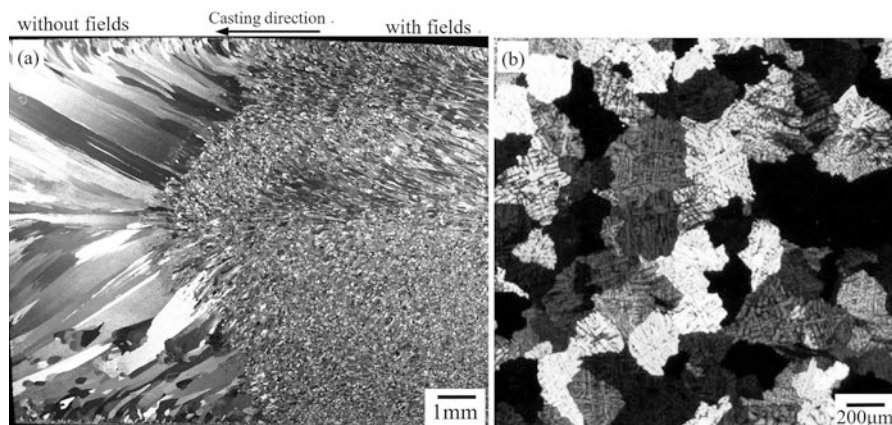


**Fig. 4.10** Macrostructure (a) and microstructure (lower part of the ingot with the electromagnetic stirring) (b) of an AA3004 aluminum alloy billet prepared by horizontal direct chill casting technology with the application of electromagnetic stirring (adapted from [51])

convection, the temperature and composition fields in the entire melt become relatively uniform, which reduces and even eliminates the constitutional undercooling near the liquid–solid interface. This provides a uniform and isotropic environment for the growth of the nuclei to globular grains.

In summary, the enhanced heterogeneous nucleation, the uniform and isotropic growth environment, and the delayed transformation from spherical to dendritic growth are believed to be the main reasons to produce fine, uniform, and spherical equiaxed grain structure of Al alloys under electromagnetic stirring.

Other than the transformation from coarse equiaxed dendrites to fine spherical equiaxed grains, the electromagnetic stirring also promotes columnar-to-equiaxed transition (CET). Figure 4.10a shows the macrostructure of an AA3004 aluminum alloy billet prepared by horizontal DC casting with the application of electromagnetic stirring [51]. Without the electromagnetic field, the structure consists of coarse columnar grains. When the electromagnetic field is applied, it is transformed to fine columnar grains in the upper and equiaxed grains in the lower parts of the billet. To more clearly reveal the morphology of the grains, Fig. 4.10b shows the microstructure in the lower part of the ingot cast with EMS. As can be observed, the equiaxed grains are actually dendritic with many fine arms, which is different from the spherical equiaxed grains. Therefore, the refining of this alloy should be dominated by the fragmentation of arms due to the forced convection by the electromagnetic fields. Meanwhile, the mechanism mentioned above for the Al–Zn–Mg–Cu alloy may also contribute to this CET transformation.

As for the fine columnar grains in the upper part of the ingot cast with EMS, it is related to the effect of gravity. As the contacting pressure between the top mold and the ingot surface is lower than that between the bottom mold and the ingot surface, the melt in the upper side has a low undercooling and then a lower surviving rate of the detached arms. As a result, fine columnar grains are formed as a temperature gradient exists at the solidification front.

## 4.4 Effects of Low-Frequency Vibration on Heat/Mass Transfer and Solidification Structures

In industrial production of metallic alloys, fine-grained equiaxed structures are always desirable as they can improve low temperature strength and toughness, reduce anisotropy, microsegregation, and hot tearing tendency, and favor heat treatment. So far, it has been extensively shown that the application of external forces during the solidification process of alloys can refine grain size by the induced fluid flow. The methods of imposing external forces include rotation of the mold, mechanical, or electromagnetic stirring (as mentioned above) and rheocasting. Moreover, it has also been found that mechanical vibrations of both sonic and ultrasonic character promote the development of a fine-grained equiaxed structure when applied during the solidification of metals and alloys [52–55]. (Ultrasonic melt processing is considered in Chap. 5, and contactless excitation of cavitation in melt using EMP is considered in Chap. 3 [56, 57]). Based on these effects, Vivès [58, 59] developed a magnetohydrodynamic method of transmitting forced vibrations to solidifying aluminum alloy melts—electromagnetic vibration, which was produced by the application of two different electromagnetic force patterns. With this method, extensive grain refinement has been observed in both continuous casting and batch-type mold casting. In this section, we will give a brief introduction of the principles of electromagnetic vibration, and then present the effects of low-frequency vibration on heat/mass transfer and solidification structures.

### 4.4.1 *Vibration Forces Induced by an Oscillatory Electric Field and a Steady Magnetic Field*

According to Vivès [58, 59], this method refers to the simultaneous application of a stationary magnetic field  $B_0$  and of a sinusoidal electric current of low frequency  $N$  and of intensity (listed as Eq. (4.31)) during the solidification process of an alloy.

$$i = I \sin(\omega t) \quad (4.31)$$

The alternating current density  $j = J \sin(\omega t)$  induces a periodic magnetic field  $b = B \sin(\omega t + \phi)$  of the same frequency, according to the Maxwell equation  $\nabla \times B = \mu J$  (on account of the low frequency of the electromagnetic parameters, the displacement current is negligible here). From the hydrodynamic standpoint, the melt flow may be considered as the superposition of three motions: two alternating flows of  $N$  and  $2N$  frequency, respectively, and an unstable recirculating flow which may be resolved into a steady component and a random component. The imposed stationary magnetic field  $B_0$  interacts with the electric current of density  $j$  and then results in a vertically directed periodic electromagnetic force  $j \times B_0$  of frequency  $N$ , which in turn forces the solidifying melt into vibration.

On the other hand, the  $j \times b$  force consists of an oscillating component of frequency  $2N$  and of a time-independent component. Though the time-smoothed component is mainly irrotational (pinching force), the strength of its rotational part is sufficient enough to engender relatively unstable recirculating flows characterized by rather slow local velocities on the order of a few cm/s, whereas the periodic component has a tendency to set the melt vibrating.

#### ***4.4.2 Vibration Forces Induced by a Variable Magnetic Field and a Steady Magnetic Field***

Different from the vibration induced by an oscillatory electric field and a steady magnetic field, this method refers to the simultaneous application of a stationary magnetic field  $B_0$  and of a variable magnetic field  $b$  in the vicinity of the molten metal. Both  $B_0$  and  $b$  are nearly parallel to the vertical axis of the ingot. The stationary magnetic field is generated by driving direct current through one or more coils. The alternating magnetic field is created by inputting an alternating current of frequency  $N$  into another inductor of similar geometry. The periodic current in the inductor produces a variable field  $b$  in the melt and then results in an induced periodic current of density  $j$ . The interaction of  $B_0$  and  $j$  generates a vibrating force of frequency  $N$ , while the  $j \times b$  force consists of a time-independent component and an oscillatory component of frequency  $2N$ . The electromagnetic vibrations mainly originate inside the electromagnetic skin depth area and are propagated throughout the melt due to the medium elasticity. The time mean electromagnetic body force may be resolved into a radial component (primarily irrotational) and a vertical component (primarily rotational). Hence, the potential forces give rise to the formation of a convex surface meniscus, whereas the rotational forces cause an electromagnetic stirring.

In summary, the first method takes the vibrating force as the principal force applying into the whole melt, whereas the second method applies the vibration and stirring together into the skin depth of the melt. Furthermore, a larger stationary magnetic field is needed to cause vibration of the melt for the method one, and a variable electromagnetic field with a lower frequency is necessary to increase the acting region of electromagnetic force for the method two. Therefore, the low-frequency electromagnetic vibration based on the simultaneous application of a stationary magnetic field and of a variable magnetic field can be applied widely.

#### ***4.4.3 Effects of Low-Frequency Electromagnetic Vibration on Heat/Mass Transfer***

In this section, we will give a brief introduction on the effects of electromagnetic vibration on the heat transfer during DC casting of aluminum alloys. As we have

already explained, in the steady-state process of DC casting, the water-cooled mold wall first cools the melt. At this stage, high heat extraction rate occurs for a brief period of time. Afterwards, as the solidified shell pulls away from the mold wall due to shrinkage and thermal contraction, the thermal contact of the melt with the mold and, hence, the heat flux decrease abruptly. When electromagnetic vibration is applied, the melt is subject to the vibrating force in the radial direction at a certain frequency, which generates the electromagnetic pressure  $P$ :

$$P = BJ(V/A) \sin(2\pi ft), \quad (4.32)$$

where  $f$  is the frequency,  $t$  is the time,  $V$  is the volume of the liquid, and  $A$  the area of the surface normal to the direction of the force that puts the liquid under compression and tension in two successive halves of a cycle. Under the effects of this pressure, the electromagnetic oscillatory wave translates throughout the entire melt inside the mold due to its elasticity, which increases the rate of liquid superheat removal and heat transport inside the melt. It has been observed from the temperature measurements that the temperature distribution in the sump is strongly modified by the simultaneous application of a stationary magnetic field  $B_0$  and a variable magnetic field  $b$ : the escape of superheat is enhanced, and the melt temperature is rapidly homogenized [58, 59]. During this specific electromagnetic vibration casting, which combines both stirring and vibration effects, the pool temperature is about 8 °C below the liquidus [58].

In this section, solute distribution in a DC cast aluminum alloy ingot is used to characterize the effects of electromagnetic vibration on the mass transfer.

In the presence of electromagnetic vibration, the applied magnetic field generates forced liquid flow inside the melt, which tends to suppress the settling of the solute-depleted dendrites to the bottom of the sump so that the segregation of alloying elements throughout the billet is decreased. Furthermore, the changed shape of the grains by the electromagnetic vibration also plays an important role in modifying the macrosegregation behavior. During solidification, the solute is rejected continuously from the solid phase to the surrounding liquid, causing the liquid to become richer in solute elements (here hypoeutectic alloys are meant). In order to feed the solidification shrinkage, the solute-rich liquid moves toward the periphery of the billet through the interdendritic channels, resulting in a positive segregation at the periphery region [60]. Dahle and StJohn showed that grain refinement or a more globular grain morphology lowers the dendrite coherency temperature, at which the dendrites started to impinge on each other [61]. In the case of the electromagnetic vibration, the structure of the billet is greatly refined and the grain shape changes from large-irregular dendrites to fine-equiaxed dendrites. Thus, it can be concluded that the dendrite coherency in the mushy zone is postponed by the electromagnetic vibration. As solidification proceeds, a stage where a coherent network is formed is considered as the start of linear thermal contraction [62, 63]. Therefore, the refined and equiaxed dendritic grains in the melt postpone the start of linear contraction, which results in increasing the contribution of convection to macrosegregation. In addition, the globular and smaller grains decrease the contribution of shrinkage-induced flow

[28, 63]. Thus, the time available for interdendritic fluid flow during billet solidification may be shortened. As a result, the macrosegregation in the billet is considerably reduced by the electromagnetic vibration.

As a result of solute rejection at the solid–liquid interface and incomplete diffusion in liquid, the dendrite boundary exhibits a higher solute concentration, causing the solute to diffuse into the interior regions of the grain due to the concentration gradient within the grain. If the solidified grain is fine, the solute diffusion path inside the grain is short and the relatively high concentration gradient within the fine grain provides conditions for more efficient back diffusion. Therefore, in comparison to large grains, the minimum concentration of solute at the refined grain is larger. As aforementioned, the electromagnetic vibration technique can effectively refine the grains size. As a result, the solute concentration inside the grain should be raised accordingly.

#### 4.4.4 *The Effects of Electromagnetic Vibration on Solidification Structure*

Figure 4.11 shows microstructures of the ingots prepared by DC casting in the absence and presence of electromagnetic vibration. As can be observed, the microstructure of the ingot is changed from coarse dendritic to fine and uniform equiaxed grains by the electromagnetic vibration. In general, such a structural change can be a result of two distinct phenomena: cavitation and fluid flow.

However, the cavitation phenomena cannot occur in this process, because the level of the fluctuating pressure peak is significantly lower than the pressure peak required to reach the cavitation threshold, which is on the order of 0.7 bar [52, 59]. The role of cavitation in solidification upon ultrasonic melt processing is considered in Chap. 5, while the possibility of achieving cavitation by EMP is discussed in Chap. 3. Vibration, however, also gives rise to considerable agitation

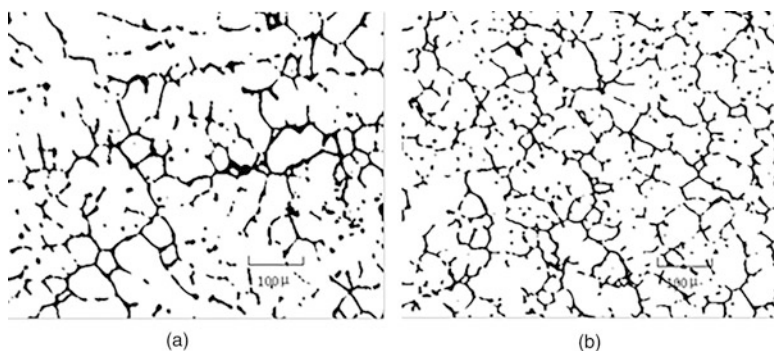


**Fig. 4.11** Microstructures of the ingots produced by DC casting in the absence (a) and presence (b) of electromagnetic vibration (adapted from [64])

of the melt and results in the newly formed nuclei being distributed throughout the solidifying pool, so that the crystallization takes place uniformly inside the entire volume. Moreover, the vibration has much the same effects as turbulence in dispersing and multiplying small crystals.

Therefore, the refining results in Fig. 4.11 are mainly because of the forced convection by the electromagnetic stirring component during DC casting process in the presence of electromagnetic vibration.

Vives [58] showed that the gain refinement obtained by the simultaneous application of a variable magnetic field and a steady magnetic field was better than that achieved by the a variable magnetic field acting alone, probably because of increasing nucleation provoked by the additional effect of the electromagnetic vibrations.

## 4.5 Casting Technologies Based on Electromagnetic Stirring and Vibration

In order to obtain excellent solidification structures of ingots, some casting technologies have been developed based on the electromagnetic stirring, e.g., Casting, Refining, ElectroMagnetic (CREM) and Low-Frequency Electromagnetic Casting (LFEC), and based on the electromagnetic vibration, e.g., Electromagnetic Vibration Casting (EVC) and Low-Frequency Electromagnetic Vibration Casting (LFEVC).

### 4.5.1 *Casting, Refining, ElectroMagnetic and Low-Frequency Electromagnetic Casting Processes*

The casting technique called CREM process was developed by Charles Vivès in the late 1980s [30]. Figure 4.12a shows the schematic of the CREM process. This technology is characterized by the presence of a strong forced convection of electromagnetic origin that leads to the significant reduction of the grain size. In this process, liquid metal is inductively stirred, using an inductor supplied with a 50-Hz alternating current. The coil surrounds the ingot mold following its shape. Under the effect of periodic current, the inductor generates a variable magnetic field in the melt which, in turn, gives rise to the induced current. Thus, the melt is subject to electromagnetic body forces caused by the interaction of eddy currents  $J$  and magnetic field  $B$ . As we showed before, the time mean electromagnetic body forces may be resolved into a radial component (primarily irrotational) and a vertical component (primarily rotational). The potential forces, balanced by a pressure gradient, result in the formation of a convex surface meniscus, while the rotational forces are responsible for an electromagnetic stirring. The action of such a vigorous convection results in refining of the grains and a higher degree of homogeneity in crystallization.



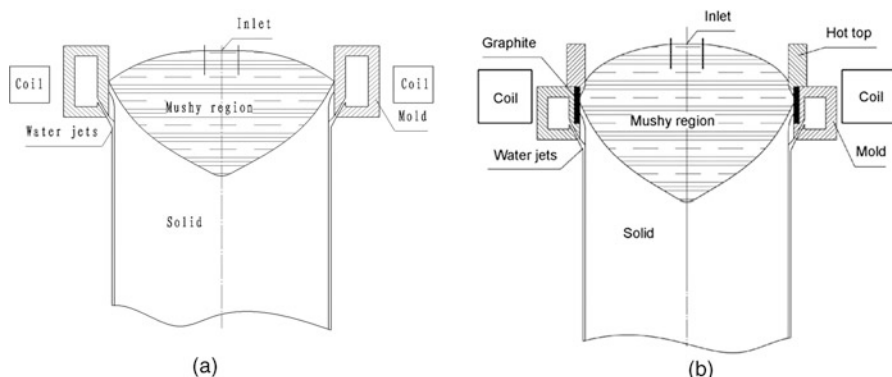


**Fig. 4.12** Schematics of the (a) casting, refining, electromagnetic (CREM) and (b) low-frequency electromagnetic casting (LFEC) processes (adapted from [3])

This cast technology has been applied in DC casting of a 320-mm diameter AA2214 aluminum alloy billet [30]. The potential forces can decrease the height of metal in contact with the mold, which results in modification of the heat flux profile, and then results in the progressive decrease in exudation and a smaller segregation zone. Therefore, the billet surface becomes very smooth, and the thickness of the segregated surface layer tends toward zero [30]. The temperature field in the sump is strongly affected by the electromagnetic stirring. This intense forced convection promotes the evacuation of superheat, and makes the bulk liquid temperature lower than the liquidus (within 1 °C). Moreover, for the case of aluminum alloys vigorously stirred and characterized by a wide freezing range (AA2214, for instance), the transition region may occupy the whole volume of the sump. The mechanism of the grain refinement provoked by the forced convection has been described in the previous sections.

To summarize, by means of this original technology, both the stirring intensity and the level of the contact line of the metal with the ingot mold are modulated at will, without direct contact with the melt and, therefore, without risk of pollution. Moreover, it should be emphasized that the supporting effect of the mold, though substantially reduced by the electromagnetic confining forces, continues to exist (in difference to the electromagnetic casting [65] not considered here).

Despite the advantages mentioned above, CREM process is not applied widely because of two reasons:

(a) The range of the electromagnetic force is narrow.

The alternating magnetic field with a frequency of 50 Hz is used in the CREM process, which results in the electromagnetic force being confined to a narrow range (i.e., the skin depth) and the forced convection is not uniform in the molten pool. So, the microstructure across the cross-section of the ingots is not uniform, and this phenomenon becomes more pronounced with increasing the billet diameter.

(b) The mold design is outdated.

The coil used in the CREM process is difficult to fit in modern molds.

Based on the CREM process, Jianzhong Cui [38] developed another casting technique—LFEC process, as schematically shown in Fig. 4.12b. The basic principle of LFEC process is the same as that of CREM. The difference is that the frequency of the electromagnetic field used in the LFEC process is 15–30 Hz, which is lower than that in the CREM process. As a result [3, 14, 33, 66, 67], the range of electromagnetic force in LFEC process becomes relatively large, leading to more uniform forced convection in the liquid pool. With this technique, the distribution of temperature in the liquid pool becomes uniform, and the casting stress is decreased. Moreover, the size of grains is decreased remarkably, the micro- and macro-segregation is alleviated significantly, and the hot tearing and cold cracks are reduced. Due to its advantages, the LFEC process has been applied widely in many Chinese factories to cast large-scale Al- and Mg- alloy billets.

In addition, some further applications based on LFEC are also developed, such as Horizontal direct chill casting under Low-frequency Electromagnetic field (HLEC) [68], DC casting of Hollow Billets under Electromagnetic field (HBEC) [69], Electromagnetic Modifying of hypereutectic Al–Si alloys (EMM) [70], Air Film Casting under static Magnetic field (AFCM) [71], and ElectroMagnet-Air knife Casting (EM-A Casting) [72].

#### 4.5.2 Electromagnetic Vibration Casting and Low-Frequency Electromagnetic Vibration Casting Processes

A casting technique called EVC process was also developed by Charles Vivès [58] in the late of 1980s. The schematic diagram of EVC process is shown in Fig. 4.13a. The electromagnetic vibration is produced by a simultaneous application of a

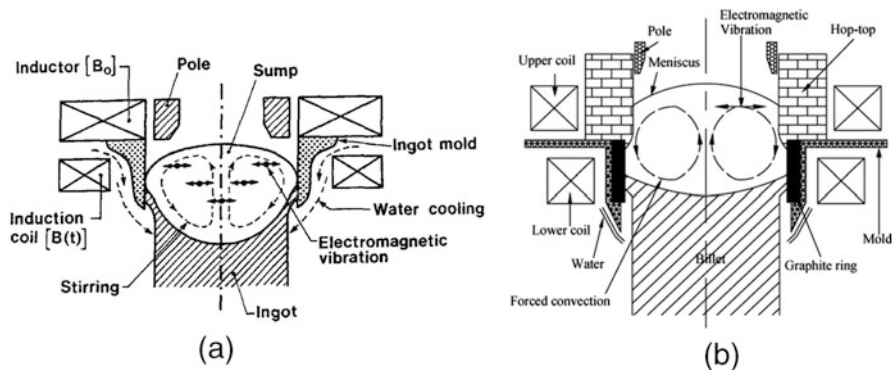


**Fig. 4.13** Schematic of the (a) electromagnetic vibration casting (EVC) (adapted from [58]) and (b) low-frequency electromagnetic vibration casting (LFECV) processes (adapted from [73])

stationary magnetic field  $B_o$  and a variable magnetic field  $B(t)$  created by two coils around the billet mold. These two magnetic fields are nearly parallel to the vertical axis of the billet. A ring of a pole is embedded in the upper coil to increase the stationary magnetic field. Under the effect of the variable magnetic field, an induced current is generated in the skin region of the melt, and vibration is generated inside the electromagnetic skin depth area of the melt due to the medium elasticity and propagated throughout the melt inside the mold. At the same time, stirring is produced in the melt by the interaction between the induced current and the applied variable magnetic field in the mold.

This cast technology has been applied in DC casting of a 320-mm diameter AA1085 aluminum alloy billet without addition of grain refining master alloys [58]. It is found that the billet cast by the conventional DC casting exhibits a columnar structure, whereas that cast with electromagnetic vibration shows a fine-equiaxed structure (the mean grain size is on the order of 150  $\mu\text{m}$ ). Application of EVC process to billets and slabs of an AA2214 aluminum alloy, which is characterized by a broad freezing range, has confirmed that the grain refinement obtained by the simultaneous application of  $B_o$  and  $B(t)$  is better than that achieved by the CREM process acting alone.

The EVC process is not used widely because of the same reasons as the CREM process. Based on the EVC process, Jianzhong Cui [64, 73] developed another casting technique—LFEVC process. Figure 4.13b shows a schematic of the LFEVC process, the principle of which is the same as that of EVC process. The difference is that the frequency of the electromagnetic field used in the LFEVC process is 15–30 Hz, which is lower than that in the EVC process (50 Hz). Similarly, the range of the electromagnetic force in LFEVC process becomes large, giving rise to more uniform forced convection and macro- and micro-structure across the sections of the ingots.

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# Chapter 5

## High-Frequency Vibration and Ultrasonic Processing



Dmitry G. Eskin and Iakovos Tzanakis

### 5.1 Historical Overview of Ultrasonic Cavitation Science and Applications

The application of ultrasound to the processing of liquids and slurries has a long history. The theory of oscillations was developed by Lord Rayleigh who laid the foundation for nonlinear acoustics. He also theoretically quantified the pressure pulse resulted from the imploding cavitation bubble and suggested that the acoustic pressure is directly related to the wave energy and velocity [1], which was experimentally confirmed by Altberg [2].

Significant contribution to the theory of cavitation was made by Frenkel [3] and Harvey [4] who explained why the cavitation threshold in liquids is well below the theoretical tensile strength of the liquid phase, suggesting a model of cavitation nuclei in real liquids as stable gas pockets at the surface imperfections of suspended particles. The pulsation of a cavitation bubble was described analytically by Nolting and Neppiras [5]. They introduced the resonance radius of the bubble. A bubble smaller than or around the resonance size will rapidly grow and then implode within one or two sound wave cycles. Each imploded bubble will generate large pressure pulse and create many even smaller bubbles, starting a chain reaction of bubble multiplication. A bubble larger than the resonance size will not implode but, being relatively stable, will pulsate around its size. The product of the number of cavitation bubbles in the unit volume and the maximum volume of a single bubble is called

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153



cavitation index. When this index approaches unity, the amount of bubbles in the unit volume becomes so big that they substitute the liquid phase and the ultrasonic power transmitted to the liquid declines rapidly [6, 7]. This is the base of the so-called shielding effect of the cavitation region, when the acoustic energy rapidly attenuates within the cavitation zone and does not propagate to the liquid volume.

The practical aspects of ultrasonic cavitation started to attract the attention of physicists, chemists, and other applied scientists and researchers. Wood and Loomis in the late 1920s observed intensive acoustic streaming and fountaining, ultrasonic degassing, emulsification and atomization, cavitation damage of organic tissue, etc. [8].

The direct observation of cavitation became possible with the development of high-speed film cameras, high-brilliance impulse lamps, and, eventually, laser illumination in the 1950–1960s [9–14]. The images taken with the exposure 0.5–5 ms enabled the in situ study of the cavitation development, bubbles collapse, and sonoluminescence. In recent years, in situ studies of cavitation in liquid metals became possible using synchrotron radiation [15–17].

The application of vibrations to treating metals dates back to the 1870s when Chernov reported that shaking molten steel solidifying in a mold resulted in the formation of very fine crystals [18]. The effects of low-frequency vibration on liquid and solidifying metals were reviewed by Balandin [19] and Campbell [20].

The ultrasonic processing of liquid and solidifying metals has been reviewed on numerous occasions, e.g., by Hiedemann [21], Eskin [22, 23], Flinn [24], von Seemann et al. [25], Abramov and Teumin [26], Kapustina [27], Abramov [28], Buxmann [29], and Campbell [20].

Extensive studies on solidification of various metals and alloys under ultrasonic fields of different frequencies and intensities were performed by von Seemann et al. [25, 30, 31], and Schmid et al. [32, 33] in the 1930–1940s. A significant refining of grain structure was achieved in these experiments, and crystal fragmentation was suggested to be responsible [33]. At the same time, a group of scientists advocated the cavitation-induced nucleation of the solid phase [34–37]. Danilov and Teverovsky [36] suggested cavitation-assisted heterogeneous nucleation through activation of insoluble impurities. A. P. Kapustin observed the formation of new crystallization centers under sonication of very pure liquids, hence something different from activation of impurities might have happened [26]. Hunt and Jackson [38] demonstrated through calculations and dedicated experiments on water that the collapse of cavitation bubbles and the resultant surge of pressure might be responsible for the nucleation due the local change of phase equilibria, increase of the melting point (by tens of degrees!), and the effective local undercooling.

The application of ultrasound to processing of commercial alloys started with the works of von Seemann et al. (e.g., [31]) who demonstrated efficient refinement of the duralumin ingot grain structure and an improvement of its mechanical properties. This group also reported structure refinement of tin and zinc [25] as well as brass and steel [25, 39]. Eskin [23] applied ultrasonic cavitation treatment to a variety of model and commercial foundry Al alloys (hypo- and hypereutectic Al–Si alloys), and demonstrated that the grain structure, intermetallics, and primary crystals were

refined under cavitation conditions. Later, ultrasonic processing (USP) was shown to be advantageous for receiving refined grain structure and improved mechanical properties of direct-chill (DC) cast wrought magnesium alloys [40].

The proper choice of the material for sonotrodes (horns, and ultrasonic tips) was treated with special care, and Nb and its alloys were recommended for use in molten aluminum [23]. Direct introduction of ultrasound to high-temperature melts is, however, almost impossible. Consumable steel horns were reported to be used to treat Fe-based alloys [28]. Indirect ways were tested including transmission of the oscillations via mold, through solid substrate upon ark vacuum remelting, or through the layer of molten slag upon electro-slag remelting [41, 42]. Most recently, a contactless excitation of cavitation in liquid aluminum through a combination of induction coils was developed [43], see Chap. 3 for details. Such indirect ways open the way to treat virtually all metals.

An important effect of ultrasonic vibrations and cavitation that attracted the interest of metallurgists was degassing of the melt. The nature of ultrasonic degassing was first revealed on water. Lindström [44] suggested that the ultrasonic degassing of water is due to the diffusion of dissolved oxygen into the cavitation bubbles, their oscillation and growth and, finally flotation to the surface. Kapustina [27] concluded that the most important role is played by the oscillations of the bubbles in the acoustic field, while ultrasonic cavitation takes the supportive role in intensification of the bubble formation and acceleration of bubble/liquid interfacial diffusion. Eskin [23] argued that the cavitation is essential for ultrasonic degassing of metallic melts where the natural gas bubbles are not typically present, unlike those in water. Therefore, the formation and multiplication of bubbles (essential for degassing) can be only achieved by cavitation.

Another important effect of ultrasound is atomization and dispersion of liquid and solid phases with obvious metallurgical applications in manufacturing composite materials as well as immiscible alloys. Schmid and Ehret [32] and Becker [45] described Al–Pb and Zn–Pb alloys produced with ultrasonic melt processing as stable suspensions. Nonmetallic and solid particles can also be introduced into liquid metals, forming metal–matrix composites. Pogodin-Alekseev and Zaboileev-Zotov reported in 1958 the introduction of particulate (from 2 to 20  $\mu\text{m}$ ) alumina, silicon carbide, and titanium nitride in liquid aluminum in quantities of 10–50 wt% [46]. Seemann and Staats published in 1968 an important paper where they summarized their earlier works on the dispersion of metallic (Ti, Fe) and ceramic (carbides, oxides) particles in molten aluminum using 20-kHz magnetostrictive transducer and an alumina sonotrode [47].

Herrmann described, already in 1958, many pilot installations for ultrasonic processing (USP) of molten metal [48]. The versatility of the treatment was illustrated by examples with ultrasonic processing conducted in the furnace, melt flow, feeders of castings, and in the molds with the aim to remove dissolved gases, refine structure, and improve casting properties.

One of the early pilot-scale trials of ultrasonic melt processing of aluminum alloys during aluminum semicontinuous casting was described by Seemann and Menzel in 1947 [31]. Commercial size (290 mm) billets from a duralumin (AA2024)

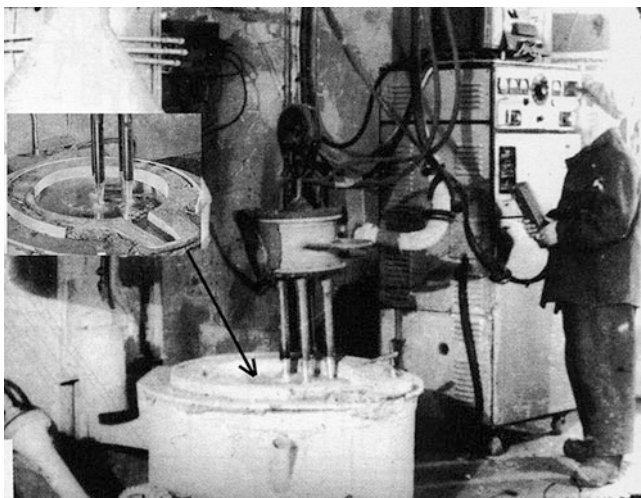


**Fig. 5.1** Aluminum degassing by submerged sonotrodes in the 1960s (courtesy of G. I. Eskin)

were cast with ultrasonic processing of the melt in the sump of the billet. In these experiments, a powerful ultrasonic generator (up to 25 kW) excited four 2-kW magnetostrictive transducers at 40 kHz. The efficiency of the entire assembly was 14% and it was able to deliver an intensity of  $2.0 \text{ W/cm}^2$  to the cross-sectional area of the billet ( $660 \text{ cm}^2$ ), which was sufficient to achieve grain refinement, reduced porosity, and increased ultimate strength.

The first industrial ultrasonic degassing installation (UZD-200) was developed in 1959 to treat 100–200 kg of melt in a crucible before casting [23]. The UZD-200 unit included a 10-kW lamp ultrasonic generator and a special switching circuit allowed for the alternate operation of four magnetostrictive transducers with Ti or Nb sonotrodes, Fig. 5.1. Similar installations were used for DC casting of aluminum alloys when the UST was performed in the sump of a billet or in the launder [49].

This brief historical overview shows that the ultrasonic melt processing has a long tradition. It originated from advances in physics that led to the design of modern equipment; followed by technological developments and trials that started in the 1930s and continued through the 1980s, leading to the first industrial implementations.

## 5.2 Brief Theoretical Introduction to Ultrasonic Cavitation Processing

Generally, acoustic phenomena are classified with respect to their frequencies: ultrasound is commonly bordered on the lower side by 16,000 Hz. Commercial ultrasonic transducers are capable of generating power densities about  $10^5$ – $10^6 \text{ W/m}$

<sup>2</sup> at frequencies of 18–20 kHz, which is sufficient for treatment of liquid and solidifying melts. High-frequency transducers (up to the MHz range) are also commercially available and are typically used in cleaning and chemical processing.

When a source of ultrasonic oscillations is introduced into the liquid pool, it induces an ultrasonic field whose characteristics depend on the oscillation parameters and on the properties of the treated medium.

One of the basic parameters is the propagation velocity of elastic oscillations. This velocity is governed by the physical properties of the medium where the wave propagates. At a given temperature, the velocity [m/s] of (ultra)sonic longitudinal waves in the solid phase with density  $\rho$ , Young's modulus  $E$ , and Poisson's ratio  $\mu_p$  is determined by:

$$c = \sqrt{\frac{E(1 - \mu_p)}{[\rho(1 + \mu_p)(1 - 2\mu_p)]}} \quad (5.1)$$

In the liquid phase, where elastic properties depend on the compressibility, the velocity of acoustic wave can be determined from

$$c = \sqrt{1/(\beta_{ad}\rho)}, \quad (5.2)$$

where  $\rho$  is the liquid density and  $\beta_{ad}$  is the adiabatic compressibility. For gases, the molecular motion is related to the adiabatic index  $\gamma = c_p/c_v$  (the ratio of specific heats at constant pressure and volume), gas pressure  $P_0$ , and density  $\rho$ :

$$c = \sqrt{\gamma P_0/\rho}. \quad (5.3)$$

Generated at any point in the medium (solid, fluid, or gas), oscillating disturbances propagate through the medium as elastic waves of alternating compressions and rarefactions. As follows from Eqs. (5.1), (5.2), and (5.3), the velocity of elastic waves in an unbound medium is independent of the frequency and, up to certain magnitudes, of the intensity (this relation is referred to as the linear approximation).

The product of propagation velocity  $c$  and density  $\rho$  ( $\rho c$ ) is called the wave (or acoustic) impedance of the given medium. It is equal to

$$\rho c = P_A/v = P/2\pi fA, \quad (5.4)$$

where  $P_A$  is the sound pressure in the travelling wave and  $v$  is its oscillation velocity that is determined by frequency  $f$  and amplitude  $A$  of the oscillations. Here,  $2\pi f$  is called angular velocity  $\omega$ .

The sound pressure  $P_A$ , therefore, can be expressed as:

$$P_A = v\rho c = \rho cA_0\omega \cos\left(\omega t - \frac{\omega x}{c}\right) \quad (5.5)$$

A very important parameter of the ultrasonic field determining to a great extent the efficiency of processing is the ultrasonic intensity  $I$ , or power flux  $W_a$  normalized by area  $S$ . In the simplest case of a plane wave, the intensity  $[W/m^2]$  is given by

$$I = \frac{W_a}{S} = \frac{1}{2} \rho c v^2 = \frac{1}{2} \rho c (A_0 \omega)^2 = \frac{1}{2} P_{AV} \quad (5.6)$$

The acoustic intensity is, therefore, proportional to the squared amplitude and frequency, which largely determines the selection of processing equipment and regimes.

When cavitation develops in the melt, the temporal characteristics of force and velocity at the sonotrode radiating face and in the melt containing cavitation bubbles vary, so Eqs. (5.5) and (5.6) may be used to describe the actual technological processes of melt sonication only in the first, or linear, approximation.

In the presence of cavitation, the acoustic impedance of the melt that is a function of oscillation amplitude or velocity rapidly decreases, as the sound velocity and the pressure in the cavitating liquid phase are no longer the same as in the non-cavitating liquid. The intensity or transmitted power can still be considered proportional to the squared oscillation velocity, but with the acoustic impedance rapidly decreasing after the cavitation threshold has been reached.

Figure 5.2 shows the dimensionless parameter  $K$ , which is the ratio of acoustic impedance under cavitation to the acoustic impedance in the absence of cavitation, versus the oscillating amplitude of the sonotrode at 18 kHz for water (1) and

**Fig. 5.2** Relative acoustic impedance  $K$  versus the amplitude  $A$  of the sonotrode at 18 kHz. (1) Water and (2) aluminum melt (after [49])

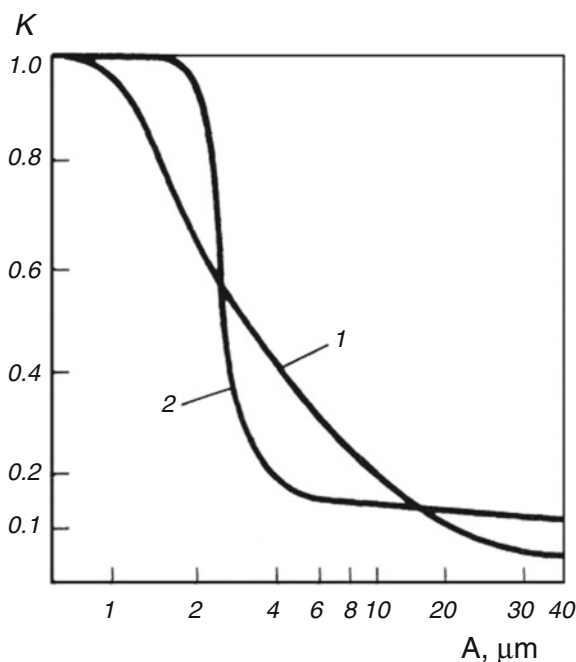
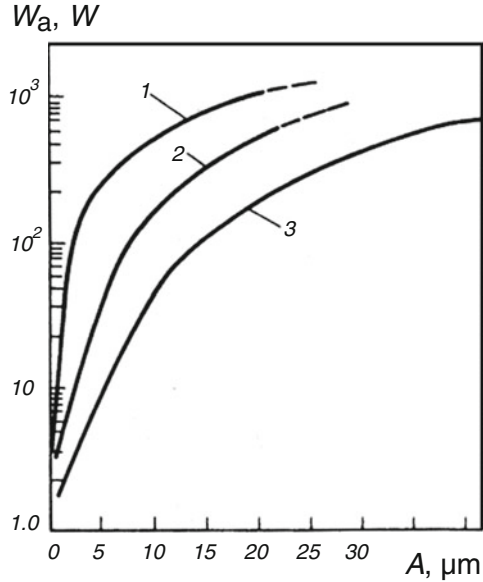


**Fig. 5.3** Power  $W_a$  transferred into the melt versus the amplitude  $A$  of the sonotrode at a resonance frequency of 18 kHz for three sonotrode diameters: (1) 65 mm, (2) 40 mm, and (3) 20 mm (after [49])



aluminum melt (2) [49]. When the null-to-peak amplitude exceeds  $0.5 \mu m$  for water at  $20^\circ C$  and  $2\text{--}3 \mu m$  for an aluminum melt, the wave resistance decreases to values ten times smaller than for sonication without cavitation.

On the other hand, when acoustic cavitation begins, the acoustic power transferred to the fluid increases. Figure 5.3 gives the relation between the oscillation amplitude and the acoustic power generated by standard ultrasonic equipment and transmitted into an aluminum melt of commercial purity at a resonance frequency of 18 kHz for different surface areas of the sonotrode radiating face.

Only recently, the instrumental facilities have been developed that allow the measurements of cavitation activity in liquid aluminum [50–52], whereas the evaluation of flow patterns and detailed study of cavitation are still mostly reserved to transparent liquids and, increasingly, to computer modeling and simulation.

The propagation of ultrasound is accompanied with losses of oscillation energy. The amplitude and intensity of a plane ultrasonic wave decrease exponentially with the propagation distance  $x$ :

$$A = A_0 e^{-\alpha x}, \quad (5.7)$$

$$I = I_0 e^{-2\alpha x}, \quad (5.8)$$

where  $\alpha$  is the loss coefficient or sound absorption, or attenuation factor.

Recent studies in Al melt [53] showed that the variation of the maximum pressure with distance from the sonotrode surface obeys a power law (Fig. 5.4). The decay of pressure with distance is with an exponent of 1.45/m. This pressure dependence on distance is in agreement with quantitative experimental measurements with a

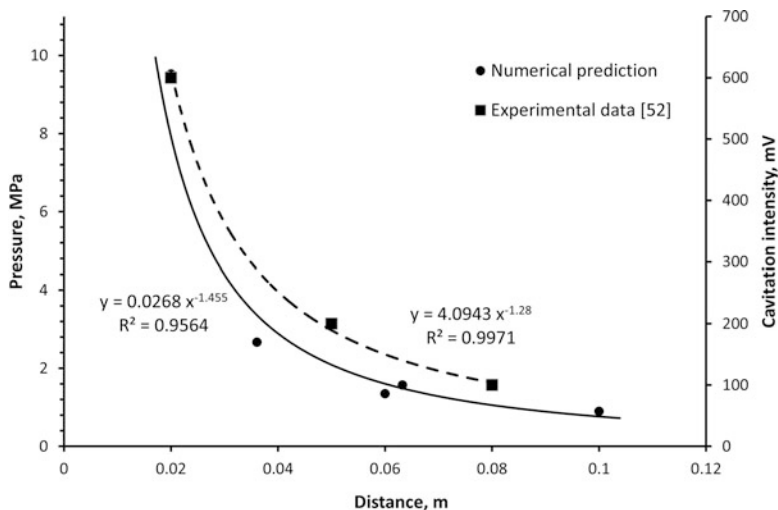


**Fig. 5.4** Attenuation of acoustic pressure (calculated numerically in MPa and experimentally measured as intensity) in liquid aluminum with the distance from the sonotrode (ultrasonic frequency 17.7 kHz)

high-temperature cavitometer [51] also plotted in Fig. 5.4, with a decay exponent of 1.28/m [54]. The experimental values are quoted in mV (pressures can be different as shown in Fig. 5.5 due to the shielding effect [54]). This large decay is expected, as the efficiency in acoustic radiation is proportional to the ratio of horn radius to wavelength. The large wavelength in aluminum and the comparatively small sonotrode makes the pressure decrease with distance more pronounced.

Apart from distance, which according to [55] plays a predominant role (74% of contribution) in attenuating cavitation intensity and hence the efficiency of cavitation treatment in the melt, acoustic power, and melt temperature also affect the cavitation development in the melt with the corresponding contributions of 14 and 12%.

The absorption of ultrasound in the liquid phase is related to the viscosity and thermal conductivity of the melt, and changes with the ultrasound frequency. The attenuation factor depends on the squared frequency:

$$\alpha = \frac{\omega^2}{2\rho c^3} \left( \frac{4}{3}\mu + \mu' + a \left( \frac{1}{c_v} - \frac{1}{c_p} \right) \right), \quad (5.9)$$

where  $\mu$  and  $\mu'$  are the shear and volume viscosities;  $a$  is the thermal conductivity; and  $c_v$  and  $c_p$  are the specific heats at constant volume and pressure, respectively. This dependence demonstrates that very high ultrasonic frequencies would be impractical for melt processing because of their strong attenuation (even without taking into account the shielding effect of the developed cavitation region).



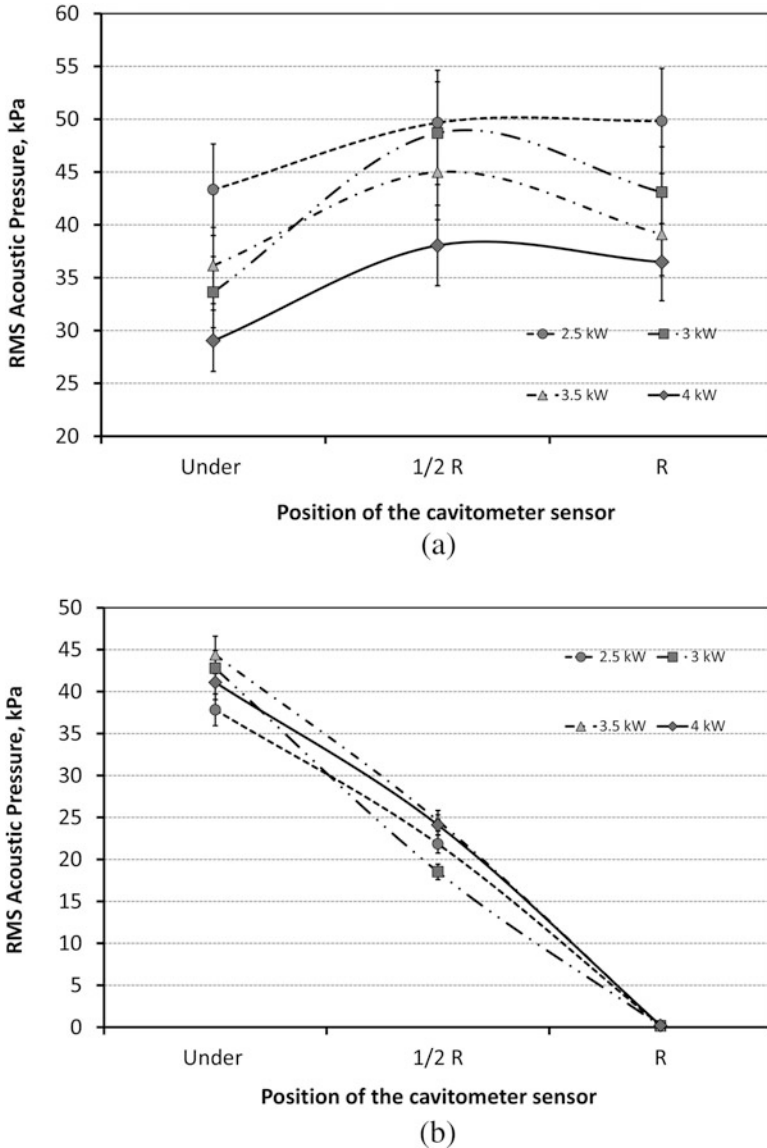


**Fig. 5.5** Variation in RMS acoustic pressures of the driving frequency (17 kHz) at three different positions (under the sonotrode, at  $1/2R$ , and at  $R$  from the source) across the crucible in (a) water and (b) liquid Al. (I. Tzanakis, D. Eskin, 2015)

In addition to that, nondimensional analysis of an ultrasonically treated aluminum melt showed that heat conductivity would be the dominant heat transfer process over convection, and the attenuation of the acoustic waves propagation (sound converts to heat) in this medium is significant [56]. On the other hand, the same report showed

that in nonmetallic liquids that are good heat insulators the heat dissipation will be controlled by viscous forces (convection).

The interfaces between the liquid phase and suspended particles (nonmetallic inclusions, and crystals) may significantly affect absorption [57]. The attenuation factor increases with the amount of particles and with their fineness. Similar effect is produced by gas bubbles whose interfaces with the melt act as scattering sources. As we will show below, the very same interfaces of gaseous and solid inclusions act as cavitation nuclei and favor the development of cavitation, absorbing additional ultrasonic energy.

Cavitation development in water closely resembles that of liquid aluminum [57]. This allows researchers to experimentally investigate cavitation activity in water using advanced experimental equipment and techniques such as advanced cavitometers and particle image velocimetry (PIV) and subsequently feed numerical models to replicate and validate the cavitation development in liquid aluminum [53].

Tzanakis et al. [52] directly measured cavitation acoustic pressures in liquid aluminum using an advanced high-temperature cavitometer (Fig. 5.5). Results showed that shielding and acoustic damping are more pronounced in liquid aluminum, in contrast to a more uniform pressure regime measured in water. The extent of the cavitation zone was quantified in both tested liquids.

According to well-adopted views on the cavitation threshold, the tensile stress-induced disruptions in liquids are not governed by molecular forces, but rather by the presence of cavitation nuclei such as vapor and gas bubbles, solid gas-adsorbing suspensions, and hydrophobic inclusions.

The cavitation strength is related to the surface tension at the liquid–gas interface and the initial bubble radius. The viscosity  $\mu$  also markedly influences the cavitation response of the liquid, increasing the cavitation threshold and the critical resonance radius of a cavitation bubble. The cavitation threshold or critical pressure is directly proportional to the  $\ln(\mu)$  [58] or to  $\mu$  [59].

The dynamic behavior of a single vapor–gas cavity in an incompressible liquid is described (neglecting gas diffusion to the cavity) by the Noltingk–Neppiras equation [60, 61]:

$$\begin{aligned} \rho \left( \ddot{R}R + \frac{3}{2} \dot{R}^2 \right) + 4\mu \frac{\dot{R}}{R} + \frac{2\sigma}{R} - \left( P_0 - P_v + \frac{2\sigma}{R_0} \right) \left( \frac{R_0}{R} \right)^3 \\ + P_0 - P_v - P_A \sin(\omega t) = 0 \end{aligned} \quad (5.10)$$

Here,  $R$  is the radius of the cavity,  $R_0$  is the initial radius of the cavity,  $\sigma$  is the surface tension of the melt,  $\mu$  is the viscosity of the melt,  $\rho$  is the melt density,  $P_v$  is the vapor pressure,  $P_A$  is the sound pressure,  $P_0$  is the static ambient pressure, and  $\omega = 2\pi f$  is the angular velocity.

The critical radius of a cavitation bubble can be related to the surface tension  $\sigma$  and viscosity  $\mu$  of the liquid phase as:

$$R_{cr} = \left( \frac{3\kappa - 1}{3\kappa} \right) \frac{\sigma}{P_g} \left[ -1 + \sqrt{1 + \frac{24\kappa\mu^2 P_g}{(3\kappa - 1)^2 \sigma^2 \rho}} \right], \quad (5.11)$$

where  $\kappa$  is the polytropic exponent varying from 1 to  $c_p/c_v$  [62],  $P_g$  is the initial gas pressure, and  $\rho$  is the liquid density [63].

Neglecting the surface tension, the critical radius depends directly on the liquid viscosity [63]:

$$R_{cr} = \frac{2\sqrt{2\mu}}{\sqrt{3\kappa P_g \rho}}. \quad (5.12)$$

This critical radius can also be described as [64]:

$$R_{cr} = \sqrt{\frac{9kT_b R m_g}{8\pi\sigma}}, \quad (5.13)$$

where  $k$  is the Boltzmann constant,  $R$  is the gas constant,  $m_g$  is the mass of gas inside the bubble, and  $T_b$  is the temperature of the bubble. The bubbles smaller than the critic radius will be stable.

The resonance radius  $R_r$  has been defined from the Minnaert resonance condition [65]:

$$f = \frac{1}{2\pi R_r} \sqrt{\frac{3\kappa}{\rho} \left( P_0 + \frac{3\sigma}{R_r} \right)}. \quad (5.14)$$

From curves in Fig. 5.6, it follows that if the sound pressure is small enough ( $P_A < P_C$ , where  $P_C = 0.6$  MPa is the cavitation threshold), the cavities pulsate and do not collapse during this time. The pressure in gaseous bubbles varies very little. As the sound pressure  $P_A$  increases to values above 1 MPa and exceeds  $P_C$ , the majority of cavities with  $R_0 > R_{cr}$  behave like typical cavitation bubbles, collapsing at the end of the first or second period of oscillations. With a further increase in sound pressure, i.e., for  $P_A \gg P_C$ , cavitation becomes developed and all cavities expand during one or two periods of the ultrasound wave and then collapse. The pressure inside the bubbles varies by several orders of magnitude.

This analysis is done with an assumption of spherical bubbles, which holds only for the first cycle of oscillations. In reality, the curved interface between the denser liquid and the less dense gas inside the bubble strongly accelerates inward, especially during last stages of collapse [66]. This results in the distortion of initially plane interface with the formation of kinks and folds. This phenomenon as well as the collapse of the bubbles resulting in the formation of a cloud of new, much smaller bubbles has been observed experimentally [13, 66]. This is illustrated in Fig. 5.7. The shape instability is counteracted by the smoothing effect of surface tension and the energy dissipation by viscosity [66].

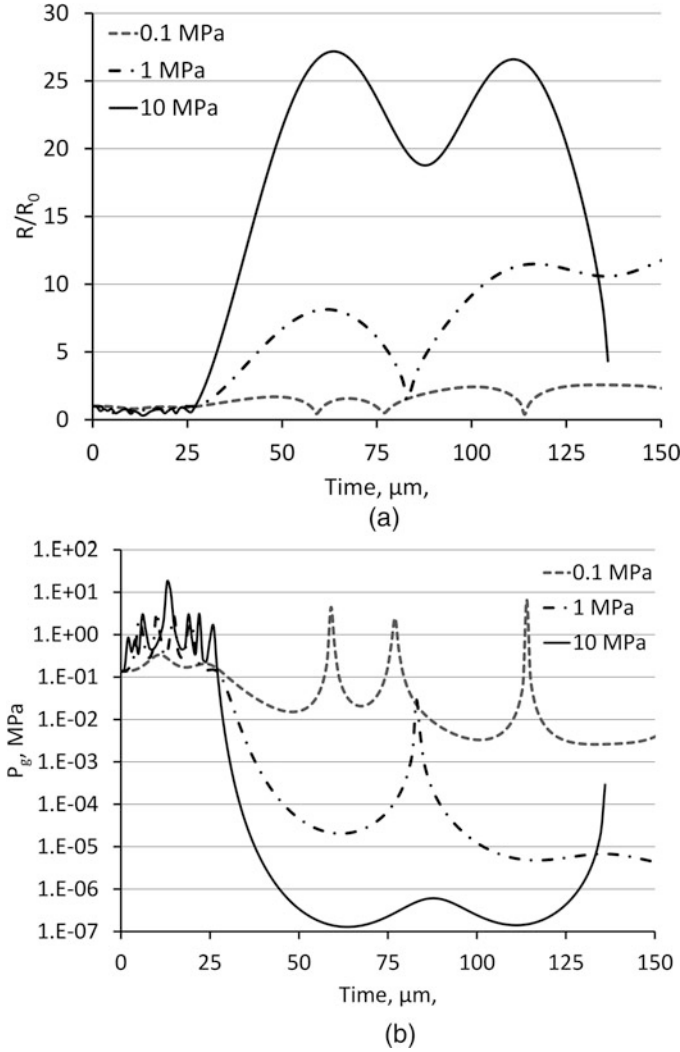


**Fig. 5.6** Evolution of cavities with initial radii  $R_0 = 50 \mu\text{m}$  in aluminum melt (a) and corresponding gas pressures (b) for acoustic pressures  $P_A$ : 0.1, 1.0, and 10.0 MPa (courtesy of G. S. B. Lebon)

The given results for bubble dynamics, though account for the gas contents inside the bubble, did not take into account the diffusion of gas dissolved in the liquid into the cavity. Allowing for this diffusion would increase the survival chances of the bubble due to gas diffusion in melts with low saturated vapor pressure or due to vaporization from the bubble walls in liquids with high saturated vapor pressure [49].

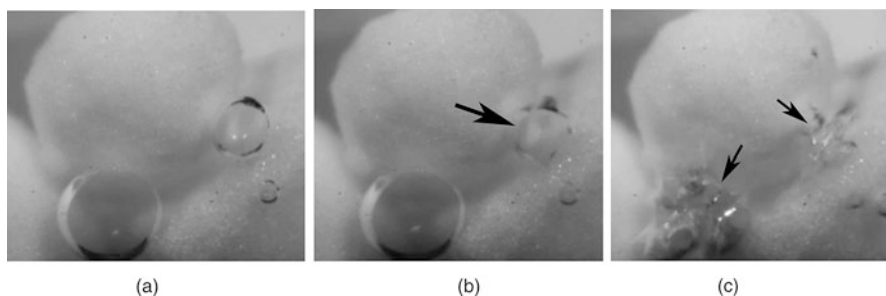


**Fig. 5.7** Evolution of gas bubbles in water with MgO agglomerates: (a) initial state, (b) shape distortion (shown by arrow), and (c) implosion and multiplication of bubbles (shown by arrows). (I. Tzanakis, F. Wang, D. Eskin, 2016)

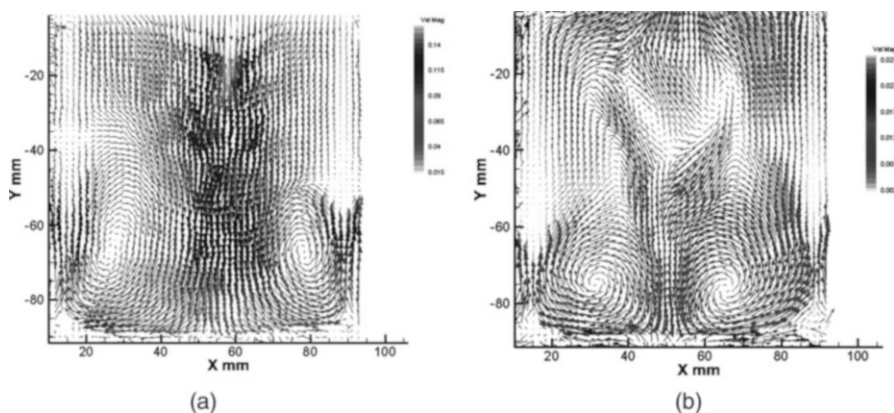


**Fig. 5.8** Typical velocity fields below the sonotrode tip in water at 100% (a) and 50% (b) transducer power settings. Velocity magnitude scale in m/s (0.01–0.15 in (a), and 0.01–0.03 in (b)). The upper central part of each image is the cavitation zone. (I. Tzanakis, 2015)

Details of numerical solutions can be found in a review by Plesset and Prosperetti [62] and works of Fyrrillas and Szeri [67, 68], Crum [69], and Lebon [70].

The observation of bubbles 25  $\mu\text{m}$  in size in liquid aluminum performed in a synchrotron showed that the cavitation bubbles exhibited a nonlinear stable behavior surviving for prolonged period of time in the melt, enhancing the broadband cavitation signal intensity and thus the cavitation treatment potential [56].

The size and geometry of the cavitation zone is not a very well-studied subject. The empirical observations show that the cavitation originates on the interfaces (radiating face of the sonotrode, walls, and solid and gaseous inclusions) as well as inside the melt volume, forming a concentrated region close to the ultrasound source with complicated, changing in time configurations at a distance (Fig. 5.8). These configurations gradually transform to streams, jets, and flows.

The rule of thumb says that the average dimensions of the cavitation zone are on the same scale as the diameter of the sonotrode. A rough estimate of the

**Fig. 5.9** A typical cavitation pattern in water

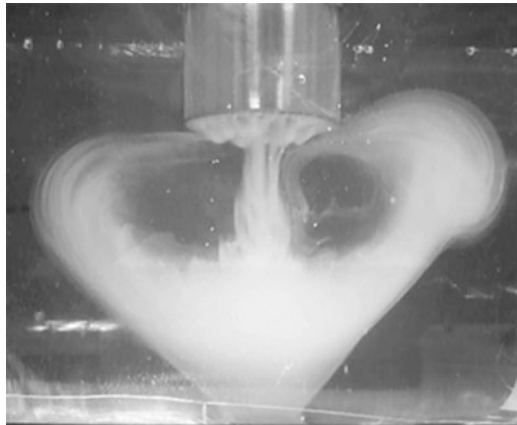


dimensions of the cavitation zone can be obtained by direct observations, erosion of a thin foil placed under the sonotrode, or by measuring the loss of mass of special samples immersed into the liquid. When cavitation is established, the cavitation region has a volume with the cross-section ranging approximately from  $\lambda/4$  to  $\lambda/2$ . For example, this size is 20–40 mm for water and 50–100 mm for aluminum melts.

Figure 5.9 illustrates a typical cavitation region generated by a cylindrical horn (the type that is frequently used in metallurgical applications). There is a very densely cavitating zone close to the sonotrode (also with a specific pattern at the sonotrode face resulting from lateral distribution of wave nodes), which then develops into a cone-like structure with loose boundaries.

Sonication also generates directed hydrodynamic flows in melts (on the velocity scale of several cm/s). These flows are represented by: (1) acoustic streams that originate from the pressure wave caused by high-frequency vibration of the sonotrode and pulsation of the cavitation region and (2) secondary, forced convective flows. They occur both in the bulk of the liquid and near the walls, particles, and other objects within the volume subjected to the ultrasonic field. The general flow pattern induced in a limited volume by an ultrasonic horn is shown in Fig. 5.10 (visualized by cavitation in viscous glycerin) [56]. A fully vortex-like structure is developed with a clear recirculating pattern as the streamlines are going back into the main streamer (see also Fig. 5.8). The origin of streams relates to the momentum acquired by the liquid when it absorbs the wave. Therefore, the velocity of acoustic streams increases with the ultrasonic intensity and the sound absorption.

**Fig. 5.10** Development of acoustic streams in glycerin. (I. Tzanakis, 2015)



### 5.3 Mechanisms of Ultrasonic Melt Processing

#### 5.3.1 Degassing

Boyle was probably the first to point at the potential of ultrasound to degas liquids [71]. Krüger [72, 73] used low-power piezoceramic vibrators for degassing liquid metals, and successfully used ultrasound for degassing molten glass. As early as in 1950, Eisenreich [74] compared vacuum ultrasonic degassing with vacuum degassing and chlorine lancing. Eskin et al. [75] demonstrated that the removal of hydrogen from liquid aluminum alloys depends greatly on the acoustic power transferred to the melt and on the development of cavitation, and showed that ultrasonic degassing is more efficient than degassing with chlorine salts and by vacuum.

According to modern views, liquid metals and alloys are colloid systems, in which dispersed nonmetallic inclusions, e.g., oxides in liquid Al or Mg, serve as hydrogen concentrators as well as the cavitation nuclei. Experimental results [76] show that pure alumina and even more so alumina contaminated with transition metals adsorbs hydrogen in considerable quantities, which makes these particles efficient cavitation nuclei and decreases the cavitation threshold.

The formation of individual hydrogen bubbles near nonmetallic inclusions determines the start of cavitation and degassing, i.e., in liquid metals the cavitation threshold coincides with the degassing threshold.

The efficiency of degassing, irrespective of physical and technical means, is a function of the concentration of dissolved gas in the liquid. This concentration is not a constant but depends on several factors, most important of which are temperature, vapor pressure, and limit solubility.

Liquid aluminum and its alloys react with atmospheric moisture to form alumina and hydrogen. The latter actively dissolves in the melt while the former deposits at the melt surface.



It is important to understand that the solubility of hydrogen in liquid aluminum is not a constant or a fixed number. The solubility depends on the conditions at the interface between the hydrogen-containing medium (atmosphere or bubble) and the liquid metal (surface or bulk). The quasi-equilibrium solubility exists for each combination of the hydrogen concentration in the atmosphere (humidity), in the melt (dissolved hydrogen), and the pressure (air pressure and partial pressure of hydrogen). The higher the humidity and melt temperature, the larger the quasi-equilibrium solubility of the hydrogen [77, 78].

Thermodynamic analysis [79, 80] shows that the partial pressure of hydrogen is extremely high even at low pressures of water vapor. At 727 °C and a water vapor pressure of 1.33 kPa (typical atmospheric value), the equilibrium partial pressure of hydrogen at the liquid–gas interface reaches a huge value of  $8.87 \times 10^6$  GPa, so the hydrogen content of the melt might be as high as  $3.24 \times 10^5$  cm<sup>3</sup>/100 g. This means that all available hydrogen can be dissolved in liquid aluminum, and that relatively small atmospheric humidity may lead to high hydrogen concentration in the melt.

When, however, the hydrogen concentration reaches the quasi-equilibrium between liquid aluminum and molecular hydrogen, the dissolution stops and atomic hydrogen will have a driving force to recombine into molecules and leave the melt. As a result of these two processes, there will be a dynamic equilibrium between atomic hydrogen intake (regassing) and molecular hydrogen expel from the melt (degassing). This equilibrium can be shifted if the pressure, temperature, humidity, or interface conditions change. The general possibilities for the variation of hydrogen content in liquid aluminum after ultrasonic degassing are illustrated in Fig. 5.11

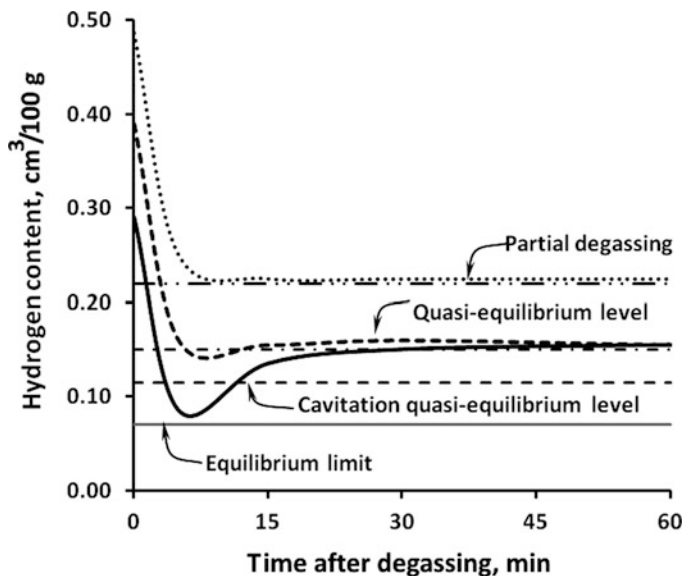


Fig. 5.11 Different scenarios of degassing kinetics. (After [82])

[81]. It is important to note that degassing process is usually faster than the regassing [27].

Aluminum alloys would typically have different levels of hydrogen depending on the alloy composition: commercially pure Al will have between 0.2 and 0.3 cm<sup>3</sup>/100 g; Al–Si and Al–Cu alloys from 0.4 to 0.5 cm<sup>3</sup>/100 g; and Al–Mg alloys between 0.4 and 0.6 cm<sup>3</sup>/100 g. For a given charge of liquid aluminum, hydrogen content can be naturally reduced to 0.1–0.2 cm<sup>3</sup>/100 g (degassing) giving time (up to 1 h) and typical conditions (750 °C, 30% humidity) [80, 82]. Natural degassing takes long time and is impractical for industrial applications, so different methods have been proposed for accelerating this process. Two types of degassing methods are currently used for aluminum alloys: gas purging (rotary and lance systems) and vacuum degassing. Ultrasonic degassing has also been suggested quite some time ago as an environment friendly, robust, and efficient means of melt degassing [23, 49].

Let us now consider the mechanisms of ultrasonic degassing of molten metal in detail.

The oscillation of a bubble in the acoustic field results in rectified diffusion of the dissolved gas into a bubble. As a result, the gas transfer from the liquid phase into the bubble becomes possible even when the difference between the average gas concentration in the liquid  $C_0$  and the gas concentration at the bubble/liquid interface  $C_g$  is not large. The gas concentration at the bubble interface can be written as [27]:

$$C_g = C_p (1 + 2\sigma/(R_0 P_0)), \quad (5.15)$$

where  $R_0$  is the equilibrium bubble radius,  $P_0$  is the hydrostatic pressure, and  $C_p$  is the equilibrium gas concentration in the liquid phase.

When the bubble compresses, the gas concentration inside increases and the gas diffuses to the liquid. Upon bubble expansion, the opposite process takes place. As the bubble surface (hence, interface available for diffusion) becomes larger upon expansion than that upon compression, the diffusion rate is higher in the rarefaction stage than in the compression stage of the oscillation. Also during compression, the boundary layer (where the hydrogen concentration gradient is maximum) increases in thickness while it thins during expansion. This difference in the boundary layer thickness also promotes more gas to enter the bubble during expansion than leave during compression. In other words, the oscillating bubble acts as a pump extracting gas from the liquid phase. In addition to the rectified diffusion, microscopic acoustic streams generated in the viscous boundary layer around the bubble take their part in the mass transfer, bringing fresh liquid phase to the surface of the pulsating bubble.

The actual gas solubility in the liquid phase under conditions of cavitation will be lower than the quasi-equilibrium solubility (see Fig. 5.11). There exists a limit until which the gas can be extracted from the liquid phase by cavitating bubbles. This limit was estimated to be about 50% lower than the quasi-equilibrium gas solubility under given environmental conditions. This was first established for degassing water from oxygen [27] and then confirmed for degassing aluminum from hydrogen [44, 49]. The actual value can be even smaller due to the hysteresis of gas diffusion [44]. Under conditions of cavitation, the instantaneous solubility can be described as [44]:

$$C = \frac{C_0}{2} + \frac{1}{\pi} \left[ \frac{C_0}{\sin\left(\frac{C_0}{C_A}\right)} - C_A + \sqrt{C_A^2 - C_0^2} \right], \quad (5.16)$$

where  $C_0$  and  $C_A$  are the gas solubilities at the atmospheric and acoustic pressure, respectively.

The ultrasonic degassing of liquid metal is a process of three simultaneous stages [23, 27, 74, 83]: (1) gas bubbles form on cavitation nuclei and grow in the ultrasonic field accumulating hydrogen through rectified diffusion (if the liquid contains small bubbles, this stage consists only of their diffusion growth); (2) separate bubbles coalesce under the action of the Bjerknes and Bernoulli forces; and (3) bubbles float to the surface of the molten metal.

### 5.3.2 *Wetting and Sonocapillary Effect*

The characterization of wetting and surface tension under dynamic conditions such as under the action of ultrasonic waves and cavitation is not well developed and indirect methods are most commonly used instead. There have been however attempts to quantify the effect of ultrasonic vibrations on the wetting and surface tension using various experimental techniques adapted to dynamic conditions.

It was shown that the wetting angle of Al–Ti and Al melts on graphite decreases significantly when the ultrasonic vibrations are applied, from 150–160° before processing to 45–50° after 10 min of holding after the ultrasonication [84]. The reason behind the improved wetting is the destruction of alumina film surrounding the droplet in the case of wetting of graphite with liquid aluminum and enhanced reactive wetting by forming TiC in the case of wetting graphite with Al–Ti alloys. The improved wettability of graphite and alumina by liquid aluminum has been demonstrated in other experiments as well [85, 86]. The experiments with various low-melting alloys and metallic or ceramic substrates showed that the application of ultrasonic vibrations to the substrate results in almost immediate wetting. This effect is enhanced by increasing temperature and ultrasound amplitude. Summary of experimental results can be found elsewhere [87].

A sonocapillary effect, i.e., the penetration of liquid into thin channels assisted by cavitation, was extensively studied and the results were summarized in a monograph [88]. The crucial role of cavitation in the sonocapillary effect was proved both theoretically and experimentally [89, 90]. The liquid rise in a capillary increases by an order of magnitude under developed cavitation conditions. A sonocapillary theory [88] includes asymmetry in the boundary conditions for a collapsing cavity, when it loses its spherical shape and implodes emitting a cumulative jet of liquid. This cumulative jet is assumed to be responsible for the elevation of liquid level in the capillary. Repeated with a frequency determined by the probability of bubble occurrence and collapse near the capillary entry, the cavity collapse and jets produce

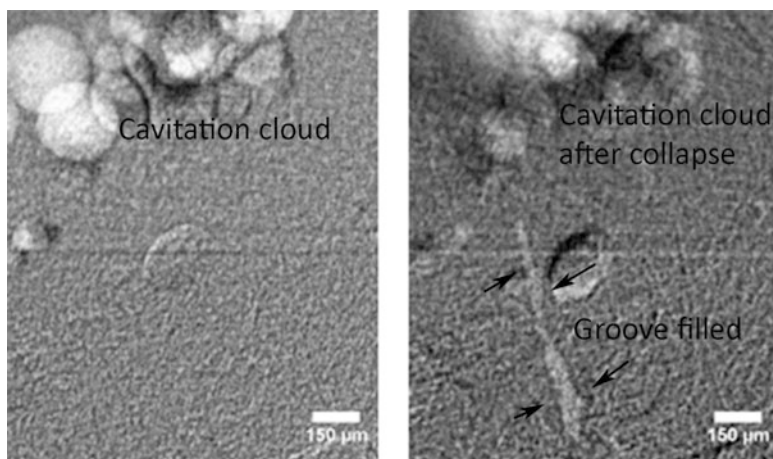


**Fig. 5.12** Radiographs of the preexisting groove which (a) is not visible as it is filled by liquid melt until the moment when, after the cavitation bubbles collapse, it is refilled and revealed (b). After [91]

accumulated liquid rise  $\Delta H$ , resulting in the sonocapillary effect. In the interval between two successive jets reaching inside the capillary, the liquid can escape from the capillary and the liquid column can decrease. The sonocapillary effect in liquid aluminum was recently confirmed by a small-scale experimental study, where the refilling of a preexisting oxide film tube-like groove, with the action of ultrasound upon an Al–10% Cu melt was monitored using in situ synchrotron X-ray radiography [91]. Analytical solutions of the hydrodynamic impact pressure exerted from the cavitation implosion jet and the hydrodynamic pressures required to fill the studied groove in Fig. 5.12 have shown that the mechanism responsible for the refilling of the groove with the melt is the collapse of cavitation bubbles near by the groove inlet. Specifically, the pressure delivered by the high-speed micro-jet at the inlet of the groove after the collapse of bubbles at a distance of 300  $\mu\text{m}$  from that inlet is in the range of 0.3–46 MPa which, on the upper side, is enough to fill the groove.

Additionally, during the refilling process a secondary effect was observed, related with the mass transfer of oxide particles inside the groove. The particle delivery was due to the action from the high-speed liquid micro-jet. The concentration percentage of oxide particles that are captured in the groove during melt entrainment was quantified and found to increase with time and hence with the amount of bubble collapse events. The observed phenomenon is related to the ultrasound-assisted filtration of the melt from oxide inclusions.

Although the fundamental studies of this phenomenon are ongoing, the importance of its role in many processes and mechanisms is beyond any doubt. For a number of metallurgical procedures, such as melt degassing, filtering, wetting of solid inclusions, forming of cavitation and solidification nuclei, manufacturing of composite materials, insert casing, precision casting; the sonocapillary phenomena are essential.

### 5.3.3 Grain Refinement

The cavitation-induced nucleation can go along the two main mechanisms: (1) undercooling of the cavitation bubble surface during the expansion phase of oscillations and (2) undercooling of the liquid phase resulted from the instantaneous increase of pressure during cavitation bubble collapse (according to the Clapeyron equation). The latter mechanism seems most probable as the decrease of bubble surface temperature does not exceed 1 K while the change of the melting point as a result of bubble collapse can reach tens of degrees and approach  $0.2T_m$  [38]. For example, for 99.99% pure aluminum the increase in melting temperature changes with the pressure as shown below:

|            |       |       |       |       |       |
|------------|-------|-------|-------|-------|-------|
| $P$ (MPa)  | 0.1   | 500   | 1000  | 2000  | 4000  |
| $t_0$ (°C) | 660.5 | 690.0 | 720.0 | 780.0 | 830.0 |

These mechanisms of cavitation-induced nucleation are seldom realized as they consider homogeneous nucleation, which is not a common phenomenon in real metals.

Multiplication of solidification nuclei by activation of heterogeneous substrates was suggested in the 1930–1950s by Danilov et al. [92, 93] and Kazachkovsky [94]. In this case, the dynamic action upon solid/liquid interface improves wetting, decreases surface tension, and promotes heterogeneous nucleation on the available insoluble substrates such as oxides, carbides, etc., being assisted by penetration of the liquid phase into discontinuities of the substrate surface and the formation of the adsorbed boundary layer at the substrate surface.

Early direct observations of transparent analogues seem to confirm that nucleation is indeed facilitated by ultrasonic cavitation [23]. More recently, advances in high-speed imaging allowed for more specific observations of the interaction between cavitation and solidifying material. Swallowe et al. [95] demonstrated both nucleation of the solid phase in the ultrasonic field and fragmentation of growing dendrites by oscillating cavitation bubbles in camphene. Interesting evidence of dynamic nucleation of 15 wt% water solution of sucrose was reported by Chow et al. [96]. The nuclei were formed at a distance from the sonotrode almost immediately after an ultrasonic pulse, and then grew to equiaxed crystals.

Nucleation of primary intermetallics on alumina inclusions was demonstrated in aluminum alloys both *ex situ* (Fig. 5.13a) and *in situ* (Fig. 5.13b) [97, 98].

The fragmentation of the solid phase under dynamic action is accepted by many as the main mechanism of structure refinement [19, 20, 28, 95, 99]. Chvorinov [99] suggested that the dendrites growing in the two-phase transition region are separated from the solidification front by forced convection and the resultant crystals move to the bulk of the melt and act as nuclei for new grains, providing that they are not completely remelted. Balandin [19] enriched this idea with the thesis that the insoluble inclusions deactivated by alloy melting with high superheat reactivate once the solid phase is formed around them. After separation from the two-phase

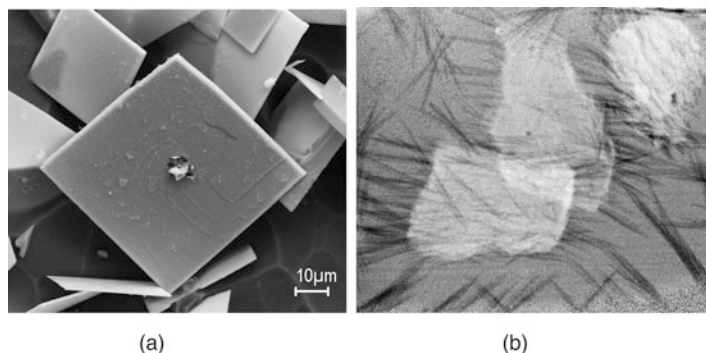


**Fig. 5.13** Nucleation of primary intermetallics on oxide particles after ultrasonic processing: (a) ex situ observation of extracted  $\text{Al}_3\text{Zr}$  crystals nucleated on alumina (small particle in the center) and (b) in situ observation in synchrotron of the formation of  $\text{Al}_2\text{Cu}$  (dark needle-shaped particles) on alumina plates (courtesy F. Wang)

zone by forced convection, a solid crystal containing this activated inclusion is transported to the liquid phase and the solid phase is melted away leaving behind the active insoluble substrate. These concepts have not, however, explained the mechanisms of dendrite (crystal) separation from two-phase zone or its fragmentation.

One of the earliest suggested mechanisms was the seemingly obvious fragmentation of dendrites by mechanical fracture caused by melt flow. This mechanical fracture assisted by bending deformation, formation of large-angle boundaries, and liquid metal embrittlement is still considered as one of the possibilities [20, 100].

On the mesoscopic scale, forced melt flow can bring hot melt from the liquid pool into the undercooled two-phase zone and cause its partial remelting with subsequent washing-out of loose solid crystals. On the microscopic scale and in the absence of cavitation, the most realistic mechanism of fragmentation is dendrite arm separation by root remelting effects because of thermal, solute, or capillary effects. Solute accumulation at the solidification front causes the fluctuations in growth velocity that has direct effect on the kinetics of dendrite branches growth and coarsening [101]. The coarsening of dendrite branches results in their necking [102, 103] and accumulation of solute at their roots both by rejection from the solid phase and by convection in the interdendritic space [104]. The local solute enrichment results in local superheating of the solid phase and its melting. Along with the local change of equilibrium, capillary effects cause dendrite roots to be more soluble than other regions. The forced flow assists further by transporting the fragments to the solidification front and farther to the bulk of the liquid. The fragmentation assisted by acoustic streaming is especially applicable to elongated crystals that are subjected to alternating flow, facilitating the root remelting and fatigue-type fracture [105].

In the presence of cavitation accompanied by the implosion of bubbles, the destruction of dendrites has been demonstrated on transparent analogues [95, 106] and recently on intermetallic crystals subjected to cavitation in water [107].

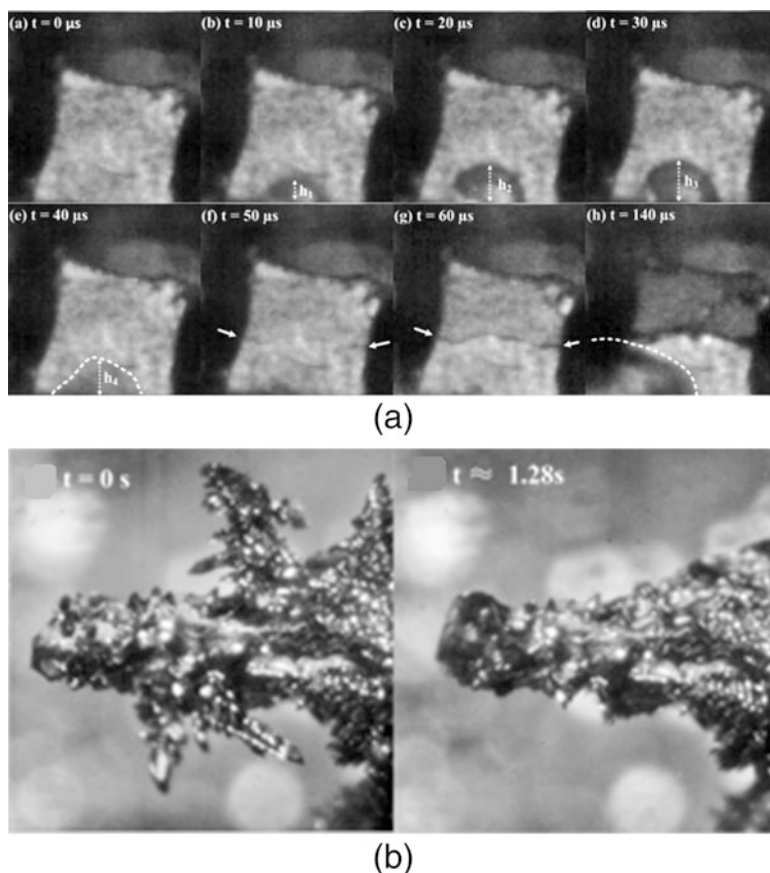


**Fig. 5.14** Fragmentation of intermetallic crystals by cavitation: (a) a sequence of images showing the fatigue crack propagation and fracture of a primary  $\text{Al}_3\text{Ti}$  crystal interacting with a pulsating cavitation bubble (a changing bubble radius is shown by  $h$ ) and (b) fragmentation of a primary  $\text{Al}_3\text{V}$  dendrite after ultrasonic processing with the input power 200 W in distilled water for around 1.28 s [107]

Figure 5.14 gives a sequence of frames capturing the fragmentation of primary intermetallics by oscillating and imploding bubbles as well as a result of cavitation processing. Before fracture, oscillations of the future fragments with obvious crack propagation were observed. A fatigue-like brittle fracture mechanism was most likely responsible for the fragmentation.

The ultrasound-induced streaming flow can be effective in transporting cavitation bubbles toward the dendrites to promote continuous fragmentation of the growing dendrites, and in transporting the fragments to the bulk of the melt.

Solidification of real melt always occurs heterogeneously and on available substrates that are either naturally present (indigenous impurities) or deliberately added (exogenous, grain refiners) to the melt. In aluminum and magnesium alloys, the



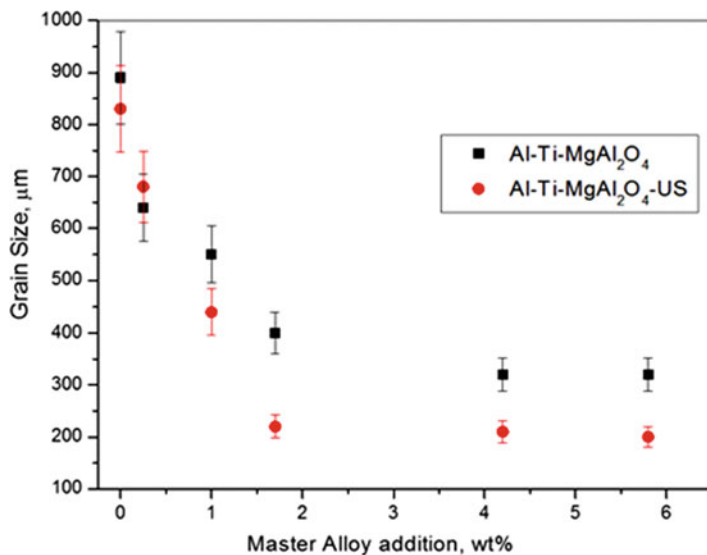


**Fig. 5.15** Relation between grain size of an A357 alloy and the level of Al-Ti-MgAl<sub>2</sub>O<sub>4</sub> master alloy addition with and without ultrasonic processing (adapted from [110])

former are represented by oxides and carbides and the latter by borides, carbides, and primary phases. The term “activation” is usually applied to indigenous particles and includes the phenomena of wetting, formation of stable or metastable surface layers, deagglomeration, and nonequilibrium solidification.

Let us look closer at the particles that can be activated and involved in solidification in light alloys.

The activation of inclusions by ultrasonic cavitation has been observed for pure aluminum with mixed in oxide surface film [108] and for Mg–Al alloys with added carbon black nanoparticles [109]. Recently, an ultrasonic activation of spinel particles (potent substrates for aluminum) from an Al–1.3% Ti–1.8% MgAl<sub>2</sub>O<sub>4</sub> master alloy added to an aluminum casting alloy has been demonstrated as shown in Fig. 5.15 [110].

Cavitation treatment may turn particles into active solidification sites by the following mechanism [49].

Any microscopic solid particle that has affinity to the solidifying phase has a potential to become an active solidification site. This affinity can be due to the match of crystal structures, or due to the presence of a special adsorbed layer or even the matrix solid phase on its surface. In the latter case, the stability of such a solidification site can be assured only when the adsorbed layer or the solid phase is thermally stable within some temperature range above the liquidus of the alloy. Such conditions can be met in discontinuities like microcracks where, due to the capillary effect, the melting temperature of the alloy is much higher than the equilibrium liquidus.

The increase in the melting point under conditions of negative curvature (concave particle) is described by the Gibbs–Thompson equation [111]:

$$T_m^r = T_m^\infty - \frac{2\Gamma}{r}, \quad (5.17)$$

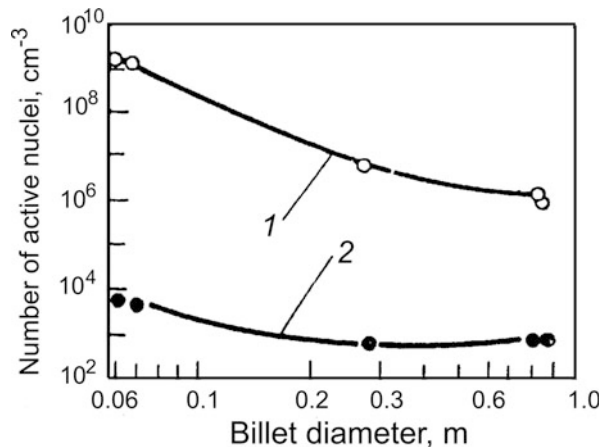
where  $T_m^r$  is the melting point of a concave particle inside a crevice,  $T_m^\infty$  is the melting point of a particle with flat interface,  $r$  is the curvature (negative in the case of the concave particle), and  $\Gamma$  is the Gibbs–Thompson coefficient depending on the surface tension, density, and latent heat.

However, the presence of a gaseous phase at the surface and in the surface imperfections of nonmetallic particles hinders the access of the liquid phase to the inclusion, wetting, and filling of the imperfections with the melt. Therefore, the majority of the inclusions remain inert with regard to the solidification.

During USP with intensity higher than the cavitation threshold, a cavitation bubble is formed close to the capillary opening filled with gas. In this place, the cavitation strength of the melt is weakened by the presence of a gaseous phase. Then, the sonocapillary effect takes over, filling the capillaries of almost submicroscopic sizes (see Sect. 5.3.2). At the same time, the particle is stripped of absorbed gas and becomes accessible by the surrounding melt. As a result of this activation, the solidified alloy inside capillary openings (cracks) of the particle stays solid at a temperature of the surrounding melt and acts as a perfect solidification site for the matrix melt. The same mechanism should be valid for any primary solidifying phase: solid solution, intermetallic, or silicon. Actually, the activation of nonmetallic impurities facilitates nucleation and refinement of any primary phase as shown in Fig. 5.13.

A comparison between ingots from a high-strength aluminum alloy produced with and without ultrasonic cavitation treatment during DC casting shows that the number of active nuclei increases by several orders of magnitude after the cavitation treatment (Fig. 5.16). For example, the cavitation treatment in the case of small-sized

**Fig. 5.16** A change in a number of active nuclei upon solidification of a direct-chill cast billets from a 7XXX-series (Al–Zn–Mg–Cu–Zr) alloy with ultrasonic melt processing (1, with ultrasonic processing and 2, without ultrasonic processing) (adapted from [86])



ingots (65–74 mm) enables the activation of nucleation substrates with the density up to  $10^9/\text{cm}^3$  as compared to  $10^3/\text{cm}^3$  without sonication. In the case of middle-sized ingots (270–285 mm), this difference reduces to four orders of magnitude; for large-sized ingots (830–845 mm), this difference reaches three orders of magnitude.

Deagglomeration and dispersion of nucleating particles is another mechanism of grain refinement. The high-intensity ultrasonic oscillations create vast number of microscopic bubbles that are distributed within the volume by acoustic and secondary flows. The bubbles preferentially form at the interfaces and gas pockets. Therefore, the agglomerates of the particles and particles themselves are ideal nuclei for cavitation. The mechanisms of deagglomeration can be represented as follows: the cavitation bubbles are formed at the interfaces particle/gas pocket/liquid. These bubbles pulsate intensely, implode, loosening the agglomerate and chipping off particles. The local pressure generated (up to 500 MPa) far exceeds the forces that hold together the particles in agglomerates, i.e., up to 1 MPa (capillary and adhesive forces) [112, 113]. The acoustic flows generated by the cavitation zone distribute the particles further in the volume.

Some practically important analytical calculations show (though semiquantitatively due to the assumptions) the dependence of processing time on the surplus in pressure at the capillary entry (difference between the capillary pressure and the pressure from cavitation) and relative sizes of capillary channels (depth/radius) as illustrated in Fig. 5.17a; as well as the requirement for the minimum acoustic pressure at the entry to the capillary in dependence on the agglomerate size and processing frequency in Fig. 5.17b [114]. It is important to make two notes: (1) the deagglomeration is not an instantaneous process but takes time and (2) the ultrasonic frequency is preferable over sonic frequencies.

Grain refinement can be achieved by additions of elements that form primary intermetallics with good crystallographic match with the matrix solid solution, i.e.,

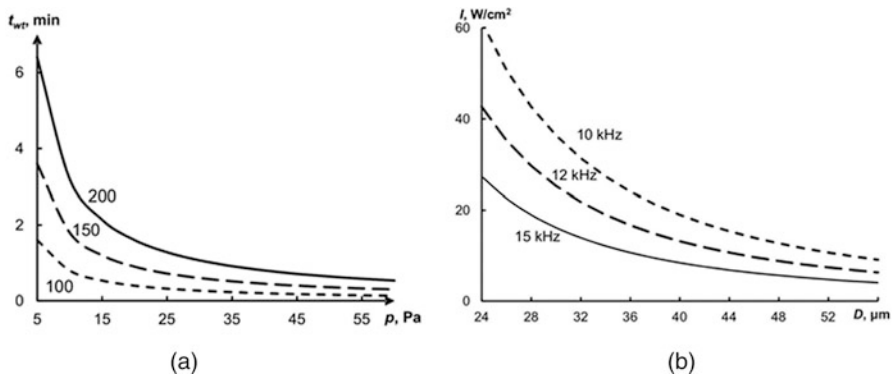


**Fig. 5.17** (a) The dependence of the processing time required for liquid penetration into an agglomerate on the surplus pressure at the entry to a capillary channel (numbers show the relative size of the channel, i.e., depth/radius) and (b) dependence of the threshold (ultra)sound intensity for breakup of agglomerates in liquid aluminum on the particle diameter for various values of the sound frequency (after [114])

aluminum or magnesium. In aluminum alloys, titanium aluminide and scandium aluminide are well known to possess structural features required for powerful grain refinement effect; in magnesium alloys, zirconium forms a primary phase that is used in Al-free alloys for grain refinement.

It has been known since the 1960s that the addition of Zr in combination with USP results in considerable grain refinement of aluminum alloys [23]. Later on, the essential role of small Ti additions has been demonstrated [49] and the combined effect of Zr, Ti, and ultrasonic processing has been explained [108, 115]. The fragmentation of primary intermetallic particles by cavitation is one of the mechanisms for grain refinement of the main primary phase, e.g., Al. Fracture by oscillating and collapsing bubbles can happen to the primary intermetallics in the range of their formation, in addition to the enhanced nucleation on insoluble inclusions [116, 117]. In this case, the alloy would be considered liquid from technological point of view as the formation of these particles and the ultrasonic processing occur well above the liquidus temperature of the matrix solid solution.

The fragmentation of dendrites can also result in spectacular structure refinement, when ultrasonic processing happens in the solidification range of the matrix [118]. Despite very good grain-refining effect of fragmentation, the practical application of this mechanism is limited to small volumes. There might a potential to use this mechanism in direct-chill casting or other continuous processes (e.g., arc remelting) where the position of the solidification front is fixed in space and the cavitation can be applied throughout the process in the locations below the liquidus isotherm. The limitation in this case would be lateral spread of the effect, i.e., multiple cavitation sources would be required for processing of larger cross-sections.

### 5.3.4 Emulsification (*Immiscible Alloys*)

The emulsification of immiscible liquids under the action of ultrasound is known since the 1920s and was demonstrated for water and oil, and water and mercury [8, 119]. The decisive role of cavitation in the process of emulsification was soon recognized [120]. Already in the 1930s, first successful experiments on high-frequency (10 kHz) introduction of Pb in liquid Al and Cd in Al–Si melt were reported [32] and the possibility to produce emulsions of 7–10% Pb in Al and Zn stable even upon remelting was demonstrated [45].

The physics of ultrasonic emulsification is considered elsewhere [121–125]. Some basic factors controlling the process can be summarized as follows. The size of droplets in the emulsion decreases with the increasing ultrasonic frequency. At the same time, the higher density requires a greater sound intensity applied. With the increasing intensity and processing time, the emulsion concentration increases up to a certain value when saturation occurs. This saturation is a result of the equilibrium reached between the processes of emulsification (dispersion) and coagulation. A running sound wave is more efficient than a standing wave, with coagulation processes prevailing in the latter case. Pre-cavitation sound processing

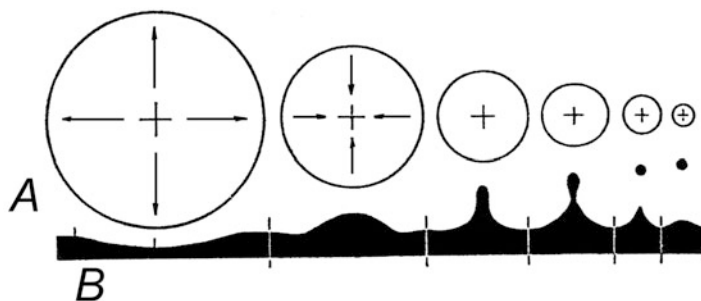


**Fig. 5.18** A diagram illustrating the mechanisms of ultrasonic emulsification

results in de-emulsification. Therefore, cavitation is the important requirement of the process. A low viscosity and a lesser difference in viscosities between the components facilitate emulsification. Additions of surfactants (decreasing the surface tension at the interface) and stabilizers (coating of droplet surface) promote the stability of the emulsion and allow for higher concentrations. In general, the emulsification occurs through local disturbances at the interface between two immiscible liquids with typically only one liquid undergoing dispersion, while the other liquid acts as the source of cavitation bubbles. The disturbance occurs during the expansion phase of the bubble oscillation, while the dispersion happens upon bubble collapse. Figure 5.18 illustrates the formation of a wave disturbance in liquid B caused by an expanding bubble in liquid A. When this bubble starts to contract, it draws the crest of the wave of liquid B upwards, and this crest extends with acceleration following the accelerated contraction of the bubble. When bubble collapses, the crest disintegrates forming a droplet.

With respect to liquid metals and alloys, ultrasonic emulsification has practical value for manufacturing free-machining and bearing alloys. These alloys contain additions of low-melting, soft elements such as Pb, Bi, and Sn that have either a miscibility gap with Al that causes stratification (Al–Pb, and Al–Bi) or a very large solidification range that triggers gravity segregation (Al–Sn).

It was demonstrated that application of ultrasonic cavitation significantly decreases macrosegregation and promotes the uniformity of structure in an immiscible Al–Sn–Cu alloy. With a single ultrasonic source, the uniform distribution of monotectic Al–Sn–Al<sub>2</sub>Cu cells was obtained close to the cavitation region, while nonuniformity triggered by gravity separation of Sn from Al remained in the areas farther from the ultrasonic source where only acoustic streaming was acting [126]. It was also observed that the monotectic cells nucleate on cavitation-affected substrates. An innovative scheme of ultrasonic processing with three orthogonal sources was developed and applied to the solidification of a similar immiscible alloy [127]. In this case, the homogeneous monotectic structure was obtained in the entire  $30 \times 30 \times 100$  mm volume, due to the uniform cavitation field created in the melt.

5.4 Practical Implementations of Ultrasonic Melt Processing

5.4.1 Degassing

The ultrasonic degassing of aluminum was implemented in foundries for precision investment, sand, gravity, low-pressure, and high-pressure die casting [23]. Let us look at the example of sand casting. A special ultrasonic degassing system UZD-200 has been developed in 1959 for degassing up to 250 kg of melt in stationary volume (Fig. 5.1). The installation (in stationary and mobile versions) consisted of a 10-kW generator that fed 4 magnetostrictive transducers that worked in a sequence with a time gap of 15–20 s. The frequency was 19.5 kHz and the total acoustic power—1.6 kW. Table 5.1 summarizes the results for castings of an A361.1 alloy. It can be easily seen that ultrasonic degassing significantly increases the density of cast metal and makes it possible to obtain almost pore-free castings (rank 1 in the porosity scale).

In recent years, a design that includes a moving sonotrode has been tested for degassing of up to 500 kg of aluminum melt [128]. This principle is based on the idea that the degassing involves (as we have discussed in Sect. 5.3.1) three stages: generation, growth, and flotation of the bubbles. When the sonotrode is moving through the volume, it generates bubbles in the volume part, and then moves to the next part to cause cavitation there, while the bubbles in its wake grow in the sound field (that covers much larger volume than the cavitation zone) and float to the surface. One moving sonotrode, therefore, effectively substitutes for several stationary ones. The degassing performance was shown to be very similar to the commercial Ar-rotary degassing with 4–5 times less dross formed at the melt surface. Figure 5.19 shows the degassing prototype based on a robotic arm, magnetostrictive transducer, and Nb sonotrode.

The requirement for processing of large, industrial-scale volumes of melt, especially in large foundries and continuous casting plants, shows a limit for batch degassing operations. Another approach needs to be used and the processing of the melt flow seems like a logical and viable possibility. In large melting/casting operations, it is more appropriate to relocate the cleaning of melts from gaseous and

**Table 5.1** Comparison of various degassing methods for an A361.1 alloy [87]

| Degassing method     | H <sub>2</sub> content (cm <sup>3</sup> /100 g) | Density (g/cm <sup>3</sup> ) | Porosity rank | Tensile properties |        |
|----------------------|-------------------------------------------------|------------------------------|---------------|--------------------|--------|
|                      |                                                 |                              |               | UTS (MPa)          | El (%) |
| Starting melt        | 0.35                                            | 2.660                        | 4             | 200                | 3.8    |
| Ultrasonic degassing | 0.17                                            | 2.706                        | 1–2           | 245                | 5.1    |
| Vacuum treatment     | 0.2                                             | 2.681                        | 1–2           | 228                | 4.2    |
| Argon blasting       | 0.26                                            | 2.667                        | 2–3           | 233                | 4.0    |
| Hexachloroethane     | 0.3                                             | 2.665                        | 2–3           | 212                | 4.5    |

**Fig. 5.19** Ultrasonic degassing machine with a moving ultrasonic source in the process of degassing 500 kg of a liquid aluminum alloy (courtesy J. Tort Guzman, Doshormat, FP7 project No.606090)



**Table 5.2** Concentration of hydrogen before and after ultrasonic degassing upon DC casting of aluminum alloys [86]

| Alloy type | Ingot/bullet size (mm) | Casting speed (mm/min) | Hydrogen concentration (cm <sup>3</sup> /100 g) |                      |
|------------|------------------------|------------------------|-------------------------------------------------|----------------------|
|            |                        |                        | No degassing                                    | Ultrasonic degassing |
| AA1030     | 1040 × 300             | 123                    | 0.28                                            | 0.18                 |
| AA2024     | 1480 × 210             | 123                    | 0.41                                            | 0.24                 |
| AA2117     | 460 dia                | 35                     | 0.4                                             | 0.21                 |
| AA1070     | 350 dia                | 44                     | 0.2                                             | 0.10                 |
| AA5017     | 350 dia                | 65                     | 0.42                                            | 0.3                  |

oxide inclusions from the melting or holding furnace to the zone of metal transfer, somewhere en route from the furnace to the mold.

First industrial trials on ultrasonic degassing in melt flow were performed in the USSR in the early 1960s during DC casting of aluminum alloys using a setup similar to that described above for the batch ultrasonic degassing (UZD-200) (Fig. 5.1). The difference was in the arrangement of sonotrodes, they were put in line [129]. With taking into account that DC casting involves high flow rates and relatively low melt temperatures, a principle of multiple ultrasonic processing of melt flow was used. The launder contained a section of ultrasonic processing and a section of gas release. The melt flow rate was about 70 kg/min and the ultrasonic intensity about 5 W/cm<sup>2</sup>. The results demonstrated that the ultrasonic degassing in the melt flow allowed for 1.5–2 times decreased hydrogen concentration in the melt, as demonstrated in Table 5.2. One can notice that the efficiency of degassing commercially pure aluminum is less than for more concentrated alloys. This might be a consequence of its higher purity in solid inclusions with corresponding lesser cavitation



**Table 5.3** Hydrogen content ( $H_2$ ) and porosity ( $P$ ) in flat  $1700 \times 300$ -mm ingots of an AMg6 alloy for various acoustic powers used in ultrasonic degassing in the melt flow during DC casting [86]

| Acoustic power (kW) | $H_2$ in melt ( $\text{cm}^3/100 \text{ g}$ ) |              | Ingot properties                               |         |                                                |         |
|---------------------|-----------------------------------------------|--------------|------------------------------------------------|---------|------------------------------------------------|---------|
|                     | No degassing                                  | US degassing | No degassing                                   |         | Ultrasonic degassing                           |         |
|                     |                                               |              | $H_2$ in solid ( $\text{cm}^3/100 \text{ g}$ ) | $P$ (%) | $H_2$ in solid ( $\text{cm}^3/100 \text{ g}$ ) | $P$ (%) |
| 4                   | 0.60                                          | 0.45         | 0.41                                           | n/a     | 0.36                                           | n/a     |
| 5                   | 0.60                                          | 0.42         | 0.44                                           | 0.6     | 0.35                                           | 0.51    |
| 7                   | 0.58                                          | 0.39         | 0.41                                           | 0.66    | 0.33                                           | 0.55    |
| 11                  | 0.56                                          | 0.29         | 0.38                                           | 0.56    | 0.20                                           | 0.40    |

development. The amount of defects (porosity, and nonmetallic inclusions) decreased by a factor of 5–8, e.g., from  $0.82$  to  $0.1 \text{ mm/cm}^2$  in a  $460$ -mm billet of an AA2117-type. The mechanical properties were also improved.

This experience was later extended to DC casting of various aluminum alloys including Al–Mg (2–6% Mg), Al–Zn–Mg–Cu (AA7055-type), and Al–Cu–Mg (AA2038- and AA2214-type). The number of ultrasonic sources was varied depending on the ingot cross-section, melt flow rate, and the desired degree of degassing.

Industrial-scale degassing plant was designed and manufactured for casting large flat ingots ( $1700 \times 300 \text{ mm}$ ) from an AMg6 Russian Grade (6% Mg, and 0.6% Mn). The degassing was performed in a specially designed section of a launder at  $20 \text{ m}$  from a  $40$ -ton holding furnace. The melt flow rate was up to  $100 \text{ kg/min}$ . Each of four to twelve  $4.5\text{-kW}$  magnetostrictive transducers was delivering up to  $1 \text{ kW}$  of acoustic power into the melt. Two schemes of ultrasound input were tried, from the bottom of the launder and from the top of the melt [130]. The latter version proved to be more reliable and efficient.

The efficiency of ultrasonic degassing with regard to the acoustic power introduced to the melt, other acoustic parameters, and the dimensions of the ingot/billet is given in Tables 5.3 and 5.4. The efficiency of this process shows a distinct dependence on the metal flow rate and acoustic power (or the number of sources) conveyed to the melt [49].

Despite these successful industrial applications, the further development and spreading of this experience was hindered by the bulkiness of the equipment and lack of optimization of melt flow. Current efforts are concentrated on understanding the interaction between the melt flow, cavitation field, and acoustic streaming via physical and numerical modeling. Also, new schemes of ultrasonic processing in the melt flow are under scrutiny.

One of the possible schemes involves using a plate sonotrode placed at the bottom of a launder [131]. This allowed the similar degassing efficiency in the flow as could be achieved in the stationary volume with a conventional cylindrical sonotrode as illustrated in Table 5.5.

**Table 5.4** Efficiency of the ultrasonic in-flow degassing of an AMg6 alloy in relation to the billet diameter, and the number and intensity ( $A$  is the oscillation amplitude, and  $W$  is the input acoustic power density) of ultrasonic sources with a 40-mm diameter radiating face [86]

| Billet diam. (mm) | Number of sources | Ultrasonic parameters |                          | Hydrogen content <sup>a</sup> (cm <sup>3</sup> /100 g) |       | Degassing efficiency (%) |
|-------------------|-------------------|-----------------------|--------------------------|--------------------------------------------------------|-------|--------------------------|
|                   |                   | $A$ ( $\mu\text{m}$ ) | $I$ (W/cm <sup>2</sup> ) | Initial                                                | Final |                          |
| 127               | 1                 | 15                    | 30                       | 0.4                                                    | 0.25  | 37                       |
| 204               | 1                 | 5                     | 3                        | 0.67                                                   | 0.46  | 25                       |
| 204               | 1                 | 10                    | 15                       | 0.67                                                   | 0.39  | 40                       |
| 204               | 1                 | 20                    | 60                       | 0.67                                                   | 0.28  | 58                       |
| 370               | 1                 | 12                    | 40                       | 0.31                                                   | 0.26  | 13                       |
| 370               | 2                 | 20                    | 60                       | 0.48                                                   | 0.24  | 50                       |
| 370               | 3                 | 20                    | 50                       | 0.51                                                   | 0.19  | 60                       |

<sup>a</sup>Data obtained by vacuum extraction from the billet**Table 5.5** Results of ultrasonic degassing in batch and continuous operation using different schemes of ultrasonication [131]

| Degassing method              | Density index before degassing (%) | Density index after degassing (%) | H <sub>2</sub> (cm <sup>3</sup> /100 g) before degassing | H <sub>2</sub> (cm <sup>3</sup> /100 g) after degassing | Degassing efficiency (%) |
|-------------------------------|------------------------------------|-----------------------------------|----------------------------------------------------------|---------------------------------------------------------|--------------------------|
| Natural                       | 15.7                               | 16.3                              | 0.22                                                     | 0.23                                                    | −4.5                     |
| Cylindrical sonotrode (batch) | 20.3                               | 14.7                              | 0.36                                                     | 0.195                                                   | 46                       |
| Plate sonotrode (batch)       | 22.45                              | 9.24                              | 0.44                                                     | 0.11                                                    | 75                       |
| Plate sonotrode (flow)        | 22.9                               | 15.5                              | 0.46                                                     | 0.21                                                    | 54                       |

Other suggestions are to combine the ultrasonic degassing with Ar lancing in a vessel through which the melt is constantly flowing [132] or using a hollow sonotrode through which a carrier gas is supplied to the melt [133].

### 5.4.2 Grain Refinement During Casting

DC casting on the one hand simplifies the application of ultrasonic melt treatment as the melt containers (launder, mold, and melt distribution systems) are simple and constant in shape with well-defined temperature profiles. On the other hand, DC casting requires processing of larger melt volumes in a continuous manner, which creates some challenges for the technology of ultrasonic processing.

The first industrial DC casting installation with ultrasonic melt processing (USP) was built in the 1970s at one of Soviet metallurgical plants. A standard DC caster with a 10-t holding furnace was equipped with an ultrasonic processing station that could be controlled remotely. The ultrasonic processing was performed by dipping several sonotrodes (each fed by an individual water-cooled 4.5 kW transducer) into the sump of a billet or an ingot. The horns were made of a Nb alloy that assured the stable and continuous operation in the melt during the entire casting process. The choice of Nb alloys as the most suitable material for ultrasonic horns for liquid aluminum processing was proven in the 1960s [23].

The main casting parameters of DC casting with ultrasonic melt processing are given in Table 5.6 [86]. Depending on the size of the billets, one to ten transducers with sonotrodes placed into the sump of the billet were used in a single casting in order to achieve uniform nondendritic structure in the entire billet.

It was possible to refine grains substantially, especially in aluminum alloys containing Zr and Ti. In some cases, a uniform structure with nondendritic grains was obtained for billets from 74 to 1200 mm in diameter. Figure 5.20 gives some examples. Billets and ingots with such a structure exhibit higher mechanical

**Table 5.6** Main processing parameters for DC casting of round billets with ultrasonic melt processing in the sump [49]

| Billet diameter (mm) | Casting speed (mm/min) | Acoustic power (kW) <sup>a</sup> |
|----------------------|------------------------|----------------------------------|
| 70–100               | 180–240                | 0.6–0.8                          |
| 100–200              | 90–180                 | 0.8–1.0                          |
| 200–300              | 36–90                  | 1.0                              |
| 300–400              | 24–36                  | 1.0–3.0                          |
| 400–500              | 18–24                  | 3.0–7.0                          |
| 600–1200             | 12–18                  | 7.0–10.0                         |

<sup>a</sup>The maximum acoustic power produced by a single 18-kHz source used is 0.6–1.0 kW

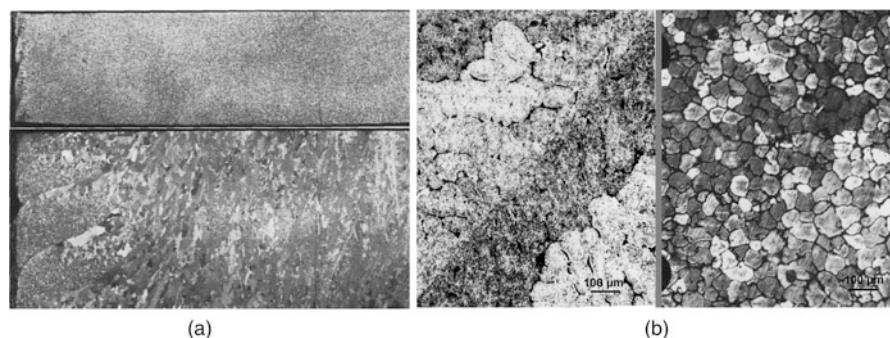


**Fig. 5.20** Effect of ultrasonic melt processing in the billet sump on the grain structure of (a) 830-mm billet from an AA7474 alloy (top—with USP, bottom—without USP) and (b) 285-mm billet from an AA7055 alloy (left—without USP, right—with USP) (courtesy G. I. Eskin)

properties, improved casting properties, better response to heat treatment and deformation [49, 86]. Fine equiaxed grains were also characterized by reduced microsegregation and finer nonequilibrium eutectic particles, which resulted in shorter homogenization times.

The uniformity in structure and chemical composition translates in the uniformity and high level of mechanical properties. As a consequence, the susceptibility of the cast metal to hot and cold cracks decreases. It is well known that higher ductility of semisolid and solid metals plays decisive role in the occurrence of hot and cold cracks, respectively [134–137]. In the solid state, the ductility at temperatures below 300 °C should be larger than 1.0% in order to prevent cold cracks (as the cast metal is subjected to tensile strains in an order of 0.55–0.6% [138]). Nondendritic structure assures that the ductility stays above 2% that guarantees crack-free billets.

Large deformed items for aircrafts made from high-strength alloys require high characteristics of fracture toughness and fatigue endurance. These requirements are typically met by increasing the purity of the alloys with regard to Fe and Si. This, however, results in coarsening of the grain structure and higher susceptibility to cracking upon and after casting. Ultrasonic melt processing and the formation of nondendritic structure in larger billets and ingots made it possible to meet the challenge and solve the problem of producing large castings without cracking and with uniform fine structure [49, 80, 139–142]. As a result of gained experience in industrial DC casting with ultrasonic melt processing of various alloys and different-scale billets, it became possible in the 1980s to commercially produce large-scale crack-free billets 960 mm (AA7055) and 1200 mm (AA2324) in diameter. These billets were used for special forgings and extrusions for transport airplanes [143, 144]. This experience was extended to flat ingots of an AA2324 alloy where the nondendritic structure was successfully obtained in ingots 450 × 1200 mm in cross-section.

The ultrasonic melt processing can be applied to the melt flow, during the transport of the melt from the holding durance to the mold. This technological way is more versatile as the processed melt can be directed to several molds but also poses a number of challenges related to the treatment time–melt volume–acoustic power ratios. The grain refinement can be achieved by ultrasonic melt treatment in the flow [86] but its efficiency for grain refinement is less that for processing in the mold. In this case, the mechanisms of substrate activation and refinement of primary particles are acting. The efficiency may be improved by managing the melt flow by dams and baffles.

Figure 5.21 shows the grains refinement achieved in an 85-mm billet after the melt was treated in different ways [145]. In this case, the comparison is made between a 6XXX-series alloy with a commercial AlTiB grain refiner addition (a), the alloy containing small additions of Zr and Ti cast without USP (b), and the alloy with USP either in the melt outside the DC casting mold (c) or in the sump of the billet (d). It is clear that the USP results in a significant grain refinement as comparison with a commercial grain refiner, and that the processing in the sump

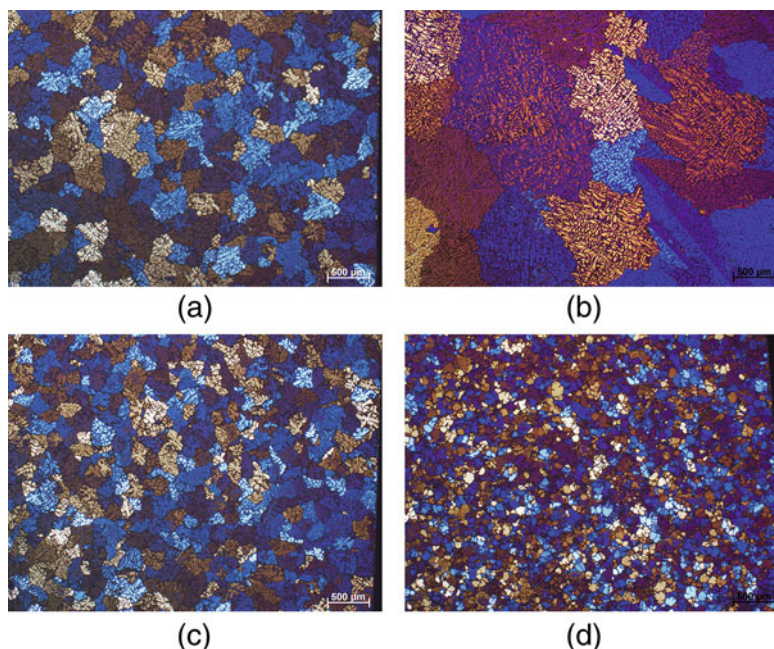


**Fig. 5.21** Grain structure of an AA6XXX-series alloy direct-chill cast in an 85-mm billet: (a) with standard AlTiB grain refiner, No USP; (b) with Zr + Ti addition, no USP; (c) with Zr + Ti addition, USP outside the mold; and (d) with Zr + Ti addition, USP in the sump (courtesy G. Salloum-Abou-Jaoude)

gives smaller grains than the processing outside the mold. This difference is most likely due to the action of the additional refining mechanisms, i.e., dendrite fragmentation.

Grain-refining additions of Zr and Ti can be added to the melt using an Al–Zr–Ti master alloy with simultaneous ultrasonic melt processing [146].

The application of ultrasonic cavitation to introduction of grain-refining master alloys is very promising. The application of an Al–Ti–B grain-refining rod was suggested in the 1970s [147] but was widely adopted later in the 1980s [148]. One of the deficiencies of grain-refining rod introduction is the agglomeration of  $\text{TiB}_2$  particles, wide size distribution of these particles, and, as a consequence, low efficiency, i.e., only several percent of particles are acting as nucleation substrates [148, 149]. Ultrasonic melt processing improves the performance of standard AlTiB master alloys by dispersing agglomerates and activating substrates as has been confirmed by a number of studies [113, 150, 151].

Figure 5.22 illustrates this by an example of AlTiB introduction into Al–Si alloys that usually show grain coarsening at higher concentrations of Si.

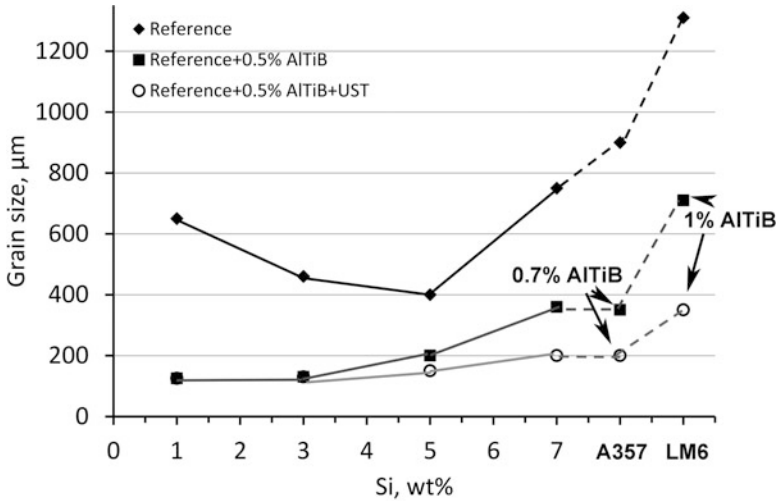


**Fig. 5.22** Effect of a commercial AlTiB grain refiner and ultrasonic treatment (UST) on the grain size in binary and commercial Al–Si alloys

### 5.4.3 Composite Materials and Immiscible Alloys

Ultrasonic cavitation and streaming are widely used for making metal–matrix composite materials (MMC) through a liquid-metal route, and for composites with nanoparticles (MMNC) this is a main technique used nowadays. The mechanisms of ultrasonic processing such as wetting, deagglomeration, and dispersion are used.

The simplest technique of introducing the particles is spraying them onto the surface of the melt using a trough or a tube. These particles are then drawn into the bulk of the melt by vortex (in the case of impeller) or by gravity and surface flows [152–155]. This technique works quite well in magnesium MMCs but have limitations in aluminum MMCs due to the strong oxide film at the melt surface. A combination of the impeller and protective atmosphere are required.

Particles can be also wrapped in a metallic foil (e.g., in aluminum foil for Al MMCs) to form a sort of a compact rod that is then slowly fed into the cavitation region, where the foil dissolves releasing the particles and exposing them to cavitation [156, 157]. A double wrap in aluminum foils of different thicknesses has been suggested for controlling the release rate [158]. A special feeder device can be used to deliver particles into the cavitation region. Such a system using a worm-type feeder and Ar-atmosphere protection of particles was developed and tried in Mg alloys [159]. The selection of material for the feeding tube is important and maybe cumbersome, especially for aluminum. For Mg alloys, steel can be used.

The delivery of particles in the cavitation region can be also achieved using perforated container (e.g., from Nb) placed underneath the sonotrode [160]. In this



case, the geometry of the container, and the number and size of holes control the release rate.

A next logical step would be to use a kind of master alloy containing a metallic matrix with large concentration of particles, similar to grain-refining rods. The particles can be spatially distributed in such a composite master alloy and wetted by the matrix. The master alloy can be produced by a powder metallurgy route, using mechanical alloying for mixing and hot extrusion for consolidation and better particle distribution. Such a scheme was first suggested in the 1960s and implied the direct contact of a sintered aluminum powder (SAP) rod with the sonotrode [47]. Later, this approach was used in grain-refining practice and tried in MMNC processing [154, 161, 161].

The application of hollow sonotrodes has been also suggested for introduction of the particles into the melt and in the cavitation region [47, 163, 164].

All these techniques are currently tried on the laboratory scale and, obviously, have advantages and disadvantages. The finer the particles, the more complicated their introduction to the melt is. In the case of microscopic (5–100  $\mu\text{m}$ ) particles, mechanical or electromagnetic mixing with subsequent or simultaneous ultrasonic processing is sufficient [153, 165].

Most of the successful experiments are performed under conditions of developed cavitation with amplitudes 10–40  $\mu\text{m}$  at frequencies 17–22 kHz. It seems that there is a consensus that cavitation is the basis of successful ultrasonic processing of composites, especially at the stage of wetting and deagglomeration. Physical modeling using transparent solutions and mixtures and variable ultrasonic parameters (17–20 kHz, 1.4–4 kW) demonstrated that a better distribution of particles in the volume could be achieved at a higher frequency and lower power [166]. In this case, the re-agglomeration is prevented and particles are well distributed by acoustic flows in the volume.

Figure 5.23a demonstrates a reasonable distribution of alumina nanoparticles in an aluminum alloy, while Fig. 5.23b shows that USP really results in deagglomeration of nanoparticle agglomerates (evidenced by ultra-small angle X-ray scattering, USAXS).

Bearing alloys containing up to 10% Pb (additionally up to 10% Sn, and up to 4% Sb) can be produced by the following route [167]. The melt is superheated to 1100–1200  $^{\circ}\text{C}$  that allows for dissolution of 18–30% Pb in liquid aluminum. The melt is then poured through a water-cooled ultrasonic funnel (magnetostrictive transducer arranged around the pouring channel). The ultrasonic processing then occurs simultaneously with melt cooling. This creates conditions for nucleation of Pb droplets under intensive mixing that prevents sedimentation. The process ends with DC casting of billets where high cooling rate helps to preserve the emulsion in the solid state. Lead particles 5–40  $\mu\text{m}$  in size were uniformly distributed in the billet volume.

Another technological approach was suggested by G.I. Eskin [49] and tested under laboratory conditions (casting of a 6XXX-series alloy in a metallic mold 95 mm in diameter, 300 mm in height, and processed volume 5 kg). The idea was to avoid addition of the low-melting and immiscible components in the furnace,



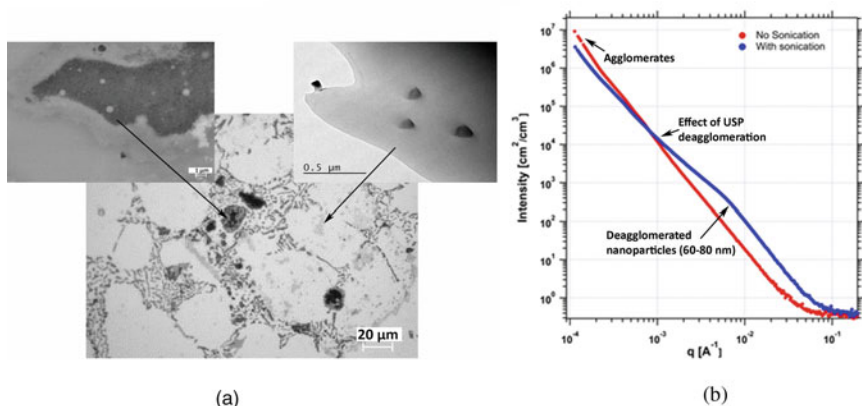


**Fig. 5.23** Distribution of  $\text{Al}_2\text{O}_3$  nanoparticles (<100 nm) in the matrix of an Al alloy: (a) metallography with insets showing loose particles in agglomerates (top left) and in the solid solution (top right) (J. Tamayo, W. Lefebvre, D. Eskin, 2015) and (b) USAXS results showing deagglomeration of nanoparticles as a result of USP (courtesy P. Srirangam)

preventing contamination and necessity for high melt superheat. Relatively small (up to 6%) additions of such elements were done using a master alloy or pure-metal rod with ultrasonic processing in the launder.

The same approach was used in DC casting of a 6XXX-series alloy with addition of Pb in the melt flow with simultaneous ultrasonic processing of the melt [86].

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# Chapter 6

## High Magnetic Field Processing of Metal Alloys



Yves Fautrelle, Jiang Wang, Dafan Du, Xi Li, and Zhongming Ren

The use of direct current (DC) magnetic field in electromagnetic processing of materials becomes widespread in metallurgy, especially in metals and semiconductor industries. The main goals are to control the behavior of melts during solidification, to improve process performance and to achieve better quality products. DC magnetic fields are usually known for their magnetohydrodynamic effects, e.g., flow damping which are commonly used in continuous casting process for steels or crystal growth elaboration [1–6]. In parallel, the development of super conducting technology, which is able to produce high magnetic fields in rather large space, has open many new possibilities in controlling the processing of materials, in solid and liquid state. The novelty comes from the use of magnetization forces acting on non-magnetic or feeble-magnetic materials. Indeed, most metallic materials exhibit magnetic properties, and some special effects have been discovered [7–11]. For example, it has been realized quite recently that thermo-electric phenomena under a high DC magnetic field can produce quite strong electromagnetic forces in solid and liquid metals, leading to a phenomenon called Thermo-Electric-Magnetic Convection (TEMC) [12]. The forces due to TEMC are able to generate significant liquid motion, especially when temperature gradients are present, thus may strongly influence the solidification of metallic alloys [13–19]. Processing of materials under DC magnetic fields is at the cross point of two scientific fields, namely Electromagnetic Processing of Materials and Magnetosciences. Theroies and

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195

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**Table 6.1** Type, function, and utilization of static magnetic fields on materials

| Type of magnetic field                                 | Function and utilization                                                                                     | Typical $B$ values |
|--------------------------------------------------------|--------------------------------------------------------------------------------------------------------------|--------------------|
| <i>Moderate magnetic fields</i>                        | Damping of flow fluctuations                                                                                 | up to 0.1 T        |
| Effect of the Lorentz force                            | Flow control<br>MHD actuators, pumping, propulsion power generators (coupled with applied electric currents) |                    |
| <i>Moderate to high magnetic field</i>                 | Thermo-electric effects—pumping of liquid metals                                                             | 0.1–0.5 T          |
| Effect of the thermo-electric magnetic (Lorentz) force | Influence on solidification                                                                                  |                    |
| <i>High magnetic fields</i>                            | Crystal orientation                                                                                          | up to 1 T          |
| Effect of magnetization force or torque                | Structural alignment                                                                                         |                    |
|                                                        | Vapor deposition                                                                                             |                    |
|                                                        | Phase transformation                                                                                         |                    |
|                                                        | Change of physical properties                                                                                |                    |
| <i>High magnetic fields</i>                            | Levitation                                                                                                   | up to 1 T          |
| Effect of the magnetic field gradients                 | Phase separation                                                                                             |                    |

practice from the two fields were combined and used in “Electromagnetic Processing of materials” (EPM), and triennial International Symposia were established to discuss and publish the scientific advance in the field of EPM. The first of which was held in Nagoya, Japan in 1994 co-chaired by the pioneer scientists, Prof. Shigeo Asai and Doctor Marcel Garnier. Readers may find many valuable papers, examples, and applications in the proceedings of the past eight symposia. This chapter is an updated review of the major progresses and applications related to the uses of strong/intense DC magnetic fields in processing of materials (essentially metallic alloys) during the solidification processes.

In the first section, we review the basic principles and underlying physics, namely the magnetohydrodynamic and magnetic effects. In the second section, we discuss the main phenomena induced by DC magnetic fields in materials processing. We describe in particular the flow damping effects on liquid metals and control of the structures of materials during solidification, the texture, phase separation, and thermo-electric effect. Finally in the last section (Sect. 6.3) we give two examples of successful industrial applications. Table 6.1 summarizes the various effects and utilizations.

## 6.1 Physical Principles of High Magnetic Field Processing

The effects of a DC magnetic field on a material are based on two principles:

- Magnetohydrodynamic effects resulting from the electromagnetic forces (or Lorentz forces)  $\mathbf{F}_{em} = \mathbf{j} \times \mathbf{B}$  acting on liquid or solid materials,  $\mathbf{j}$  is the electric current density inside the materials.



- Magnetization effects which are based on the magnetization force on feeble-magnetic materials.

Each type of force leads to a specific action. For example, the Lorentz forces are commonly used to modify or damp fluid flow and any associated turbulence. In practice, moderate amplitude magnetic fields are sufficient to create significant effects (see Table 6.1). However, for feeble-magnetic materials, high amplitude magnetic fields are necessary to compensate their weak magnetic susceptibilities. The magnetization forces may exert attraction or repulsion actions dependent on the nature of the materials. This will be discussed later on. Table 6.1 summarizes the different types of DC magnetic fields and their functions and utilizations.

### 6.1.1 Magnetohydrodynamics of Liquid Metals

In the present section we describe the principles for understanding of the magneto-hydrodynamic (MHD) phenomena. Magnetohydrodynamic interactions are based on the uses of the Lorentz force for various purposes, i.e., the interaction between an electric current density  $j$  and a magnetic field  $B$ . An electric current density may be created by various mechanisms, for example, applying electric potential gradients, fluid flow across magnetic field lines, and thermo-electric currents when temperature gradients are present in solidification processes. Significant actions may be produced by using moderate magnetic fields ranging from 0.1 to 0.5 T. The main variables used in this chapter are gathered in Table 6.2 below.

**Table 6.2** Main variables, their symbols, and definitions in magnetohydrodynamics

| Symbol                        | Definition                                                                                                                                   | Unit                                           |
|-------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------|
| $H$                           | Magnetic field                                                                                                                               | A/m                                            |
| $B$                           | Magnetic flux density related to $H$ by $B = \mu H$ , $\mu$ is magnetic permeability of the medium. $B$ is conservative $\nabla \cdot B = 0$ | Tesla                                          |
| $E$                           | Electric field                                                                                                                               | V/m                                            |
| $j$                           | Electric current density which is conservative $\nabla \cdot j = 0$                                                                          | A/m <sup>2</sup>                               |
| $V$                           | Electric scalar potential                                                                                                                    | V                                              |
| $\mu$                         | Magnetic permeability of the medium                                                                                                          | H/m                                            |
| $\mu_r$                       | Relative magnetic permeability $\mu_r = \mu/\mu_0 = 1 + \chi$                                                                                | –                                              |
| $\mu_0 = 4\pi \times 10^{-7}$ | Magnetic permeability of vacuum                                                                                                              | H/m                                            |
| $\chi$                        | Magnetic susceptibility                                                                                                                      | –                                              |
| $S$                           | Thermo-electric power of the medium                                                                                                          | V/K                                            |
| $\sigma$                      | Electric conductivity of the medium                                                                                                          | Ohm <sup>-1</sup> m <sup>-1</sup> or Siemens/m |
| $\rho$                        | Density of the medium                                                                                                                        | kg/m <sup>3</sup>                              |
| $\nu$                         | Kinematic viscosity of the fluid                                                                                                             | m <sup>2</sup> /s                              |

### 6.1.1.1 Maxwell Equations

Under the MHD approximation [20], steady-state Maxwell equations are based on two fundamental laws:

*Ampère's law :*

In an electrically conducting medium, an electric current density creates a magnetic field, and it is expressed by Eq. (6.1).

$$\nabla \times \mathbf{H} = \frac{1}{\mu} \nabla \times \mathbf{B} = \mathbf{j} \quad (6.1)$$

*Ohm's law :*

Ohm's law relates the electric current density to the generalized electric field by

$$\mathbf{j} = \sigma \mathbf{E}_t. \quad (6.2)$$

The generalized electric field  $\mathbf{E}_t$  may be created by various mechanisms, e.g., the gradients of an electric scalar potential  $V$ , velocity  $\mathbf{u}$  of the medium, and temperature gradients  $\nabla T$ :

$$\mathbf{E}_t = -\nabla V + \mathbf{u} \times \mathbf{B} - S \nabla T. \quad (6.3)$$

The last term of Eq. (6.3) is the thermo-electric current generated by temperature gradients in the medium. The constant  $S$  is the thermo-electric power of the medium [12]. Its value is usually very small (of order of  $10^{-6}$  V/K). However, thermo-electric effects may become important in the presence of high magnetic fields (see Sect. 6.1.1.4).

### 6.1.1.2 Laplace-Lorentz Forces and Momentum Equations

Any unit volume in a conducting material is submitted to a body force  $\mathbf{F}_{em}$ , called Lorentz force which is expressed as:

$$\mathbf{F}_{em} = \mathbf{j} \times \mathbf{B} \text{ (N/m}^3\text{)}, \quad (6.4)$$

Different decompositions of Eq. (6.4) can be made for understanding the different phenomena. The physical properties are defined in Table 6.2.

#### First Decomposition

Using Eq. (6.1), an expression involving magnetic field only can be obtained.

$$\mathbf{F}_{em} = \frac{1}{\mu} (\nabla \times \mathbf{B}) \times \mathbf{B} \quad (6.5)$$

Equation (6.5) can be also split into two parts:

$$\mathbf{F}_{em} = -\nabla \left( \frac{B^2}{2\mu} \right) + \frac{1}{\mu} (\mathbf{B} \cdot \nabla) \mathbf{B}. \quad (6.6)$$

From Eq. (6.6) it can be seen that the Lorentz force contains two parts:

- A curl-free part for electromagnetic pressure  $p_m \equiv \frac{B^2}{2\mu}$ ,
- A rotational part for generating fluid motions.

## Second Decomposition

Combining Eqs. (6.2), (6.3), and (6.4) yields:

$$\mathbf{F}_{em} = -\sigma (\nabla V + S \nabla T) \times \mathbf{B} + \sigma \mathbf{B} (\mathbf{u} \cdot \mathbf{B}) - \sigma B^2 \mathbf{u}. \quad (6.7)$$

In Eq. (6.7), the last term of the R.H.S. is a force that always oppose to fluid motion. This term is the damping part of the electromagnetic forces. It is noticeable from Eq. (6.7) that the damping force is anisotropic and dependent on the direction of the flow with respect to the magnetic field. This is clear when the two last terms of Eq. (6.7) are considered. However, it must be emphasized that the gradient of the scalar potential may also compensate the action of the damping (sometimes called braking) forces.

Liquid metals are generally considered as weakly compressible Newtonian fluids. The fluid velocity field  $\mathbf{u}$  is thus governed by incompressible Navier-Stokes equations.

Momentum equation:

$$\rho \frac{\partial \mathbf{u}}{\partial t} + \rho (\mathbf{u} \cdot \nabla) \mathbf{u} = -\nabla p + \mathbf{F} + \rho \nu \nabla^2 \mathbf{u}, \quad (6.8)$$

along with mass conservation equation:

$$\nabla \cdot \mathbf{u} = 0. \quad (6.9)$$

The physical properties in Eqs. (6.8) and (6.9) are defined in Table 6.2.

### 6.1.1.3 Characteristic Scales and Non-Dimensional Parameters

To use the above equations more conveniently, some characteristic time scales and non-dimensional parameters were defined and listed in Table 6.3. The Thermo-Electric-Magnetic Convection (TEMC) is dealt separately in Sect. 6.1.1.4.

When the magnetic Reynolds number  $R_m$  is small, the externally applied magnetic field is weakly modified by the presence of a conducting load. Then,  $\mathbf{B}$  behaves

**Table 6.3** The characteristic times and non-dimensional parameters

| Definition                                                                                                                                  | Formula                                                       |
|---------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------|
| Magnetic diffusion time (s)                                                                                                                 | $\tau_d = \frac{L^2}{\eta}$                                   |
| Typical time for electromagnetic action (s)                                                                                                 | $\tau_m = \left( \frac{\sigma B_0^2}{\rho} \right)^{-1}$      |
| Convection time (s)<br><i>L</i> and <i>U</i> are the domain length and typical velocity of the medium, respectively                         | $\tau_c = \frac{L}{U}$                                        |
| Turbulence turn-over time (s)<br><i>l</i> and <i>u'</i> are the turbulence length scale and typical velocity fluctuation, respectively      | $\tau_t = \frac{l}{u'}$                                       |
| Magnetic Reynolds number: ratio between convection of the magnetic field and its diffusion                                                  | $R_m = \frac{UL}{\eta} = \mu\sigma UL$                        |
| Interaction parameter or Stuart number: measure of the influence of the electromagnetic forces on the fluid motion                          | $St = \frac{\tau_c}{\tau_m} = \frac{\sigma B_0^2 L}{\rho U}$  |
| Interaction parameter of turbulence (or Stuart number for turbulence): measure of the influence of the electromagnetic forces on turbulence | $N' = \frac{\tau_t}{\tau_m} = \frac{\sigma B_0^2 l}{\rho u'}$ |
| Hartmann number: ratio between Lorentz force and viscous force                                                                              | $Ha = \left( \frac{\sigma B_0^2 L^2}{\rho \nu} \right)^{1/2}$ |

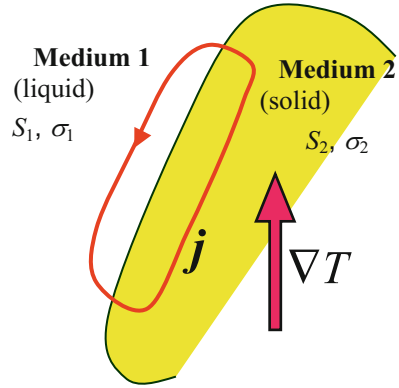
like in vacuum and is curl-free. In DC magnetic fields, the Hartmann number  $Ha$  is one of the most important parameters to measure the flow damping effect, and it describes the damping action and strength of the magnetic field. The most effective damping is caused by friction near the walls of a fluid domain in a special viscous boundary region called Hartmann layers [20]. If the Hartmann number is in the range of 100–1000, the damping effect due to the magnetic field is considered effective as demonstrated by the examples given in Sect. 6.3.

The second important parameter is the Stuart (or Stewart) number  $St$ . It quantifies the efficiency of the magnetic field to act on fluid flows (damping but also deflection, modification of the flow pattern, etc.). This is especially relevant in cases of non-uniform magnetic fields often found in industrial applications (see Sect. 6.3).

#### 6.1.1.4 Thermo-Electric-Magnetic Convection (TEMC)

Thermo-electric (TE) effect occurs in metallic materials when they are submitted to temperature gradients as described in Eq. (6.3). Thermo-Electric-Magnetic Convection (TEMC) is present when materials are submitted to a high DC magnetic field. Peltier-Seebeck effect occurs at the interface between two media having different thermo-electric powers, whilst Thomson effect takes place in the bulk. In the bulk medium, an electric current density  $j \approx -\sigma \nabla T$  is created as stated by Eq. (6.3). At the interface between two media, e.g., liquid and solid (Fig. 6.1), the interface

**Fig. 6.1** A sketch of the thermo-electric current distribution near the interface between two media



behaves like a battery, and a TE current is generated due to the following condition at the boundary [12]:

$$\left[ \left( \frac{j_1}{\sigma_1} - \frac{j_2}{\sigma_2} \right) + (S_1 - S_2) \nabla T \right] \cdot \mathbf{t} = 0, \quad (6.10)$$

$\mathbf{t}$  is unit vector tangent to the interface.

In solidification processes, all possible conditions to produce a Peltier-Seebeck effect are present. Eq. (6.10) indicates that the existence of TE currents depends on three conditions [21]:

- The liquid and solid thermo-electric powers must be different,  $(S_1 - S_2) \neq 0$ ,
- There exists a temperature gradient in the vicinity of the interface,
- The temperature gradient must not be perpendicular to the interface,  $\nabla T \cdot \mathbf{t} \neq 0$ .

The thermo-electric powers of common metallic alloys are generally weak, in the order of  $10^{-6}$  V/K (Table 6.4). However, in the presence of high magnetic fields where the Lorentz force is calculated by

$$F_{TE} \approx \mathbf{j} \times \mathbf{B} \approx -\sigma \nabla T \mathbf{B}, \quad (6.11)$$

It may become important.

In metal solidification, the solid and the liquid phases usually have different thermo-electric powers, and therefore, thermo-electric current is produced near the solidification front. Under DC magnetic fields, the Peltier-Seebeck effect can be magnified hugely. The evolution of the thermo-electric power of both tin and lead with temperature is illustrated in Fig. 6.2 [22]. The data clearly show an abrupt change of the thermo-electric power near the liquid–solid interface and the difference between  $S_s$  and  $S_l$ . Kaldre et al. [22] showed that the sign of  $(S_s - S_l)$  depends on the nature of the metal and the chemical composition in the case of an alloy.

According to [21] the typical thermo-electric-magnetic velocity scales are calculated by

**Table 6.4** The typical physical properties of liquid aluminium, steel, and silicon

| Type of materials | Physical property                                                              | Unit                        | Value                                                                         |
|-------------------|--------------------------------------------------------------------------------|-----------------------------|-------------------------------------------------------------------------------|
| Aluminium         | Density $\rho$ near the melting point<br>$T \sim 660\text{ }^{\circ}\text{C}$  | $\text{kg/m}^3$             | 2700 at solid state<br>2400 at liquid state                                   |
|                   | Kinematic viscosity $\nu$                                                      | $\text{m}^2/\text{s}$       | $0.54 \times 10^{-6}$                                                         |
|                   | Electrical conductivity $\sigma$ near the melting point                        | $\Omega^{-1}\text{ m}^{-1}$ | $\sim 12 \times 10^6$ at solid state<br>$3.8 \times 10^6$ at liquid state     |
|                   | Thermo-electric power $S$                                                      | V/K                         | $-5.4 \times 10^{-6}$ at solid state<br>$-3.8 \times 10^{-6}$ at liquid state |
| Liquid steel      | Density $\rho$ near the melting point<br>$T \sim 1510\text{ }^{\circ}\text{C}$ | $\text{kg/m}^3$             | 7000                                                                          |
|                   | Kinematic viscosity $\nu$                                                      | $\text{m}^2/\text{s}$       | $0.54 \times 10^{-6}$                                                         |
|                   | Electrical conductivity $\sigma$ near the melting point                        | $\Omega^{-1}\text{ m}^{-1}$ | $0.8 \times 10^6$                                                             |
| Liquid silicon    | Density $\rho$ near the melting point<br>$T \sim 1414\text{ }^{\circ}\text{C}$ | $\text{kg/m}^3$             | 2510                                                                          |
|                   | Kinematic viscosity $\nu$                                                      | $\text{m}^2/\text{s}$       | $0.29 \times 10^{-6}$                                                         |
|                   | Electrical conductivity $\sigma$ near the melting point                        | $\Omega^{-1}\text{ m}^{-1}$ | $\sim 1.5 \times 10^6$                                                        |

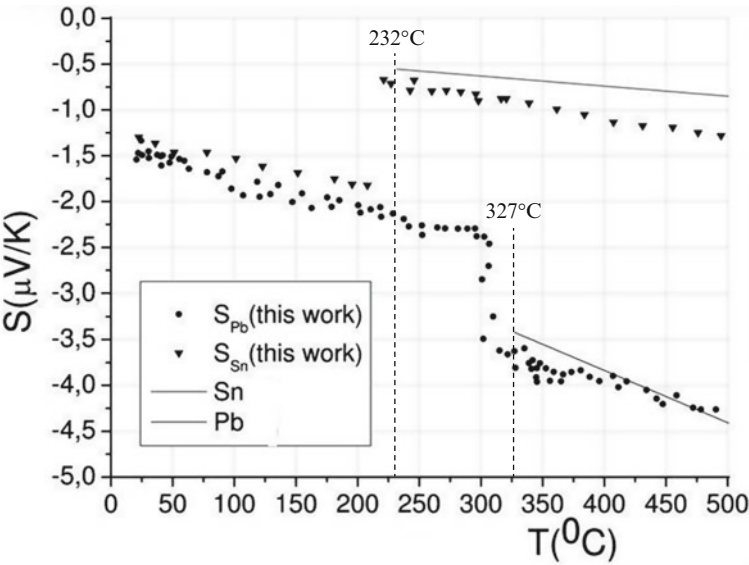


**Fig. 6.2** The absolute thermo-electric powers as function of temperature for pure tin and pure lead [22]. The vertical dashed lines indicate the melting temperatures of each metal. The straight lines are the results obtained by N. Cusack and P. Kendall (Proc. Phys. Soc. 72–5, 1958)

- For moderate magnetic field amplitudes ( $Ha \leq 10$ )

$$U_1 \approx \frac{\sigma SGL^2 B}{\rho \nu} \quad \text{or} \quad U'_1 \approx \sqrt{\frac{\sigma SGLB}{\rho}}, \quad (6.12)$$

in viscous or inertial regimes.

- For very strong magnetic fields (Hartmann regime, i. e.,  $Ha \geq 10$ )

$$U_2 \approx \frac{SG}{B}. \quad (6.13)$$

$G$  stands for the temperature gradient and  $L$  is a typical length of the system.

The above calculations indicate that, as the magnetic field amplitude increases, TE convection first increases then decays in the larger magnetic field region (Fig. 6.3). Thus TE convection reaches a maximum value with the Hartmann number around 10 [23]. Since the Hartmann number is proportional to the length scale of a system, the smaller the length scale, the higher the magnetic field in order to be in the Hartmann regime as illustrated in Fig. 6.3.

Let us consider a liquid aluminium melt with the following values:

$\sigma = 3.8 \times 10^6$  S/m,  $S = 10^{-6}$  V/K,  $\rho = 2.4 \times 10^3$  kg/m<sup>3</sup>,  $\nu = 0.54 \times 10^{-6}$  m<sup>2</sup>/s,  $\nabla T \equiv G = 2 \times 10^3$  K/m,  $B = 1$  T, the TE forces calculated by (6.11) is  $0.76 \times 10^4$  N/m<sup>3</sup>. Note that the value is very high and is of the same order as gravity force density  $\rho g = 2.35 \times 10^4$  N/m<sup>3</sup>. In typical dendrite spacings in solidification where  $L = 100$   $\mu$ m, then the velocity estimates are:

$$U_1 = 0.058 \text{ m/s or } U'_1 = 0.178 \text{ mm/s, } U_2 = 2 \text{ mm/s, } Ha = 5.41.$$

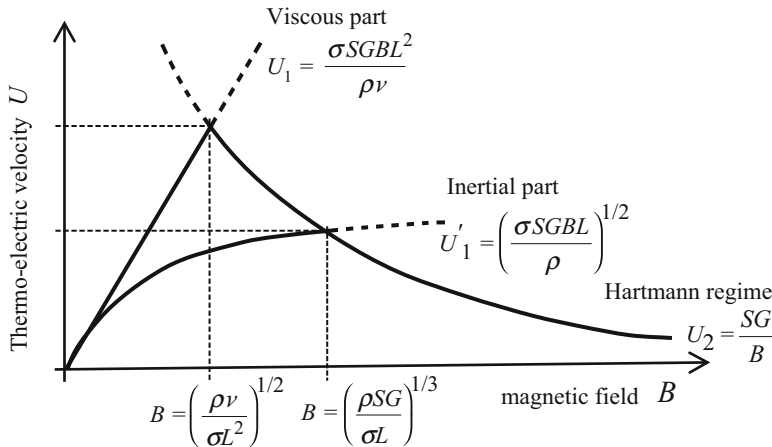


**Fig. 6.3** A schematic illustration of the evolution of the TEM velocity,  $U$  as a function of the applied magnetic field,  $B$



It is noteworthy that the above estimates are significantly larger than the usual growth velocity encountered in solidification with a typical value in the range of 1–200  $\mu\text{m/s}$  approximately. This shows that the effect is restricted not only in the bulk material but also in the mushy zone where the interfacial area density is high. More examples will be provided in Sect. 6.2.

### 6.1.2 Magnetization Effects in Feeble-Magnetic Materials

Most materials in nature are non-magnetic, especially at a temperature above the Curie point. This applies to most liquid metals. The magnetic moment  $M$  is non-zero but very weak compared to the ferromagnetic materials, e.g., some iron-based alloys. However, the magnetic effects become significant under high magnetic fields, e.g., in the range of 1–20 T [3]. For an isotropic medium, the magnetic moment is related to the magnetic field by

$$M = \chi H, \quad (6.14)$$

$\chi$  is the volume magnetic susceptibility, and is related to the magnetic permeability by

$$\mu = \mu_0(1 + \chi)$$

#### 6.1.2.1 Magnetization Forces

For ferromagnetic materials  $\chi$  is normally in the order of  $10^3$ , whereas for non-magnetic media  $\chi$  is in the range of  $10^{-5}$  to  $10^{-3}$ . The magnetization body force acting on the materials is calculated as follows:

$$\mathbf{F}_m = \mu_0 (\mathbf{M} \cdot \nabla) \mathbf{H} = \frac{\chi}{\mu_0} (\mathbf{B} \cdot \nabla) \mathbf{B}. \quad (6.15)$$

$\mathbf{F}$  is proportional to the square of  $B$ . When the external magnetic field is not distorted by the presence of the materials (curl-free magnetic field density), Eq. (6.15) can be simplified as:

$$\mathbf{F}_m = \chi \nabla \left( \frac{B^2}{2\mu_0} \right). \quad (6.16)$$

Equation (6.16) indicates that the magnetization force also depends on the magnetic field gradients. The magnetization force is curl-free and cannot generate directly any fluid motion. It behaves like an effective gravity force acting on the materials, and any unit volume of the material is submitted to a torque.

### 6.1.2.2 Magnetization Energy

The magnetization energy  $E_m$  is defined as

$$E_m = - \int_0^H \mu_0 \mathbf{M} d\mathbf{H}.$$

For non-magnetic materials, the magnetization energy can be written as:

$$E_m = -\mu_0 \chi \mathbf{H}^2 / [2(1 + \chi N)^2], \quad (6.17)$$

$N$  is the demagnetization factor. If the value of the magnetic susceptibility is near zero, then the magnetization energy is approximated by:

$$E_m = -\frac{1}{2} \mu_0 \chi \mathbf{H}^2. \quad (6.18)$$

### 6.1.2.3 Magnetic Susceptibility

Materials can be classified into different types depending on the value and the sign of their magnetic susceptibility. Table 6.5 gives the definitions and some typical examples. The magnetic susceptibility may be isotropic or anisotropic. For example, an anisotropy exists in crystal materials due to the crystalline atomic structure. To describe anisotropy in susceptibility, a susceptibility tensor is used, and Eq. (6.14) becomes:

$$\mathbf{M} = \chi \cdot \mathbf{H}, \quad (6.19)$$

where  $\chi$  is a second order symmetric tensor.

**Table 6.5** Classification of magnetic materials and their susceptibility

|                        | Type of materials                | Order of magnitude of the volume magnetic susceptibility $\chi$                                                                                                     |
|------------------------|----------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Magnetic materials     | Ferromagnetism<br>Ferrimagnetism | $\chi > > 1$<br>Example:<br>$\chi_{\text{Fe}} \approx 200$ (774 °C)                                                                                                 |
| Non-magnetic materials | Paramagnetism $\chi > 0$         | $\chi \approx 10^{-3}$ to $10^{-5}$<br>Example:<br>$\chi_{\text{Al}} \approx 2.2 \times 10^{-5}$ (20 °C)<br>$\chi_{\text{O}_2} \approx 0.37 \times 10^{-5}$ (20 °C) |
|                        | Diamagnetism $\chi < 0$          | $\chi \approx -10^{-5}$<br>Example:<br>$\chi_{\text{Cu}} \approx -2.0 \times 10^{-5}$ (20 °C)<br>$\chi_{\text{H}_2\text{O}} \approx -0.9 \times 10^{-5}$ (20 °C)    |

The components of  $\chi$  are usually related to the crystal symmetry properties. For example, for a crystal having an hexagonal symmetry, the susceptibility tensor is diagonal in a principal reference frame, and its components have the following form:

$$\chi = \begin{bmatrix} \chi_1 & 0 & 0 \\ 0 & \chi_2 & 0 \\ 0 & 0 & \chi_3 \end{bmatrix}. \quad (6.20)$$

By neglecting the influence of the demagnetizing factor, the magnetization energy becomes:

$$E_m = -\frac{1}{2}\mu_0 \sum_{i=1}^3 \chi_i H_i^2. \quad (6.21)$$

Assuming that firstly the materials are paramagnetic ( $\chi_i$  is positive for  $i = 1, 2, 3$ ), and secondly  $\chi_1 > \chi_2, \chi_3$ . Then, from Eq. (6.21), the following inequality holds:

$$E_m = -\frac{1}{2}\mu_0 \chi_1 \sum_{i=1}^3 \frac{\chi_i}{\chi_1} H_i^2 > -\frac{1}{2}\mu_0 \chi_1 H^2. \quad (6.22)$$

Equation (6.22) indicates that, for a given crystal, the magnetization energy of the system is minimum when the 1-axis of the crystal is aligned with the magnetic field. For example, in hexagonal crystals,  $c$  is the principal axis, and  $a, b$  are the perpendicular directions of the crystal. Furthermore, if the crystal has rotational properties around the  $c$ -axis. We may write  $\chi_a = \chi_b \equiv \chi_\perp$  and  $\chi_c \equiv \chi_\parallel$ . If  $\chi_\parallel$  is positive and larger than  $\chi_\perp$ , then the magnetization energy is minimum when the magnetic field is parallel to the crystal axis. The latter effect may cause crystal orientation as discussed in Sect. 6.2.

#### 6.1.2.4 Magnetic Levitation in Magnetic Field Gradients

Equation (6.16) shows that a magnetic force may be created on any materials if a high magnetic field (and gradients) is applied. The sign of the force depends on the sign of the magnetic field gradient and on its para- or diamagnetic nature. This principle has been exploited widely to levitate liquid (water, organic liquids) or metals (bismuth) or even gas (oxygen) or to separate two materials that have different magnetic susceptibilities within a fluid medium (blood red cells, for example).

One striking example is the action of magnetic field gradient on diamagnetic liquid free surfaces. Free surfaces may be deformed in magnetic field gradient [7–10]. Levitation of water droplets is another example. In order to achieve liquid levitation or free surface deformations, the magnetic force must be in the same order as gravity [8, 9]. Considering a liquid volume  $V$  located in a magnetic field gradient, the liquid pool can be levitated if the total magnetic forces exceed its weight, and it can be calculated:

$$\int_V \chi \nabla \left( \frac{B^2}{2\mu_0} \right) dv \geq \rho g V \text{ or equivalently } \chi \frac{B^2}{\mu_0 l \rho g} \geq 1, \quad (6.23)$$

$l$  is a typical variation length of the magnetic field gradient and  $g$  is gravity. For example, levitation of water (a diamagnetic material) requires a magnetic field,  $l(\mathbf{B} \cdot \nabla) \mathbf{B}$  of 1360 T<sup>2</sup>/m for  $\chi \approx -0.907 \times 10^{-5}$  [24],  $g = 9.81$  m/s<sup>2</sup>. Assuming  $l \approx 0.1$  m, the required magnetic field is  $\sim 11$  T. The condition defined by Eq. (6.20) is necessary, but not sufficient. Indeed, stable levitation of liquid droplets involves the spatial distribution of the total magneto-gravitational energy such that

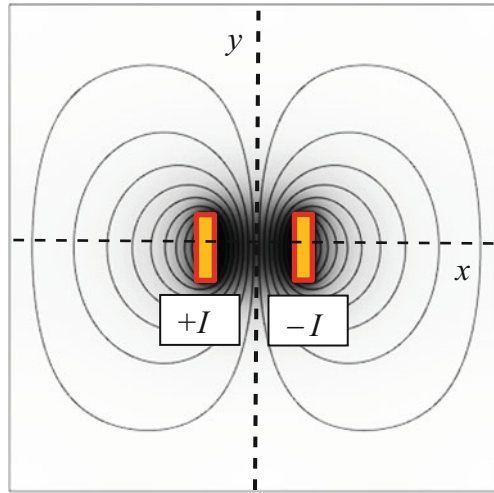
$$E_{mg} = \rho g y - \chi \frac{B^2}{2\mu_0}, y \text{ in the vertical coordinate direction} \quad (6.24)$$

Stable magnetic levitation may be achieved only if the droplet is submitted to a restoring force and located in a region where  $E_{mg}$  reaches its minimum [24]. A heuristic example of stable magnetic levitation system is shown in Fig. 6.4. Let us consider a simple two-dimensional coil supplied with an intense DC electric current (Fig. 6.4a). The magnetic induction reaches its maximum inside the coil and decays outside the inductor. The right part of Fig. 6.4b shows the spatial distribution of the magnetization force  $\vec{F}_m$  in the case of a diamagnetic fluid like water.  $\vec{F}_m$  is directed upward in the upper half of the domain and oriented toward the axis. The profile of its modulus along the vertical  $y$ -axis illustrated in the left part of Fig. 6.4b reaches its maximum value which may exceed the gravity body force for a sufficiently high magnetic field amplitude. Thus, magnetic levitation is possible. The circle indicates the location where magnetic levitation may be achieved in a stable manner.

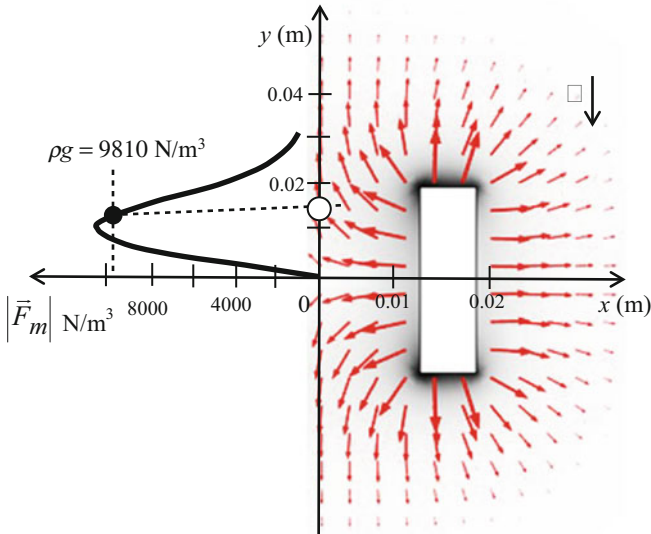
### 6.1.2.5 Phase Separation

Other than the orientation of crystals, their location is another crucial factor in determining metallic materials properties [25]. The positions of primary phases are decided by the nuclei, the inclusions, and the local melt condition (content of solutes, for instance). If there is a method to affect these factors, primary phase position may be controlled [26]. Fortunately, the difference in the magnetic property between the nuclei, the inclusions, the solutes, and their surrounding melt allows uniform or gradient static magnetic field to modify their distribution [27]. It should be pointed out that different to the electromagnetic levitation introduced in Sect. 6.1.1.2, the gradient of the static magnetic field is another approach to levitate substance, which is called magneto-Archimede levitation [28]. The remarkable difference between the two types of levitation is that the former is achieved by means of AC magnetic fields, whereas the latter levitates substance by the static magnetic field [29].

Thanks to magneto-Archimede levitation, any substance in gradient magnetic field is subjected to a magnetic force as defined by Eq. (6.16). Therefore, at the equilibrium condition, different objects should be at different positions if they are



(a) Magnetic field lines generated by a two-coil inductor



(b) Right side: Computed magnetization force density distribution for a diamagnetic fluid like water (arrows in logarithmic scales). Left side: profile of the magnetization force modulus along the centerline of the coil. The circle indicates the location of possible stable levitation.

**Fig. 6.4** An example of a magnetic levitation system consisting of two parallel conductors supplied with intense DC electric currents. The magnetic induction amplitude is 6.8 T in the center of the coil. The magnetization force (b) is upward in the upper part of the coil. The black dot in (b) indicates the location where the magnetization force is equal to the gravity body force for water. (a) Magnetic field lines generated by a two-coil inductor. (b) Right side: Computed magnetization force density distribution for a diamagnetic fluid like water (arrows in logarithmic scales). Left side: profile of the magnetization force modulus along the centerline of the coil. The circle indicates the location of possible stable levitation

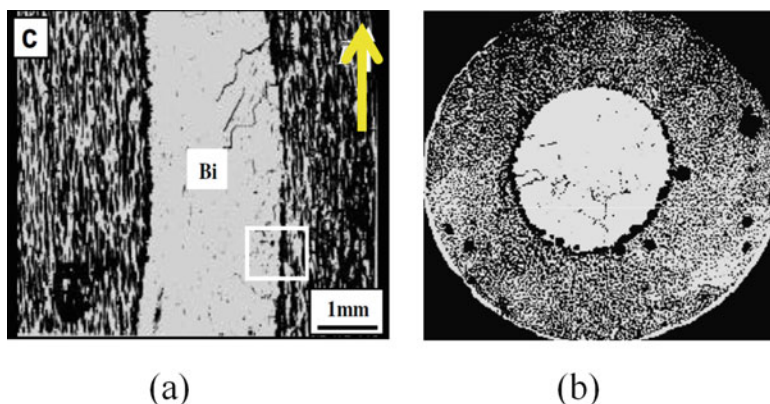


**Fig. 6.5** Radial migration and alignment of primary phase in Mn–Bi alloy under gradient static magnetic field [33]. (a) longitudinal cross-section. (b) transverse cross-section (reproduced with permission)

put in the same magnetic field. This provides an approach to separate the mixed objects via imposing a suitable magnetic field. As shown in [30] feeble-magnetic particles are separated by a 12 T magnetic field. By using the gradient static magnetic field, Tagami et al. [31] in situ observed the solidification of a levitated water droplet and investigated the containerless crystal growth. Wang et al. [32] utilized a high gradient magnetic field to grade the Mn solutes in Mn–Sb melts and achieved the compositional gradient composites. As shown in Fig. 6.5, Li et al. [33] studied the effect of magnetic field on the migration of primary MnBi phase in the melt and found that distribution of primary phase can be controlled via modifying magnetic fields and varying the holding time during solidification. Finally, it is noticeable that the principle may be extended to biology. Maki et al. [34] reported results of the crystal growth of hen-egg lysozyme by magnetically levitating crystals in a small amount of buffer solution. The concentrations of lysozyme and the precipitating agent (gadolinium chloride) were 6.53 wt% and 0.362 mol/kg, respectively. Gadolinium chloride, which induces the magneto-Archimedes effect, was utilized to levitate the crystals under a magnetic field gradient.

## 6.2 Effects of High Magnetic Fields on Structures and Properties of Solidifying Metals

### 6.2.1 Damping of Melt Flow During Solidification

Solidification process is an important sector in metallurgy and the widely used method to make metallic materials. It was consciously treated as an independent discipline from the late 1950s to the early 1960s [35]. Although electromagnetic fields had been used in several metallurgical processes at that time, most of them

were time-changing or mechanically moving magnetic fields [36–38]. The first attempt of applying static magnetic fields during solidification was to damp melt flows that may otherwise cause solute segregation and banding in the solidified metals [39]. Since then, studies of the influence of static magnetic field on solidification have attracted more interest with focus on the promotion of columnar structures because of weak convection conditions. Meanwhile, numerous new phenomena were discovered, particularly when solidification occurs in high static magnetic fields [40, 41]. Clearly, a static magnetic field has a significant influence on the solidified structures, and the effects are governed by two opposing distinct mechanisms:

1. Electromagnetic damping of the flow
2. Thermo-Electric-Magnetic convection which produces a non-negligible flow in the vicinity of the solidification front as discussed later in Sect. 6.2.4.

### 6.2.2 *Impact on Crystal Orientation and Phase Alignment*

For improving the physical and mechanical properties, materials are often aligned in a specific crystallographic direction. Magnetic fields are more effective with materials of high magnetic anisotropy. Using magnetic fields to control the aligned or textured structures is also an active research field. By applying a strong magnetic field, magnetic forces/torques are generated when the crystals have anisotropic magnetic properties.

As early as 1981, Mikelson and Karklin [13] found that oriented solidification structures could be obtained for Al–Cu and Cd–Zn alloys solidified in 0.5–1.5 T magnetic fields. Savitsky et al. [42] found that during the solidification of a Bi–Mn alloy in a magnetic field, the MnBi phase in the alloy aligned along the direction of the magnetic field. They proposed that the magnetocrystalline anisotropy of primary phase caused the rotation and alignment of crystal. However, their study did not differentiate between preferred crystallographic orientation and preferred morphological orientation strictly. In order to avoid a signal distortion due to skin effects, the samples were ground and the powders were suspended in an epoxy [43]. The *c*-axis grain orientation was obtained by placing the samples in a 9.4 T magnetic field until the epoxy hardened. The *c*-axis of the grains were preferentially aligned along the magnetic field direction. De Rango et al. [44] investigated the solidification of a paramagnetic material,  $\text{YBa}_2\text{Cu}_3\text{O}_7$  and obtained bulk textured crystal structure in a magnetic field.

Based on the above method, ceramic powders (Figs. 6.6 and 6.7) with magnetocrystalline anisotropy suspended in a liquid medium tend to be oriented with the smallest magnetic susceptibility axis parallel to the applied magnetic field in the case where the anisotropic energy is higher than the thermal energy [45–47]. Recently, many efforts have been made on binary eutectic alloys [48, 49], peritectic alloys, multi-component alloys, and high-temperature superconducting



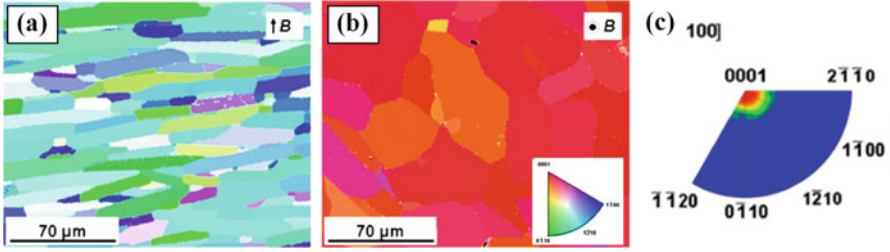


**Fig. 6.6** Electron back-scattered diffraction mappings of the sintered alumina surface (a) and cross-section (b), which are, respectively, parallel and perpendicular to the magnetic field direction. (c) The colormap, indicating the color-coded orientation of (a) and (b) [45] (reproduced with permission)

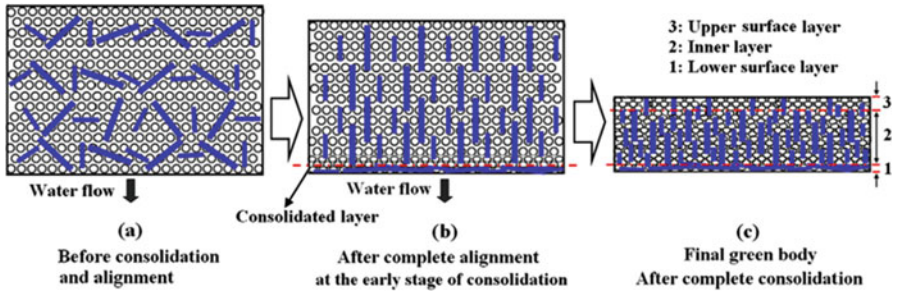


**Fig. 6.7** Schematic illustration of the alignment of  $\beta$ - $\text{Si}_3\text{N}_4$  whiskers during slip casting in a strong rotating magnetic field of 12 T [46] (reproduced with permission)

materials by melting treatment [50], semi-solid forming process [51–53], and directional solidification process [49, 54–56].

Based on the above research, theory of crystal alignment under a magnetic field was proposed. However, for the solidification of metallic alloys, the growth of crystal was affected by crystallographical characteristics and solidification conditions. Thus, the mechanism of crystal orientation and alignment should be studied further. This chapter describes the physical mechanisms of crystal orientation and the alignment for ferromagnetic and non-ferromagnetic metals under the influence of a magnetic field.

For magnetic alignment, a crystal (tetragonal, for instance) needs to have magnetic anisotropy, i.e., the magnetic susceptibility is different in different crystallographical directions. The magnetic free energies in different directions are calculated by:

$$E_m^{a,b} = \frac{\chi_{a,b}}{2\mu_0} B^2 \quad (6.25)$$

$$E_m^c = \frac{\chi_c}{2\mu_0} B^2 \quad (6.26)$$

where  $\chi_{a,b}$  and  $\chi_c$  are the magnetic susceptibilities in the  $a$ -,  $b$ -, and  $c$ -axes of the crystal, respectively. When the magnetic free energy difference  $\Delta E_m$  between different axes is larger than the thermal energy [57], the magnetic field will have significant effect on the crystal.

$$|E_m^{a,b}| = |E_m^c - E_m^{a,b}| = \left| -\frac{(\chi_c - \chi_{a,b})^2}{2\mu_0} \right| B^2 > k_B T \quad (6.27)$$

where  $k_B$  is the Boltzmann constant. If Eq. (6.27) is fulfilled, the crystal/particle will be aligned to the direction with the lowest system magnetic energy. It means that the  $c$ -axis of the crystal will be aligned to the magnetic field direction when  $E_m^{a,b} > E_m^c$ , where as the  $c$ -axis will be aligned perpendicular to the magnetic field direction when  $E_m^{a,b} < E_m^c$  (see Fig. 6.10). The system tends to minimize its total magnetic energy  $E_m$  as stated in Eq. (6.22). During the solidification of a liquid metal, it is necessary to know the critical radius of the nuclei for achieving magnetic alignment. If the particle is assumed to be spherical in Eq. (6.27), the critical radius  $r$  can be calculated by:

$$r > \sqrt[3]{\frac{3\mu_0 k_B T}{2\pi(\chi_c - \chi_{a,b}) B^2}} \quad (6.28)$$

For instance, for bismuth the critical radius is 16.5 nm [58]. According to the theory of magnetic anisotropy [59], it is not necessary for the crystal to have a non-cubic structure, while it is more common for non-ferromagnetic materials with non-cubic crystal structures to have magnetic alignment [57]. In some cases, magnetic alignment can also be induced by the shape magnetic anisotropy due to the shapes of the crystals, for instance, needle-like phases precipitated from a liquid metal [60]. Because of shape anisotropy, the particle is aligned to the direction where the anisotropic demagnetizing field gives a lower system energy as explained by Eq. (6.29) [8]. The detailed derivation can be found in [60].

$$\Delta U \propto \frac{B^2}{2\mu_0} (\chi_P^2 - \chi_M^2) (N_{\perp} - N_{\parallel}) \quad (6.29)$$

where  $\Delta U = U_{\perp} - U_{\parallel}$  is the difference between the magnetic energies of the particle aligning in perpendicular to and parallel to the magnetic field direction.  $\chi_P$  and  $\chi_M$  the magnetic susceptibilities of the particle and liquid metal, respectively.  $N_{\perp}$  and  $N_{\parallel}$  the demagnetizing coefficient in perpendicular to and parallel to the needle axis of the particle.

When a particle has a needle-like shape, such as a primary dendrite arm,  $N_{\perp}$  is larger than  $N_{\parallel}$  in most cases [49]. Therefore, if  $\chi_P > \chi_M$ ,  $\Delta U > 0$  and the particle should be in parallel to the imposed magnetic field direction. If  $\chi_P < \chi_M$ ,  $\Delta U < 0$  and the particle is aligning in perpendicular to the magnetic field.

Morikawa et al. [60] found that the application of a magnetic field made the primary dendrite arms of MnBi in a Bi-4 wt% Mn alloy align along the magnetic

field and the AlFeSi intermetallic compounds crystallized from Al–Fe–Si melt align in perpendicular to the magnetic field. Moreover, on the basis of magnetization energy theory, some theoretical work was developed to support the experimental results. Li et al. [56] have studied the alignment behavior of the MnBi primary phase in Bi–Mn alloy under the magnetic field and found that the *c*-axis of the MnBi crystal (i.e., the easy magnetic axis) was aligned along the magnetic field direction. Textured crystal growth of Bi-2201 [61] and Bi (Pb) 2212 [62] has been obtained in a high magnetic field. All these studies have shown that a high magnetic field has a strong influence on the solidification microstructures and further research is needed. Dendrite growth, as one of natural phenomena and fundamental of processing materials, is an interesting and important topic for research. However, up to now, few works have been undertaken on the influence of a high static magnetic field on the dendrite growth. It is expected that dendrite growth may be modified by the presence of a high magnetic field, and the field may be a useful tool to control the solidification processes. Li et al. [48] studied the influence of a high magnetic field on the primary dendrite of  $\alpha$ -Al, and more detailed work was reported in [49]. Experimental investigations were made to study the growth of  $\alpha$ -Al, Al<sub>3</sub>Ni, and MnBi dendrites in directionally solidified Al–Cu, Al–Ni, and Bi–Mn alloys under an axial high magnetic field (Fig. 6.8). It was found that the growth behaviors of the dendrites under a high magnetic field changed significantly. The magnetic field was capable of aligning the primary dendritic arms, but the alignment behaviors were different for different dendrites. At a moderate growth speed, the magnetic field caused deflecting growth of the dendrite. At a higher growth speed, the magnetic field ( $B \leq 10$  T) increased the  $\alpha$ -Al primary dendrite arm spacing, although it was not capable of aligning the primary dendrite arms. Moreover, it was also found that the field can enhance the growth of the high-order dendrite arms and the formation of twin planes.

For the Bi-0.85 wt.% Mn alloy, the magnetic field increased the ratio of length to diameter and made the alignment of the MnBi dendrite more regular. This means that the field enhanced the growth of the MnBi dendrites along the solidification direction. However, for the Al-4.5 wt.% Cu alloy, the primary dendrite arms were deflected from the solidification direction and aligned at 45° to the solidification direction (Fig. 6.8b). For the Al-12 wt.% Ni alloy, the magnetic field caused the primary dendrite arms to align in perpendicular to the solidification direction (Fig. 6.8c). These results indicate that, for different dendrites, the influences of the magnetic field on the primary dendrite arms are different.

Magnetic alignment is frequently used in different processes, for example, in solidification processes (Fig. 6.9a), vapor deposition (Fig. 6.9b), and heat treatment [57, 63–67]. So far, metals with relatively low melting points are usually aligned in the solidification processes, while heat treatment is commonly used for Fe-based alloys.

Fig. 6.9a gives an example of magnetic alignment of primary crystals during solidification where chains of primary crystals are formed simultaneously due to the magnetic field enhanced interactions [63]. Vapor deposition is standard route for preparing metallic films and unique morphologies due to magnetic alignment can be achieved when a strong magnetic field is applied as illustrated in Fig. 6.9b [64]. The

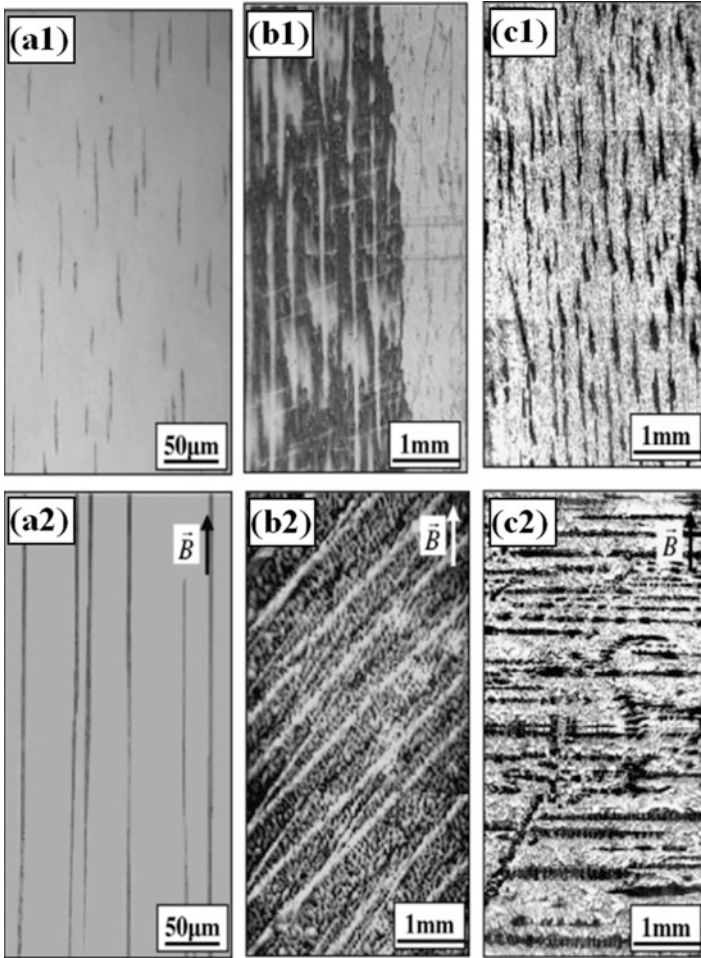


**Fig. 6.8** The influences of a 10 T magnetic field on the primary dendrite arms during the directional solidification of: (a) a Bi-0.85 wt.% Mn alloy, (b) an Al-4.5 wt.% Cu alloy, and (c) an Al-12 wt.% Ni alloy. The primary phases in above alloys are MnBi,  $\alpha$ -Al, and  $\text{Al}_3\text{Ni}$ , respectively [49] (reproduced with permission)

aligned structures may provide anisotropic physical properties and enhance the film performance. To improve magnetic alignment of metals especially during solidification, a number of techniques can be combined together. For example, unidirectional solidification or a thermal gradient can be easily imposed in parallel to the easy magnetization axis [64]. An improvement on alignment of  $\text{Tb}_{0.3}\text{Dy}_{0.7}\text{Fe}_y$  ( $1.85 < y < 1.95$ ) alloy was realized by using a 1 T magnetic field coupled with a unidirectional thermal gradient [58, 68]. Rotating magnetic fields are also applied to increase the magnetic alignment when the  $c$ -axis of the crystal is not the easy magnetization axis [57]. Figure 6.10 shows the magnetic alignment process of

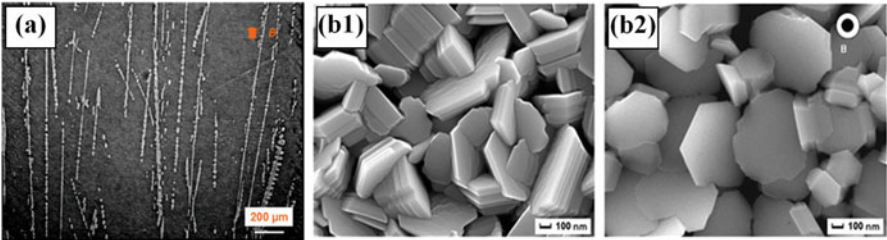


**Fig. 6.9** Alignment of metallic alloys under a high magnetic field: (a) alignment of primary Co in Co-B melt under a 3 T magnetic field [63] (reproduced with permission); (b) morphology of Zn-film by vapor deposition under a magnetic field, without (b1) and with (b2) magnetic field [64] (reproduced with permission)

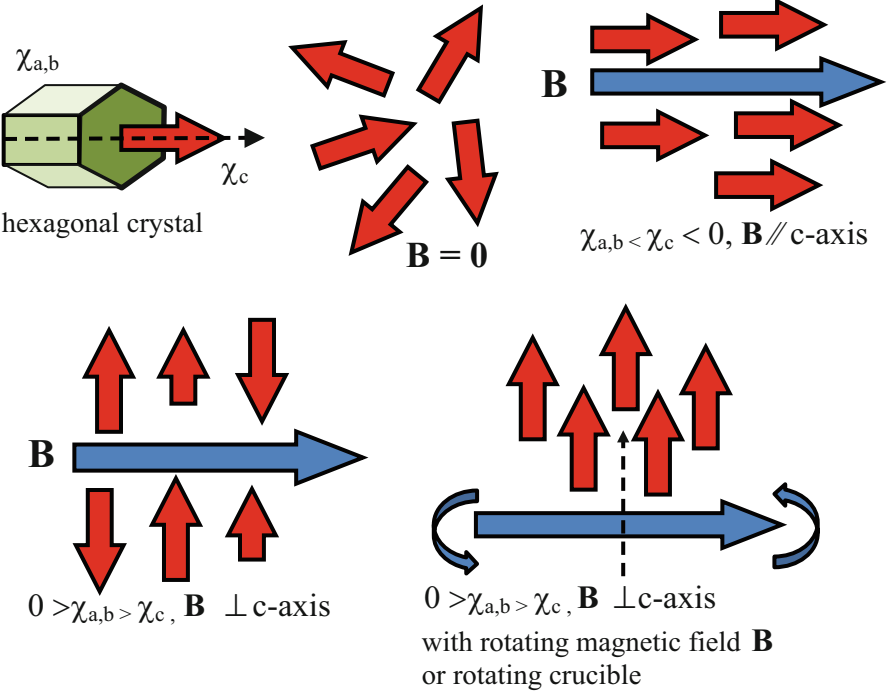


**Fig. 6.10** A schematic illustration of magnetic alignment of hexagonal crystals with different magnetic properties for diamagnetic materials. When  $\chi_c < \chi_{a,b}$ , a uni-axial alignment can be reached by applying a rotating strong magnetic field (from Tanaka S et al (2009) *c*-axis oriented ZnO formed in a rotating magnetic field with various rotation speeds. J European Ceramic Society, 29: 955–959)

some crystals with different magnetic anisotropy (assuming hexagonal crystals). When the magnetic susceptibilities  $\chi_c > \chi_{a,b}$ , i.e.,  $E_c < E_{a,b}$ , the *c*-axis of the crystal is aligned parallel to the magnetic field direction to achieve the lowest system energy. If  $\chi_c < \chi_{a,b}$ , the *c*-axis of the crystal will be perpendicular to the magnetic field direction, and it is difficult to reach a uni-axial alignment as shown in Fig. 6.9.

In this case, a rotating magnetic field can be used as indicated in Fig. 6.10, the magnetic field can be considered to be imposed in every direction in the  $ab$ -plane when the magnetic field is rotating (see the examples showed by Sun et al. [11] or Asai [3]). The axis with the smallest magnetic susceptibility ( $c$ -axis) will be perpendicular to the magnetic field and a uni-axial alignment is realized. Since it is difficult to rotate a superconducting magnet, an equivalent technique by rotating the sample is usually adopted.

### 6.2.3 Effects on Solidification Temperature

The effects of magnetic fields on the solidification temperature of metallic liquid, particularly the non-magnetic materials, were noticed just in the recent decade. The research in this field therefore is far from being completed. The present chapter reviews the relevant works that have been published so far.

In theory, the characteristics of any materials could be affected by magnetic fields because an external magnetic energy is imposed by the magnetic fields. But for non-magnetic materials, the magnetic energy induced even by a 10 T magnetic field is still far less than the thermal energy [69]. It has been known that magnetic fields have little effect on the phase transition of non-magnetic materials in thermodynamics. Therefore, a small amount of works have been done on the impact of magnetic fields on the phase transition temperature of non-magnetic materials. However, using a high-precision measuring method, a number of researchers have discovered a shift of phase transition temperature caused by the high magnetic fields. Rosenblatt [70], for the first time, experimentally observed the effect of magnetic fields on the nematic-isotropic phase transition temperature of octyl-cyanobiphenyl (8-OCB). The change of the phase transition temperature is proportional to the square of magnetic fields as illustrated by Fig. 6.11. This is in good

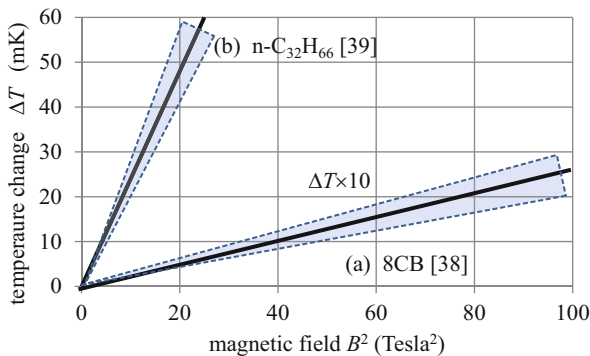


**Fig. 6.11** Relationship between the change of temperature and the square of magnetic field. The curves are fitted from the experimental data [70, 71]. Curve (a) nematic-isotropic phase transition temperature of octyl-cyanobiphenyl [70]; curve (b) melting temperature change of n-C<sub>32</sub>H<sub>66</sub> [71]. The shaded regions show the uncertainty of the experimental data

agreement with the theoretical prediction. By using high-precision DSC, Inaba [71] found that the melting temperature of  $n\text{-C}_{32}\text{H}_{66}$  increased by approximately 60 mK under a 5 T magnetic field. They found that magnetic fields could also affect the melting of  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  [72]. Indeed, their melting temperatures increased by 5.6 mK and 21.8 mK, respectively, under a 6 T magnetic field. Such changes are proportional to the square of magnetic fields or the magnetic energy. These results did not fit the theory well and cannot be explained by the Clapeyron equation. In order to interpret the results, instead of static susceptibility they used, the dynamic one was used to estimate the influence of magnetic field on the phase transition temperature.

For the effects on solidification temperature, Valko et al. [69] theoretically analyzed the liquid-to-solid transition temperature of non-magnetic materials under magnetic field. They proposed that the thermodynamic parameters of the liquid-to-solid equilibrium phase transition could be affected by the magnetic fields and derived the following equations to calculate the influence of magnetic field on solidification pressure and temperature:

$$\Delta P = P_H - P_0 = \frac{1}{2}\mu_0(\chi_l - \chi_s)H^2 \frac{1}{\Delta V_0} \quad (6.30a)$$

$$\Delta T = T_H - T_0 = \frac{1}{2}\mu_0(\chi_l - \chi_s)H^2 \frac{1}{\Delta S_0} \quad (6.30b)$$

where  $\chi_l$  and  $\chi_s$  are the volume susceptibilities of the liquid and solid phase, respectively,  $\Delta V_0$  is the volume change,  $\Delta S_0$  is entropy change,  $\mu_0$  is the magnetic field permeability of vacuum. For paramagnetic and diamagnetic materials, their susceptibility commonly is in the order of  $\chi \approx \pm 10^{-(5-6)}$  under a 100 T magnetic field,  $\Delta P \approx \pm (0.1 - 0.01)$  bar,  $\Delta T \approx 10^{-(3-5)}$  K, on condition of normal melting ( $dT/dP > 0$ ), the melting temperature of paramagnetic material ( $\chi > 0$ ) increases, whereas the diamagnetic materials ( $\chi < 0$ ) melting temperature decreases.

Li et al. [73] argue that Valko's theory relies on the hypothesis that the entropy and susceptibility of materials are invariable. But, both entropy and magnetic susceptibility are affected by magnetic fields. To take both factors into account, Magomedov [74] derived the following equations:

$$\Delta P = P_H - P_0 = - \left\{ \frac{\Delta(\chi)}{\Delta[d\chi/dP]_{T,H}} \right\} \times \ln \left\{ \left| 1 + \frac{\Delta V - \Delta V_0}{\Delta V_0} \right| \right\} \quad (6.30c)$$

$$\Delta T = T_H - T_0 = - \left\{ \frac{\Delta(\chi)}{\Delta[d\chi/dT]_{P,H}} \right\} \times \ln \left\{ \left| 1 + \frac{\Delta S - \Delta S_0}{\Delta S_0} \right| \right\}, \quad (6.30d)$$

where  $P_H$  and  $T_H$  are phase transition pressure and temperature under  $H$  magnetic field, respectively,  $P_0$  and  $T_0$ , respectively, stand for the phase transition pressure and temperature with no magnetic field,  $\Delta V$  and  $\Delta V_0$  are the volume changes, and  $\Delta S$  and  $\Delta S_0$  are the entropy changes. Many researchers found that the phase transition



temperature of the non-magnetic materials changed dramatically under high magnetic fields. In 1992, Hasegawa et al. [75] studied the solidification of a copper melt under magnetic field and found that the maximum undercooling temperature under magnetic field was higher than that without magnetic field. Li et al. [73] measured the solidification temperature of Bi, and found that the solidification temperature of Bi increased by about 6 K under a 12 T magnetic field. Zhang et al. [76] studied the undercooling behavior of pure Sb under a gradient magnetic field, and found that the nucleation temperature decreased under a positive gradient magnetic field while the magnetic field is raising. Liu et al. [77] found that the nucleation temperature of a Ni-90 at.% Cu alloy and pure Sb decreased, and the undercoolings increased under a 11.5 T magnetic field. Wang et al. [78] investigated the recalescence behavior of an undercooled CoSn alloy under magnetic field, and found that the nucleation and the maximum recalescence temperature of the undercooled melt were affected by the magnetic field. Using differential thermal analysis, Li et al. [79–82] systematically studied the nucleation temperature and undercooling of non-magnetic metals (pure Bi, pure Al and Al–Cu alloy, etc.) during solidification. They found that the solidification temperature of pure Al and Al–Cu alloy decreased, but that of pure Bi increased with magnetic fields.

#### **6.2.4 Thermo-Electric Magnetic (TEM) Effects**

Before discussing the thermo-electric magnetic (TEM) phenomena and effects in the solidification processes, the historical development on the thermo-electric magneto-hydrodynamics phenomena is briefly reviewed here to provide the historical and technological background.

##### **6.2.4.1 Interactions Between Thermo-Electric Currents and Magnetic Fields**

The thermo-electric currents (TEC) is the electric currents induced by heat only and three serial phenomena make up of the thermo-electric effect. They are Seebeck effect that converts temperature difference directly into electricity, Peltier effect that produces heating or cooling at an electrified junction of two different metals, and Thomson effect that generates heating or cooling for a current-carrying conductor in a thermal gradient. The three phenomena were discovered successively in 1821 by Thomas Johann Seebeck, in 1834 by Jean-Charles Peltier, and in 1851 by Lord Kelvin [83]. Although the thermo-electric effect was discovered as early as in the 1850s, its interaction with an external magnetic field was studied almost one hundred years later during an attempt to pump liquid metal though the Lorentz force induced by TEC and magnetic field in nuclear fusion generator [84, 85]. In order to convey the heat generated by nuclear fusion to a hot engine, liquid metal coolant was chosen as the medium to transfer the heat. Thermal gradient exists along the heat

**Table 6.6** The key development and progress concerning the interactions between thermo-electric currents and magnetic fields

| Year | Key researcher                      | Events                                                                                                                              |
|------|-------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------|
| 1951 | W. Murgatroyd                       | Improvements in or related to heat transfer systems. <i>U.K. Patent Appl.</i> 20911/51 [86]                                         |
| 1954 | E. Luebke<br>L. B. Vandenberg       | Compact reactor power plant with combination of a heat exchanger thermoelectric pump (also <i>U.S. Patent</i> 2.748.710, 1956) [85] |
| 1956 | K. F. Schoch                        | An experimental liquid metal thermoelectric electro-magnetic pump-heat exchanger [87]                                               |
| 1961 | D. von Rex                          | Thermoelectric pump for liquid metal [88]                                                                                           |
| 1964 | J. F. Osterle<br>S. W. Angrist      | The thermoelectric hydromagnetic pump [89]                                                                                          |
| 1964 | S. R. Rocklin                       | Thermoelectric pump <i>U.S. Patent</i> 3.116.693 [90]                                                                               |
| 1965 | M. A. Perlow<br>K. A. Davis         | The development of the SNAP-10 thermoelectric pump (also <i>U.S. Patent</i> 3.288.070, 1966) [91]                                   |
| 1969 | M. de Cachard<br>P. Caunes          | Fuel elements of sodium thermosyphon for irradiation cell [92]                                                                      |
| 1969 | V. S. Makarov<br>A. Kh. Cherkasskii | Pressure-consumption characteristic and efficiency of a thermoelectromagnetic pump [93]                                             |

exchanging tube naturally. Meanwhile, for confining/stabilizing the plasma and protecting windings from neutron bombardment, the fusion reactor blanket must be immersed in a magnetic field. In this senario, the fusion reactor blanket generators provided the enviroment where TEC interacts with a magnetic field. Under intensive demands for developing fusion reactor generators by taking the advantage of the interactions between TEC and magnetic fields, relevant progresses had been achieved and patents filed in the context of fast fission reactors cooled by liquid metal. Table 6.6 lists the key developments and patents concerning the interactions of TEC and external magnetic fields.

Similar to the paper published by Hannes Alfvén in 1942 that marked the establishment of fully-fledged magnetohydrodynamics theory, the paper published by Shercliff in 1979 [12] marked the establishment of the thermo-electric magneto-hydrodynamics (TEMHD) theory, and the accomplishment of cross-diciplinary field by coupling TEC and magnetic fields together. Although his paper was in the context of fusion reactors and dealt with the flows of liquid metal coolants in heat exchange process, he proposed and showed the possibility of applying TEMHD to metallurgical processes as well, which is an important topic for this chapter. Shercliff published three more papers to enrich the theory and describe other interesting phenomena and applications [94, 95]. It is natural to think about whether and how can this new discovery and theory be used, especially for processing of materials. In this section, we review the researches on TEMHD in the solidification processes.

#### 6.2.4.2 TEM Flows in Solidification

Hereafter, the term, Thermo-Electric-Magnetic Convection (TEMC), is used to replace the term TEMHD used by Shercliff, in order to link more logically to the concept of “thermo-electric magnetic (TEM).” Initially, Shercliff’s attention was mostly focused on TEM flows in nuclear reactors, the attempt to apply such phenomenon to metallurgical processes was firstly made by some former Soviet Union scientists in crystal growth processes [13, 14, 96], and then by others in the solidification of metallic alloys [97–99]. In 1981, Mikelson and Karklin [13] investigated the control of crystallization processes by magnetic fields. They found that currents generated by the thermal electromotive force in the crystallizing body might affect the crystal growth if a magnetic field was present. They proved the existence of TEC on the conditions that the magnitude of TEC cannot be constant as a direct current. Consequently, it should induce a variation for the magnetic fields they observed. However, the paper did not clearly indicate where the influence was originated from, by the TEM flows ? TEM force? or both?

Some years later, an explicit proof that TEM flows can influence the growth of bulk single crystals was given by Gorbunov in 1987 [14]. He provided an experimental evidence to demonstrate the existence of TEM flows by visualizing the motion of an In–Ga–Sn melt surface under an imposed temperature gradient in the presence of a vertical static magnetic field. The velocity measurement of the melt surface showed that the rotating velocities increased to its maximum when the magnetic field was about 0.1 T, and then decreased with continuously increasing of the magnetic field. The similar trend was confirmed numerically by Kaddeche et al. seven years later [100]. Such behavior is consistent with the theoretical prediction described in Sect. 6.1 (Fig. 6.3). Furthermore, Gorbunov observed that when the direction of magnetic field was reversed, immediately, the rotation direction of the flow reversed, demonstrating clearly that flows must be linked to the imposed magnetic field. Gorbunov and Lyumkis [96] also explained that the strong deformation of crystal shape occurred in growing InSb single crystal under a magnetic field was caused by the TEM flows as well.

Exploration of the beneficial effects of TEM flows on the solidification of metallic alloys was firstly made in 1991, Alboussière et al. [97] proposed that the Lorentz forces in dendritic zones produced by the interactions between TEC and imposed magnetic fields can enhance the mixing of solutes. In order to prove the existence of TEM flows during solidification under magnetic fields, they directionally solidified Bi–Sn and Pb–Sn alloys without and with a magnetic field. They found that, for Bi–Sn alloy, solute convection under magnetic field was much stronger than that without as shown in Fig. 6.12. But for Pb–Sn alloy, no effect was detected under a magnetic field. Actually, Pb–Sn has much smaller absolute thermo-electric power ( $0.1 \mu\text{V/K}$ ) than Bi–Sn ( $70 \mu\text{V/K}$ ), these results indeed demonstrated the existence of TEM flows in solidification. To obtain deeper understanding, in 1994 Moreau et al. [101] studied the dendritic regime during directional solidification of metallic alloys. A numerical model was developed to estimate the velocity of typical interdendritic

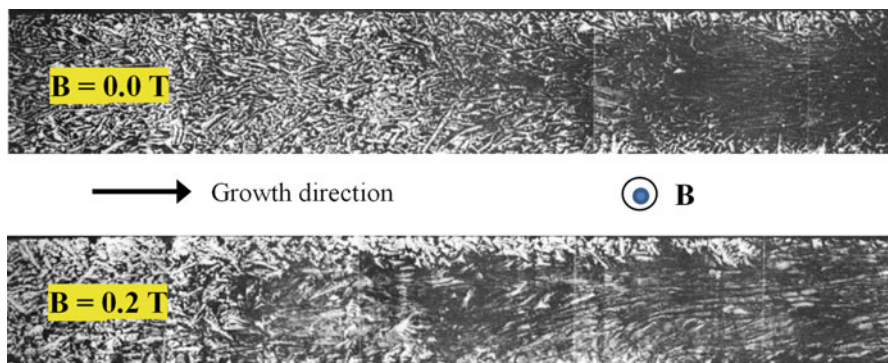


**Fig. 6.12** Directional solidification of a Bi-40 wt% Sn alloy without and with a transverse magnetic field [97] (reproduced with permission)

TEM flows. In addition, Seebeck and Peltier effects in the absence of an external magnetic field were also analyzed. They found that both effects could have a destabilizing influence on liquid–solid interface stability. Lehmann and Moreau did further investigations on TEM flows in solidification [15, 102, 103]. They modified interdendritic convections by taking into account the effects of TEM flows and introduced a simple model to simulate the TEM flows in the mushy zones. Comparison between the modelled and the experimental results is made as well. Figure 6.13a–c shows some typical microstructures obtained under different TEM flows.

In parallel, the influences of TEM flows on crystal growth were also studied by numerous researchers. Cröll et al. [105] found a new type of pronounced dopant striations that was quite different from the ones caused by buoyancy or surface tension driven convections. They proposed that the new type of striations was caused by TEM flows during growth, when they grew the silicon using a floating-zone method under a strong static axial magnetic field [105]. Khine and Walker [21] studied TEM flows during Bridgman semiconductor crystal growth under a uniform axial strong magnetic field, and found the similar change trend between the magnitude of TEM flows and the imposed magnetic fields as demonstrated by Gorbunov [14]. They estimated the azimuthal component velocities of TEM flows and found it could reach several micrometers per second. Consequently, such flows may generate the rotational-like striations during crystal growth. Khine et al. [106] extended their works to study TEM flows in crystal growth with a moderate or weak magnetic field, and tried to find out how TEM flows varies with magnetic field strengths and temperature difference along crystal–melt interface. They found that the velocities reached its maximum value in a magnetic field corresponding to a Hartmann number of the order of 10. Yesilyurt et al. [107] numerically simulated the effect of TEM flows on Bridgman growth of  $\text{Ge}_{1-x}\text{Si}_x$ , and found that the meridional convection altered the composition of melt and then the shape of growth interface. By optimizing their numerical model, they predicted the TEM flows under varying gravity

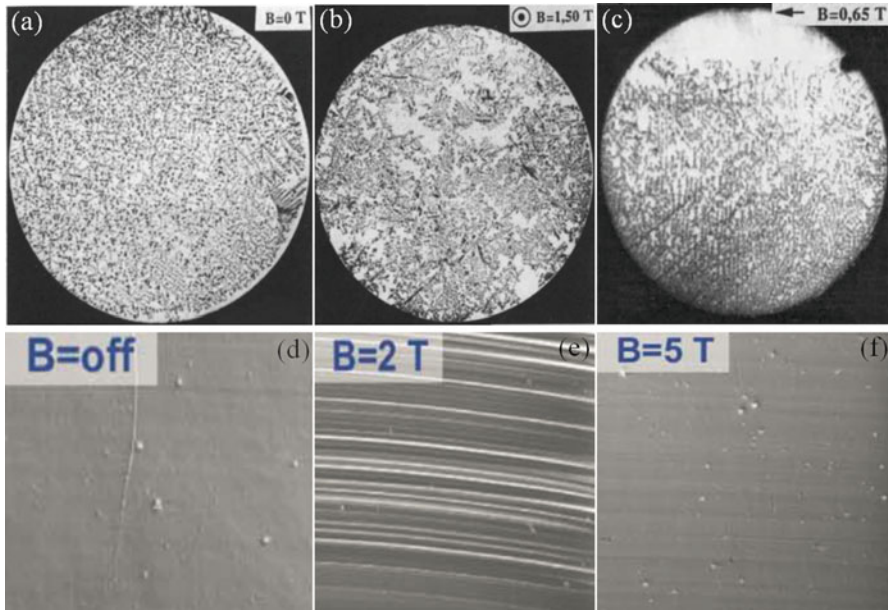


**Fig. 6.13** Transverse structures of Cu–Ag alloys directionally solidified without magnetic field [15] (a), under a 1.5 T longitudinal magnetic field (b), and under a 0.65 T transverse magnetic field (c); GeSi crystal grown under different longitudinal magnetic field flux strength [104], (d) 0 T; (e) 2 T; (f) 5 T [104] (reproduced with permission)

[108]. Walker et al. [109] further strengthened the explanation used in their previous paper by numerical calculation. The latest research on influence of TEM flows during crystal growth was performed by Dold et al. [104]. They again experimentally proved that there is a maximum velocity of TEM flows if the imposed magnetic field continuously increased as shown in Fig. 6.13d, e. The findings agreed with the measurement performed by Gorbunov [14] and numerical prediction by Khine et al. [106].

In the new century, research on the effects of TEM flows during solidification of metallic alloys continued in Liaoning Technical University, China. The influences of TEM flows on the microstructures of Al–Cu and Al–Si alloys were reported in two PhD theses in 2002 and 2006, which provided experimental evidence of the existence of TEM flows during solidification of metallic alloys under a static magnetic field that could modify the microstructures [23, 110, 111]. Other research groups began to move onto this research direction because of the growing interest in this field. For example, the successful cooperations between Grenoble Institute of Technology/SIMAP-EPM laboratory in France and Shanghai University in China led by Prof. Yves Fautrelle on the French side and Prof. Zhongming Ren and Prof. Xi Li on the Chinese side have made significant progresses and impact in this field.

Many new types of phenomena resulted from the effects of TEMC on solidification were found. By summarizing the published informations so far in this field, it is

confident to declare that the TEMC effects are responsible for many striking and unexpected phenomena as described below:

- Significant bulk flows in the vicinity of the solidification front,
- Enhanced liquid percolation in the mushy zone,
- Action of the TEM forces on the solid.

It must be stressed that the amplitude of the magnetic field is an important factor. However, other factors such as its orientation (axial or transverse) with respect to the solidification interface as well as the temperature gradient are also playing very important roles.

### Bulk TEM Flow

As already discussed, many evidences of TEM flows in the liquid zone as well as their effects on solidification microstructures have been published. Nevertheless, the solidification structures span across several length scales, from the largest one, i.e., bulk geometry, to the smallest one, i.e., the primary dendrite arm spacing (PDAS) and secondary dendrite arm spacing (SDAS). The remaining question is that how the TEM convection varies at the different length scales. Li et al. qualitatively evaluated the TEM flows in different typical length scales and compared the solid structures obtained under different axial magnetic field intensities [17, 23, 112]. It was found that the effects of magnetic fields vary at different length scale. Generally, as the structure become smaller, a larger magnetic field is needed to damp the TEM flows. Table 6.7 shows the maximum TEM velocity shifted toward large magnetic field strengths as the length scale decreases. Note that the orientation of the magnetic field with respect to the solidification front may lead to different force distributions and flow configurations. Investigating the TEM force acting on the spherical particle, Baltaretu et al. [113] showed that when the magnetic field is in parallel to the applied temperature gradient, the liquid around the particle is submitted to a torque which caused the rotation of the liquid. In the case of a transverse magnetic field

**Table 6.7** Values of the parameters deduced from the analysis of the order of magnitude provided in Sect. 6.1 for several solidification scales [17]

|                                                                              | $\lambda = R = 1500 \mu\text{m}$ | $\lambda = 100 \mu\text{m}$ | $\lambda = 1 \mu\text{m}$ |
|------------------------------------------------------------------------------|----------------------------------|-----------------------------|---------------------------|
| $B_{\max} = \left( \frac{\rho SG}{\lambda \sigma} \right)^{1/3}$             | 0.17 T                           | 0.43 T                      | –                         |
| $u_{\max} = \left( \frac{\lambda \sigma}{\rho} (SG)^2 \right)^{1/3}$         | 72 mm/s                          | 29 mm/s                     | –                         |
| $B'_{\max} = \frac{1}{\lambda} \left( \frac{\rho \nu}{\sigma} \right)^{1/2}$ | –                                | –                           | 25 T                      |
| $u'_{\max} = SG \lambda \left( \frac{\sigma}{\rho \nu} \right)^{1/2}$        | –                                | –                           | 0.5 mm/s                  |
| Reynolds number $Re$                                                         | 108                              | 2.9                         | $5 \times 10^{-4}$        |



(with respect to the temperature gradient), the particle itself is subjected to a transverse TEM force, and a complex vortical flow is developed around the particle. The order of magnitude of the TEM body force density  $F_{TEM}$  acting on a spherical conducting particle is [113]

$$F_{TEM} = O\left(\frac{\sigma_s \sigma_l}{(\sigma_s + 2\sigma_l)} (S_s - S_l) \bar{G} B\right), \quad (6.31)$$

where  $\sigma_i$ ,  $S_i$ ,  $\bar{G}$ , and  $B$ , respectively, denote the electrical conductivity and the absolute thermo-electric power of each phases, the local temperature gradient, and the magnetic flux density. It is noteworthy from Eq. (6.31) that for liquid metals the product  $\sigma S$  is usually of the order of one (cf. Table 6.4) and  $F_{TEM}$  may be very large for significant temperature gradient and magnetic flux density. For example, let us consider an aluminium solid particle in a liquid aluminium bath. Using the numerical values provided in Table 6.4, the value of  $F_{TEM}$  is 7445 N/m<sup>3</sup> for  $B = 1$  T and  $\bar{G} = 2000$  K/m. The latter value is significant compared to gravity body force  $(\rho_s - \rho_l)g$  acting on the particle. Figure 6.14 illustrates the two types of flows around a conducting spherical particle, in the case of an equiaxed grain, both in a transverse and axial magnetic field. This will be also illustrated in Fig. 6.17 below. Similar results were obtained by Li et al. who thoroughly investigated TEM flows and its effects on solidification in a low axial and transverse magnetic field [115]. The distribution of TEC and velocities of TEM flows were simulated by Wang et al. [116] and agreed reasonably well with the experimental results. They clearly show the difference on the flow patterns due to the magnetic field orientation. Figure 6.15 illustrates the influence of the magnetic field orientation on the flow near

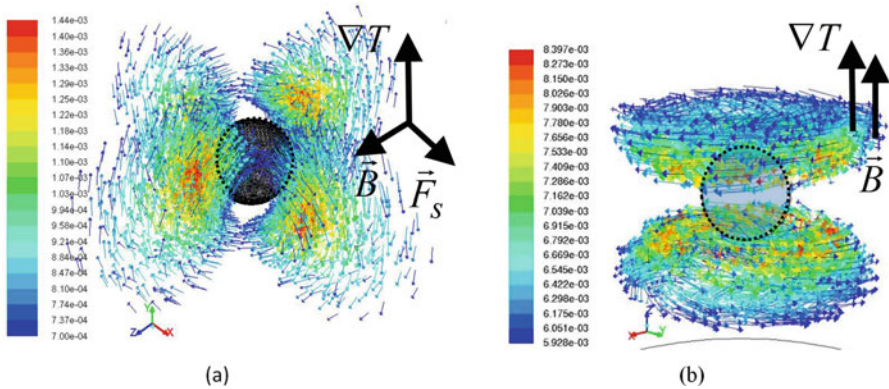


**Fig. 6.14** The flow patterns around an electrically conducting spherical particle under a DC magnetic field. The vertical temperature gradient at infinity is  $G_\infty = 3000$  K/m whereas the magnetic field amplitude is  $B = 0.08$  T. **(a)** A transverse magnetic field with a particle of the radius  $R = 0.050$  mm, the image shows the direction of the transverse TEM force density  $\vec{F}_s$  acting on the particle. The velocity scale is m/s. **(b)** An axial magnetic field with a particle of the radius  $R = 0.15$  mm. The unit for the velocity is m/s [113] (reproduced with permission)



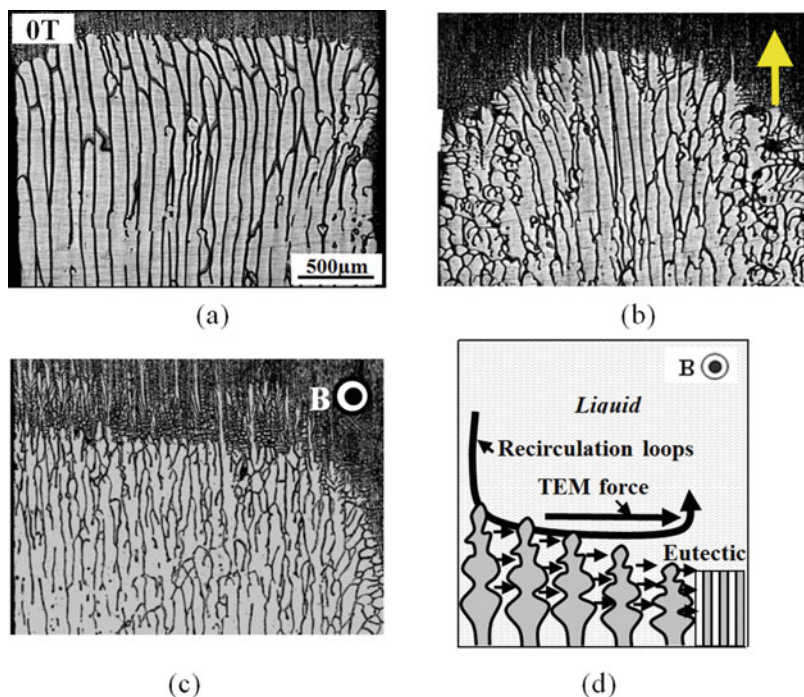


**Fig. 6.15** Modification of the interface shape profiles under transverse and axial magnetic field Al-2.5 wt% Cu alloy, diameter of the sample 3 mm (pulling velocity  $R = 10 \mu\text{m/s}$ , axial temperature gradient  $G = 60 \text{ K/cm}$ ). (a)  $B = 0 \text{ T}$ , (b) axial magnetic field  $B = 0.5 \text{ T}$ , (c) transverse magnetic field  $B = 0.5 \text{ T}$ , and (d) sketch of the TEM flow both in the liquid bulk and in the mushy zone under a transverse magnetic field [115]

solidification cells. In situ observations by X-ray imaging were performed by Yasuda in Japan [117]. It was believed that he was probably the first researcher to make in situ observation of the TEM flows during directional solidification of metallic alloys. With the increasing interest on TEM flows, more and more systems were investigated and reported. For example, TEM flows were validated in superalloys DZ417 by Ren et al. [118], and they found a dramatic increase of the number of dendrites. For hypereutectic Al–Al<sub>2</sub>Cu alloy, Shen et al. found that the distance between primary Al<sub>2</sub>Cu dendrites and eutectic interface was changed [119].

### Enhanced Liquid Percolation in the Mushy Zone

Since the thermo-electric currents are generated mainly near the liquid–solid interfaces, the mushy zone is obviously an active region where the TEC has an effect. In addition, the variation of density is particularly an important characteristic in the mushy zone. Alboussi re et al. [97] derived a theoretical expression to calculate the TEM force acting on the liquid phase in the mushy zone in a transverse magnetic

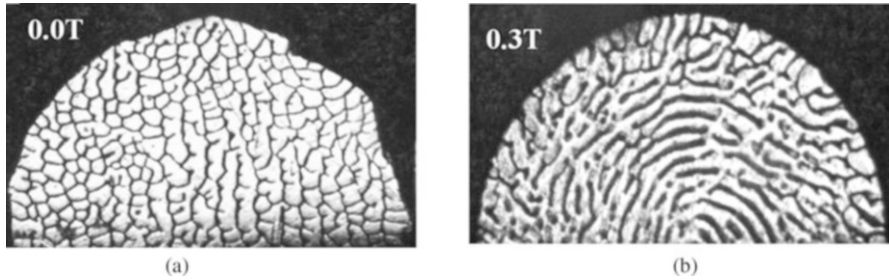


**Fig. 6.16** Transversal structures of an Al-0.85 wt.% Cu directionally solidified (a) without and (b) with DC magnetic field. The temperature gradient in the liquid is 62.8 K/cm. The cross-sections correspond to a distance of 3 mm below the columnar front [23] (reproduced with permission)

field. They showed that the liquid in the mush is subjected to a transverse TE force, which is capable of producing a significant draining of the mushy region. Other experiments also showed that, in transverse magnetic fields, the columnar front is deformed by the development of a large segregated channel, due to the TEM force acting on the liquid in the mushy zone. Directional solidification of an Al-4 wt.% Cu alloy coupled with in situ X-ray imaging confirmed the effect.

When an axial magnetic field (i.e., parallel to the temperature gradient) is applied, TEM force is mainly in azimuthal direction, not in the transverse direction. Thus, the flow in the mushy zone may be very different from the previous case. Global transverse recirculation loop shown in Fig. 6.15d doesn't exist anymore. It is remarkable to find that the mush flow may re-organize the solidifying structures. Figure 6.16 shows how the interdendritic region, hence the grain boundaries, is completely re-organized in a ring-like structure deep in the mushy zone [23]. It must be noted that the latter structure is possible only if the TEM convection exceeds the solidification velocity.

### TEM Forces Acting on the Solid

TEM forces act on both liquid and solid simultaneously when the solid is electrically conducting. Because the flows are easily detected in liquid but difficult in solid, researches of TEM forces acting on solid have just emerged more recently. TEM forces are proportional to the electrical conductivity of the medium, so for a good solid conductor, the TEM forces are larger in the solid than that in the liquid. Effect of TEM forces in solid was firstly pointed out by Li et al. in 2007 [112], when they tried to validate the TEM flows, they found cells were broken and liquid–solid interface became uneven under a higher magnetic field. Initial calculations showed that TEM flows should be mostly suppressed under such high magnetic field, but the breaking cells and uneven interface were believed to be caused by the TEM forces acting directly on the solid. Further experimental and theoretical investigations in five years found three important effects. There exist TEM forces in solid causing

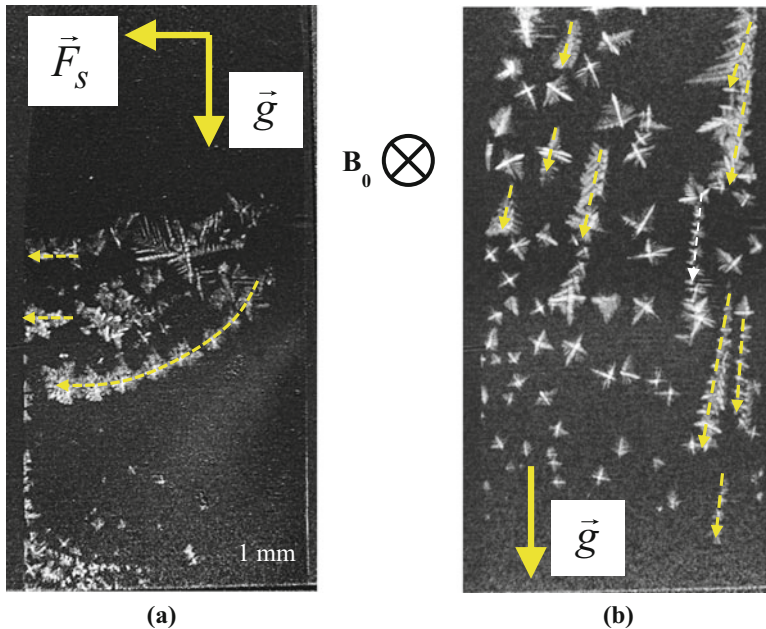


**Fig. 6.17** Images obtained by overlaying successive radiographs of the same solidification experiment, showing the effect of the vertical temperature gradient on the motion of equiaxed grains which are deflected on the left side of the sample due to the TEM force  $\vec{F}_s$  acting on each equiaxed grain. The alloy is an Al-4 wt% Cu, cooling rate = 2 K/min, in a transverse permanent magnetic field of  $B = 0.08$  T, (a) temperature gradient  $G = 20$  K/cm, (b) temperature gradient  $G \sim 0$  K/cm [114] (reproduced with permission)

columnar-to-equiaxed transitions (CET), TEM forces in solid causing solid particle displacements and liquid–solid interface instability. Displacement of equiaxed grains occurring during solidification was demonstrated by in situ X-ray observations [114]. Figure 6.17 shows that with magnetic field and without temperature gradient, the equiaxed particles fall freely; whereas under a transverse magnetic field in a vertical temperature gradient, they are deflected horizontally.

Li et al. [113, 120–122] studied the morphological instability of cells and dendrites during directional solidification under a high magnetic field, and found that at lower growth rates, cells and dendrites were twisted and deflected from the solidification direction. At moderate growth rates, side-branching of primary trunks and tip-splitting of cells were observed. They suggested that TEM forces in solid changed the surface chemical potential of the solids and alternated the surface tension of cellular and dendrite tips. In 2009 [120], combined with numerical simulations Li et al. confirmed the existence of a torque generated by a TEM forces at the top and the bottom of a cell or dendrite and pointed out the capability of TEM forces in causing fragmentation, hence CET, during directional solidification. In order to prove the CET could be triggered by TEM forces, Li et al. directionally

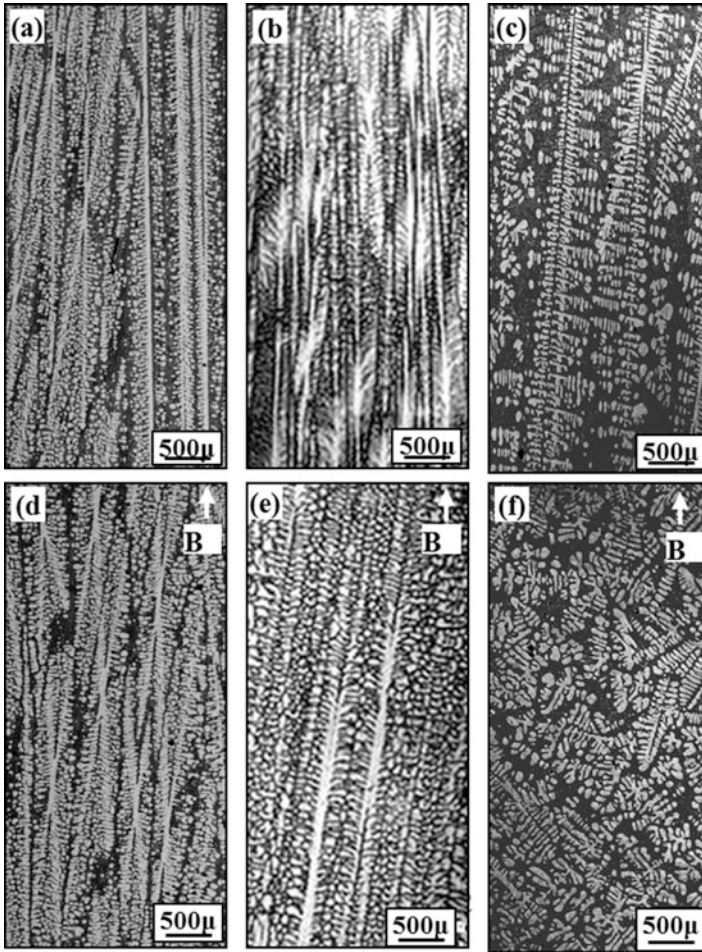


**Fig. 6.18** Effect of a 12 T high magnetic field on the  $\alpha$ -Al columnar dendrites in three Al-based alloys during directional solidification ( $G = 30$  K/cm and  $R = 100$   $\mu$ m/s). Without magnetic field: (a) Al-7 wt% Ni alloy, (b) Al-4.5 wt% Cu alloy, (c) Al-6 wt% Si alloy; with magnetic field: (d) Al-7 wt% Ni alloy, (e) Al-4.5 wt% Cu alloy, (f) Al-6 wt% Si alloy [124] (reproduced with permission)

solidified various alloys, such as Al-Cu, Pb-Sn, superalloys, Zn-Cu, Al-Si, and Al-Ni without and with high magnetic fields [123]. Electron back-scattered diffraction (EBSD) examination of the microstructure revealed that CET did occur under a sufficient high magnetic field. Figure 6.18 shows how a strong magnetic field may trigger a CET in Al-Si alloys (Fig. 6.18c, f) by dendrite fragmentation, whereas it is more difficult to generate an equiaxed structure in Al-Ni and Al-Cu alloys as shown in Fig. 6.18a, b, d, e [123, 124].



Li et al. [125] examined the local misorientation map of samples, and found that the crystal mismatch of sample solidified under 10 T magnetic field was more severe than that without magnetic field, which demonstrated that TEM forces did exist when magnetic field was applied. Figure 6.19 shows the drastic decrease in the quality of the Kikuchi pattern (31%) under the magnetic field which suggests that during the solidification process, the formation of the crystal has suffered strong distortion. This distortion certainly originates from some stresses.

The importance of the TEM forces acting on the solid may also be realized by analyzing the structure of the solidified material. Figure 6.20 clearly shows the

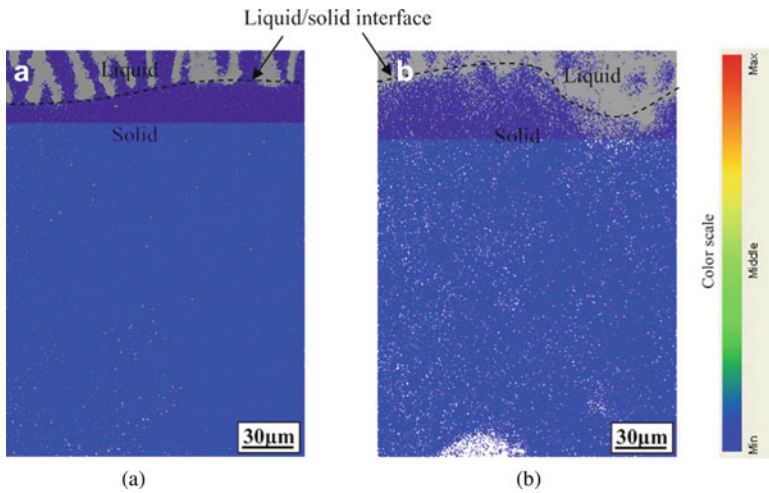


**Fig. 6.19** Local misorientation map of the sample without and with a 10 T magnetic field and the color scale. The local misorientation is averaged on  $3 \times 3$  neighboring pixels: (a) without the magnetic field; (b) with a 10 T magnetic field [125] (reproduced with permission)

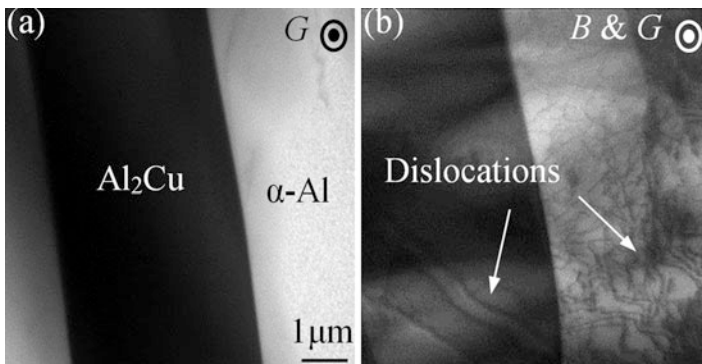


**Fig. 6.20** Bright field transmission electron microscope images of Al-40 wt.% Cu alloys obtained without (a) and with a 10 T magnetic field (b) at the growth rate of  $2 \mu\text{m/s}$  and the thermal gradient of  $6000 \text{ K/m}$  (provided by ZM. Ren and co-workers)

significant increase in the number of dislocations in a crystal solidified under a 10 T magnetic field.

### **6.3 Casting Technologies Using High Magnetic Fields and Applications**

In addition to the research and theories discussed previously, in material manufacturing processes and the related technology development, static magnetic fields are used mostly for their damping effects. When a magnetic field is applied to a free surface liquid flow, the motions of the fluid flow are subject to braking. Note that electromagnetic braking is not isotropic, and there is a tendency to re-organize the flow, making it two-dimensional parallel to the magnetic field. Magnetohydrodynamic effects of DC magnetic fields are mainly used for flow damping in the solidification processes, for example, in continuous casting of steels and in crystal growth.

#### **6.3.1 *Utilization of DC Magnetic Fields in Continuous Casting of Steel***

In steel continuous casting, DC magnetic fields are oftenly used. The so-called electromagnetic brake (EMBr) proposed by the ABB company is one of the mostly used devices. They are mainly located in the upper part of the casting as shown in Fig. 6.21. EMBr demonstrated its capability to improve the quality of the cast products by reducing inclusion/bubble entrapment, bulk and surface turbulence, and allowing higher casting speeds.

Many works are being performed in order to characterize the efficiency and to optimize such devices. The readers are referred to the many review articles [4, 6, 126–129]. The important effects are:

- Control of the flow in the liquid bulk, especially the liquid jet from the nozzle,
- Control of the triple point liquid–solid–mold at the beginning of the solidification
- Action on the free surface turbulence.

It is difficult in practice to achieve all the above objectives with a single device. Many types of electromagnetic brakes are designed according to the function to be fulfilled. This is illustrated in Fig. 6.22

Firstly, from a general point of view the EMBr stabilizes the flow pattern in the liquid. Under magnetic fields, the melt flow is nearly symmetrical and the jets behave more stationary but long period oscillations are not easy to suppress [4]. Moreover, the transverse magnetic field deflects the jet flowing out of the nozzle and prevents it from impinging the solidification front as sketched in Fig. 6.21. Part of the liquid jet

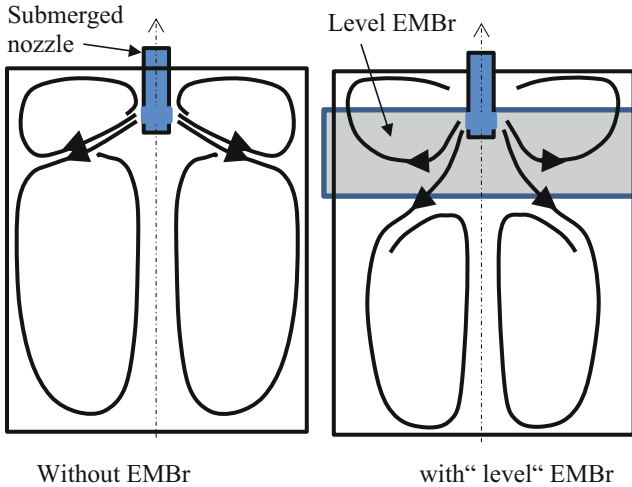


**Fig. 6.21** Sketch of the flow on mold wide centerplane: (a) without magnetic field, (b) with a “level”-type magnetic field

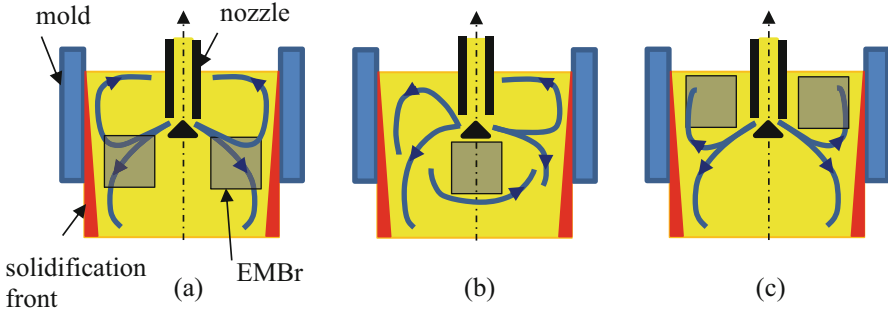


**Fig. 6.22** Various types of DC damping device (EMBr) for thin slab casting according to the required functions. (a) Deflection of the submerged nozzle jet minimizing the solidification front impingement; (b) local control of the exit jet and the left-right instability; (c) damping of the meniscus fluctuations [130]

is deflected upwards and accelerates inclusions and bubble decantation (see, for example, Fig. 6.21). Accordingly, the device minimizes the entrapment of argon bubbles contained in the liquid metal. The required magnetic field strength must be large enough but not too high. The order of magnitude of the magnetic field can be calculated by balancing the convection time  $\tau_c = \frac{L}{U}$  (Table 6.3 in Sect. 6.1) and the electromagnetic damping time



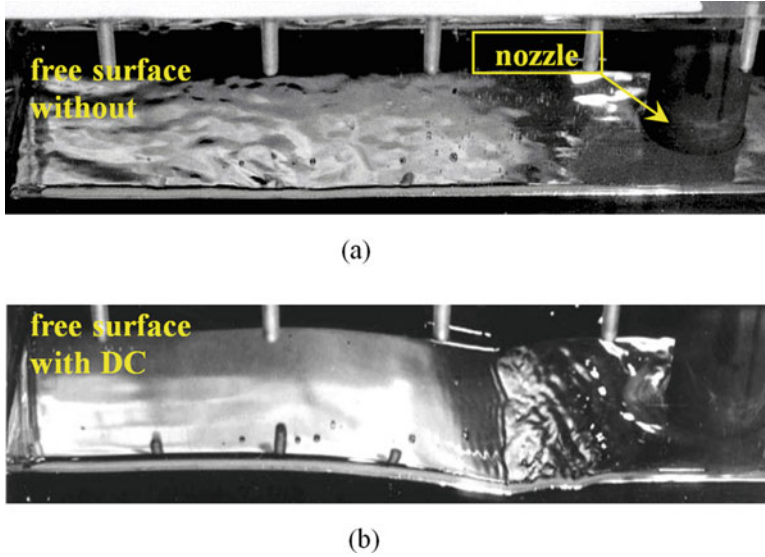


**Fig. 6.23** Free surface of a mercury model of a slab casting showing the damping of meniscus fluctuations [131] under a transverse DC magnetic field. (a) Without any magnetic field, small amplitude free surface oscillations corresponding to the free oscillation modes of the mold may be observed; (b) with a transverse magnetic field. The small wavelengths are suppressed, and there only remains a large amplitude wave with a long time period (reproduced with permission)

$$\tau_m = \left( \frac{\sigma B_0^2}{\rho} \right)^{-1},$$

$U$  and  $L$ , respectively, denoting a typical velocity in the liquid and the slab size.

The ratio between the two characteristic times is provided by the Stuart number  $St$  defined in Table 6.3. The electromagnetic forces must exceed inertia, meaning that the Stuart number must be significantly higher than unity. For example, let us consider a case with the following values:

$$L = 1.5 \text{ m}, U = 0.5 \text{ m/s}, \rho = 7000 \text{ kg/m}^3, \sigma = 0.7 \times 10^6 \text{ S/m}.$$

In order to fulfill the condition  $S \approx 10$  the magnetic field strength  $B_0$  must be equal to 0.18 T, a typical value which is usually found in practical situations.

As far as the free surface is concerned, it is usually needed to decrease the surface agitation which may responsible for oxidation or slag entrapment when the liquid–steel interface is covered by a slag. Another interesting consequence of the application of DC magnetic field relates to the decay of the free surface fluctuations as shown in Fig. 6.23. The efficiency of the damping depends on the position of the EMBR with respect to the free surface as indicated by Fig. 6.22c. Damping is caused by the breaking part of the electromagnetic forces expressed in Eq. (6.11) and other factors. The viscous wall friction in the Hartmann layer is also significant [132]. Figure 6.23 clearly shows by means of a 1/3 mercury model of a steel caster [131], how the free surface fluctuations are damped. In order to adapt more accurately the effect of the magnetic field to the sizes and shapes of the cast product, various

configurations have been designed. For example, direct action on the flow exiting near the nozzle exit may be exerted by the so-called local field configurations, whereas rule-type EMBr (or “level” field) has a more global effect on both the internal flow and the free surface swelling [127]. A combination of several EMBrs with a proper location in the upper part brings more flexibility and may be adapted to several configurations, especially for thin slab castings as shown in Fig. 6.22 [130, 133].

### 6.3.2 Utilization of DC Magnetic Fields in Crystal Growth

Single crystals for electronic applications are solidified or grown from semiconductor melts. While many different techniques have been developed, the Czochralski (Cz) and the floating zone (crucible less) methods are perhaps the two most popular ones. In the electronics industry, the majority of commercial crystals are grown using the Czochralski method, while the floating zone method is primarily used for the growth of single crystals of extra-high purity demanded for infrared sensor and detector applications [2, 5].

Both semiconductor crystal growth and metal casting involve solidifying liquid into solid and have similarities in process-design concepts. However, the quality demand for single crystals differs greatly from that for metals. Accordingly, the details of solidification-processing operation and required thermal and flow management are quite different. It is essential to control both the level of impurities, e.g., contamination of oxygen from the free surface or silica crucible, and to eliminate any major defects like striations. Moreover, the level of dislocations on the crystal must be as low as possible. That level is linked to the temperature distribution in the vicinity of the solidification front, especially temperature fluctuations, which are responsible for several defects. It is also important to control the convex shape of the liquid–solid interface. This requires that the temperature gradient be carefully controlled at the crystal–melt interface so that liquid atoms are given sufficient time to incorporate into equilibrium-lattice positions of the crystal. Thus, semiconductor crystals are usually small in size (100–500 mm in diameter), and growth rate is slow (of order of  $\mu\text{m/s}$ ) in comparison with metal ingots in order to avoid the so-called planar solidification front instability.

Semiconductors are good electrical conductors at liquid state. This property allows the use of electromagnetic fields to achieve a thermal and flow environment favorable for growing crystals of better quality. The details of operation, such as field configurations and process-control parameters, are different from metal solidification and are tailored to satisfy the more restricted processing and quality requirements imposed by the semiconductor industry. The trend is to process larger size crystals. However, as the pool dimension increases, thermal convection becomes more and more unsteady which justify use of damping systems like DC magnetic fields.

DC magnetic field has been proven to reduce effectively the level of turbulence and temperature fluctuations as well as the level of striations. In the present case, flows are mainly generated by natural convection and Marangoni effects caused by the surface temperature gradients. Magnetic fields of order of 0.05–0.3 T are commonly used. Those values may be retrieved by a simple analysis of order of magnitude. As for natural convection, the required order of magnitude of the magnetic field may be estimated from a balance between buoyancy forces and electromagnetic ones. The latter balance involves non-dimensional numbers such that:

- The Rayleigh number

$$Ra = \frac{g\beta\Delta TL^3}{\nu\alpha},$$

- The Hartmann number  $Ha$  already defined in Table 6.3,  $g$ ,  $\beta$ ,  $\alpha$ ,  $\Delta T$ , and  $L$ , respectively, denoting gravity, thermal expansion coefficient, thermal diffusivity, liquid pool overheat, and typical pool size.

The magnetic field damping action is effective if  $Ha^2 \geq Ra$  [134]. For example, let us consider a silicon pool with the following values:

$\beta = 1.1 \times 10^{-4} \text{ K}^{-1}$ ,  $\alpha = 2.2 \times 10^{-5} \text{ m}^2/\text{s}$ ,  $L = 0.3 \text{ m}$ ,  $\rho = 2510 \text{ kg/m}^3$ ,  $\sigma = 1.5 \times 10^6 \text{ S/m}$ . The Hartmann number must be at least equal to 1950. The corresponding value of the magnetic field amplitude is 0.14 T, a value which is usually encountered in practical situations.

Many works have been performed so far and readers are referred to some reviews (for example, [2, 5]). Nevertheless, it is not possible to entirely suppress any turbulence fluctuations due to partly the phenomenon which tends to make turbulence two-dimensional parallel to the magnetic field. Indeed, any vortex having its axis parallel to the magnetic field is weakly influenced by the breaking effect except near the walls. Note also that as mentioned in Sect. 6.2 thermo-electric magnetic convection was responsible for the generation of striations (Dold et al. [109] of Sect. 6.2). Furthermore, even though the magnetic field lowers the level of fluctuations, it also generates an electromagnetically driven flow because of the rotations of both the crucible and the solid crystal. The liquid rotation interacts with the applied magnetic field to create induced electric currents, producing an additional electromagnetic force contribution. The resulting flow may be quite complex. Many different magnetic-field configurations have been applied to achieve an adequate damping effect on convection in the melt pool (see, for example, Fig. 6.24), namely

- Transverse magnetic fields [135–137],
- Axial magnetic fields [138–141],
- Cusped magnetic fields [142–144].

The three configurations are globally efficient. However, axial or cusped magnetic fields are easier to use in large-scale configurations than transverse magnetic fields. Transverse fields break the axial symmetry of the flow and temperature, as

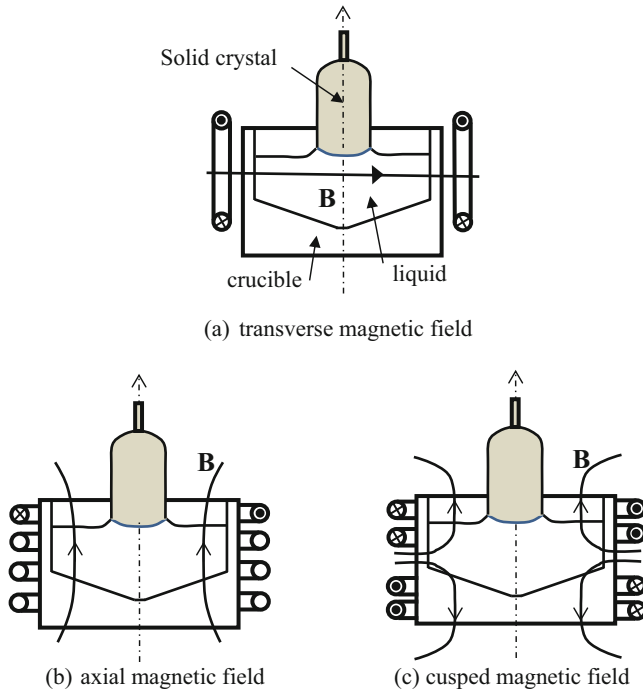


**Fig. 6.24** Sketch of the various electromagnetic devices used in Czochralski processes for single crystal growth. (a) transverse magnetic field. (b) axial magnetic field. (c) cusped magnetic field

well as the shape of the liquid–solid interface, whereas in axial configurations the magnetic field action is also effective in the vicinity of the solid crystal. Regarding horizontal magnetic fields, special types of defects, e.g., double spiral patterns [145] are observed. The situation may be even more complex when the crucible is rotating. Cusped magnetic field could be a good compromise.

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# Chapter 7

## Pulse External Fields Processing of Metal Alloys



Jiawei Mi

In 1831, Michael Faraday discovered the phenomenon of electromagnetic induction. Subsequently, Franz Ernst Neumann, James Clerk Maxwell [1], and Oliver Heaviside [2] proposed and formulated the governing equations for electromagnetic induction and its propagation. These are the fundamental laws and bases for electromagnetic processing of conductive liquid materials. From 1930s to 1970s, research and applications of electromagnetic processing of materials were mainly on using electromagnetic induction for (1) heating or melting metal alloys, (2) stirring melt for temperature and chemical homogenization, (3) applying electromagnetic force for levitating or shaping melt against gravity, and (4) applying electromagnetic brake for controlling liquid metal flow or reducing turbulence [3, 4]. At approximately the same period of time, study of the magnetic properties of electrically conducting fluids, originated in the field of astrophysics and plasma physics, was gradually developed into a new scientific discipline, i.e. magnetohydrodynamics (MHD) [4]. However, it was not until the 1970s that researchers and engineers in materials and metallurgical sectors started to realize that the established theories and knowledge in MHD could be used to solve the MHD phenomena in metallurgical processes where an electromagnetic field is present [5]. Following early research in Europe [3], the former Soviet Union and East Europe [4], the Iron and Steel Institute of Japan (ISIJ) recognized the huge potential of exploring the benefits of MHD in steel making and selected it as one of the major innovative subjects for future steel making technology. At that time, the term “Electromagnetic

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Metallurgy” was used [5], and later in 1989, Asai named it as “Electromagnetic Processing of Materials” (EPM) [5]. Since then, eight series of international Symposiums have been dedicated to the developments in this field [6], and the ninth Symposium (EPM 2018) will be held in Awaji Island, Hyogo, Japan on 14–18 Oct 2018 [<http://www.epm2018.org/>]. This Chapter primarily describes the historical and recent research and technological developments on pulse external fields with a focus on their applications to the solidification processes. Pulse field methods are relatively new compared to other types of electromagnetic processing methods. Two major types of pulse fields, i.e. pulse electrical currents and pulse magnetic fields, are described with a critical review on the most recent developments in this field. Most of the fundamental governing laws that are already covered in Chapters 3 and 6 will not be repeated here. Only those relevant to the nature of pulses are described. Finally, a summary is given to highlight the scientific issues that remain to be solved in the future.

## 7.1 Pulse Electric Current Processing of Metal Alloys

### 7.1.1 *Grain Refinement Due to Alternating and Pulse Electric Current*

Research on applying alternating and pulse electric currents into liquid metal alloys during the solidification processes has been seen reported since the 1970s. The main objectives of those works were to investigate mechanisms and effectiveness on grain refinement of different metal alloys. Some of the important work and findings are summarized and critically reviewed here.

In 1974, Vashchenko et al. [7] were probably the first to report the application of electric current in a cast iron during solidification. They found that electric current could suppress the occurrence of impurities and increase the mobility of carbon in cast iron [7]. Just a year later in 1975, Nishimura of Osaka Prefectural Industrial Research Institute and Kawano of Kyoto University, Japan [8] reported the effects on grain refinement of metal alloys by applying an alternative electromagnetic field into solidifying melts using the apparatus schematically shown in Fig. 7.1. Pure Al, Al–Cu, and Al–Zn alloys were investigated. The maximum magnetic flux density of the magnetic field imposed was  $\sim 0.27$  T, while the electric currents applied were from 0 to 20 A with an increasing step of 5 A for the different experiments [8]. They found that the grain refinement effect was roughly proportional to the applied current intensity, i.e. the vibration amplitude. The refinement effect was most appreciable in pure Al but not pronounced in the alloys containing a higher amount of an alloying element, nor in the titanium-treated alloys. Compared to mechanical vibration, electromagnetic vibration can remarkably decrease microporosities, but the segregation of a solute element near the interface of precipitates was not eliminated. They stated that the mechanism of grain refinement by this method was not clear, but may be due to the accelerated nucleation effect and by detachment of dendrite tips due to thermal fluctuations [8].

In 1985, Misra of the Indian Institute of Technology reported, in a short communication [9], that applying direct electric potential to the solidifying melt contained

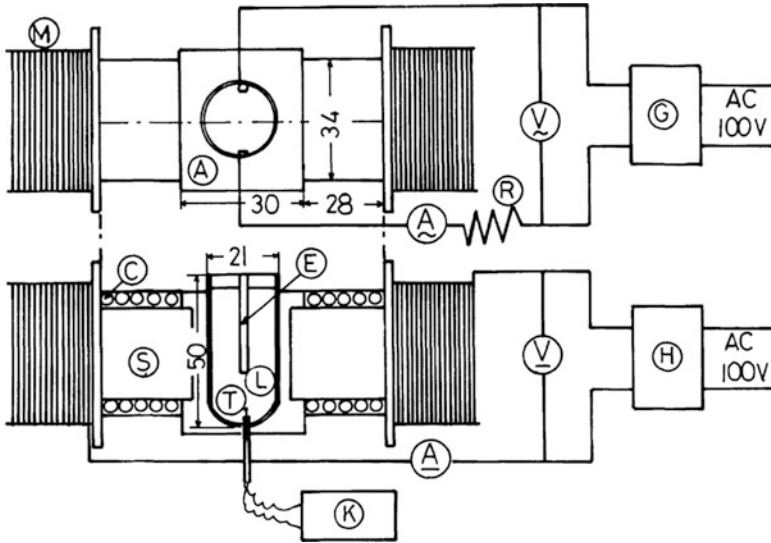


**Fig. 7.1** A schematic representation of the apparatus used for generating electromagnetic vibration in solidifying metal alloys in Nishimura's experiment [8]. A: refractory, C: cooling coil, E: two electrodes, G: transformer, H: rectifier, K: recorder, L: molten metal, S: mild steel, T: thermocouple (adapted from [8])

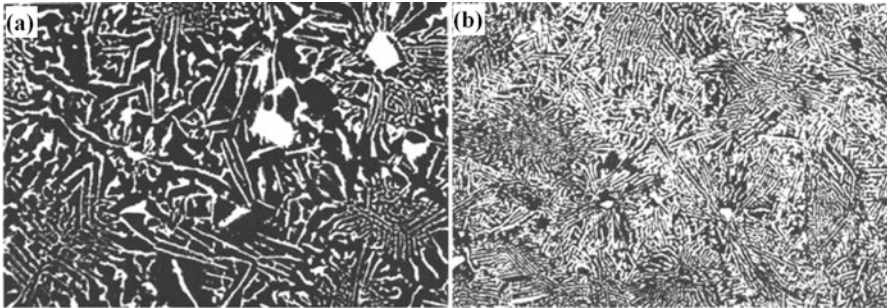


**Fig. 7.2** (a) The microstructure of a Pb-15%Sb-7%Sn alloy solidified without applying electric potential ( $\times 100$ ), (b) The modified microstructure of the Pb-15%Sb-7%Sn alloy solidified with a direct current ( $30\text{--}40\text{ mA/cm}^2$  at  $\sim 30\text{ V}$ ) passed through the melt until the completion of solidification with a cooling rate of few degrees a minute ( $\times 100$ ), (adapted from [9])

inside a glass tube (5 mm in diameter and 100 mm long) can change the normal process of nucleation and growth of equilibrium phases. A Pb-15%Sb-7%Sn alloy was used in the experiment [9] and part of the results are reproduced here and shown in Fig. 7.2. Unfortunately, Misra did not give any explanation on the mechanism for the changes of microstructures [9]. In 1986, Misra [10] applied a similar method (a direct current of  $-50\text{ mA/cm}^2$  at  $\sim 20\text{ V}$ ) to a high temperature alloy, Ni-Mg bearing cast iron during solidification. Again clear microstructural changes were



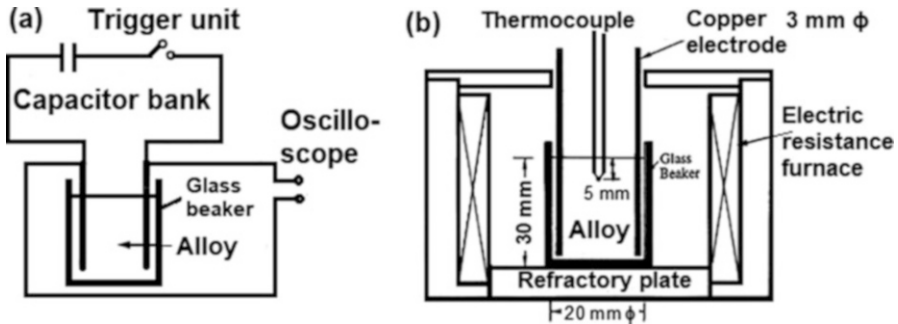


**Fig. 7.3** (a) The electric circuit for discharging pulse electric current, and (b) a schematic for the experimental apparatus and experimental setup (adapted from [11])

found due to the passing of direct current during solidification, but no explanation on the mechanism was given [10].

In 1990, Nakada, Shiohara and Flemings of Massachusetts Institute of Technology, USA reported a systematic experiment on “modification of solidification structures by pulse electric discharging [11]”. The experimental apparatus used and the circuit for discharging electric current is shown in Fig. 7.3. The capacitor bank (Fig. 7.3a) had 320  $\mu\text{F}$  capacitance and could be charged to a predefined voltage of up to 5000 V by using a regular AC electric source.

An Sn–15w%Pb hypoeutectic alloy was used in the experiment [11]. This alloy has a liquidus temperature of  $\sim 488$  K, and solidification is complete at the eutectic temperature of 456 K. The alloy samples were melted in an electric furnace and heated to 553 K (65 K of superheating), and then cooled at different cooling rates of 18, 11, and 6 K/min, respectively. The onset of solidification (nucleation of primary Sn phase) took place at  $\sim 480$  K. Pulse electric discharging (PED) was then carried out with different initial capacitor bank voltages, and different capacitor triggering times after the onset of solidification. Multiple capacitor dischargings were also used [11]. The voltage drop across the specimen during PED was measured using a digital oscilloscope (Fig. 7.3a). From the voltage drop, the discharge time and oscillating frequency were determined.

Figure 7.4a is an example of the measured voltage drop across the specimen after discharging the capacitor bank with an initial voltage of 2500 V. The voltage drop oscillated with a frequency of  $\sim 3$  kHz, and the discharging time was about 1 ms. A series of experiments were conducted [11], and it was found that (1) the time of triggering after onset of solidification, (2) cooling rates, and (3) initial capacitor bank voltage are the dominant control factors on determining the microstructure change from dendritic to transient to globular morphology. For example, Fig. 7.4b indicates how, at a cooling rate of 6 K/min, the transition from dendritic to global structure occurred with increasing of capacitor bank voltage and shortening of the time of trigger of PED. In addition, the voltage required for exact structural transition increased with increasing time of trigger after the onset of solidification.

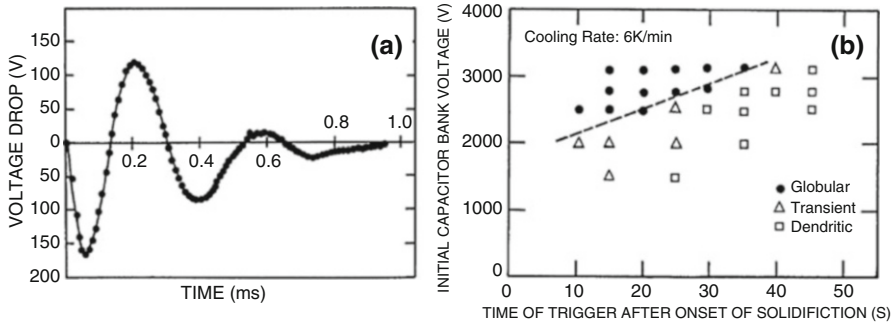


**Fig. 7.4** (a) An example of the measured voltage drop across a specimen during discharging with an initial capacitor bank voltage of 2500 V. (b) The relationship between microstructures, initial capacitor bank voltages, and time of trigger after onset of solidification at a cooling rate of 6 K/min (adapted from [11])

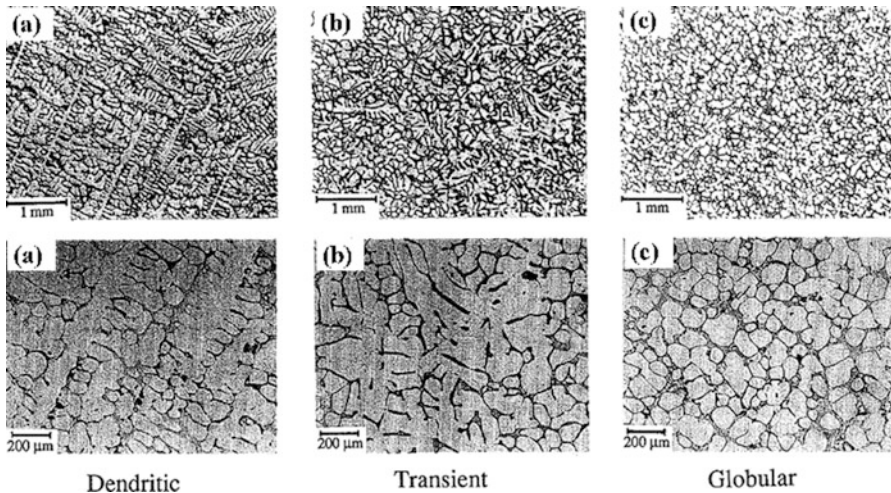


**Fig. 7.5** Typical examples of (a) the dendritic (the one below is the enlarged image), (b) transient, and (c) globular microstructures obtained in Nakada’s experiments (adapted from [11])

The typical examples of the dendritic, transient, and global structures obtained in Nakada’s experiments are shown in Fig. 7.5. Actually, the fraction of solid phase presented in the solidifying melt at the instant of triggering PED is critical for the transition from dendritic to globular microstructures. Figure 7.6a shows the relationship between the calculated fraction of solid and time of triggering PED after the onset of solidification for three different cooling rates [11].

In Fig. 7.6a, the critical upper limit of the fraction of solid in the melt in order to obtain globular microstructures is highlighted with shaded areas for three different initial capacitor bank voltages, 2500, 2700, and 3200 V, respectively. Figure 7.6b shows the relationship between the upper limit of the fraction of solid at which the

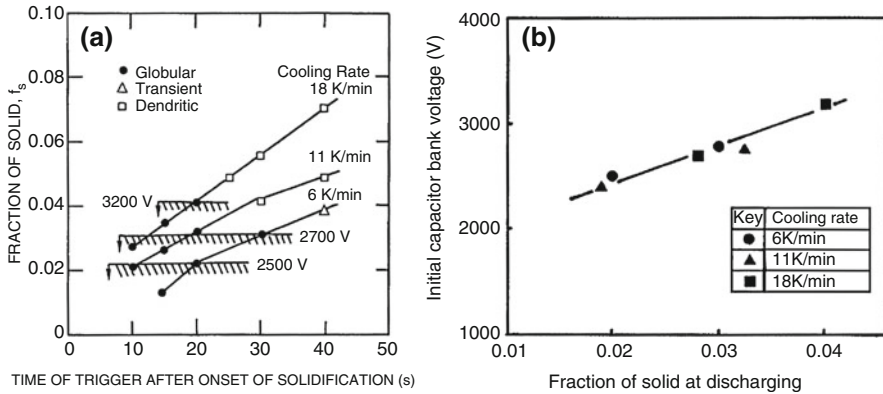


**Fig. 7.6** In the conditions of forming globular microstructures, (a) the upper limit for the solid fraction in the melt when different cooling rates and initial discharging voltages were used. (b) The relationship between the upper limit for the solid fraction and the initial discharging voltage (adapted from [11])

globular microstructure was obtained, and initial capacitor bank voltages. This figure shows more clearly that the limit of fraction of solid depends on the initial capacitor bank voltage and is independent of cooling rate [11]. Nakada et al. argued that when PED was conducted, the shock wave caused by discharging was observed on the surface of the molten metal. This is supposed to be the result of the pinch force at the moment of discharging. The strength of the pinch force can be calculated at any arbitrary position in the specimen and at any time during the discharging. The magnetic flux density and current density vary at each point of the specimen, which give rise to a pinch force gradient, resulting in local velocity differences in the molten metal and generating shear stresses. When the shear stress is high enough, dendrites are expected to be broken into globular fragments. However, in their paper, Nakada et al. did not calculate the shear stresses inside the specimen at PED during the experiments [11].

In 1994, Bamak, Sprecher, and Conrad of North Carolina State University, USA published a short communication in *Scripta Metallurgica et Materialia*, and attempted to provide more evidence for the mechanisms of grain refinement caused by applying electric current pulses into solidifying melts [12]. They used two commercial near-eutectic alloys, Sn–40%Pb and Sn–37%Pb. The alloys were melted and poured into a preheated Pyrex glass tube (8 mm I.D. and 10 mm O.D.), which had been bent into a flat-bottomed “U” shape (65 mm long flat). Cu wire electrodes (3.2 mm in diameter) were positioned at each upright end of the U-tube to apply electric current pulses. Their results showed that when an electropulsing of 1426 A/cm<sup>2</sup> was applied, the undercooling was increased to 9–13 °C as compared to just ~0.5 °C for the case without electropulsing (Fig. 7.7a). Associated with the increase in undercooling (Fig. 7.7b), the slope of  $dT/dt$  (the temperature rate change between the minimum undercooled temperature and the thermal arrest temperature) decreased, and the duration for arrest (solidification) time decreased as well.

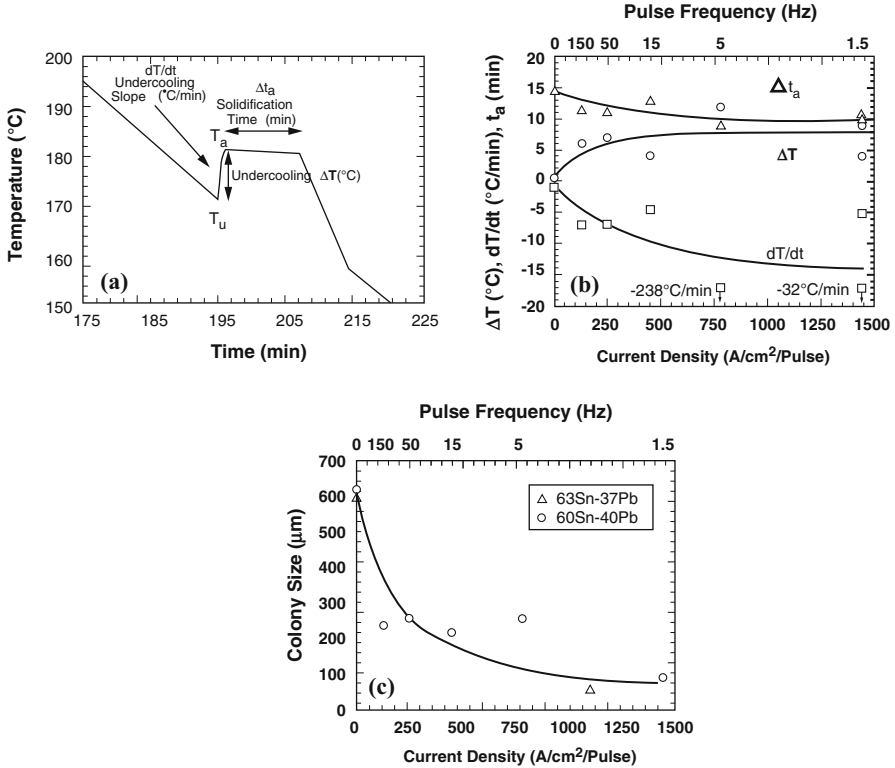


**Fig. 7.7** (a) The cooling curve during the solidification of a Sn-40%Pb with concurrent electropulsing of 1426 A/cm<sup>2</sup> and 1.5 pulses per second, and (b) the effect of electropulsing conditions on the characteristics of the cooling curves during solidification of the Sn-40%Pb. As defined and showed in (a),  $\Delta T$  is the undercooling, and  $dT/dt$  is the average rate of temperature change between the minimum undercooled temperature  $T_u$  and the thermal arrest temperature  $T_a$ .  $\Delta t_a$  is the time duration of the thermal arrest. (c) The effect of electropulsing current density and frequency on the eutectic colony size of the Sn-40%Pb and Sn-37%Pb alloys (adapted from [12])

Figure 7.7c also shows that the size of the eutectic colony decreased with the increase of current density, even though the pulsing frequency was decreased. With a current density of 1000–1500 A/cm<sup>2</sup> applied at a frequency of 1.5–5 pulses/s during the whole solidification process, the eutectic colony size was reduced to approximately an order of magnitude smaller. However, no big difference in the eutectic lamellae was observed.

In contrast to what was found and reported by Nakada et al. in [11], in all cases they studied, the dendrites in the electropulsed specimens were of the same form and size as those without electropulsing, indicating that the dendrites had not been broken [12]. They argued that, because the lamellae spacing was not reduced, the electropulsing applied mainly influenced the nucleation of the eutectic colonies rather than their rate of growth. They also discussed the possible reasons that cause the increase in undercooling by the electropulsing, and excluded the skin

and pinch effect, and the possibility of decreasing liquid diffusivity by the applied electropulses. Then, it is down to whether the electropulsing could decrease the Gibbs free energy,  $\Delta G = \Delta H_f \Delta T/T_f$  ( $\Delta H_f$  is the enthalpy of freezing,  $\Delta T$  is undercooling, and  $T_f$  is the equilibrium freezing temperature) or increase the liquid–solid interfacial energy,  $\gamma_{L-S}$ . Unfortunately, they did not have sufficient experimental evidence to determine which is more important in the observed increase in undercooling and in turn the nucleation rate with electropulsing [12].

In 1996, Vives of the University of Avignon, France reported a systematic study on the “effects of forced electromagnetic vibrations during the solidification of Al alloys [13, 14]”. The forced vibration is produced by applying simultaneously a sinusoidal electric current (intensity:  $i = I \sin \omega t$ , and frequency:  $N$ ) and a stationary magnetic field,  $B_o$  inside alloy melt contained in a parallelepipedic tank as schematically shown in Fig. 7.8a. Such an arrangement is very similar to that used in Nishimura’s experiment in 1975 [8]. Figure 7.8b highlights the alloy melt part and vectors of the magnetic field, the electric current applied, and the velocity and pressure generated inside the solidifying Al melt. The stationary magnetic field  $B_o$ ,

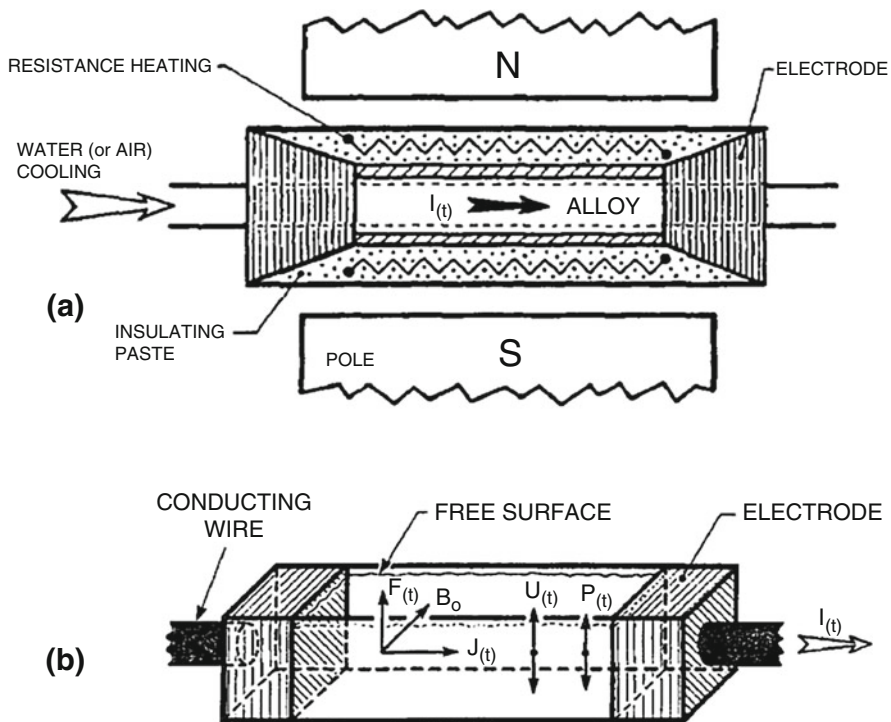


**Fig. 7.8** (a) A schematic illustration of the experimental device (a top view). (b) The enlarged part of the Al melt inside the parallelepipedic tank (the internal dimensions are width:  $a = 2$  mm, height:  $h = 4$  mm, and length:  $L = 12$  mm). A stationary magnetic field,  $B_o$ , and a sinusoidal electric current (intensity:  $i = I \sin \omega t$ , and frequency:  $N$ ) are simultaneously applied to the Al melt. The electrodes used are stainless steel with  $2 \times 4$  cm cross section (adapted from [13])

interacts with the electric current of density  $j$  giving rise to a vertically directed periodic electromagnetic force  $\mathbf{J} \times \mathbf{B}_o$  of frequency  $N$ , which in turn forces the solidifying melt into vibration. The resultant vertical electromagnetic force applied to the whole melt volume is given by  $\mathbf{F} = \mathbf{B}_o \mathbf{I} L \sin \omega t$ , creating an electromagnetic vibrating pressure of  $P = \mathbf{B}_o \mathbf{I} L \sin \omega t / (L \times a) = \mathbf{B}_o \mathbf{I} \sin \omega t / a$ . Assuming an ideal condition, i.e. the solidifying alloy was not in contact with the mould wall, and hence no friction loss, the whole liquid, or semi-solid mass was set in uniform vibration under the action of  $\mathbf{F}$  (the whole melt behaves as a rigid body, and the solidifying phases vibrated in phase).

Therefore, at the peak parameter values, a simple calculation gives that the displacement  $e = \mathbf{J} \mathbf{B}_o / \rho \omega^2$ , velocity  $u = \mathbf{J} \mathbf{B}_o / \rho \omega$ , and acceleration  $\gamma = \mathbf{J} \mathbf{B}_o / \rho$ . For example, if an electric current of  $N = 50$  Hz and a peak value of  $\mathbf{I} = 3500$  A was applied between the stainless steel electrodes ( $2 \times 4$  cm cross section), the peak current density would be  $J = 4.38 \times 10^6$  A m<sup>-2</sup>. In a magnetic field of  $\mathbf{B}_o = 0.7$  T, the magnetic force density would be  $\mathbf{F} = j \times \mathbf{B}_o = 3.06 \times 10^6$  Nm<sup>-3</sup>. Hence, the pressure would be  $P = [\mathbf{F} \times (a \times L \times h)] / (a \times L) = 122,500$  Pa (i.e. 1.21 bar). Assuming that the Al melt has a density of  $\sim 2400$  kg m<sup>-3</sup>, the peak value of the vibrating electromagnetic force is approximately  $\sim 130$  times higher than the gravity force acting on the Al melt [13].

Wide or narrow freezing range Al alloys, including A356, 2024, and 1050 Al alloys, were cast using the above experiment setup, and the experiments were conducted under different electromagnetic vibration pressure amplitudes through controlling the electric current density and the magnetic flux density. Figure 7.9 shows three typical pressure amplitudes and the corresponding microstructures of an A356 alloy formed under those conditions. Figure 7.9d shows typical as-cast columnar-dendritic structures solidified without any electromagnetic vibration. While in the presence of an electromagnetic vibration with pressure amplitude profile as that shown in Fig. 7.9b (peak pressure of  $P = 0.52$  bar), globular grains with an average diameter of  $\sim 120$   $\mu$ m were formed, which were predominantly caused by the shearing effects generated by the vertical velocity (a peak value  $> 1$  m s<sup>-1</sup> [13]) during vibration. This shearing process breaks dendritic particles and deforms them into a spheroidal shape which are quite similar to those encountered in rheocasting techniques [13, 14].

The microstructure displayed in Fig. 7.9f was obtained in the cavitation conditions due to the presence of electromagnetic vibrations. The production of cavitation in liquid metals strongly depends on the most volatile undissolved gas content inside the liquid. It has been established that, in the case of Al melts, the hydrogen content is the controlling factor. The solubility of hydrogen in Al is dependent on both the partial pressure of gas and the melt temperature. At a constant temperature, the equilibrium concentration of gas in solution is proportional to the square root of the partial pressure. For example, at a melt temperature of 650 °C, the hydrogen level is in the order of 0.3 ppm and the corresponding equilibrium pressure is 0.29 bar [13]. Cavitation takes place with full efficiency during the negative pressure part of a vibration cycle (Fig. 7.9c). Grain nucleation is enhanced either by the increase in the equilibrium temperature (hence the effective undercooling) caused by



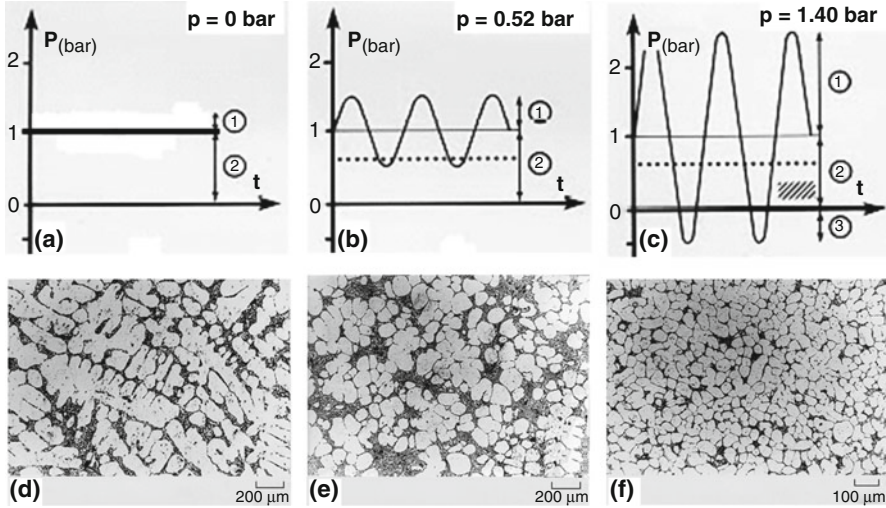


**Fig. 7.9** The pressure waves generated by interaction between the magnetic field and the electric field with the amplitude of (a)  $P = 0$  bar, (b)  $P = 0.52$  bar, and (c)  $P = 1.40$  bar. The resulting solidification microstructures of an A356 Al alloy due to the refinement effect by electromagnetic vibration: (d) the as-cast dendritic structures (i.e. without vibration); (e) globular grains with an average diameter of  $\sim 120 \mu\text{m}$  at  $P = 0.52$  bar, caused by predominantly the hydrodynamic effects (a velocity peak value  $> 1 \text{ m s}^{-1}$  [13]; and (f) globular grains with a mean diameter of  $\sim 50 \mu\text{m}$  at  $P = 1.16$  bar (similar condition to that shown in Fig. 7.8c), caused by predominantly the cavitation effect [13] (adapted from [13, 14])

the pressure spike during the collapse of cavitation bubbles or as a result of cooling the surface of the bubbles by evaporation during its growth. Hence, cavitation renders grain refinement by (1) increasing grain nucleation rate, and (2) increasing grain multiplication effect by disrupting and fragmenting growing phases. In the case shown in Fig. 7.9f, negative pressure peaks of 1.16 bar were transmitted 50 times per second to the solidifying melt for 12 min from the liquidus and with a cooling rate of  $4^\circ\text{C min}^{-1}$ . The effects of cavitation resulted in much finer grains ( $50\text{-}\mu\text{m}$  mean size) and less globular than those produced by shearing effect in the absence of cavitation (Fig. 7.9b, e). Moreover, the cavitation effects resulted in the total disappearance of the numerous large clusters observed in Fig. 7.9e. Similar significant reduction in grain size under the action of cavitation was also obtained in a 2024 alloy and a 1050 alloy, which have a relatively narrow solidification temperature range [13, 14]. Compared to the cases of mechanically vibrated melts, the electromagnetically irradiated semi-solid alloy mixtures exhibited uniform grain refinement across the entire section. This was due to the fact that, in this experiment, the electromagnetic forces which induced oscillating motion acted uniformly throughout the semi-solid melt. Moreover, it should be noted that the cavitation effects, which are provoked by electromagnetic pressure fluctuations, are not likely to be present in the mechanically vibrated melts (excluding those where ultrasound is applied into the melt mechanically). However, from the industrial application point



of view, which often involves an alloy grain refinement process, such process has a serious drawback, because, for large-scale ingot castings, substantial energy consumption is required to reach the cavitation threshold. Indeed, it is not easy to apply relatively intense steady magnetic field strength inside an air gap of 30 cm width and to inject current intensity of about 40,000 A [13]. To solve such problems, Vives proposed to apply a Helmholtz resonator to an enclosed casting chamber containing a solidifying melt. By adjusting the electromagnetic vibration frequency at the small opening of the chamber, the resonance of the melt could be achieved and then sufficient electromagnetic energy could be irradiated into the melt to achieve the vibrating and cavitation effect. Under such conditions, the magnetic field strength and the electric current intensity would be markedly lowered, and consequently, the facility cost and the energy expense would be decidedly reduced [13, 14].

After the new millennium, research in this field has become active in China, and researchers in Zhai's group of Shanghai University, China have done a systematic study on using pulse electric current (they call "electric current pulse", hence the acronym "ECP" used here) to refine grain structures of metal alloys. Some of their important work and findings are summarized and critically reviewed here.

In 2007, Liao et al. designed a series of experiments using a similar experimental approach to that in Nakada's work shown in Fig. 7.3a [11]. The electrodes were instead arranged in an up-down manner inside a melt contained inside a sand mould. One electrode was at the bottom of the crucible and the other at the top of the crucible. The ECP with a peak value of 2000 A and a frequency of 1000 Hz was applied into pure Al melt during the solidification processes. One interesting experimental design was that a wire netting was positioned in the middle of the mould with the aim of preventing any nucleus outside the netting from entering the netting.

The melt was poured at 1113 K into a sand mould of room temperature. Two specimens were cast at the same time, and just one specimen was treated by applying ECP during the whole solidification process. Figure 7.10a shows that, for the untreated specimen, the macrostructures inside and outside the netting are similar, mainly coarse columnar crystals. However, for the specimen (Fig. 7.10b) treated with ECP, outside the netting, there were fine globular crystals, especially at the top of the netting. Liao et al. claimed that such evidence indicated that the crystal nuclei fall off from the mould wall continued under the action of ECP, but they could not enter the netting because the top of the netting was sealed. Combined evidence obtained from other experiments, Liao et al. [15] made a strong claim that (1) solidification structure cannot be refined when ECP is applied to pure Al in liquid state or during crystal growth period. ECP has no inoculation effect on liquid melt. (2) grain refinement occurred when applying ECP during nucleation stage, and the crystal nucleus formed on the mould wall falls off and drifts in the liquid, leading to crystal nuclei multiplication and grain refinement. The skin effect of ECP particularly enhances this effect [15]. However, Liao et al. did not give any detailed theoretical analyses, for example, as Nakada et al. did in [11], to support their strong argument.

In 2008, Li et al. used parallel electrodes (Fig. 7.10c) to apply ECP in pure Al melt during solidification and observed the similar phenomena, i.e. grain refinement

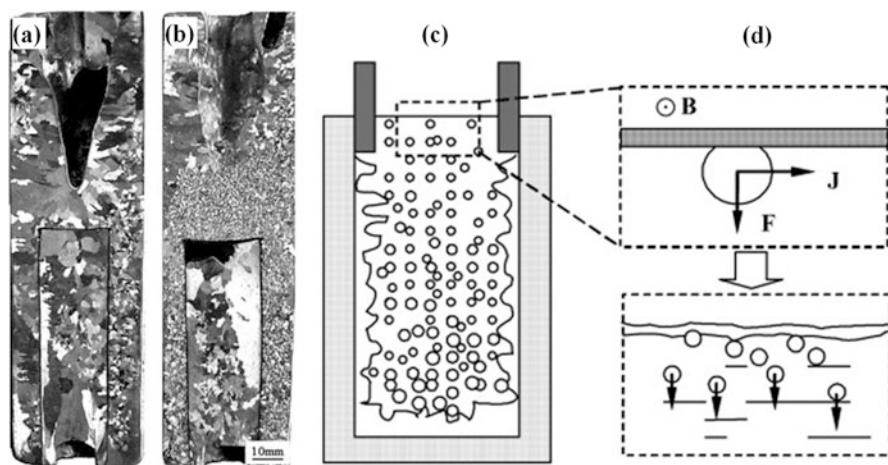


**Fig. 7.10** The macrostructures of two pure Al specimens cast at the same time by pouring the melt at 1113 K into a sand mould (inner cavity of 40 mm in diameter, and 160 mm in height) of room temperature. A wire netting was inserted into the mould. (a) Without ECP, (b) with ECP (top-bottom electrodes arrangement) during the whole solidification process; the peak value of the pulse current was 2000 A with a frequency of 1000 Hz [15] (adapted from [15]). (c) A schematic illustration of the crystal rain during solidification caused by applying ECP (parallel electrodes arrangement); and (d) the force and movement of the nuclei below the top surface under the action of ECP [16] (adapted from [16])

effect was significant when the ECP was applied in nucleation stage, but no effect was found when the ECP was applied in the liquid state [15, 16]. Under the same cooling conditions and ECP parameters, the grain refinement efficiency of the parallel electrodes arrangement was better than that of the up-down arrangement. They also argued that ECP with high frequency would increase atom vibration frequency and enhance the adsorption probability. In addition, ECP also changes the Gibbs free energy of liquid and solid, and the diffusion activation energy [16]. All these effects promote heterogeneous nucleation. Figure 7.10c schematically illustrates the crystal rain effect due to the action of ECP. After liquid Al was poured into the mould, a small thermal undercooling was generated at the upper surface, leading to formation of a thin solidified shell or an oxide layer, which provided an appropriate substrate for heterogeneous nucleation. The atomic clusters locating at or near the surface had more opportunities to collide with each other and agglomerated into a stable nucleus under the action of ECP. At the same time, ECP also induced pulse magnetic field within the melt, producing periodic Lorentz force ( $F = J \times B$ ) that was acting on the upper surface and pointing downward (Fig. 7.10d). Such force created a shock wave that broke up the thin solidified shell and made the nuclei to separate from the top surface and move downward into the undercooled melt below. This could be viewed as crystal rain. Some of them grew into equiaxed crystals, and some impinged continuously on the tip of the primary columnar crystal growing from the mould wall. Such impingement prevented the primary columnar crystal from growing into

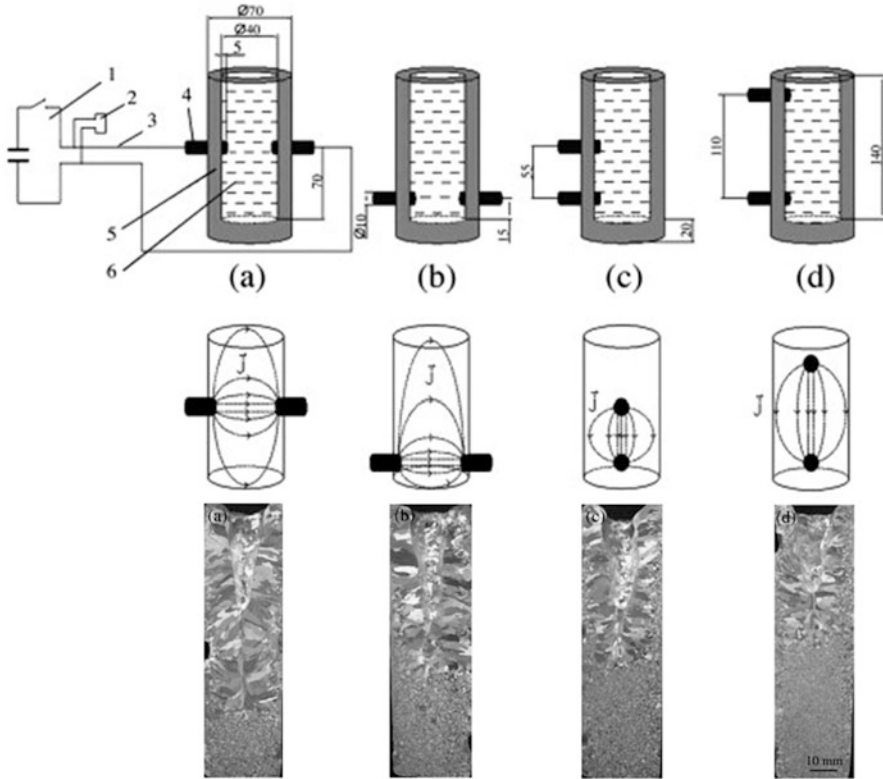


**Fig. 7.11** Schematic illustration of the electrode arrangement in different experiments (a) Mode I; (b) Mode II; (c) Mode III; and (d) Mode IV. 1—pulse generator; 2—digital oscillograph; 3—copper strip; 4—electrodes; 5—sand mould; and 6—sample. The corresponding solidification macrostructures of the pure Al under ECP (the current pulse peak was 2000 A with a frequency of 200 Hz and width of 100  $\mu$ s) in each mode (adapted from [17])

coarse columnar crystal. Hence, an overall fine equiaxed solidification structure was formed [16].

In 2009, Ma et al. [17] reported an interesting experimental study on the effects of grain refinement of a pure Al by applying ECP by electrodes arranged at different positions inside the mould. Figure 7.11 shows four different electrode arrangements for applying ECP. In Mode I, the electrodes (0Cr18Ni9 stainless steel) were placed at middle lateral wall of the mould (Fig. 7.11a). In Mode II, the electrodes were at lower lateral wall of the mould (Fig. 7.11b). In Mode III, one electrode was at the middle lateral wall, and the other was at the lower lateral wall (Fig. 7.11c). In Mode IV, two electrodes were placed at the upper and lower lateral wall, respectively (Fig. 7.11d). Figure 7.11 also shows the solidification structures after applying ECP in different modes (a: mode I, b: mode II, c: mode III, and d: mode IV). The solidification structure of each sample can be divided into equiaxed and columnar grain regions. In Mode I and Mode II, the upper part of the samples mainly consisted

of large columnar crystals, yet the lower part of the samples had fine equiaxed grains, and the area fraction of fine grains was about 38.3% and 51.8%, respectively. In the case of Mode III, the area of coarse columnar crystal tended to be reduced, while the region of the equiaxed grains expanded more widely than that in Modes I and II. The area fraction of fine grains in Mode III was 65.6%. In Mode IV, the region of equiaxed grains expanded further, and there were some fine equiaxed grains even near the top surface. The highest proportion (82%) of fine equiaxed grain area was obtained.

Clearly, the equiaxed grains region in each specimen matched approximately the region where the ECP had an effect on as indicated by the illustration for each case in Fig. 7.11. Again, Ma et al. argued that the nuclei that were shaken off from the mould wall in ECP affected regions caused formation of the equiaxed grains. While the formation of those columnar crystals was because they were nucleated and grew into columnar morphology in the region far away from the ECP affected zones [17].

To further elucidate the effects of electrode materials and dimension on grain refinement, Yin et al. [18] used three different types of parallel electrodes that were made of (1) carbon steel, (2) carbon steel with water cooling capability, and (3) pure copper. The cross sections of the electrodes were  $15 \times 2$  mm, and  $30 \times 2$  mm, respectively. They found that, with the same ECP parameters, the electrode with the cross section of  $15 \times 2$  mm had negligible effect on grain refinement of pure Al, while that of the  $30 \times 2$  mm had marked grain refinement effect [18]. They argued that the Joule heat ( $Q = I^2 R t = I^2 (\rho L/A) t$ ,  $I$ —electric current,  $\rho$ —resistivity,  $L$ —length of the electrode,  $A$ —area of the electrode, and  $t$ —time) was determined by the cross section of the electrode,  $A$ , and the electric resistivity,  $\rho$ . When an electrode of small cross section was used, more Joule heat was produced in a small area, resulting in decrease in the undercooling in the upper surface (where the electrode was acting on) and therefore suppressed grain nucleation, leading to no obvious grain refinement [18]. In the case of the pure copper or water-cooled steel electrode (both have cross section of  $30 \times 2$  mm), the Joule heat generation was reduced and heat transfer was quicker, leading to a shorter solidification time. ECP also had no effect on refinement because the grains at the upper surface grew too quickly to be melted or shaken off by the applied pulses. Hence, they claimed that, for a parallel electrode positioned at the top of a solidifying melt, the thermal condition of the upper surface played a vital role in microstructure refinement when using ECP [18].

### ***7.1.2 Simulation of Lorenz Force, Melt Flow, and Grain Migration Due to Pulse Electric Current***

To further quantify the migration of the nuclei falling off from the relatively cold upper surface under action of ECP, Li et al. [19] developed a numerical model to simulate the migration of nuclei in pure Al melt under the action of ECP (schematically showed in Fig. 7.12a). The model used the finite difference method and volume of fluid (VOF) method to solve the equations for the momentum and energy

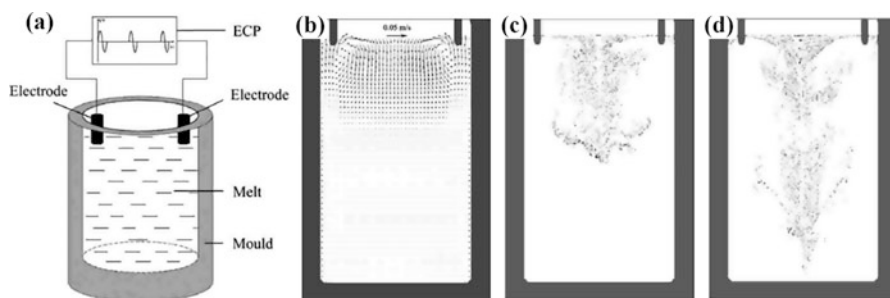


**Fig. 7.12** (a) A schematic, showing the physical arrangement used in the simulation of a pure Al solidified with ECP (peak current of 100 A, frequency of 100 Hz, and pulse width of 200  $\mu$ s). (b) The calculated typical melt flow profile near the upper surface. The movement and distribution of nuclei (50  $\mu$ m in diameter) under the action of ECP: (c)  $t = 0.7$  s and (d)  $t = 1$  s (adapted from [19])

transport of the melt, and Maxwell's equations to calculate the electromagnetic field and current induced by the application of ECP [19]. The nuclei were considered to be generated only from the upper surface of the melt and flowed down under the action of gravity and electromagnetic force. Figure 7.12b shows the calculated melt flow profile near the upper surface, flowing inwards and then downwards. The simulation showed that, for nuclei of 50  $\mu$ m diameter, they can reach the bottom of the mould filled with an Al melt (an initial temperature of 936 K) of 64.65 mm height, and distributed mainly in the central region of the mould (Fig. 7.12c, d) [19]. Of course, the simulation ignored many of the coupled physics during melt solidification, and just calculated the movement of free floating particles under the action of gravity and electromagnetic force. The model also had difficulty in capturing the movement of small size particles ( $< 10$   $\mu$ m) and that of large size particles ( $> 100$   $\mu$ m). Nevertheless, the simulation seemed to provide better and reasonable explanations for the grain refinement mechanism of ECP.

In 2014, Rabiger et al. [20] studied the directional solidification of Al-7 wt.% Si alloys under the influence of strong electric currents implemented by immersing two parallel electrodes under the free surface of solidifying alloys (Fig. 7.13a). Both direct currents and electric current pulses in rectangular profile (Fig. 7.13b) were used. Numerical simulations were conducted to calculate the Lorentz force (Fig. 7.13c), Joule heating, and induced melt flow (Fig. 7.13d). The simulation showed that the Lorentz force (Figs. 7.13c and 7.14c, f) produced an electro-vortex type flow in the melt (Fig. 7.13d), and the time-averaged axial velocity of the melt was strongly linked to the applied effective current (Fig. 7.13e). The grain refinement effect was also strongly linked to the effective current (Fig. 7.13f), and there were no marked differences with respect to the influence of DC or ECP treatment on the mean grain size and the area of equiaxed zone in the solidified samples (Fig. 7.13f), provided that the effective values of the current strength are identical. They did not observe any effect of pinch force at the instant of discharging ECP, and the calculation showed that the effect of Joule heating was confined to a very local region near the electrode end surface (Fig. 7.14b, e) and the heating input into the melt can be ignored when compared to the latent heat released from the solidifying

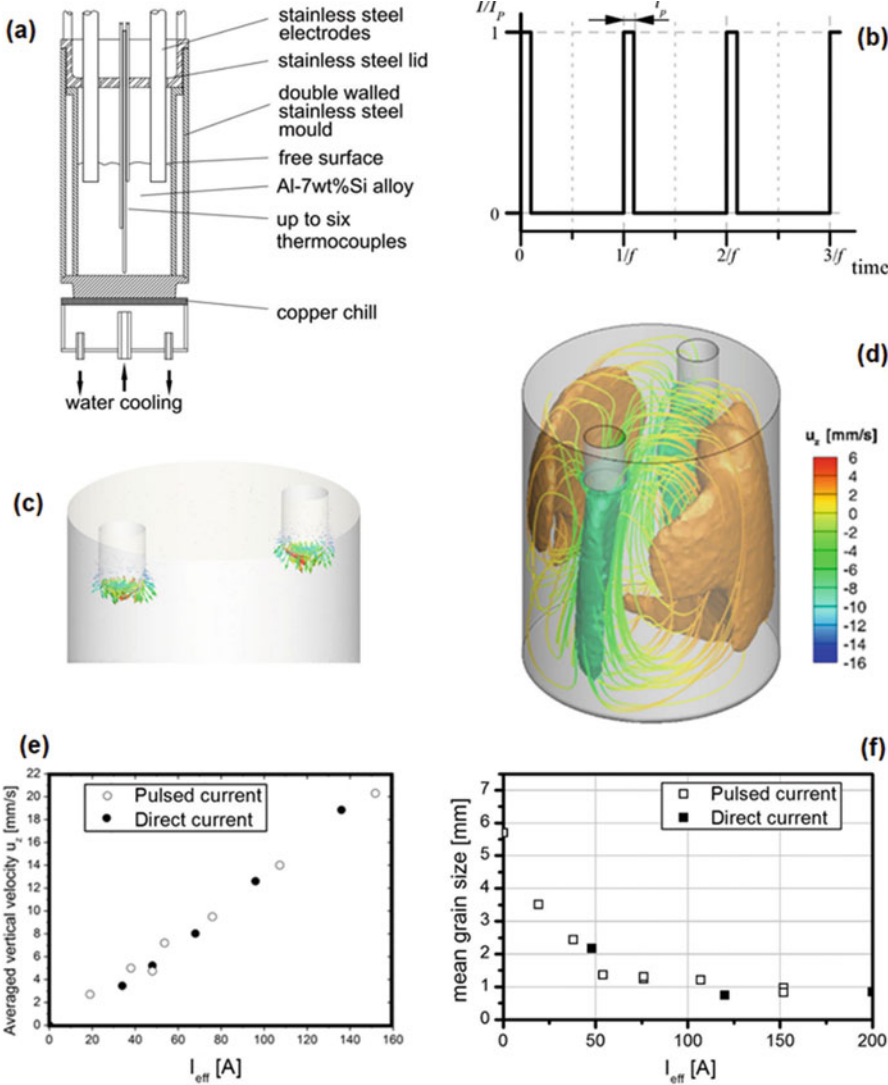


**Fig. 7.13** (a) A schematic, showing the solidification experimental setup with parallel electrode arrangement. (b) The rectangular profile of the applied ECP during solidification, (c) The simulated Lorentz force profile near the electrodes, and (d) the 3D flow pattern when the direct current applied was  $I_{DC} = 48$  A. (e) The relationship between the applied effective current and the averaged vertical velocity of the melt flow. (f) The relationship between the applied effective current and the mean grain size of the sample (adapted from [20])

phases. Hence, they argued that the grain refining effect observed in their experiments was ascribed solely to the dendrite fragmentation mechanism due to the local fluctuation in temperature and solute concentration caused by the forced melt flow driven by the Lorentz force.

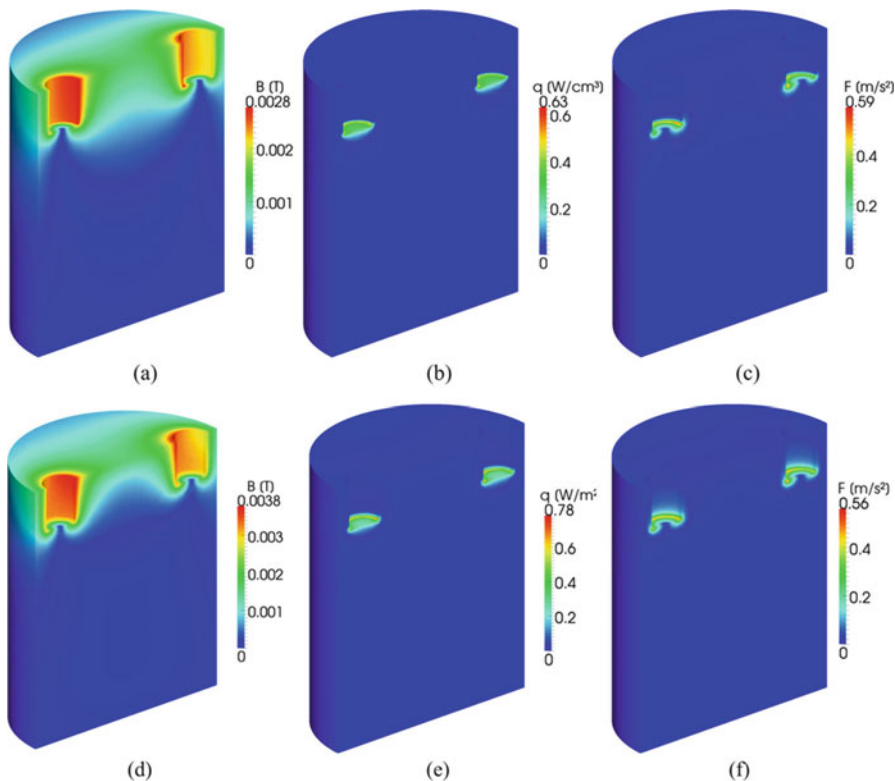


**Fig. 7.14** In the top row, the simulated (a) magnetic field strength; (b) Joule heating; and (c) Lorentz force density when the applied direct current was  $I_{DC} = 48$  A. In the bottom row, those when the applied effective alternating current was  $I_{eff} = 48$  A with the frequency of  $f = 2000$  Hz (adapted from [20])

### 7.1.3 Effect on Liquid–Solid Interface Due to Pulse Electric Current

In 2007, Liao et al. investigated the effects of ECP on the liquid–solid interface stability of an Al–4.5% Cu alloy during directional solidification [21]. Figure 7.15 shows some typical results from the experiments. In summary, the results show that the solid–liquid interface morphology transforms from dendritic to cellular or even planar interface at relative slow pulling rates. Both cellular spacing and mushy zone depth decrease with increasing current density. At higher pulling rate ( $96 \mu\text{m/s}$ ), the initial dendritic crystals with secondary dendrites were suppressed with increase of current density. The secondary dendrites gradually disappeared because of increase of temperature gradient due to Joule heating from the ECP and the homogeneous distribution of the solute.



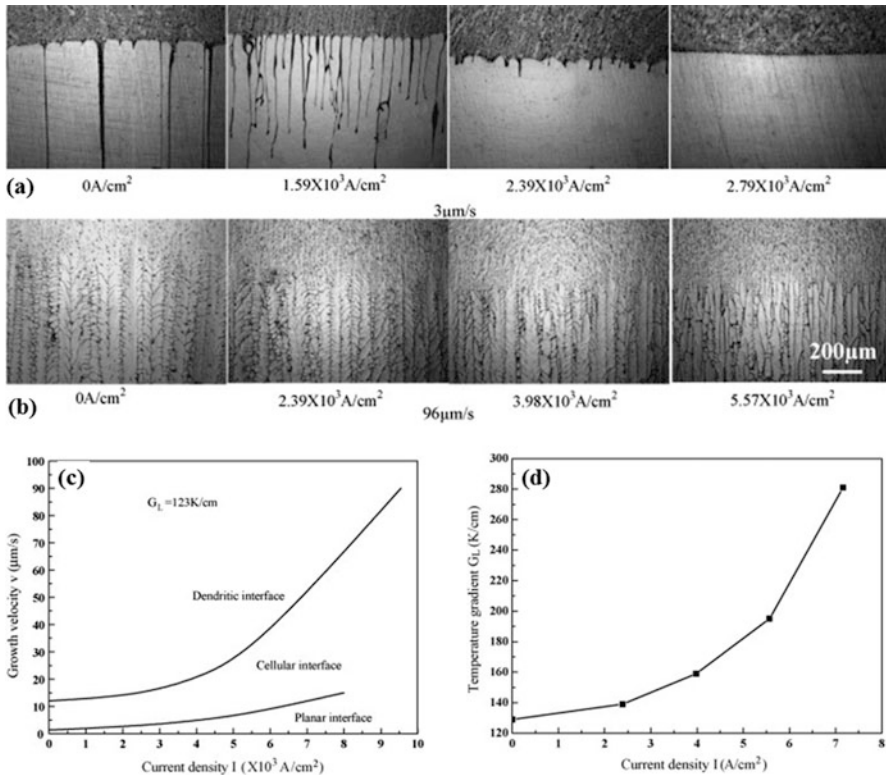


**Fig. 7.15** The effects of ECP on the liquid–solid interface morphology at different growth rates: (a) at a pulling rate of 3 μm/s with increased current density of the applied ECP, from a regular cellular morphology to splitting of the cells, and then to a planar interface (from left to right). (b) A pulling rate of 96 μm/s, starting with a cellular–dendritic type morphology and then with increase of current density, the cellular spacing gradually decreased until formation of a typical cellular morphology. (c) The transition from planar growth to dendrite growth, and (d) the effect of temperature gradient by ECP (adapted from [21])

Clearly, Fig. 7.15d shows that the temperature gradient increases with increasing pulse current density because of Joule heating and the Peltier and Thomson effect when the ECP passed through the solidifying melt and the solidified crystals. The liquid phase has higher resistivity than the solid phase, and therefore it increased the liquid temperature and the liquid temperature gradient in front of the liquid–solid interface. In addition, the electromagnetic pressure induced by the current was perpendicular to the growth direction, causing increased melt convection in front of the interface, which decreased the solute concentration gradient and constitutional undercooling in front of the interface. For these two reasons, the interface stability was improved by applying ECP after a period of transition [21]. However, in the experiments, no evidence was given as to whether ECP could enhance the interfacial energy or not.

In 2015, Zhang et al. [22] investigated the macrosegregation formation of primary silicon phases in a directionally solidified Al–20.5 wt%Si hypereutectic alloy due to pulse electric currents. They found that applying electric currents resulted in a

severe macrosegregation of primary silicon phases in the initially growing region of the directionally solidifying sample. Numerical analysis revealed a concentration of electric currents in the mushy zone's melt among the participating primary silicon particles due to their low electric conductivity, causing much higher flow intensity (forced convection) in the upwards direction. The forced flow initiated a rigorous solute exchanging between the mushy zone and the bulk melt, which leads to a continuous participation and segregation of the primary silicon in the mushy zone [22].

## 7.2 Pulse Magnetic Field Processing of Metal Alloys

### 7.2.1 Grain Refinement Due to Pulse Magnetic Field

In 2008, Gong et al. [23] developed a pulse magneto-oscillation (PMO) method to refine solidification structures of pure Al. They used a capacitor bank of 200  $\mu\text{F}$  to store electricity of voltage up to 8000 V, and then discharged it into a copper coil (Fig. 7.16a). The current in the coil with a discharge of 2500 V is shown in Fig. 7.16b. The arrangement of the crucible relative to the copper coil is shown in

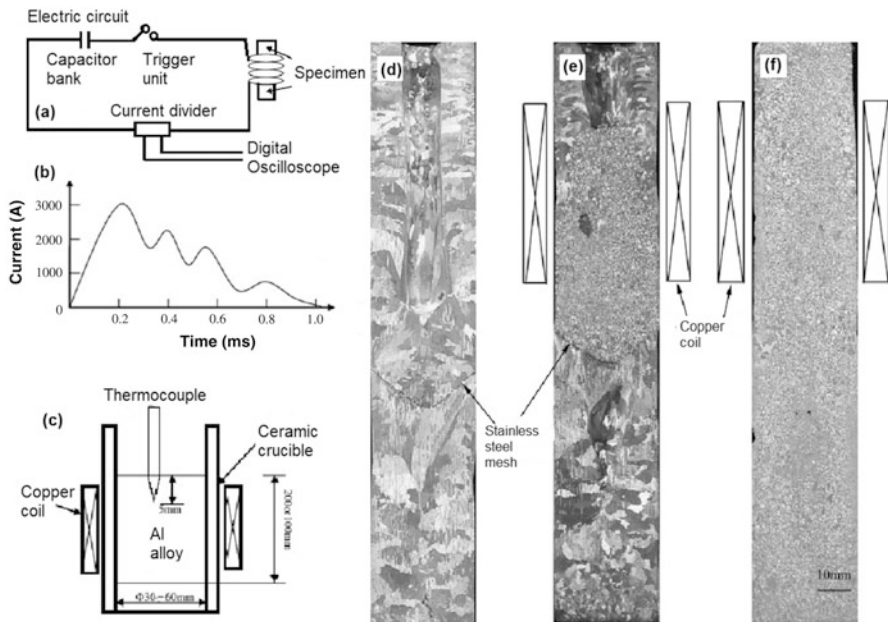


**Fig. 7.16** (a) The electric circuit and key components for generating a pulse magnetic field into a specimen. (b) The current profile inside the coil when discharging a 2500 V current from the capacitor bank. (c) A schematic, showing the coil, crucible, and melt. The macrostructures of the pure Al specimens with horizontally placed stainless steel mesh: (d) without PMO, (e) with PMO, (f) with PMO but without mesh (adapted from [23])

Fig. 7.16c. In some experiments, they placed a stainless steel mesh with sieve number of 60 inside the mould to prevent any nucleus outside from entering the mesh. Figure 7.16d–f shows the effects of PMO on refinement of solidification macrostructures. Without PMO, it was coarse grains (Fig. 7.16d). When PMO was applied and the stainless steel mesh placed below the copper coil, the macrostructure was divided into two parts by the mesh. Only the part above the mesh was refined (Fig. 7.16e). Without the mesh (Fig. 7.16f), the whole length had fine macrostructure.

From these experimental evidence, Gong et al. argued that PMO had similar effect on pure Al as ECP in terms of grain refinement. The mechanism is that the nuclei formed on the mould wall fall off and drift into the melt under the action of PMO, leading to refinement of the solidification structure. The best refinement effect due to PMO treatment can only be achieved during nucleation stage. If the pulse electric current induced by PMO has the same pulse width and intensity to those of the ECP generated by electrodes, their refinement effects on the melt should be identical since distribution of the electromagnetic field in the melt is the same [23]. However, contact electrodes are needed in ECP treatment. Such arguments are actually contradictory because the induced current inside a melt due to PMO is not the same as that due to ECP. In addition, Gong et al. also discussed how PMO sound wave pressure helped to move nuclei clusters inside the melt. Such argument was without evidence and quite confusing [23].

In 2012, Yin et al. reported a surface pulsed magneto-oscillation (SPMO) method for refining solidification structures of metals and alloys [24]. A special flat spiral type coil was used (Fig. 7.17a) and it was made from a pure copper tube (can be cooled with flowing water). The experimental apparatus is shown in Fig. 7.17b, consisting of a pulse generator, an oscilloscope for monitoring electropulse, and an electric resistance furnace. When an electropulse was passed through the coil positioned on top of the melt, a pulse magnetic field  $\mathbf{B}$  was produced around the coil (Fig. 7.17c), and a pulsed eddy current  $\mathbf{J}$  was simultaneously induced in the melt (Fig. 7.17e). The skin effect was significant because the magnetic field and the eddy current were at a relatively high frequency ( $\sim 10^3$  Hz). The skin depth was approximately 8 mm [24]. So, the pulse eddy current and its Joule heating effect owing to the resistance of melt were concentrated in the surface layer of  $\sim 8$  mm. Lorentz force,  $\mathbf{F}$ , was also exerted on the melt due to interaction between the magnetic field  $\mathbf{B}$ , and the eddy current  $\mathbf{J}$ . The direction of the Lorentz force is given by the “left-hand” rule, namely,  $\mathbf{F} = \mathbf{J} \times \mathbf{B}$ . The magnetic field was not perpendicular to the liquid surface, being at an angle of  $\theta$  to the eddy current, thus the Lorentz force can be divided into two parts, i.e.  $F_x$  and  $F_y$  (Fig. 7.17d). The Lorentz force’s direction was changing constantly with the varying electropulse, making the melt oscillate up and down. According to Lenz’s law, when the  $\mathbf{B}$  is decreasing, the coil attracts the melt to create a forced convection that is limited within the surface layer due to the shielding effect and the gravity of melt  $\mathbf{F}_g$ . When  $\mathbf{B}$  is increasing, the coil repels the melt to form another pattern of forced convection that could affect the inner liquid because of the force transmission and the constraint of the mould wall. The forced convection could have strong effects on the formation

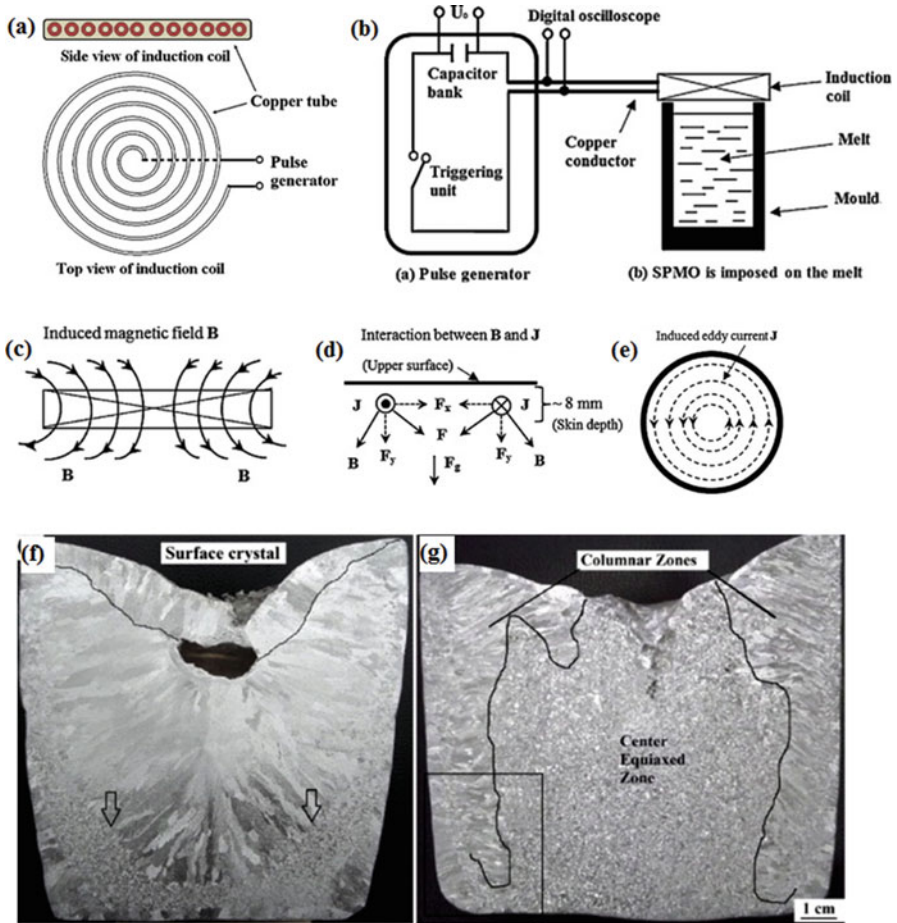


**Fig. 7.17** (a) A special type coil, (b) the schematic of the experimental setup. (c) A side view of the magnetic field induced by the coil. (d) The Lorentz force generated by the magnetic field and the eddy current in the melt. (e) A top view of the induced eddy current in the melt surface. The macrostructures of two pure Al ingots: (f) without SPMO, (g) treated with SPMO (adapted from [24])

of cast structure [24]. Under normal solidification conditions without SPMO, the surface chill zone was clearly observed, forcing the surface crystals to grow downwards and impinge on the crystals below, resulting in a clear boundary as shown in Fig. 7.17f. With SPMO, the SPMO-induced free crystals on the top tended to drift away towards the centre and then pile up on the bottom due to the forced convection (Fig. 7.17g). In addition, the macro-shrinkage cavity became smaller after the SPMO treatment, because of increase in the area of equiaxed grains, and the induced Joule heating on the upper surface, which is favourable for decrease in shrinkage cavity [24].

In 2014, Liang et al. [25] studied the effects of PMO on thermal undercooling. They found that, for pure Al melt, the thermal undercooling of the melt increased and the temperature gradient from the mould wall to the centre of the casting decreased due to melt convection induced by PMO treatment. Increasing thermal undercooling largely promoted nucleation of pure Al grains while decreasing the temperature gradient to low levels means that most of the melt was slightly undercooled, preventing remelting thus improving survivability of the nucleated grains and allowing these grains to grow. Therefore, when PMO treatment produced these casting conditions, very fine grain structures could be achieved [25].

### ***7.2.2 Effect on Liquid–Solid interface Due to Pulse Magnetic Field***

In 2008, Song et al. [26] investigated the effects of axial pulse magnetic fields on microstructure and interface morphology of an austenitic stainless steel over a wide range of growth rates from planar to dendritic growth mode. The experimental setup is schematically shown in Fig. 7.18a, consisting of a generator for pulse magnetic field, a heating coil, a pulling arrangement, a high purity alumina crucible, and a coolant of liquid Ga–In–Sn alloy [26]. The typical current profile inside the coil at discharging is shown in Fig. 7.18b.

Figure 7.18c–g shows the effect of pulse magnetic fields on the longitudinal cross-sectional microstructure and interface morphology of the austenitic stainless steel (grey phase is austenite phase, and black phase is ferritic phase) at a pulling rate of 12  $\mu\text{m/s}$ . Without pulse magnetic field, the growth mode was planar front growth (Fig. 7.18c). When a field of 0.5 T was applied, slight disturbances appeared at the interface (Fig. 7.18d), indicating the onset of interface instability. At 0.84 T, the interface changed to a cellular growth mode (Fig. 7.18e). When the field strength was increased to 1.0 and 1.54 T, the growth mode evolved into complex cellular–dendritic or dendritic growth (Fig. 7.18f, g). Clearly, the results show that application of the pulse magnetic fields changed the growth mode from planar to cellular then to dendritic front growth [26]. More results with pulling rates of 24, 64, and 96  $\mu\text{m/s}$  were presented in [26], and convincing evidence showed that applying a pulse magnetic field reduces interface stability and promotes planar–cellular–dendritic–cellular transition. In addition, increasing magnetic intensity reduces the primary spacing at pulling rates of 12, 24, and 64  $\mu\text{m/s}$ , but increases the primary spacing at 96  $\mu\text{m/s}$ . Although different mechanisms were discussed, the explanations were inconclusive [26].

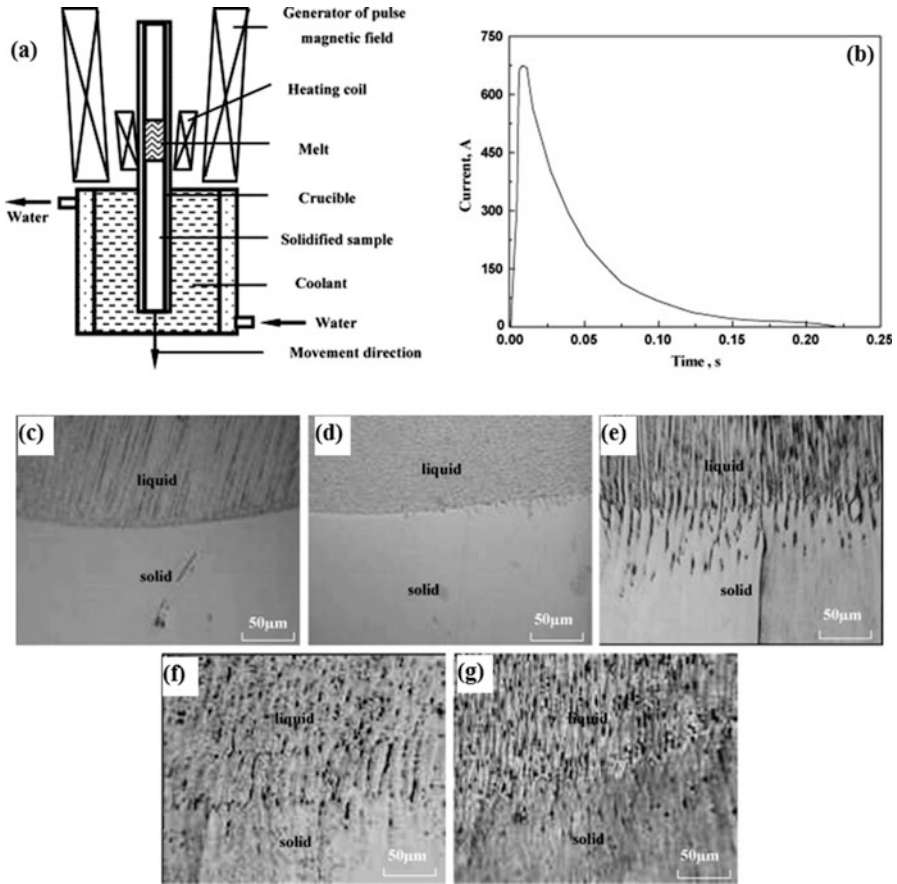


**Fig. 7.18** (a) A schematic of the experimental setup, and (b) the current profile inside the coil at one discharging. The microstructure at the liquid–solid interface region at a pulling rate of  $12 \mu\text{m/s}$  with different magnetic intensity: (c) 0 T, (d) 0.50 T, (e) 0.84 T, (f) 1.00 T, and (g) 1.50 T (adapted from [26])

## 7.3 In Situ Study of the Solidification Processes Under External Pulse Fields

### 7.3.1 In Situ Study Under Pulse Electric Current

In 2014, Liotti et al. of Oxford University [27] reported experiments using synchrotron X-ray imaging to study the effect of dendrite fragmentation by passing a pulse electric current through a thin Al–15wt%Cu sample. The sample melt was placed inside a static magnetic field. Hence, the alloy melt was subject to a pulse electro-magnetic field (PEMF) during solidification. A special solidification apparatus (Fig. 7.19a) was designed and built for these experiments. The two plate heaters



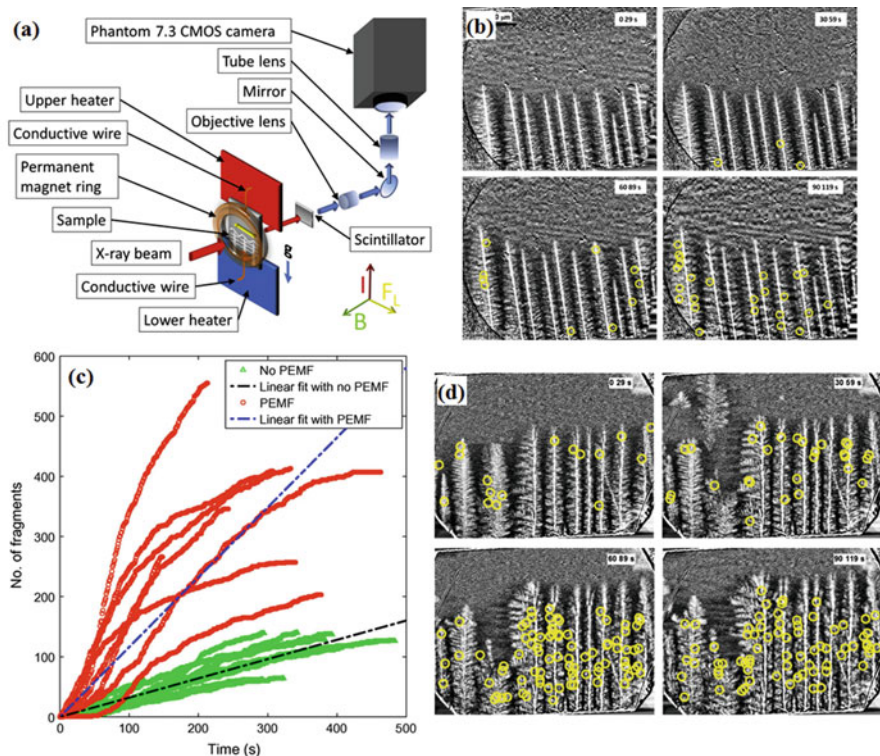


**Fig. 7.19** (a) A schematic of the sample arrangement and experimental set-up. (b) The growing Al-15wt%Cu dendrite array and the locations where fragmentation occurred (marked by yellow circles) during solidification (thermal gradient  $G = 48$  K/mm and no external PEMF) (adapted from [27]). (c) The cumulative fragmentation number curves without (4 typical images showed in b) and with the PEMF (4 typical images showed in d). (d) The fragmentation events occurred under the action of a PEMF (marked by a yellow circle) (adapted from [27])

were aligned vertically in the vertical plane and separated by an adjustable gap through which X-rays could pass. In the gap, a 200- $\mu$ m thick foil sample was placed in close contact with both heaters. This entire sample holder arrangement could be moved vertically under computer control for imaging the solid-liquid interface by the X-ray beam and imaging camera. A permanent ring magnet was placed 3 mm from the foil sample, with field lines running approximately normally in and out of the sample surface. By applying an electric current ( $I$ ) from a signal generator through the plane of the sample in the presence of the static magnetic field ( $B$ ), a pulsed Lorentz force ( $F$ ) acting on the sample can be generated ( $F = B I \sin(\theta) L$ , where  $\theta = 90^\circ$  is the angle between the electric and magnetic field and  $L$  is the active length of the sample). The current pulse magnitude, waveform, and frequency were generated and controlled by a signal generator. A common trigger signal was used to synchronize the measured thermal data with corresponding video images, so that specific events observed in the images could be linked directly to thermal data and



any pulse events. Al–15 wt%Cu alloy foil samples were used and the experiments were carried out in the B16 beamline of Diamond Light Source, UK [27]. Figure 7.19b shows that, consistent with previous studies, the “bulk” movement of liquid, i.e. convection, close to the dendrite front caused temperature and solute perturbations, which is the primary source for dendritic arm fragmentation in this type of alloy. Without PEMF, the dendrite fragmentation rate was  $0.26 \times 10^9$  fragments  $\text{m}^{-3} \text{s}^{-1}$  (Fig. 7.19b). However, it increased to  $1.18 \times 10^9$  fragments  $\text{m}^{-3} \text{s}^{-1}$  with a PEMF applied (Fig. 7.19c). They suggested that PEMF induced an enhanced movement of solute-rich inter-dendritic liquid, and caused relatively small-scale movement of liquid between both primary and secondary dendrite arms. The movement transports comparatively solute-rich liquid from within the dendrite network to more dilute regions, causing dendrite arm remelting [27].

In a further study, Liotti et al. [28] also demonstrated that the stronger the applied PEMF, the greater the induced flow and the higher the fragmentation rate. However, there was no compelling evidence for any change in fragmentation mechanism or the distribution of fragmentation events in their experiments [28].

### 7.3.2 *In Situ Study under Pulse Magnetic Field*

Recently, researchers in Mi’s group at the University of Hull, UK have used synchrotron X-ray to conduct systematic real-time studies [29–32] on solidification of metal alloys under pulse magnetic fields. A novel programmable device (Fig. 7.20) for generating electromagnetic pulses in solidifying melts was designed and built for the in situ studies. Different to that used by Liotti et al., this device was designed for processing bulk samples with a diameter of up to 30 mm, hence solidification conditions similar to those found in industry can be realized. An Al–15%Cu and an Al–35%Cu alloy were firstly used in these experiments.

Pulse magnetic fluxes generated inside the solidifying melts were simulated using finite element method. Figure 7.20b shows the physical and computational domain used in the simulation [29, 30]. The simulated magnetic flux density distribution for different discharge voltages are shown in Fig. 7.20d. In this particular arrangement, the distribution of magnetic flux density along the axial direction inside the metal alloy sample are uniform. More detailed simulation data can be found in [29, 30].

The effects of pulse magnetic fields on solidification microstructures were characterized using electron microscopy and synchrotron X-ray tomography. Figure 7.21 shows the 2D and 3D dendritic microstructures of the Al–15%Cu alloy, the micrographs show in the left-hand column are typical SEM images, and the middle ones are the reconstructed 3D tomography dataset chosen from the typical area marked by the rectangular boxes on the SEM micrographs, while the right-hand 3D rendering data are the segmented primary Al dendrites extracted from the 3D dataset shown in the middle column.

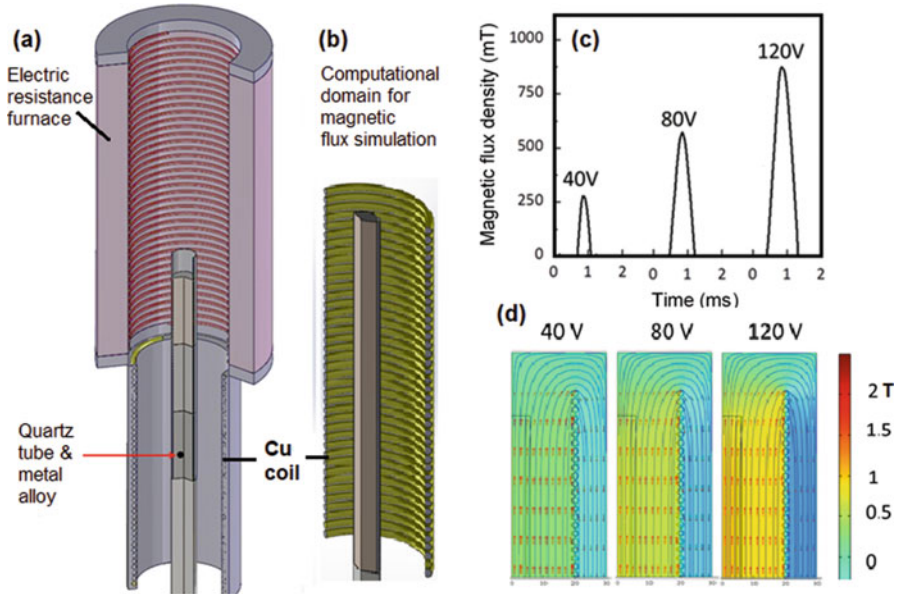


**Fig. 7.20** (a) a cut-off CAD rendering, showing the assembly of the furnace, the copper coil cemented and covered with mastics for generating magnetic pulse, the quartz tube sample holder for containing liquid metals. (b) the computational domain for simulating pulse magnetic fields, (c) The measured pulse magnetic flux density for initial discharging voltage of 40, 80 and 120 V respectively, (d) The simulated magnetic flux density distribution inside the coil (adapted from [29, 30])

Figure 7.22 shows the 2D and 3D microstructures of the Al–35%Cu alloy and the  $\text{Al}_2\text{Cu}$  phases. Using this device and a discharging voltage of 120 V, a pulse magnetic field with magnetic flux density of 0.9 T was produced into the solidifying melt (Fig. 7.20c, d). The peak Lorentz force generated inside the Al–Cu alloy melts was sufficient to disrupt the growth of the primary Al dendrites and the  $\text{Al}_2\text{Cu}$  intermetallic phases. 2D and 3D synchrotron X-ray tomography characterizations revealed that the  $\text{Al}_2\text{Cu}$  phases distribution exhibited a strong correlation to the characteristics of the applied pulses, forming a periodical pattern that reflects precisely the frequency of the electromagnetic pulses [29, 30].

Du et al. further upgraded the solidification apparatus and allowed it to be suitable for in situ studies at synchrotron X-ray beamlines. Figure 7.23 shows the upgraded apparatus, the measured magnetic flux density profiles with different initial discharging voltages and temperature profiles during heating and cooling [31, 32]. Al–15%Ni hypereutectic alloy was used in the synchrotron X-ray imaging and tomography experiments [31]. Figure 7.24 shows the typical images selected from four time-resolved X-ray image video sequences, revealing growth of the primary  $\text{Al}_3\text{Ni}$  phases during solidification under four different magnetic flux densities (0, 0.85, 1.2, and 1.5 T).

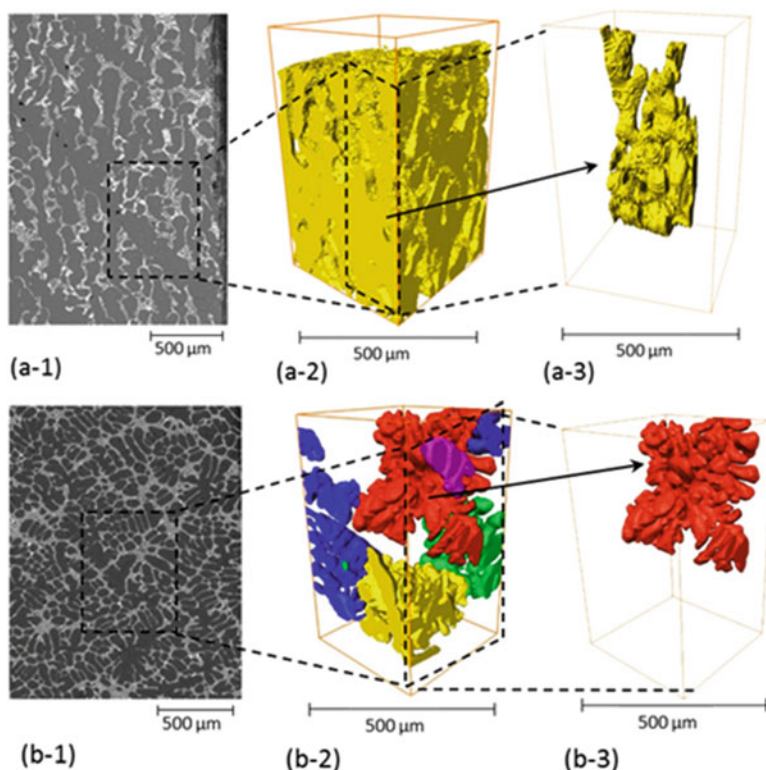


**Fig. 7.21** The 2D scanning electron microscopy micrographs (the images on the left column), and 3D dendrites of the Al-15%Cu alloy cast (a) without and (b) with pulse magnetic field of 120 V initial discharge voltage (adapted from [30])

In the four images (Fig. 7.24a1–d1) in the first row, primary intermetallic  $\text{Al}_3\text{Ni}$  phases (solid black phases) were first seen to appear in the liquid matrix. The  $\text{Al}_3\text{Ni}$  phases had different morphologies and orientations when pulses of different peak values were applied. In the case of 0 T, Fig. 7.24a1–4 shows that an  $\text{Al}_3\text{Ni}$  phase of 500  $\mu\text{m}$  length appeared at  $t = 0$  s. It floated freely in the liquid and rotated  $\sim 60^\circ$  clockwise in 0.3 s and then went downward to the location shown in Fig. 7.24a2. This is of course due to the difference in densities between the  $\text{Al}_3\text{Ni}$  phase ( $\rho_{\text{Al}_3\text{Ni}} = 3.817 \text{ g/cm}^3$ ) and the liquid melt ( $\rho_{\text{melt}} = 3.014 \text{ g/cm}^3$ ). After 16 s, in Fig. 7.24a4, many more  $\text{Al}_3\text{Ni}$  phases with almost random orientations were seen to appear in the field of view. One  $\text{Al}_3\text{Ni}$  phase (Fig. 7.24a5, highlighted by the black frame) was observed to grow from 7 to 120  $\mu\text{m}$  until it met its neighbour, and then slightly changed its direction (Fig. 7.24a5–6). After a sufficient number of  $\text{Al}_3\text{Ni}$  phases appeared, growth and coarsening continued as clearly demonstrated in Fig. 7.24a5–6.

In the cases of pulse peak values of 0.85 and 1.2 T, the  $\text{Al}_3\text{Ni}$  phases appeared firstly at the bottom of the view field (Fig. 7.24b1, c1). Majority of the subsequently

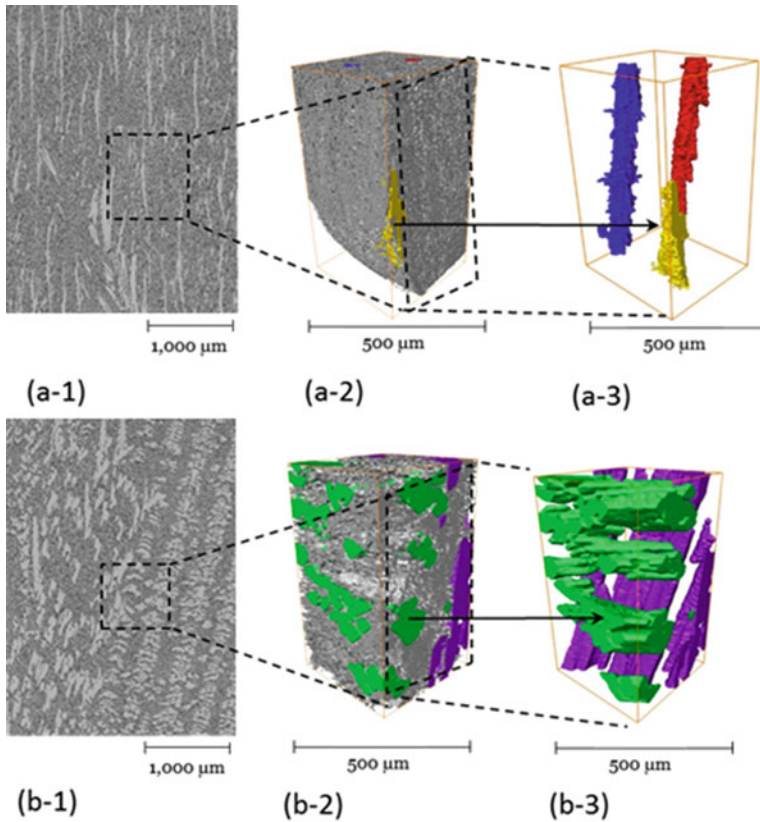


**Fig. 7.22** The 2D scanning electron microscopy micrographs (the images on the left column), and 3D microstructure and Al<sub>2</sub>Cu phases of the Al-35%Cu alloy cast (a) without and (b) with pulse magnetic field of 120 V initial discharge voltage (adapted from [30])

nucleated Al<sub>3</sub>Ni phases grew in the directions marked by the white arrows in Fig. 7.24b3, c3. At the later stage of growth (Fig. 7.24b5–6, c5–6), a lot of Al<sub>3</sub>Ni phases were seen to grow branches, or to cross over or intercept each other. However, because of the overlapping nature of the 2D images, true characteristics of the morphologies need to be resolved by tomography as discussed later. In the 1.5 T case, the first few Al<sub>3</sub>Ni phases were seen on the right-hand side (Fig. 7.24d1), aligning vertically and in parallel with the magnetic flux direction (white arrow in Fig. 7.24d3). Subsequently, more Al<sub>3</sub>Ni phases appeared as shown in Fig. 7.24d2–6 and maintained their vertical growth direction. Generally, two scenarios were often observed for the growth of Al<sub>3</sub>Ni phases. At the early stage, Al<sub>3</sub>Ni phases (for example, those labelled 1–8 in Fig. 7.24) grew freely in the liquid matrix and a single phase could grow up to 2 mm long with magnetic pulses. At a later stage and when the number of Al<sub>3</sub>Ni phases increased to a certain value, their growths were often affected by impingement onto the neighbouring phases. Then, the growth either

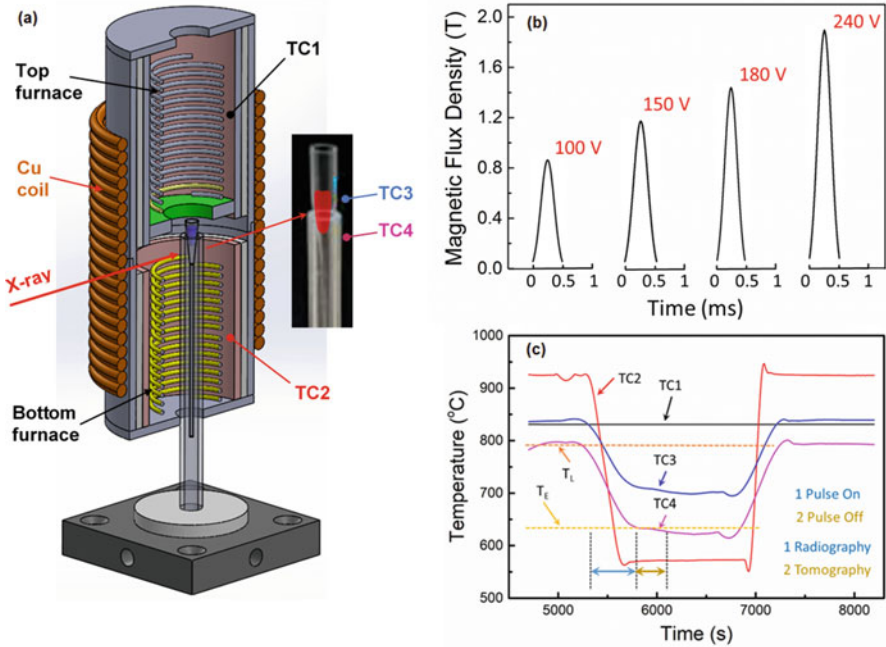


**Fig. 7.23** (a) A cut-off CAD drawing, showing the upgraded pulse magnetic field solidification apparatus with an enlarged inset on the right, showing the special quartz tube sample holder and the liquid metal alloy. (b) The measured magnetic flux density with discharging voltage of 100, 150, and 180 V respectively. (c) The measured temperature profiles at four points (TC1- top furnace, TC2- bottom furnace, TC3 and TC4 close to the metal sample), and the period when pulse was applied and when radiography and tomography were taken during the solidification experiment (adapted from [32])

stopped or changed direction. By measuring and analysing the time-evolved growing lengths of the 8 labelled free-growing  $\text{Al}_3\text{Ni}$  phases, it indicated that pulse magnetic fields increased 2–3 times the  $\text{Al}_3\text{Ni}$  phase length. At the early stage of phase growth (less than 10 s), the  $\text{Al}_3\text{Ni}$  phase free growth rates in the three pulses cases were approximately 10–40 times higher than in that of the 0 T case. Hence, pulse magnetic fields greatly increased  $\text{Al}_3\text{Ni}$  phase free growth rate [32]. At the end of each radiography acquisition, tomography was used to obtain the 3D information for each case. Pulses were switched off during tomography acquisition.

Figure 7.25 shows the 3D renderings of the four cases. In the top row, Fig. 7.25a1–d1 show the 3D structure and morphology of the  $\text{Al}_3\text{Ni}$  phases. The second row (Fig. 7.25a2–d2) shows the same but transparent primary  $\text{Al}_3\text{Ni}$  phases from Fig. 7.25a1–d1 with their skeletons; Fig. 7.25a3–d3 show phases peeled down to only their skeletons, e.g. the central line of the tracked phases. Figure 7.25a1–a1 show that, under 0 T, most of the primary  $\text{Al}_3\text{Ni}$  exhibited simple long block structure with flat surfaces. Facet-type steps were often observed on the phase surfaces, indicating that facet-type growth with planar surface are the main growth mechanism without pulse. In the case of 0.85 T, more protrusions or irregularity was



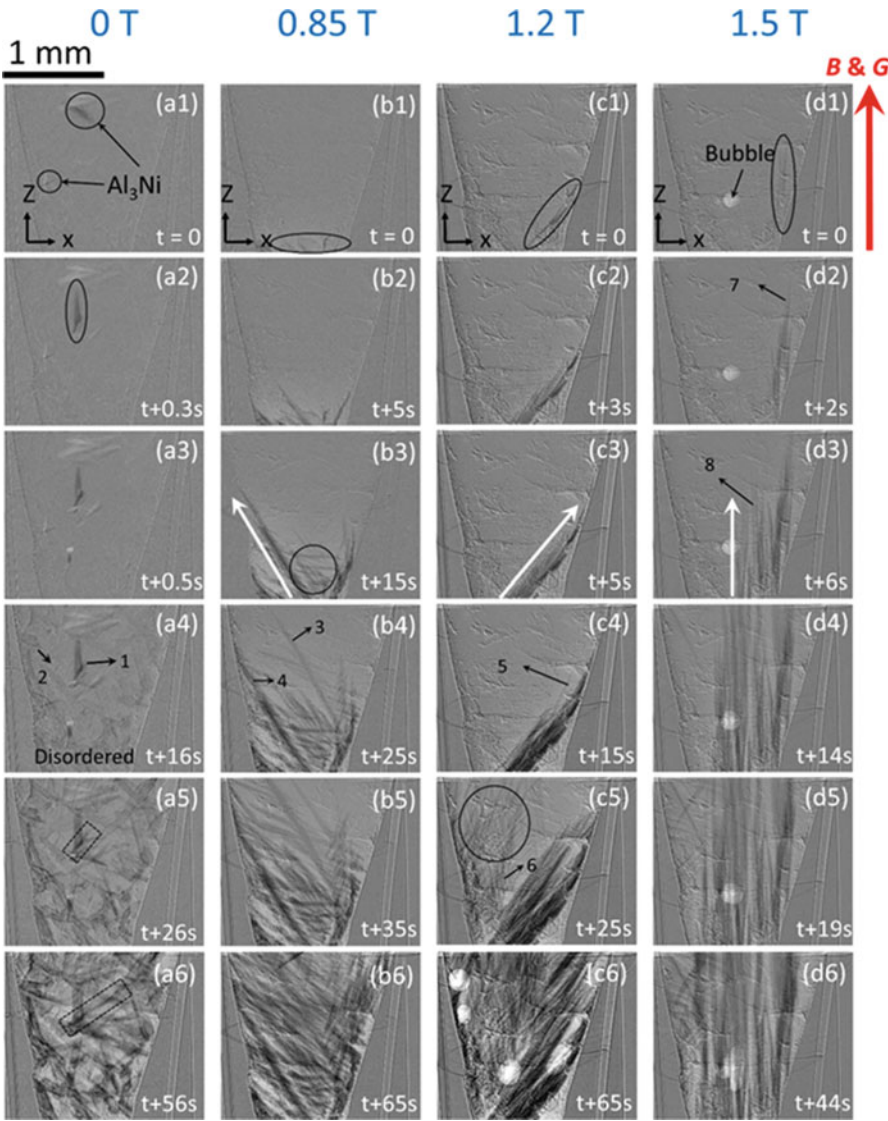


**Fig. 7.24** Four columns of synchrotron X-ray radiographs, showing growth dynamics of the primary  $\text{Al}_3\text{Ni}$  intermetallic phases of an Al–15%Ni alloy during the solidification of (a column) without magnetic pulse (0 T), and with magnetic pulse of the peak value of (b column) 0.85 T, (c column) 1.2 T, and (d column) 1.5 T. For all cases, the measured average temperature gradient was  $G = 42.5 \text{ K/mm}$ , the cooling rate was  $V = 0.35 \text{ }^\circ\text{C/s}$ , and the pulse frequency was 1 Hz (adapted from [32])

found in the phase surfaces, indicating the start of transition away from facet growth towards dendrite growth. Such trend became more clearly in the case of 1.2 T where a number of dendritically-structured phases were formed. At 1.5 T, the  $\text{Al}_3\text{Ni}$  phases grew into well-developed side branches (the secondary arms). Clearly, the transition

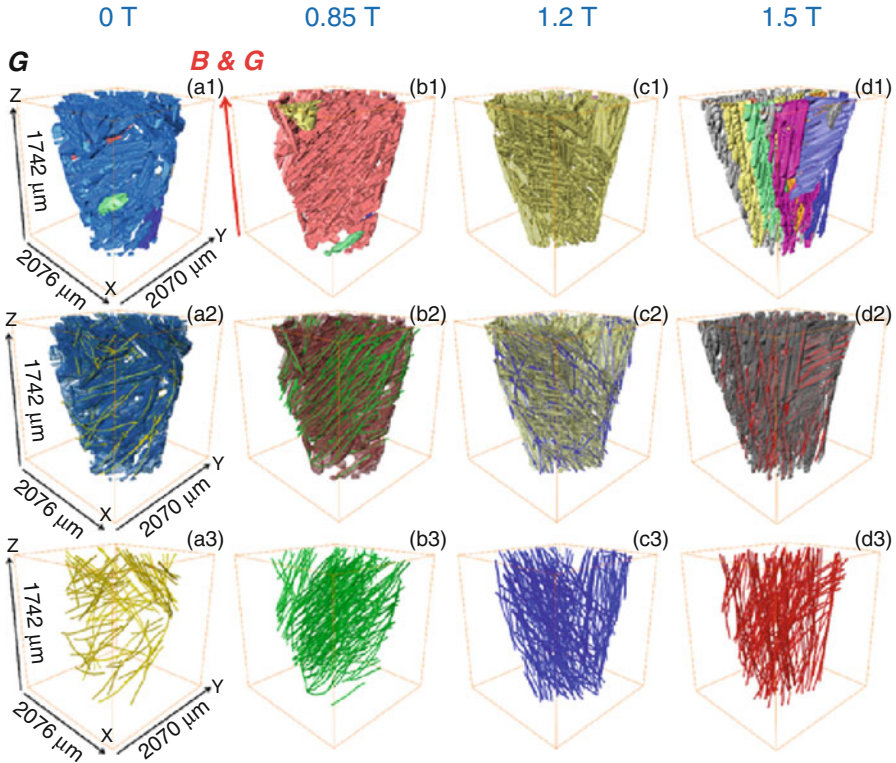


**Fig. 7.25** Four columns of tomography dataset renderings, showing 3D structure and morphology of the  $\text{Al}_3\text{Ni}$  phases, corresponding to the four cases in Fig. 7.24. Skeletonisation analysis was also used to obtain the skeletons for the phases in each dataset for further statistical analyses on phase length, phase angle and orientation distributions (adapted from [32])

from facet growth (structures with planar surfaces) to dendritic growth (tree-like) occurred at approximately at 0.85 T, because the temperature conditions were identical. The difference in the phase morphologies was the results the changes of growth modes at the liquid-solid interface due to the application of magnetic pulses. One of the most interesting phenomena found in the real-time studies was the fragmentation of  $\text{Al}_3\text{Ni}$  phases when the applied pulse was larger than 0.85 T. A video (see the attached Video 1) extracted from the bottom part of the 0.85 T case shows clearly and unambiguously the fragmentation of many primary  $\text{Al}_3\text{Ni}$  phases. The fragments often occurred in the inter-dendritic region between bigger phases; and the fragmentation events occurred clearly in the whole region of sample volume. The fragments rained down under the action of 0.85 T pulse, much different to the fragmentation events observed in dendritic structures due to enhanced fluid flow or solute remelting. This is first time that such real-time fragmentation of  $\text{Al}_3\text{Ni}$  intermetallic phases has been reported. Further analysis indicates that the mechanism of phase fragmentation was due to the shear stresses caused by the difference in pinch force acting on the liquid phase and the solid  $\text{Al}_3\text{Ni}$  phases by the pulse magnetic field [32].



## 7.4 Summary

In more than 40 years, significant progress has been made to understand the fundamental issues related to the mechanisms of grain nucleation, grain growth, and liquid–solid interface stability and morphology changes during solidification of metal alloys under pulse electric currents and pulse magnetic fields. However, most of the research has been carried out in specially designed experimental environments and with special sets of experimental parameters. Much of the research findings and explanations are only restricted to and based on those isolated experiments. Results and interpretations from different researchers are often inconsistent, and sometimes even contradictory to one another. As a result, so far there is no report of any wide uses of pulse external fields in metal industry, especially in casting industry. Fundamental research using combined in situ experimental approaches and multiphysics modelling methods need to be carried out in order to facilitate more systematic studies with the aims of obtaining in-depth and quantitative understanding of the inherent multiphysics problems in solidification processes under pulse external fields. Then, applied industry scale-up research for accelerating their uses and applications in industry can follow.

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# Chapter 8

## Thermal Melt Processing of Metallic Alloys



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### 8.1 Molten Alloy Structure

The overwhelming majority of technological processes for producing metallic alloys involve melting of initial materials and subsequent solidification of the system at various, sometimes very high, cooling rates. In an attempt to improve the structure and service properties of ingots, cast and deformed semifinished products, process engineers have paid considerable attention to the search for optimal solidification conditions. The regimes of heat and mechanical treatment of cast metal are progressively improving. The first stage of the process—the initial melt—is, however, traditionally of marginal interest to metallurgists. In most cases, attempts to affect the system at this stage are confined to additional alloying with the aim of optimizing the system composition and to cleaning the system in an effort to remove deleterious impurities, both soluble and insoluble.

At the same time, a great body of data has been accumulated in scientific periodicals over the past 40 years, which indicate that metallic melts are dynamical systems of high complexity. They can exist in different structural states and perform transitions between these states under the influence of various external actions. The role of the structural state of the initial melt in the formation of the structure and

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properties of ingots produced from this melt and, consequently, the structure and properties of deformed semifinished products is also reported. The conclusions from most studies have been drawn based on the investigations of the morphology, structure, and properties of the already solidified material and seldom from the precursor liquid itself. In this sense, the interpretations of the observed effects have been indirect.

In molten metals and alloys, the strong interaction of constituent atomic clusters substantially limits their relative positions. The resulting correlation is referred to as the local order, or short-range order. The nature of this local order and the size of clusters with strongly correlated particle positions depend on the composition of the material, on the temperature and pressure. The atomic arrangements in small clusters of simple, close-packed materials are often interpreted as being reminiscent of crystalline order. The local order can be characterized by geometric parameters that are invariant under rotations (e.g., coordination lengths and numbers, and characteristic angles in the pattern). However, it has to be realized that the structure on the atomic level of a molten system is fluctuating with time, and thus these interpretations yield time-dependent parameters.

Liquid metals and alloys can be considered as systems consisting of three different kinds of components on the atomic level, i.e., nuclei, ions, and electrons. Accordingly, the physical properties are determined by the interactions between these three kinds of particles. One might expect the local order to be strong and at least to some degree close to a crystalline local arrangement and that it does not significantly change even when the global order is lost by melting. On the other hand, the melting allows the orientations of local symmetry axes to fluctuate and become uncorrelated at some finite distance.

Whether a molten alloy after melting is homogeneous or not on the atomic scale has been an issue for many experimental investigations using a multitude of techniques. In some of these investigations, anomalies in measured property/temperature curves found at temperatures well above the liquidus temperature have been interpreted as indications for the existence of metastable micro-heterogeneous states of the melt inherited from original solid phases, and their irreversible transition into the homogeneous melt state [1–7]. It has also been suggested that the existence of atomic clusters in molten alloys might be of thermodynamic origin and that the status of the melt corresponds to specific metastable temperature- and time-dependent states [8–11]. In both interpretations, a melt may be considered as a microstructural two-phase system. Some experimentalists interpret the observed anomalies evidence for the existence of a liquid/liquid phase transition [12], while others have not observed any anomalies in the measured property/temperature curves. The existence or not of a liquid/liquid phase transition and its possible influence on the time- and temperature-dependent structure of a molten alloy is, however, a subject in itself and will not be discussed here. In this chapter, we will focus on the main features and the stability of liquid alloy structures as well as on practical applications of the related phenomena.

The properties of melts may be described on the different levels. On the macroscopic scale, we have physical properties such as density, viscosity, surface tension,

etc., while on the microscopic level there are two sublevels, one referring to the microstructure on a length scale larger than several microns and one to the atomic structure on the less-than-nm length scale. Knowledge of alloy properties on all length scales is required for the adequate prediction of alloy properties suitable for a specific technological application. In this connection, it is also important to note the differences between what are referred to as “industrial alloys” and “model alloys.” The distinction between these two kinds of alloys can be bridged by a systematic investigation of the effect of controlled amounts of impurities on some key model alloys.

Samples for studies of the physical properties of melts are very often made by arc melting the elements, and an ingot for further studies is produced by casting. In many cases, the ingot is remelted several times before and after casting in order to ensure that the sample to be studied is homogeneous with regard to its elemental composition. However, sometimes an ingot is made by casting after induction melting in order to determine its physical properties. The melt is afterwards studied during direct melting or solidification in a container that is presumably made by some inert material. The levitation techniques are sometimes used because they do not require containers and eliminate their possible influence as well as gravitational effects. It should be noted that these different production and measurement techniques do not necessarily give the same results as will be further discussed below.

Let us now briefly describe and report on studies that in our opinion are most significant for understanding the physical properties as well as the structure and microstructure of conventional molten alloys. We will thus not deal with molten immiscible alloys as they exhibit significantly different structural behavior in the molten state. A complete coverage of this subject is outside the scope of the present text.

## **8.2 Experimental Studies of Liquid Alloy Structure**

### ***8.2.1 Some Experimental Methods Used to Study the Structure and Microstructure of Molten Alloys***

The structure on the atomic length scale of liquid metals and alloys is commonly investigated by neutron and X-ray scattering techniques. Other methods based on, for example, X-ray absorption spectroscopy, are also in use but they give more limited and specific information. Numerical simulations are frequently used to complement experimental studies and may be helpful in predicting specific physical properties, such as structure, viscosity, diffusive behavior, etc.

Experimental work in this area of research is very demanding and only few systematic studies of the structure of liquid metals and alloys as a function of temperature and composition have been performed. Neutrons and high-energy X-rays that are preferably used for these studies are only available at international

facilities. Neutrons are scattered by the atomic nuclei via a weak interaction and yield, via scattering measurements, structural information of the bulk of a sample of a centimeter-size. X-rays on the other hand interact strongly with the matter via the electrons and thus X-ray measurements give structure information valid for some micron-thick surface layers only. High-energy X-rays produced at synchrotron facilities are, however, able to give accurate detailed structural information also for bulk samples of up to several hundred micron thickness.

Metallic melts are furthermore very aggressive and the interaction between the melt and the container walls is a serious problem. This has to some extent been solved by using levitation techniques in which no container is needed to house a sample [13]. In this technique, the sample is subjected to a high-frequency alternating current and performs small oscillations around an average position. The detailed studies show that an alloy heated in an ordinary furnace does not necessarily have the same structure and microstructure as the same alloy heated in an induction furnace or by the levitation technique, even if the initial ingot has been produced in the same way.

### 8.2.1.1 Small-Angle Scattering of Neutrons and X-rays

Small-angle scattering (SAS) using both X-rays and neutrons is a very powerful tool to investigate the microstructure of a material and it has been extensively used for characterization of alloys in the solid state [14, 15]. Although studies of molten alloys by these techniques are very few, these are the most powerful experimental techniques for real-time investigations of the microstructure of a molten alloy.

SAS occurs because of differences in scattering properties of a system on a length scale larger than the interatomic spacing, i.e., for features that have size larger than about 1 nm. In this case, the quantity that determines the intensity of the scattered radiation, is the contrast

$$C = \rho_p - \rho_m, \quad (8.1)$$

where  $\rho_p$  and  $\rho_m$  are the scattering length densities for a particle and for the medium, respectively.

The scattering length density  $\rho_p$  is defined by

$$\rho_p = b_p/v_p, \quad (8.2)$$

where  $b_p$  is the average scattering length of all atoms in particle  $p$  and  $v_p$  is the volume of the particle.  $\rho_m$  is determined by the corresponding quantities for the medium.

It is important to note that no SAS occurs from a homogeneous system, and also that  $\rho$  depends both on the composition and density. SAS measurements can be carried out both with X-rays (SAXS) and with neutrons (SANS) but they cannot

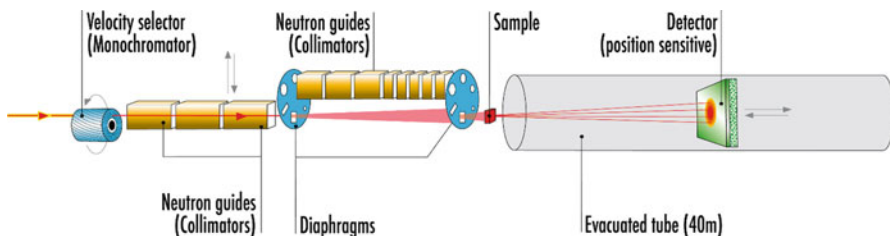


**Fig. 8.1** Schematic layout of the small-angle neutron diffractometer D11 at Institute Laue–Langevin, Grenoble, France (<https://www.ill.eu/instruments-support/instruments-groups/D11>) (kindly provided by the ILL—[www.ill.eu](http://www.ill.eu))

yield direct structural information on the atomic level. However, from the shape of the scattered intensity patterns and by combining different properties of the scattering cross section, some characteristic features of an inhomogeneous system like the concentration of particle clusters, their average composition, and their size distribution can be obtained. A detailed theoretical background for SAS can be found, for example, in [14, 15]. In order to reach as small scattering angles as possible and thus detect larger particles, a SANS diffractometer is made very long as can be seen in Fig. 8.1 that shows a schematic layout of the D11 instrument at Institute Laue–Langevin, Grenoble, France (<https://www.ill.eu/instruments-support/instruments-groups/D11>). The reactor source situated more than 140 meters away delivers a polychromatic beam of neutrons which is monochromated by the velocity selector. The divergence of the neutron beam is adjusted by the collimators and, after being scattered in the sample, the neutrons are detected in a position sensitive detector. The accessible neutron wave-vector range is about  $3 \times 10^{-4} \leq Q \leq 1 \text{ \AA}^{-1}$ . Here,  $Q$  is the wave-vector transfer of the used radiation in the scattering process and is given by  $Q = 4\pi/\lambda \sin(\theta)$ , where  $\lambda$  is the radiation wavelength and  $2\theta$  the scattering angle.

### 8.2.1.2 Neutron and X-ray Diffraction

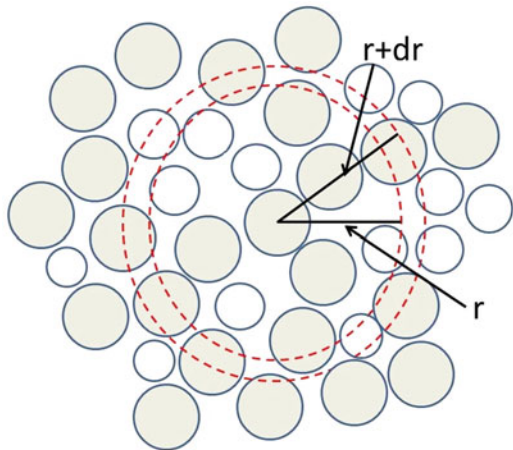
The structure on the atomic level is investigated by diffraction techniques, both using neutrons and X-rays. The structure of a disordered system consisting of atoms of two different species,  $\alpha$  and  $\beta$ , is schematically presented in Fig. 8.2. In order to describe the structure, it is convenient to define partial pair distribution functions  $g_{\alpha\beta}(r)$  that in turn are defined through radial distribution functions [16]:

$$\text{RDF}(\alpha\beta) = \rho 4\pi r^2 g_{\alpha\beta}(r) dr, \quad (8.3)$$

where  $\rho$  is the number density of the system. The  $\text{RDF}(\alpha\beta)$  functions give as illustrated in Fig. 8.2 the number of  $\alpha$  atoms within the shell of thickness  $dr$  at distance  $r$  from a  $\beta$  atom.



**Fig. 8.2** Schematic arrangement of atoms in a disordered system and definition of an atomic shell around an atom



In a diffraction experiment with X-rays or neutrons, the measured intensity is proportional to the structure factor  $S(Q)$  via [16]:

$$S(Q) = \sum_{\alpha=1}^n \sum_{\beta=1}^n c_{\alpha} c_{\beta} b_{\alpha} b_{\beta} S_{\alpha\beta}(Q), \quad (8.4)$$

where  $c_{\alpha}$  and  $c_{\beta}$  are the concentrations, while  $b_{\alpha}$  and  $b_{\beta}$  are the corresponding neutron scattering length of atomic species  $\alpha$  and  $\beta$ , respectively.  $n$  is the number of types of atoms, i.e., 2 in the case of a binary system, and  $S_{\alpha\beta}(Q)$  are the partial structure factors that in turn are related to the pair distribution functions  $g_{\alpha\beta}(r)$  via

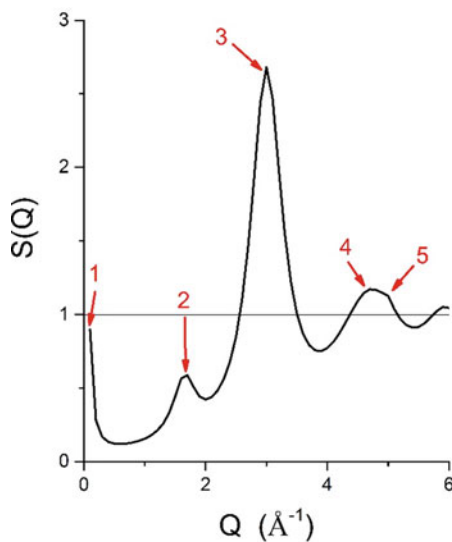
$$S_{\alpha\beta}(Q) - 1 = 4\pi\rho \int_0^{\infty} (g_{\alpha\beta}(r) - 1) \frac{\sin Qr}{Qr} r^2 dr \quad (8.5)$$

For X-ray diffraction,  $b_{\alpha}$  is to be replaced by  $f_{\alpha}(Q)$ , the atom scattering factor. The neutron scattering length,  $b$ , is a nuclear constant and is different for the different isotopes of an element thus making it possible to use the isotope substitution technique in order to determine the partial distribution function according to Eqs. (8.4) and (8.5). Equation (8.4) shows that in order to fully characterize the structure of binary system, three different measurements with different isotope composition have to be performed. However, this is very difficult (both experimentally and financially) to achieve, and in most cases only the average structure factors  $S(Q)$  are measured. As the sensitivity for different elements is different in neutron and X-ray diffraction, it is possible by combining the two techniques to determine to some extent the partial pair distribution functions  $g_{\alpha\beta}(r)$  [16, 17].

A measured static structure factor  $S(Q)$  being a weighted mean of pair interactions in a disordered binary system has some characteristic features (see Fig. 8.3) that can give some structural information directly. The presence of intensity at very small scattering angles (1 in Fig. 8.3) indicates that the system is inhomogeneous while the

**Fig. 8.3** Schematic features of a static structure factor for a disordered system measured by X-ray and neutron diffraction.

(1) Small angle scattering (SAS), (2) pre-peak, (3) main diffraction peak, (4) second diffraction peak, and (5) shoulder



existence of a pre-peak (2 in Fig. 8.3) to the left of the main peak (3 in Fig. 8.3) of the structure factor signifies a presence of a topological or chemical order in the scattering system. The existence of a shoulder (5 in Fig. 8.3) on the second peak (4 in Fig. 8.3) can be interpreted in different ways, the most popular one being that this feature signifies an icosahedral order of the atoms in the melt.

Diffraction measurements in liquid metals and alloys can be performed by using both X-rays and neutrons. As an example of an instrument suitable for these investigations, the layout of the D4 neutron diffractometer at the Institute Laue–Langevin, Grenoble, France (<https://www.ill.eu/instruments-support/instruments-groups/D4>) is shown in Fig. 8.4. A monochromatic beam of neutrons is impinging on the sample and the scattered intensity is recorded by 9 separate position-sensitive detectors fixed relative to each other in a bank. Each detector is spanning a scattering angle range of  $8^\circ$ . Thus, in order to scan the full angular range (i.e., from  $1.5^\circ$  to  $140^\circ$ ) the whole detector bank has to be rotated.

## 8.2.2 Microstructure of Molten Alloys

Arguably, the first conclusive evidence for the existence of well-defined atomic clusters existing in a molten alloy was obtained by SANS measurements on a eutectic Pb–Sn melt during heating and subsequent cooling [18]. Unfortunately, these first experiments did not cover a large enough temperature range ( $T_{\text{measured}} \leq 650^\circ\text{C}$ ) in order to fully demonstrate a complete dissolution of these structural inhomogeneities at high temperature. The derived volume-weighted particle size distributions functions (PSDF) reproduced in Fig. 8.5 clearly indicate that

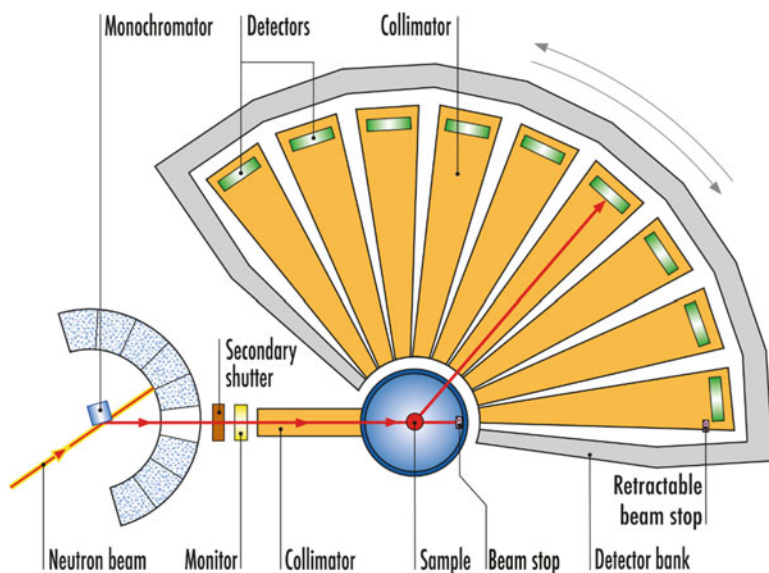


**Fig. 8.4** Layout of the D4 diffractometer at Institute Laue–Langevin, Grenoble, France (<https://www.ill.eu/instruments-support/instruments-groups/D4>) (kindly provided by the ILL—[www.ill.eu](http://www.ill.eu))

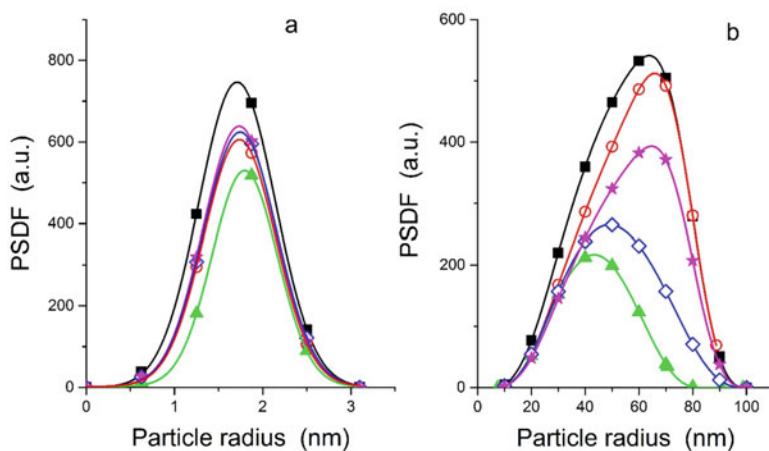


**Fig. 8.5** Volume-weighted particle size distribution functions (PSDF) for a molten eutectic Pb–Sn alloy at 250 °C (squares), at 350 °C (circles), and 650 °C (triangles) during heating and at 350 °C (diamonds) and at 250 °C (stars) during the following cooling: (a) for the small atomic clusters and (b) for the large atomic clusters (adapted from [18])

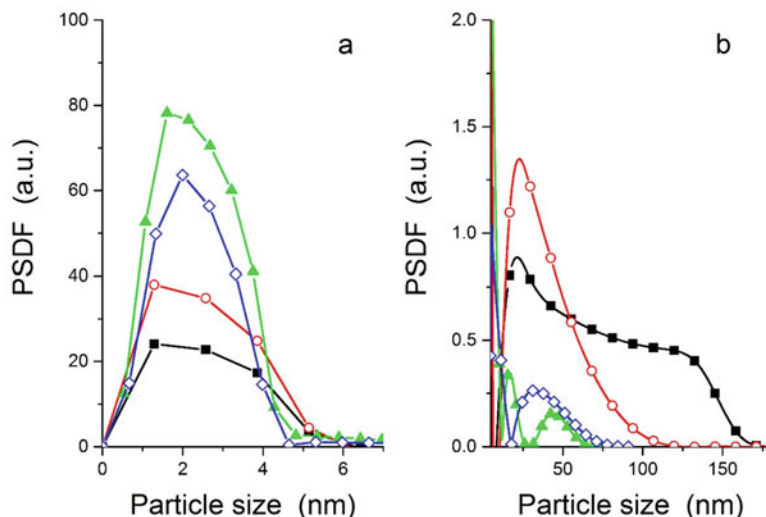


**Fig. 8.6** Derived volume-weighted PSDF for the  $\text{Al}_{80}\text{Si}_{20}$  alloy at 700 °C (squares), at 950 °C (circles), and 1200 °C (triangles) during stepwise heating and at 950 °C (diamonds) during subsequent stepwise cooling: (a) for the small atomic clusters and (b) for the large atomic clusters (adapted from [19])

the inhomogeneities continuously dissolve during heating and that they partially recombine during the subsequent cooling. Two particle size families were found to be present at all measured temperatures, one having an average size of about  $1.8 \pm 0.5$  nm and one of an average size slightly varying with temperature in the size range 30–90 nm.

Microstructures of the molten hypoeutectic  $\text{Al}_{93}\text{Si}_7$ , eutectic  $\text{Al}_{88}\text{Si}_{12}$ , and hypereutectic  $\text{Al}_{80}\text{Si}_{20}$  alloys at different temperatures were then studied in a series of SANS experiments [19]. Some of the obtained PSDFs derived from the measured SANS patterns during a stepwise heating–cooling sequence are shown in Figs 8.6 and 8.7. It can be seen that two size families of structure clusters exist in the alloys and that the shape of the PSDFs varies both with temperature and composition. The sizes of the large cluster domain decrease drastically with decreasing Si content, while the small domains instead seem to increase in size with Si content. The large clusters almost completely dissolve during heating in the hypereutectic alloys and recombine partially during subsequent cooling (Fig. 8.6). Similar behavior was observed for the hypoeutectic alloy. In the eutectic alloy (Fig. 8.7), however, the recombination tendency is strong and it can be seen that the number of clusters existing in the alloy at 700 °C is even larger after cooling from 1200 °C than immediately after melting. The number of small clusters varies significantly during the heating/cooling cycle while the shape of the PSDF remains more or less the same.

The authors [19] also performed measurements on the same alloys during continuous heating and subsequent cooling. The measured intensities as a function of

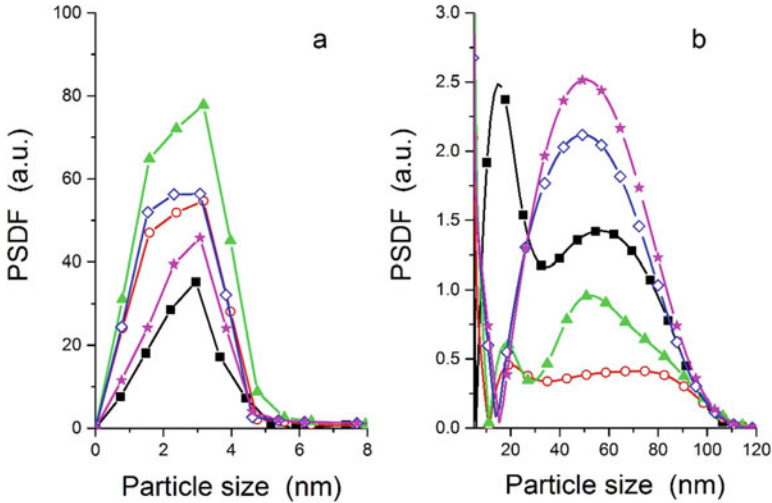


**Fig. 8.7** Derived volume-weighted PSDF for the  $\text{Al}_{88}\text{Si}_{12}$  alloy at 700 °C (squares), at 950 °C (circles), and 1200 °C (triangles) during stepwise heating and at 950 °C (diamonds) and at 700 °C (stars) during subsequent stepwise cooling: (a) for the small atomic clusters and (b) for the large atomic clusters (adapted from [19])

temperature are reproduced in Fig. 8.8 for three different  $Q$  values that very approximately correspond to domain sizes of 140, 50, and 30 nm. The measured intensities remain for all alloys more or less constant during the initial part of the heating, indicating that the microstructure does not change notably in this temperature range. For the hypereutectic alloy, the measured intensities drop monotonically during the heating up to 1200 °C in a very similar way for all three given  $Q$  values. The temperature, at which larger scattering particles dissolve, is increasing with the increasing Si content, i.e., from hypo- (Fig. 8.8c) to hypereutectic (Fig. 8.8a) composition. During the subsequent cooling to the solidification temperatures, the intensities do not change showing that the melt remains in the same temperature-independent metastable state when cooled from 1200 °C. Data are missing above 950 °C for the hypoeutectic alloy because the container broke during heating [19]. For the eutectic alloy, the change in microstructure during heating occurs in two steps, showing that the microstructure of the eutectic melt is significantly different as compared to the hypo- and hypereutectic melts [19].

More recently, small-angle X-ray scattering have unequivocally shown that melt aggregates exist in the molten hypoeutectic Al–15 wt% Cu alloy in the temperature range of about 630–1000 °C [20]. The size of the aggregates was found to be 2.7 nm and more or less independent of temperature. The analysis of the measured patterns showed that an aggregate had a core with an interfacial thickness of about 1 nm. It is interesting to note that the particles found to be present in this molten Al–Cu alloy have sizes very similar to the ones of the small particles both in molten Al–Si and Pb–Sn alloys. Moreover, Brodova et al. [5] report the presence of clusters in molten

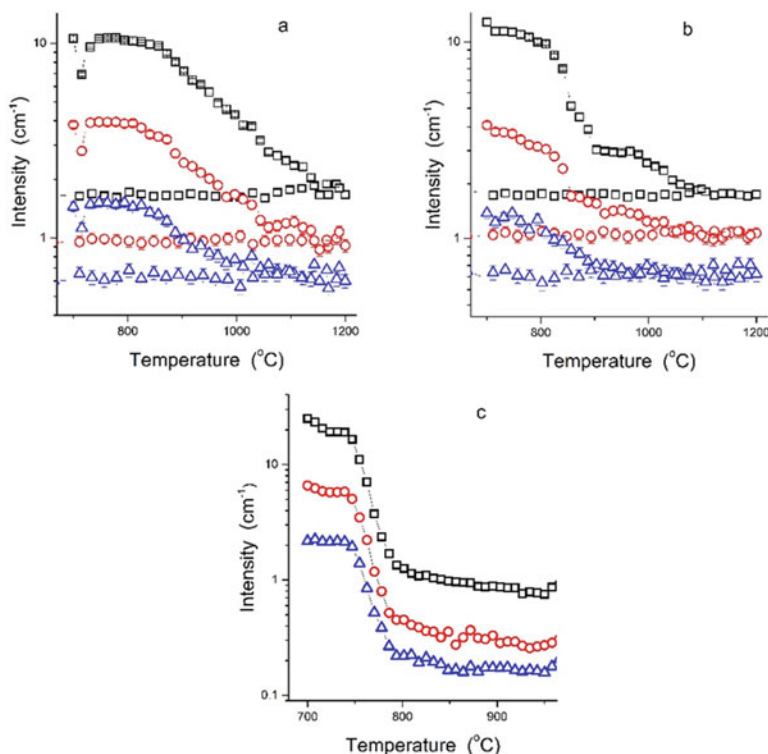


**Fig. 8.8** Measured intensities at three different  $Q$ -values during continuous heating and subsequent cooling for (a)  $\text{Al}_{80}\text{Si}_{20}$ , (b)  $\text{Al}_{88}\text{Si}_{12}$ , and (c)  $\text{Al}_{93}\text{Si}_7$  during heating only.  $Q = 0.0042 \text{ \AA}^{-1}$  (squares),  $Q = 0.011 \text{ \AA}^{-1}$  (circles), and  $Q = 0.017 \text{ \AA}^{-1}$  (triangles). The three curves correspond very approximately to particle size ranges centered round 140 nm (squares), 50 nm (circles), and 30 nm (triangles) (adapted from [19])

alloys with the radii in the range from 0.5 to 2.3 nm in Fe-, Co-, and Ni-based binary systems, and from 1.3 to 2.4 nm in the Al–Sc system, depending on the Sc concentration. It is also interesting to note in this connection that mixing in 0.075 wt.%  $\text{TiB}_2$  particles into the molten Al–15 wt% Cu alloy reduced the cluster size to about 1 nm indicating that aggregate sizes are sensitive to the presence of impurities [20].

### 8.2.3 Atomic Structure in Molten Alloys

According to Eq. (8.4), partial distribution functions can be obtained by changing the parameters  $b_i$  and  $c_i$ . For this kind of investigations, neutron diffraction is preferred as by using the isotope substitution method  $b$  is varied while the concentration of the alloy is fixed. Neutron and X-ray results on alloys of natural compositions may be

combined in order to derive partial functions either directly or via Reverse Monte Carlo (RMC) simulations [21, 22]. This method, being statistical in nature, yields one atom configuration which is consistent with the measured quantity. It has been shown that the partial functions measured by isotope substitution agree very well with the ones obtained from RMC simulation using neutron and X-ray diffraction on alloys of natural composition [17].

Well-separated pre-peaks (see Fig. 8.3) indicating the presence of a more or less pronounced topological or chemical order have been observed in many X-ray and neutron diffraction measurements on binary alloys, while in other measurements no pre-peak was observed. Very few extended elemental compositional range have been investigated. In many cases, only one composition of an alloy has been analyzed and the performed studies can be considered as tests only. This was illustrated for Al–Cu and Al–Ni alloys at two different compositions studied by XRD in a wide temperature range [23]. For the eutectic compositions, no pre-peaks were observed, while for compositions corresponding to stoichiometric crystalline phase a clear peak was observed, again indicating that the structures of these alloys at eutectic and non-eutectic compositions are considerably different. However, the absence of a pre-peak does not mean that there is no order in the molten alloy. For example, it was demonstrated that a well-defined intermediate topological order beyond 15 Å in scale existed in the molten Fe<sub>90</sub>Ni<sub>10</sub> alloy even if no pre-peak was observed [24].

Recently, neutron diffraction measurements revealed interesting features of the measured structure factors  $S(Q)$  for a molten eutectic Al–Si alloy [25]. The  $S(Q)$  obtained at two temperatures, 700 and 1100 °C, are reproduced in Fig. 8.9a. Both curves look perfectly ordinary and exhibit a clear damping of the oscillations with increasing temperature.

However, the difference between the two curves as demonstrated in Fig. 8.9b shows some obvious irregularities. In order to interpret these irregularities, the

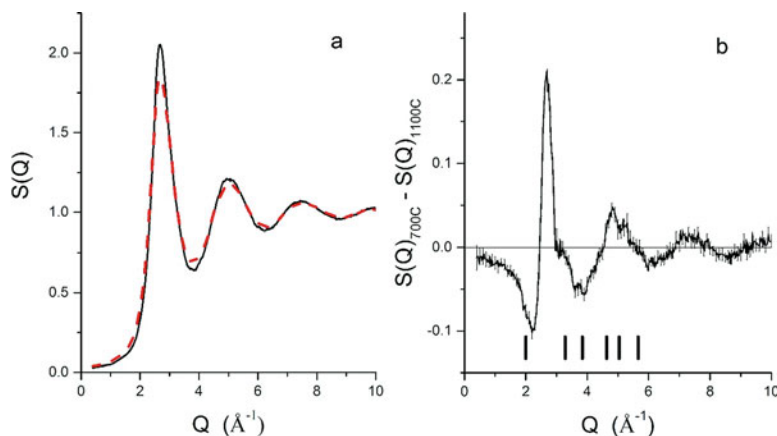


**Fig. 8.9** (a) Measured static structure factors for the molten eutectic Al–Si alloy at 700 °C (black solid curve) and at 1100 °C (red dashed curve). (b) The difference  $S(Q)_{700^\circ\text{C}} - S(Q)_{1100^\circ\text{C}}$ . The vertical bars denote position of diffraction peaks for solid Si (adapted from [25])



authors compared their positions to the diffraction peak positions for the diamond structure of solid Si, shown as vertical bars, and a very good agreement was found. Accordingly, it was concluded that the Al–Si eutectic alloy after heating to 700 °C (melting temperature is 586 °C) can be considered as a two-phase system, an aluminum-rich liquid matrix, and silicon-rich clusters. For structures to be detectable in a diffraction experiment, they must have dimensions larger than about 10 nm and have a well-defined structure. In earlier measurements, the diffraction peaks have not been observed presumably due to experimental limitations. The results presented in Fig. 8.9 [25] are in full agreement with the finding of the SANS results presented above [19].

Recently, the structure of molten Al–Ge alloys was studied at four temperatures and at 10 different compositions by X-ray diffraction [26]. Near the liquidus, the structure was found to consist of a quasi-eutectic structure in which Ge-like local clusters with covalent bonding exist. The formation of a homogeneous solution was found to be promoted by an increase in temperature and a simultaneously increased metallization of the covalent bonds. These results agree well with those obtained earlier for Al–Si alloys [19].

Similar information of the temperature-dependent structure was obtained from neutron inelastic scattering measurements on three molten Al–Cu alloys, the hypoeutectic  $\text{Al}_{90}\text{Cu}_{10}$ , the eutectic  $\text{Al}_{83}\text{Cu}_{17}$ , and the hypereutectic  $\text{Al}_{75}\text{Cu}_{25}$  during heating [27]. The greater intensity of the pre-peak with increasing the Cu content indicated an increased chemical order in the alloy. However, the most spectacular effect seen in these measurements was a significant intensity increase in the very small  $Q$  region occurring at about 900 °C for all alloy compositions. This intensity increase was not observed at 700 °C and only to a small extent at 1100 °C. The authors did not speculate about the origin of this effect but it might indicate a tendency for cluster formation or the existence of a kind of phase transition close to this temperature. Some pre-peaks have furthermore been observed in diffraction measurements on an  $\text{Al}_{60}\text{Cu}_{40}$  alloy [28] and in an  $\text{Al}_{66.7}\text{Cu}_{33.3}$  alloy [23].

Recently, some rather spectacular results on the temperature variation of  $g(r)$  for different kinds of binary molten alloys were presented [29]. The positions of the first peak in the pair distribution function  $g(r)$  were found to decrease with increasing temperature, suggesting an anomalous contraction of the first neighbor coordination shell, while the radii of the second and third ones increased. Similar effects were earlier observed in some pure molten metals [30]. The measurements in [29] were performed using the sample levitation technique while in [30] a silica capillary was used to house the sample, which showed that the results were independent of sample treatment. The experimental findings were confirmed by molecular dynamics calculations and were interpreted in terms of the cluster model and of different temperature variation of the partial pair distribution functions. Thus, these results indicated an increased short-range order with increasing temperature, which is in accordance with the temperature variation of the PSDF for molten Al–Si alloys shown in Figs. 8.6 and 8.7 [19]. However, systematic and detailed investigations of molten metals and alloys as a function of composition and temperature, that might help to understand the structure and the microstructure of liquid alloys, are still sparse.

Some investigations have been devoted to the modification of the structure of binary molten alloys by adding a third element. It is well known that small additions of Na, Sr, Cu, etc. may drastically change the structure of a solidified Al–Si alloy but the influence of additions on the structure of the melt has been studied only in very few cases and unfortunately not in a systematic way. Some extensive investigations on the effect of trace amounts of Sr (0.04 wt%) on the melt structure of Al–Si hypoeutectic alloys were reported in [31]. This study showed that at all superheat temperatures up to 800 °C (which is about 200° above the liquidus) and at all Si contents the melt structure was altered. The authors claimed that the addition of Sr had a more pronounced effect at the eutectic composition, causing a delay or even completely inhibiting the atomic clustering tendencies in the melt. In another study, it has been found that addition of Ni to a molten  $\text{Al}_{88}\text{Si}_{12}$  alloy promotes the growth of structurally ordered clusters [32].

The structure of molten X–Si and Al–X–Si (X = Ni, Co) and also of some other ternary Al-rich alloys was studied by X-ray diffraction [33–36]. The temperature range in these studies was typically restricted to some hundreds of degrees above liquidus. In all cases, it was found that the addition of a third atom had a significant effect of the melt structure and promoted the formation of heterogeneous structures in the melt. For all the alloys, the pre-peak increased in intensity with increasing the Si content, indicating a distinct inhomogeneous structure on the atomic level. The analysis of the data indicated that this might originate from both interactions between transition-metal pairs but also from ternary interactions.

## 8.3 Structure-Sensitive Properties of Liquid Metals

### 8.3.1 *Experimental Techniques*

Physical properties of molten alloys have been extensively investigated by both experimental and theoretical means in order to improve the quality of the solidified ingots in industrial applications. The properties such as density, viscosity, internal friction, surface tension, electrical resistivity, etc. have mostly been studied on binary alloys. However, in many cases the difference between results can be surprisingly large. These differences might be due to several reasons, for example, different physical status of the parent ingots, i.e., the way the ingots were produced, different external treatments of the ingot but also of the melt, the presence of impurities, etc. Moreover, it could also be due to the fact that different experimental techniques do not necessarily couple to the same microscopic features existing in the melt. It is also important to note that some published data were obtained during heating only, some only during cooling after that the sample had been heated to a high temperature, some during repeated heating/cooling cycles and yet some under melt flow. All these circumstances should be considered when comparing results found in the literature.

A great number of theories and models have been developed in order to interpret and predict the physical properties of molten alloys [37–39], with varying success. A common experience is that a model found to describe one property for one alloy does not satisfactorily describe the same physical property for another alloy. As an example, in a recent compilation of available experimental viscosity and diffusivity data for some Al-based molten alloys [40], substantial difficulties are demonstrated in comparing available experimental data to models and theories. The influence of the melt structure on the density and viscosity as well as on other physical properties of different types of alloys is the main subject to be exemplified and discussed below.

Many different experimental techniques are in use to measure the physical properties of molten alloys as can be found elsewhere [39, 40]. Here, we only briefly mention the methods for measuring the density and the kinematic viscosity of a molten alloy.

A convenient way to obtain the density is to study the attenuation of  $\gamma$ -rays that are transmitted through a liquid material. A schematic layout of the method is shown in Fig. 8.10. The intensity  $I_0$  of the  $\gamma$ -rays emitted from the source is attenuated when passing the sample according to an exponential law [41]:

$$I = I_0 \exp(-\mu\rho x), \quad (8.6)$$

where  $\mu$  is the mass absorption coefficient which depends on the exact elemental composition of the sample and on the energy of gamma radiation,  $\rho$  is the sample density, and  $x$  is the sample thickness. Thus, in order to derive the density from the measured intensity decrease, one has to know not only the sample thickness,  $x$ , but also its elemental composition in the irradiated zone. Therefore, the irradiated volume has to be representative of the entire sample.

Another important property in relation to the production of solidified alloys is the kinematic viscosity. A review of experimental techniques available for this purpose can be found elsewhere [42]. In these measurements, the molten alloy is contained in a crucible which is set in motion around its vertical axis. The

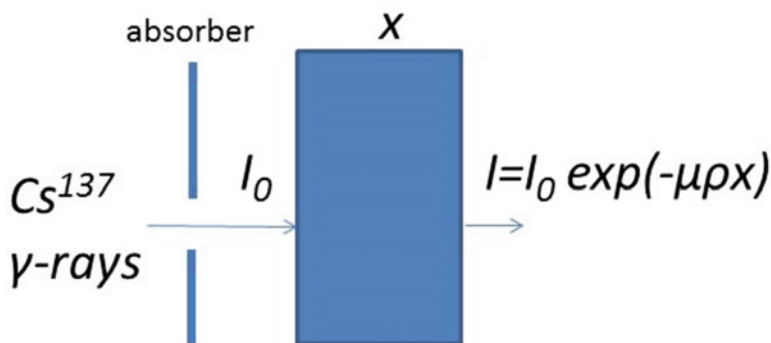


**Fig. 8.10** Schematic layout of a  $\gamma$ -ray transmission experiment

oscillatory motion of the crucible is damped by the friction between atomic layers in the melt. The viscosity is calculated from the decrement and the time period of the oscillations. It was found by measurements performed with different kinds of crucibles that the surface roughness of the crucible had a small effect on the measured viscosity of a eutectic Pb–Sn alloy [43]. The accuracy in the derived absolute viscosity is limited (2–3%) while the accuracy of a measured temperature variation is higher (~1%).

### 8.3.2 Binary Alloys

The physical properties have been measured for a large number of binary alloys. However, very few binary systems were investigated within full concentration and temperature ranges, and most studies were performed for specific concentrations chosen according to stoichiometric compositions found in the relevant phase diagram. The temperature ranges of superheat in these studies were different but mostly 50° to 1000° above the liquidus. Some investigations were devoted to studying the reproducibility of results. Out of these, we can mention the measurements of the electrical resistivity of molten In–Bi alloys after repeated heating/cooling schemes in which the anomalies found during the first heating were suggested to be due to a release of gas and/or breaking up of oxides present on the ingot [44].

Many Al-based binary alloys, especially in the Al-rich corner of the corresponding phase diagram, were studied. For a large number of alloys, but not for all, the values measured during heating and subsequent cooling were found to be different. For example, the kinematic viscosity of Al–Fe<sub>x</sub> ( $x < 10$ ) alloys heated up to about 1300 °C showed a significant difference between heating and cooling curves [45] while for Al–Co<sub>x</sub> ( $x < 0.15$ ) alloys the curves coincided [46].

Experimental quantities have been measured during continuous or stepwise heating, sometimes also during subsequent cooling and reheating. A structural relaxation time of the order of hours and longer have been found in several molten binary alloys in this kind of measurements. For example, measurements of the absorption of ultrasonic waves in molten Pb–Bi and Pb–Sn alloys of eutectic composition revealed that relaxation processes lasting for more than 10 h took place in the alloys [47] during heating/cooling sequences. This has also been demonstrated in measurements of the electrical resistivity in molten Pb–Sn alloys of two different compositions [48]. It was found that after an ultrasonic pulse the melt takes longer than 2 h to recover, i.e., to come back to the original state. However, the relaxation effects that are due to time and those that are due to temperature are generally difficult to separate. The results presented below unequivocally show that the two quantities are interrelated.

Furthermore, it has also been shown that the viscosity in Al-rich melts of the Al–Y system during isothermal holding for several hours at temperatures more than 100° above liquidus increases significantly before a subsequent exponential

decay [49]. This increase in viscosity was explained by the temporal competition of two effects, an Ostwald ripening effect in which large heterogeneities present in the melt after melting grow and a general slow dissolution and homogenization effect [50]. A similar prolonged structural decay was also observed for Al–Fe melts [51].

### 8.3.2.1 Selected Results on Physical Properties Variation in Binary Alloys

#### Al–Si

The Al–Si phase diagram is of the simple eutectic type with no equilibrium intermediate crystal phases. Nevertheless, there is a rather large discrepancy between different studies in the measured physical properties. At the same time, it is commonly agreed that the non-Arrhenius behavior of density, viscosity, diffusion, surface tension, etc. reflects the inhomogeneity of the molten alloys and that they presumably consist of a mixture of regions with different compositions and structure.

This is illustrated in Fig. 8.11 where the temperature variation of the density as obtained by measuring the transmission of  $\gamma$ -rays for three different alloy compositions is shown during heating and subsequent cooling [1, 19, 25, 51]. The difference between the heating and cooling curves was interpreted as showing that structural inhomogeneities were present in the alloy after melting and that these were continuously dissolved during heating after a specific temperature  $T_d$ . The inhomogeneities disappeared when the melt reached the temperature where the heating and cooling curves coincided, denoted as the branching temperature,  $T_b$ , which is characteristic of every alloy composition [5]. The  $T_b$  temperatures are indicated by arrows in Fig. 8.11, and interestingly  $T_b$  is the highest at the eutectic composition.

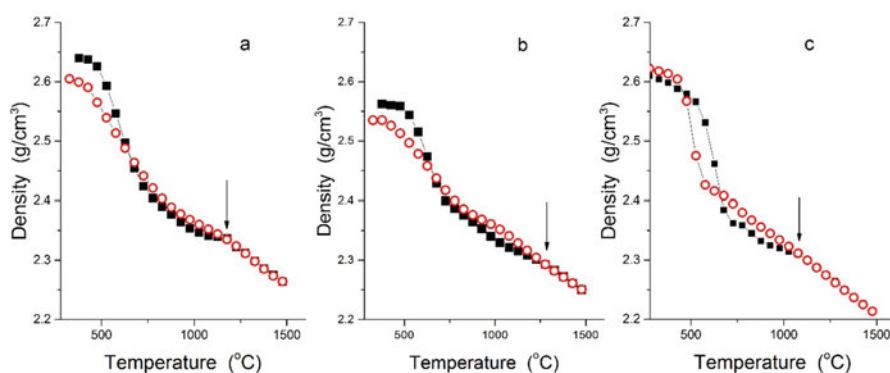
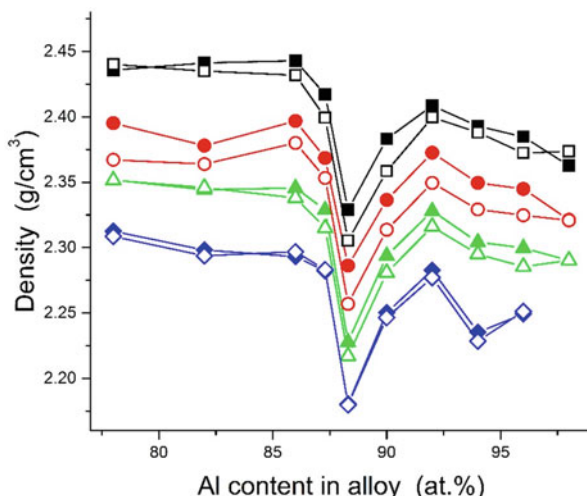


**Fig. 8.11** Densities obtained from gamma-ray transmission experiments for (a) hypoeutectic  $\text{Al}_{96}\text{Si}_4$ , (b) eutectic  $\text{Al}_{87.8}\text{Si}_{12.2}$ , and (c) hypereutectic  $\text{Al}_{82}\text{Si}_{18}$  alloys, during heating (full symbols) and subsequent cooling (open symbols). The arrows indicate the estimated  $T_b$  temperature (after [1, 25])

**Fig. 8.12** Measured densities for Al–Si alloys as function of composition at 727 °C (squares), 927 °C (circles), 1127 °C (triangles), and 1327 °C (diamonds) during heating (full symbols) and subsequent cooling (open symbols) (after [1, 19])



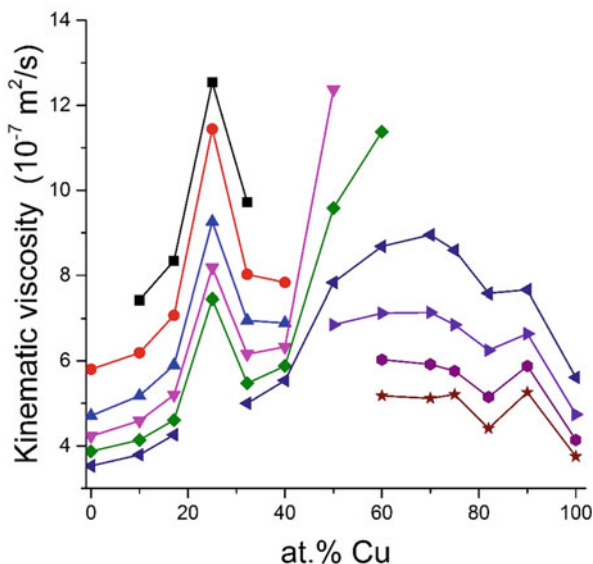
Another distinct feature shown in Fig. 8.12 [1, 19] is a clear decrease in density in a narrow composition range around the eutectic composition, both during heating and cooling. The density was derived from the transmission of a beam of  $\gamma$ -rays with a diameter of about 3 mm. The decrease of the measured density suggests that phase segregation takes place in the particular location where the beam is hitting the 40-mm high container. The magnitude of the density change does obviously not depend on whether the melt has been heated to the  $T_b$  temperature or not, and the authors suggest that it may correspond to a true thermodynamic melt state.

The measurement of the density of Al–Si alloys of several different compositions has also been performed using the sample levitation technique [52]. The measurements were performed during cooling from about 1450 °C. The density was found to increase linearly with decreasing temperature and no anomalous variation like the one shown in Fig. 8.12 was detected at the eutectic composition. Note that the levitated sample was subjected to a field produced by strong high-frequency alternating current. Thus, due to this, the melt was slowly oscillating. Consequently, the different temperature variation obtained in these measurements as compared to the ones measured during stepwise heating/cooling in an ordinary furnace (Figs. 8.11 and 8.12) illustrates the importance of considering external influences, i.e., here the electromagnetic field, when interpreting the measured values of different physical properties.

## Al–Cu

The measurements of the kinematic viscosity of many molten alloys have recently been compiled by Chen et al. [40] and compared to the current theories. The comparisons are rather discouraging as no existing theory can generally describe

**Fig. 8.13** Measured kinematic viscosities for molten Al–Cu alloys of different compositions at (from above) 600 (filled square), 700 (open circle), 800 (filled triangle), 900 (filled inverted triangle), 1000 (filled diamond), 1100 (left inverted triangle), 1200 (right inverted triangle), 1300 (filled circle), and 1400 °C (asterisk) (after [53])

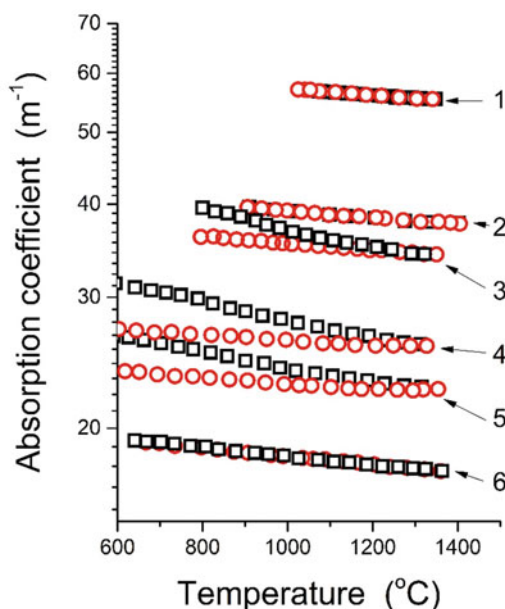


the temperature and composition variations of the measured viscosities. The complex variation of the measured viscosity presented in Fig. 8.13 [53] clearly illustrates this point. The strong maximum around 25 at.% Cu has earlier been also observed in Ref. [54]. This particular composition,  $\text{Al}_3\text{Cu}$ , does not correspond to any known crystal phase. A similar increase in viscosity taking place in a narrow composition range was observed in molten Al–Si alloys but in that case for the eutectic composition [19]. The origin of this viscosity increase is presently not well understood and could have easily been missed earlier when the studies were performed in too large composition intervals.

The densities of molten Al–Cu alloys have also been measured in wide temperature and composition ranges [55, 56]. The measurements were performed by the  $\gamma$ -ray transmission technique and the results, some of which are shown in Fig. 8.14, where the  $\gamma$ -ray absorption coefficient,  $\mu\rho$ , rather than the density is presented as a function of temperature. The reason why the authors presented the measurements in terms of the  $\gamma$ -ray absorption coefficient,  $\mu\rho$ , and not in terms of the density can be understood from Eq. (8.6): The relative amounts of matrix and clusters in the radiated zone are not known, hence one does not know the values of either  $\mu$  or  $\rho$  separately. Thus, only  $(I/I_0)$  and  $x$ , and the product  $\mu\rho$  can be experimentally determined. A difference in the values measured during heating and subsequent cooling was observed at all compositions. In a wide intermediate composition range, the differences were large indicating that the melt was in different metastable states, while in both the Al-rich and the Cu-rich regions the differences were small. The temperature variation of the absorption coefficient is probably due to the following two effects: (1) the change in the relative amount and composition of melt and clusters and (2) the sedimentation of heavy Cu-rich clusters by the gravitational force



**Fig. 8.14** Some examples of measured absorption coefficients  $\mu_p$  for some Al–Cu compositions. (1)  $\text{Al}_5\text{Cu}_{95}$ , (2)  $\text{Al}_{45}\text{Cu}_{55}$ , (3)  $\text{Al}_{55}\text{Cu}_{45}$ , (4)  $\text{Al}_{75}\text{Cu}_{25}$ , (5)  $\text{Al}_{83}\text{Cu}_{17}$ , and (6)  $\text{Al}_{95}\text{Cu}_5$  during heating (full symbols) and subsequent cooling (open symbols) (after [55, 56])



to the bottom of the sample container. It can thus be concluded from composition dependence of the measured densities and viscosities that there is no direct correlation between the composition at which anomalies are observed and the compositions corresponding to the existing solid phases on the phase diagram.

## Pd–Si

The molten Pd–Si alloy system has been studied in great detail, especially for the compositions around the two eutectic points,  $\text{Pd}_{82}\text{Si}_{18}$  and  $\text{Pd}_{80}\text{Si}_{20}$ . Moreover, Pd–Si alloys were among the first to be vitrified by rapid quenching and in this state it has been subject to many experimental studies. Figure 8.15 shows the influence of sample preparation on the measured density [51] and the sound velocity [57, 58]. Both quantities were measured during heating and subsequent cooling for the eutectic  $\text{Pd}_{82}\text{Si}_{18}$  alloy. One set of produced ingots (sample 1) was pre-melted in an induction furnace and the second set (sample 2) in an arc furnace. Sample 2 was crystallized at a somewhat higher cooling rate than sample 1. Structure investigation showed that sample 1 contained the stable crystal phases  $\text{Pd}_5\text{Si}$  and  $\text{Pd}_3\text{Si}$  while sample 2 contained metastable  $\text{Pd}_9\text{Si}_2$  in addition to the  $\text{Pd}_3\text{Si}$  phase. This structural difference shows the importance of the cooling rate for the phase composition of the solidified alloy.

Figure 8.15 shows clear difference between heating and cooling curves in the ingot produced by arc melting (sample 2) (open symbols). However, the corresponding difference for the ingot prepared by induction heating (sample 1)

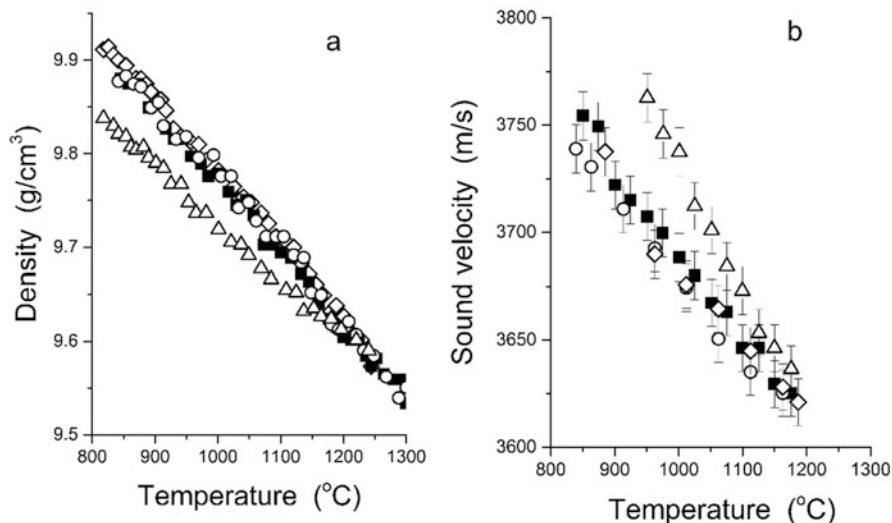


**Fig. 8.15** (a) Density [51] and (b) sound velocity [8] for molten  $\text{Pd}_{82}\text{Si}_{18}$  during heating (open symbols) and subsequent cooling (full symbols). The ingots have been produced by arc melting (triangles and diamonds) and by induction melting (squares and circles)

(full symbols) is considerably smaller. It can thus be concluded that the structures of the two initial ingots were different and that heating to  $1200^{\circ}\text{C}$  did not result in a homogeneous melt state. Nevertheless, the small difference between heating and cooling curves for the ingot produced by induction heating indicated that it was closer to such a state. The kinematic viscosities measured during heating of another ingot produced by arc melting up to about  $1300^{\circ}\text{C}$  and subsequent cooling coincided within the experimental errors (Fig. 8.16) [51]. This suggests that the melt might have reached the homogeneous solution state at  $1300^{\circ}\text{C}$ .

Furthermore, Sivkov et al. [51] reported the density of molten Pd–Si alloys in the composition range 11 to 33 at.% Si, produced in an induction furnace and measured during repeated heating up to  $1600^{\circ}\text{C}$  and subsequent cooling sequences. The measured values were fully reproducible for all alloy compositions except for the ones containing more than 28 at.% Si, indicating that heating of these hypereutectic alloys to  $1600^{\circ}\text{C}$  was not enough for reaching the fully homogeneous state.

## Pb–Bi

The time dependence of the structural homogeneity of Pb–Bi melts was studied by ultrasound techniques [47]. The ultrasound attenuation coefficient, presented as  $\alpha/f^2$ , where  $f$  is the ultrasound frequency, measured for a eutectic Pb–Bi melt is reproduced in Fig. 8.17a. The sample was continuously heated up to  $1100^{\circ}\text{C}$ , which is more than  $900^{\circ}$  above the eutectic temperature, for about 12 h and thereafter

**Fig. 8.16** Kinematic viscosity for molten  $\text{Pd}_{82}\text{Si}_{18}$  during heating (full triangles) and subsequent cooling (open diamonds) for ingots produced by arc melting (after [51])

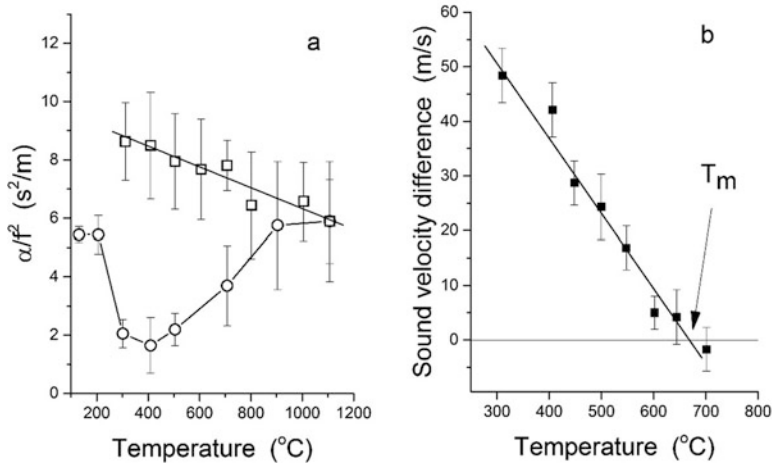
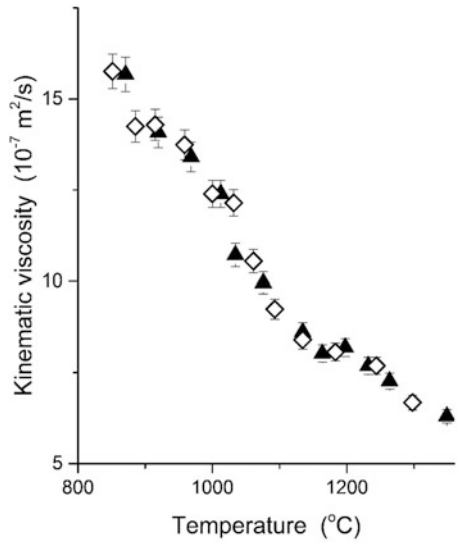


**Fig. 8.17** (a) Temperature dependence of the quantity  $\alpha/f^2$  where  $\alpha$  is the amplitude attenuation coefficient and  $f$  is the ultrasound frequency for a eutectic Pb-Bi melt measured during heating (squares) and subsequent cooling (circles). (b) Difference between the sound velocities measured close to the bottom and close to the top of the container for the eutectic Pb-Bi melt. The arrow indicates how the  $T_m$  temperature is defined. (After [47])

slowly cooled during another 12 h. A considerable decrease in the attenuation coefficient during heating and also during a part of the subsequent cooling is observed, with a branching point at about  $1100^{\circ}\text{C}$ . A similar behavior was earlier reported for molten Pd-Si alloys (see Fig. 8.15). This finding was considered as evidence that the inhomogeneities present in a molten alloy need a considerable time

to dissolve at a temperature below the branching temperature. These inhomogeneity regions were well defined and had a size comparable to the wavelength of the ultrasonic wave (about 10  $\mu\text{m}$ ). It can be concluded that the relevant time for microstructural changes to take place was of the order of hours [47] at this level of superheating. The increase of the attenuation coefficient during cooling from 300 °C corresponds to the melting points of the pure components.

Anomalous temperature dependence of internal friction, electrical resistivity, and thermopower was found in the Pb–Bi system [59]. Furthermore, accurate sound velocity measurements of liquid Pb–Bi alloys of different composition were performed [60]. The sound velocity was measured during cooling from about 900 °C. No irregularities were observed in the measured values, except close to the eutectic composition. The melting point at the eutectic composition is 123.5 °C. These results demonstrated that after heating above 900 °C, non-eutectic alloys can be considered as regular solutions.

Generally, if well-defined inhomogeneity regions are present in the melt they ought to have a different elemental composition than the matrix and, accordingly, a different density. This might in turn result in a sedimentation effect when heavier regions under the gravitational force conglomerate at the bottom of a container. This was verified by measurements of the difference of the ultrasound velocity for many molten alloys between the top and the bottom of a container [47]. The temperature variation of the difference in sound velocities is reproduced in Fig. 8.17b, and indicates that a structurally homogeneous eutectic Pb–Si alloy is obtained on the micron length scale at about 700 °C. This temperature, indicated by the arrow in Fig. 8.17 and called  $T_m$ , corresponds to the earlier defined branching temperature,  $T_b$ .

## Pb–Sn

Another molten alloy system for which the physical properties have been extensively studied is Pb–Sn, see, for example, [18, 58, 61, 62]. In these studies, like in many other systems, it has been found that the properties measured during heating are different from those measured during cooling, while in some other studies no such differences have been observed. The discrepancy between the results can be understood as follows: (1) the samples have not been produced in the same ways. (2) The measured temperature range has not been large enough. (3) The composition range has been too narrow. It has also to be emphasized that different experimental techniques are sensitive to different structural phenomena occurring in a melt. Consequently, it might be anticipated that methods kinetic in nature, such as torsion pendulum methods, yield different information regarding the melt structure than the  $\gamma$ -ray transmission technique. Moreover, measurements of the surface tension, electrical resistivity, and sound speed also correspond to different physical phenomena occurring in the melt.

Attempts have been made to represent the regions in which the melt can be considered as homogeneous in an alloy phase diagram. The pioneering work in this area was performed by Russian scientists more than 50 years ago. We refer to [5] for

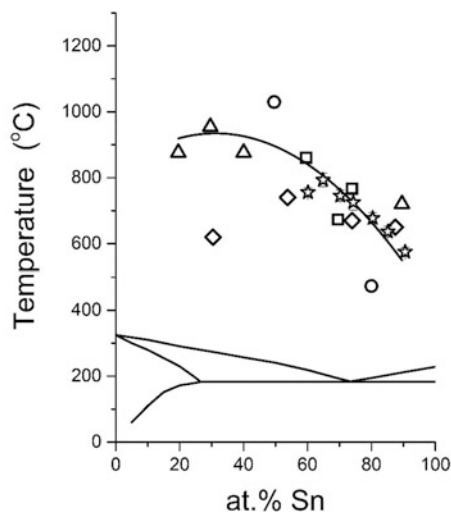


**Fig. 8.18** Branching temperatures ( $T_m$  as defined in Fig. 8.17 or  $T_b$  in [18, 19, 25]) plotted in the Pb–Sn phase diagram from the results of acoustic experiments with melts prepared by heating: (white triangle) the mixture of original components; (white square) a crystallized heterogeneous ingot obtained from a non-homogenized melt; (white circle) a crystallized heterogeneous ingot obtained from the melt overheated above the homogenization temperature. (white lozenge) refers to internal friction measurements by [62]. (white star) refers to density measurements obtained from  $\gamma$ -ray transmission technique published in [5]. The line is inserted to guide the eye

a review. This way of presenting a specific feature in a molten alloy is exemplified in Fig. 8.18 in which the branching temperatures ( $T_m$  as defined in Fig. 8.17 or  $T_b$  in [18, 19, 25]) are plotted on a schematic Pb–Sn phase diagram for alloys prepared in three different ways. The corresponding temperatures obtained from density [5] and internal friction measurements [62] are also included in the plot. The agreement between the different sets of data is very good except for the alloy with the smallest Sn content measured by internal friction. The results obtained from different ingot production methods agree very well. This shows that more or less similar metastable microheterogeneous states of Pb–Sn alloys appear in the melt, regardless of the method of their preparation.

### 8.3.3 Ternary Alloys

The effects of adding a third element to a binary alloy on its physical properties were studied in several works. In all cases, significant effects on the melt density as well as on the kinematic viscosity have been observed. For example, it was found that the viscosity of a eutectic Al–Si melt increases after the addition of P while it decreases after the addition of Sr [63]. It was furthermore shown that small additions of Li, Na, and Si to molten Al–Zn alloys have significant effects on different physical

properties during free flow of the liquid alloy in a temperature range of about 300° above the liquidus [64]. Moreover, for an Al–Co–Ce alloy it was found that the density was significantly larger in the liquid than in the solid state suggesting strong interactions between the components of the alloy melt and the existence of a distinct heterogeneous structure [65]. The temperature and composition dependencies of the viscosity of Cu–In–Sn alloys suggest the presence of inhomogeneous micro-regions [66]. For some ternary Fe-rich alloys, such as Fe–Si–B, it was also concluded from viscosity measurements that the alloy structure is heterogeneous only in a limited concentration range [67]. It can be concluded that adding even a small amount of a third element may have a strong influence on the properties of molten binary alloys.

It is obvious from the results presented above that molten alloys cannot be considered as simple homogeneous systems but that they after melting exhibit various kinds of atomic clustering phenomena. These depend both on temperature and time and can be influenced by external means, for example, by heating methods, by ultrasound, and by mixing in small amounts of additional elements. The structural recovery time after an external intervention such as an ultrasonic pulse or a rapid temperature change is found to be of the order of hours but depends on melt composition and superheating. No obvious connection between the composition of the clusters and the equilibrium solid crystalline phases has been found.

Common for all molten alloys seems to be the existence of small clusters around 2 nm in size; but clusters of larger sizes that probably are inherited from the initial ingot have been found in many cases. There are no currently available experimental methods to determine the cluster compositions but it might be conjectured that the clusters are of nearly spherical shape and have the structure of one melt component in which others atoms have been incorporated. The atomic clustering has a pronounced effect not only on the density and the kinematic viscosity of the melt but also on other physical properties. The anomalies reported in many works, between the variation of the properties upon heating and cooling, have been interpreted by defining the dissolution temperature,  $T_d$ , when the heterogeneities in the melt structure start to dissolve and the branching temperature,  $T_b$ , (or  $T_m$ ) at which the melt reaches a fully homogeneous state.

## 8.4 Effects of Melt Homogeneity on Solidification Microstructure and Properties

The presence of clusters and other micro-heterogeneities in the melt may affect its ability to nucleate the solid phase upon solidification. It is shown that the clusters present in the melt in some temperature range above the liquidus have short-range order close to the equilibrium or some other intermediate crystal phases as well as some chemical similarity, therefore providing energy incentive for nucleation on them. Elimination of these inhomogeneities through melt superheating may create condition for more difficult nucleation and lead, hence, to higher undercooling

before the nucleation starts. As a result of high undercooling, two scenarios are possible: (1) activation of small inclusions that are usually not able to nucleate due to their small size but, if nucleating, may produce very large number density of substrates and (2) homogeneous nucleation in the undercooled entire volume. In this section, we will consider experimental evidence that melt superheat (or melt heat treatment) results in structure modification and, in some cases, improvement of properties. For a more detailed account, we refer the reader to Brodova et al. [5] and Taran and Mazur [68], and Nikitin et al. [69].

### 8.4.1 Nonferrous Alloys

The effect of the melt condition (heterogeneous or homogeneous constitution) on undercooling and nucleation is supported by the observed dependence of the solid microstructure on the cooling rate as well as on the melt superheat. Figure 8.19 illustrates this for a number of primary phases in hypoeutectic and peritectic alloys. It is also shown that the increase in melt temperature reduces the size and number of primary crystals whereas the higher cooling rate promotes the dendritic morphology of the primary crystals.

For an Al–25 wt% Si alloy, a superheat of 500 degrees resulted in 4 times less primary Si crystals as compared to the equilibrium phase diagram, while the increase of the superheat to 700 degrees suppressed the primary Si formation altogether and instead a quasi-eutectic structure with branched Si crystals uniformly distributed in

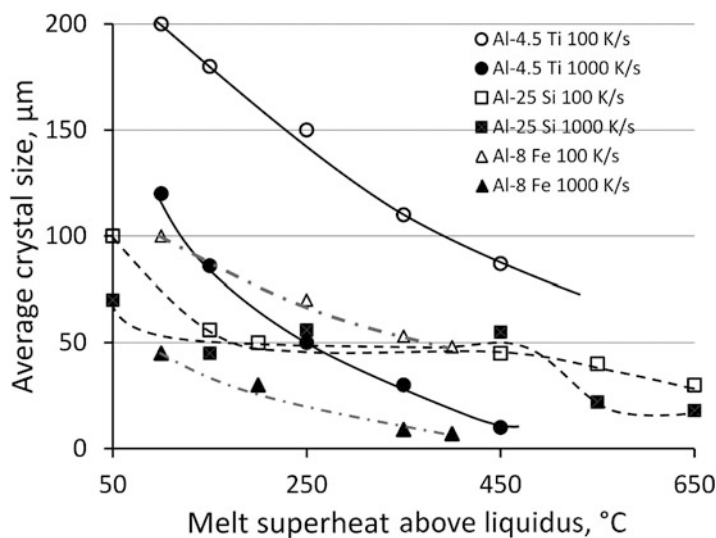


**Fig. 8.19** The effect of melt superheat on the size of primary crystals in Al–Si, Al–Ti, and Al–Fe alloys (after [5])



the aluminum matrix was formed, increasing the hardness of the alloy about twofold [5].

It was experimentally measured that the nucleation undercooling is indeed affected by the melt superheating. The nucleation temperature of the Al grains in a A357-type alloys (7 wt% Si, 0.58 wt% Mg) decreased from 591 °C after 105° melt superheat (720 °C melt temperature), to 570 °C after 185° superheat (800 °C), and to 548 °C after 285° superheat (900 °C). The eutectic temperature also decreased by about 5° [70], which resulted in eutectic modification and improved tensile strength and elongation. The observed decrease in the nucleation undercooling may signify that the critical substrate size decreases by a factor of 3. However, in this work no grain refinement has been observed. On the other hand, significant refinement of the  $\text{Sn}_3\text{Sb}_2$  primary phase was reported in a Sn–20 wt% Sb alloy where the melt heating to 1100 °C (776° superheat) and subsequent cooling to and casting from 700 °C produced 6° larger undercooling even upon slow cooling in air as compared to the superheat and casting at 700 °C [71]. Note that the electrical resistivity measurements showed that the melt homogeneity in this alloy was achieved at 980 °C and was irreversible on cooling from higher temperatures. The refinement of the primary phase was more pronounced at a higher cooling rate (30 K/s in metallic mold as compared to 0.5 K/s in air). Similar results were obtained on Pb–Sn alloys [72].

The dependence of undercooling on melt superheat may go through a maximum (at about 850 °C for aluminum and diluted Al–Si alloys) [73]. The increasing undercooling with melt superheat is explained by progressive dissolution of structural inhomogeneities and deactivation of insoluble impurities, while the decrease of undercooling at high temperatures maybe associated with the formation of some active substrates that do not require high undercooling for nucleating aluminum. We will discuss this in the next section.

The grain size (and indeed the size of other primary crystals) may also change with the melt superheat through the maximum as illustrated in Fig. 8.20 [5, 74,

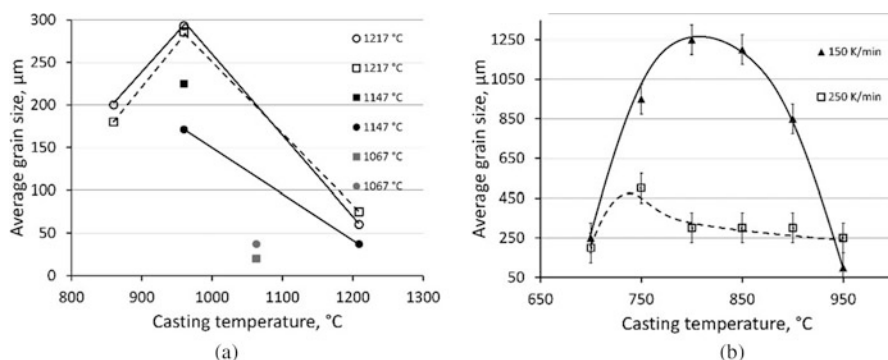


**Fig. 8.20** The effects of casting temperature and melt superheat on the grain size in (a) rapidly solidified ribbons from Al–0.6 wt% Zr (circles) and Al–0.6 wt% Zr–0.6 wt% Cr (squares) alloys (legend shows the melt superheat temperature) (after [5]) and (b) a gravity cast A319-type (Al–Si–Cu–Mg–Zr) alloy at two cooling rates (after [74])

75]. On increasing the temperature of the melt, the amount of nuclei for heterogeneous solidification decreases and, hence, primary crystals coarsen. Simultaneously, the thermal undercooling upon solidification of the melt increases. The cooling rate affects the undercooling directly. On reaching the specific overheating temperature, solidification nuclei are formed in the volume as a result of the decomposition of undercooled (supersaturated) melt. The higher is the homogeneity of the melt, the deeper is the undercooling preceding the formation of solidification nuclei, the higher is the supersaturation of the liquid solution and the smaller is the critical size of an active nucleus. Hence, numerous nuclei for primary solidification are produced (or become active) upon casting from the specific overheating temperature. In hypoeutectic aluminum alloys with the aluminum solid solution as a primary phase, one can observe the transition from progressive to spatial-progressive solidification, the latter being accompanied by grain refinement. In this case, the solidification nuclei could be crystals of transition-metal (TM) aluminides formed at the solidification front upon the decomposition of a supersaturated region in TM liquid solution. The formation of numerous solidification sites in the narrow region at the solidification front arrests the columnar zone and facilitates the formation of equiaxed grains. In hypereutectic alloys, the primary phase usually forms in the melt volume. In this case and upon undercooling, the decomposition of a supersaturated liquid solution occurs with respect to this phase, and fine primary crystals act as solidification sites. It is noteworthy that the suggested mechanism is valid only when the melt is homogeneous. If new heterogeneous factors promoting the solidification appear with increasing temperature, the undercooling decreases and this mechanism can hardly work.

It was found that the melt superheat above the homogeneity (see branching  $T_b$  or  $T_m$  temperature above) temperature affects the as-cast structure of monotectic alloys as well [5]. The distribution of In in an Al–20 wt% In alloys was completely changed: from heavily segregated after casting with a 70° superheat to uniformly distributed droplets of In after 600° superheat at a cooling rate of 1 K/s. On increasing the cooling rate to 10<sup>5</sup> K/s (melt spun ribbons), the higher superheat resulted in the formation of a quasi-eutectic structure.

In addition to the effect on the thermal undercooling (supersaturation) of a liquid solution at the solidification front, the melt superheating affects the temperature gradient at the solidification front, constitutional undercooling, and internal structure of primary dendrites. In the initial period of solidification upon pouring the melt from high temperatures, the increased temperature gradient exists in the vicinity of the solidification front and that should narrow the two-phase transition region and arrest the columnar growth. Moreover, the increased melt temperature accelerates diffusion processes and, hence, decreases the constitutional undercooling and hampers dendritic branching. Under optimum solidification conditions, one can obtain the non-dendritic grain structure which is formed due to the sharply increased amount of solidification nuclei (as a result of the decomposition of a supersaturated in TM liquid solution) and the narrowed two-phase zone (as a result of high-temperature gradient in the melt).

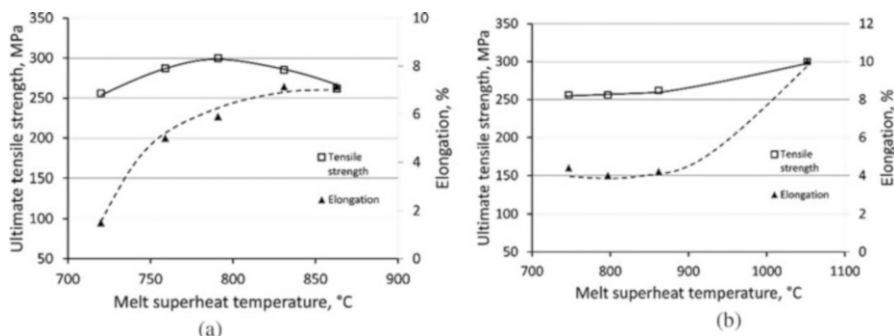


**Fig. 8.21** Dependence of the ultimate tensile strength and elongation of an A358-type alloy cast (a) from the temperature of melt superheat and (b) from 717 °C after melt superheat (after [5])

The changes in the structure (refinement of grains and other structure constituents) may result in the improved mechanical properties. Figure 8.21 shows the variation of tensile strength and elongation with the melt superheat for an A358-type alloy (Al-7 wt% Si-0.3 wt% Mg) for two types of casting schedules: (a) casting from the superheat temperature and (b) casting from 627 °C after cooling from the superheat temperature. The structural homogeneity in the melt is reached at about 945 °C according to the viscosity or density measurements [5]. The results show that on casting from the superheat temperature that is below the homogeneity temperature the strength changes slightly and even starts to decrease at higher superheat, whereas the ductility increases substantially. Casting from a higher temperature where less clusters remain may provide (in combination with high temperature gradient) essential undercooling for structure refinement. At the same time, very high melt temperatures may result in hydrogen absorption by the melt and excessive oxidation, and hence decrease of the properties. In the case of casting at a lower temperature after cooling from high superheat, yet before reaching the homogenized melt state, the elongation and strength are not changing. This can be interpreted as the retention and restoration of potential substrates (silicon clusters) in the melt which prevents the undercooling needed for structure modification. However, when the melt superheat exceeds the melt homogeneity temperature and nothing prevents the melt from being deeply undercooled, the strength and ductility are both increasing.

### 8.4.2 Ferrous Alloys

Structure and properties of steels are sensitive to high-temperature melt (HTM) treatment. As examples we present here the results for two different grades of steels, one tool steel (P6M5) containing about 6 wt% B and 5 wt% Mo and a stainless steel (C25N13) containing 25 wt% Cr and 13 wt% Ni.

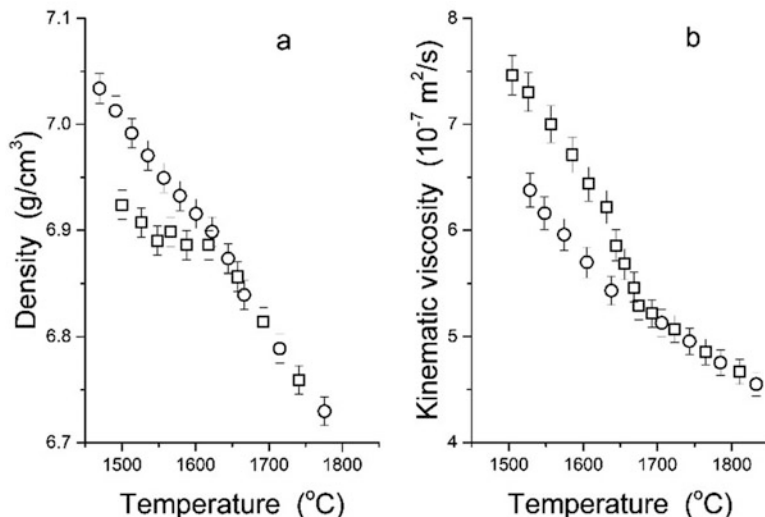


**Fig. 8.22** Temperature dependence of (a) density and (b) kinematic viscosity of molten C25N13 liquid steel containing about 25 wt% Cr and about 13 wt% Ni during heating (squares) and cooling (circles) (after [76])

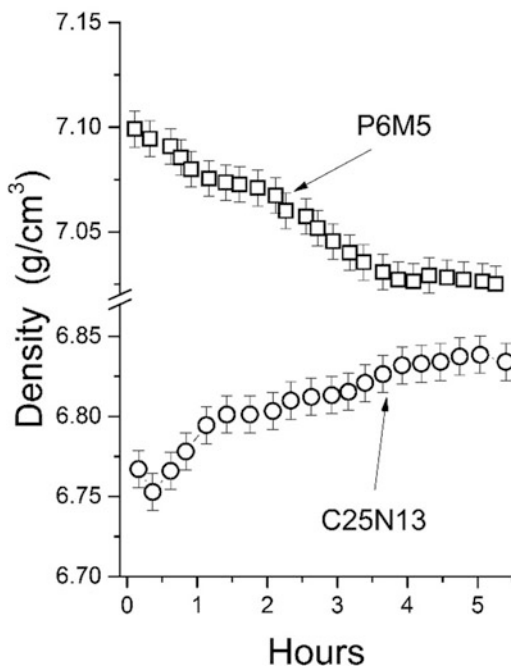
These steel grades differ from each other by their solid structure. The C25N13 steel is a solid solution alloy and its inhomogeneity is linked only to the coexistence of austenite and ferrite phases. The structure of the P6M5 ledeburite steel is essentially eutectic and contains various carbides. It has low technological plasticity and is susceptible to hot crack formation. These undesirable properties are mainly determined by the type of austenite–carbide eutectics and by the eutectic carbides morphology. Usually, the highest temperatures of the melts heating are 1540 to 1630 °C for the P6M5 steel and 1550 °C for C25N13.

In order to determine the optimal production conditions of these steels, the density and the viscosity in liquid state were measured during heating and subsequent cooling [76]. According to equilibrium phase diagram of C25N13, the different elements are expected to be distributed homogeneously in a liquid solution. The fact that there is a difference between the heating and the cooling curves that are presented in Fig. 8.22 indicates that chemical inhomogeneity is, nevertheless, present in the melt.

The measurements of density during isothermal holding at 1550 °C (Fig. 8.23) show that both the P6M5 and the C25N13 melts, when kept at this temperature, undergo a very slow homogenization over long time.

After completion of the relaxation process, the heating and cooling curves for the C25N18 alloy coincide. This shows that a solid solution-type steel, when molten, can be transformed into a homogeneous structural state at relatively low superheat above liquidus, provided the isothermal holding time is long enough. The same effect was observed in other steel grades of solid solution type [77, 78]. If the

**Fig. 8.23** Density changes of the P6M5 and the C25N13 liquid steels during isothermal treatment at 1550 °C (after [76])



C25N18 steel is solidified after full relaxation and then again melted, the micro-homogeneity is preserved.

It is not cost-effective to keep the liquid C25N13 steel at 1550 °C (the usual melting temperature in technology) during 5 h or more to homogenize it. Instead, superheating the melt up to 1820 °C for several minutes was tried in order to accelerate the relaxation process. After this heat treatment, the steel showed a more homogeneous distribution of chromium inside the austenite grains and lower segregation of nickel. The lattice parameter of austenite became somewhat smaller, the microhardness decreased from 2420 to 2020 MPa and the ferrite microhardness from 2680 to 2280 MPa. After the heat treatment, the steel also was more ductile and less prone to hot cracking. As a result, the rejection rate of cast material could be decreased and the production yield increased significantly [76].

In case of the P6M5 steel, a hysteresis of the heating and cooling curves was observed even after completion of the relaxation process at 1550 °C which shows that the melt after the relaxation is still micro-heterogeneous [76, 79]. Thus, superheat above the critical temperature is necessary to transform the melt into a true solution. Moreover, this melt even after homogenizing superheating crystallizes into a multiphase ingot with distinct heterogeneity. If it is necessary to remelt ingot (for example, for casting), the homogenizing heat treatment of melt needs thus be repeated. In order to improve this situation, it was proposed to increase the maximal temperature of industrial heating up to 1760 °C [79]. After such superheating, the

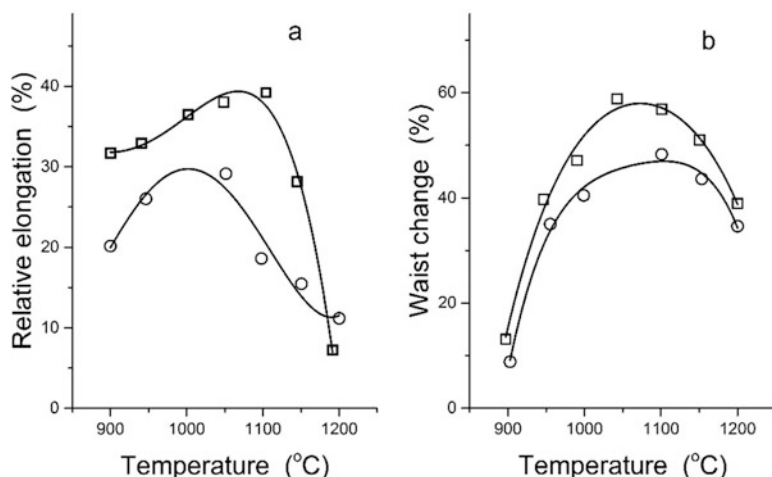


**Fig. 8.24** Measured relative elongation and reduction in area of the P6M5 steel as function of temperature after different superheat of the melt: 1760 °C (squares) and 1550 °C (circles) (after [76, 79])

volume fraction of skeleton-like and fan-like eutectics that initiate cracking of ingots during deformation decreased significantly.

Stress–strain curves at 900 to 1200 °C showed that after heat treatment the fracture stress of the steel did not change but its relative elongation and reduction in area increased (see Fig. 8.24). This difference was preserved after the deformation indicating that an HTM treatment and associated changes in the melt structure actually improve the properties of steels and widen their use for particular applications.

## 8.5 Effects of Insoluble Impurities on Solidification Microstructure and Properties

It is frequently said that the presence of oxides in the melt or on its surface can significantly affect the results of viscosity or density measurements during melt superheat. The polymorphic transformations of oxides, chemical reactions, and continuous oxide formation add to the issue [5]. The presence of oxides or other insoluble or sluggishly solvable inclusions may also control the structure upon solidification, both in favorable and unfavorable ways.

These impurities could be oxides and carbides that are usually not very well wettable by liquid aluminum or magnesium, have gaseous phase absorbed at the surface and are, therefore, excluded from the process of solidification. If, however, they could be wetted with liquid phase and form substrates either for grain refining phases (e.g., intermetallics like  $\text{Al}_3\text{Ti}$  or  $\text{Al}_3\text{Zr}$ ) or for the solid matrix phase

**Table 8.1** Crystal structure and temperature range of existence of different crystal forms of alumina [80–84]

| Alumina type      | Crystal structure                | Lattice parameters (nm)                                                      | Temperature range of existence (°C) | Crystal plane spacing closest to (Al):<br>(100)–0.404 nm<br>(200)–0.202 nm |
|-------------------|----------------------------------|------------------------------------------------------------------------------|-------------------------------------|----------------------------------------------------------------------------|
| $\eta$            | Cubic, $Fd\bar{3}m$              | $a = 0.7914$                                                                 | 270–500                             | (400)–0.197 nm                                                             |
| $\chi$            | Cubic or hexagonal               | $a = 0.557$ ;<br>$c = 0.864$                                                 | 200–750                             | (400); (104)–0.198 nm<br>(321); (202)–0.211 nm                             |
| $\gamma$          | Cubic, $Fd\bar{3}m$ or amorphous | $a = 0.7911$                                                                 | 500–850                             | (400)–0.1997 nm                                                            |
| $\delta$          | Cubic                            | ?                                                                            | 850–1050                            | (114)–0.407 nm                                                             |
| $\theta$          | Monoclinic, $C2/m$               | $a = 1.1854$ ;<br>$b = 0.2904$ ;<br>$c = 0.5622$ ;<br>$\beta = 103.83^\circ$ | 870–1150                            | (112)–0.2019 nm                                                            |
| $\kappa$          | Orthorhombic, $Pna2_1$           | $a = 0.4834$ ;<br>$b = 0.8310$ ;<br>$c = 0.8937$                             | 900–1000                            | Close-packed planes<br>0.2254 nm                                           |
| $\alpha$ (stable) | Trigonal, $R\bar{3}c$            | $a = 0.47589$ ;<br>$c = 1.2991$                                              | Above 1000                          | (113)–0.2085 nm                                                            |

(aluminum or magnesium), then they may trigger efficient refinement. This process is called activation.

In aluminum, the most likely indigenous inclusions are represented by aluminum oxide (alumina). Alumina may exist in various crystal modifications, depending on the temperature range, origin, and presence of hydrogen and other alloying elements. There is uncertainty about the crystal structure and temperature range of existence of “intermediate” forms of alumina and Table 8.1 summarizes the available data.

As one can see, each of these structure modifications exhibits some crystallographic planes that match the lattice parameter of the aluminum solid solution. The transition between the lower-temperature modifications of alumina upon heating is in reality continuous and related to the dehydration (removal of hydrogen from the crystal lattice). On increasing the melt temperature,  $\delta$ -alumina (or  $\gamma$ -alumina which is sometimes considered to be the same phase) transforms into  $\chi$ -alumina (700–850 °C) and then the stable  $\alpha$ -alumina is formed at above 1000 °C [80]. During cooling from 1000 °C, the stable modification  $\alpha$ -alumina is either retained (at high cooling rates) or is transformed to  $\chi$ -alumina (at low cooling rates) without  $\delta$ -alumina forming [80].

The activation of oxides can be done by thermal or other physical action (e.g., ultrasonic cavitation, see Chapter 4) upon the melt.

It is reported that aluminum melt superheating above 900–1000 °C may result in improved wettability of alumina with the melt [85–87]. This may be related to polymorphic transformations of alumina. In addition to the better crystallographic match with solid aluminum, hydrogen interaction with oxide particles can be affected. Hydrogen tends to dissolve in alumina and also absorbs at the surface of



oxide particles, preventing the wetting. Melt superheating results in the formation of stable  $\alpha$ -alumina which is inert to hydrogen [80]. As a result, the hydrogen absorbed layer is removed and the oxide inclusion comes into direct contact with the aluminum melt. It has been shown that very high melt superheating (above 1000 °C) of commercially pure aluminum reduces the grain size and promotes the columnar-equiaxed transition [75]. The columnar zone becomes narrower at temperatures above 950 °C and the equiaxed grains tend to refine at higher temperatures. This behavior can be explained from the fact that alumina fine particles, that are inert with respect to liquid aluminum at temperatures below 900–950 °C, start being wet by liquid aluminum and act as solidification nuclei at higher temperatures.

This way of involving alumina and other insoluble particles in solidification is, however, not very practical. An alternative is the physical action upon the melt. As we have discussed in Chap. 4, the ultrasonic cavitation-aided grain refinement has been demonstrated for pure aluminum containing oxide particles [88]. Cavitation treatment turns “hydrophobic” particles into active solidification sites by the mechanism suggested and confirmed earlier for grain refinement in aluminum alloys [89].

In the case of alloys, one can observe grain refinement due to the increased undercooling when the superheated melt reached the homogeneous state and then, on further increasing the temperature above 1000 °C—coarsening of grains and primary crystals, which is due to the same phenomenon. The introduction of high-temperature active heterogeneities in the melt prevents high undercooling and may result in less nucleation events. It also can increase the melt temperature at which one can observe the refinement. It is well demonstrated by introducing Zr in an Al–12 wt % Ni alloy, Fig. 8.25 [75].

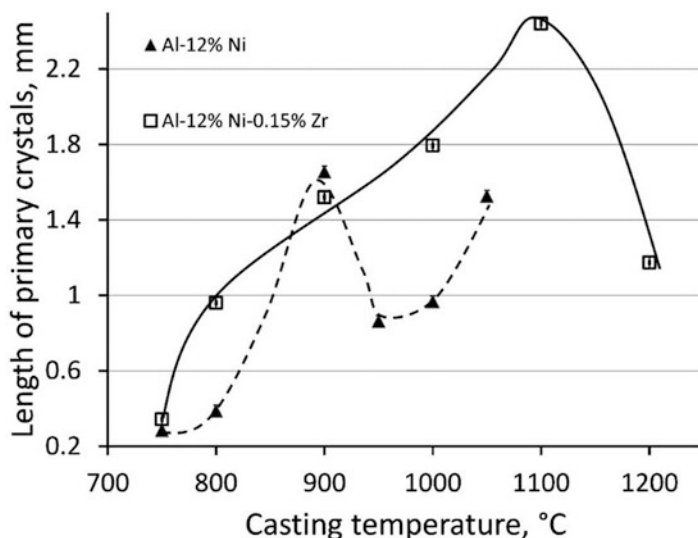


**Fig. 8.25** Effect of casting temperature on the size of primary  $\text{Al}_3\text{Ni}$  particles in Al–12% Ni alloys with and without addition of Zr (after [75])

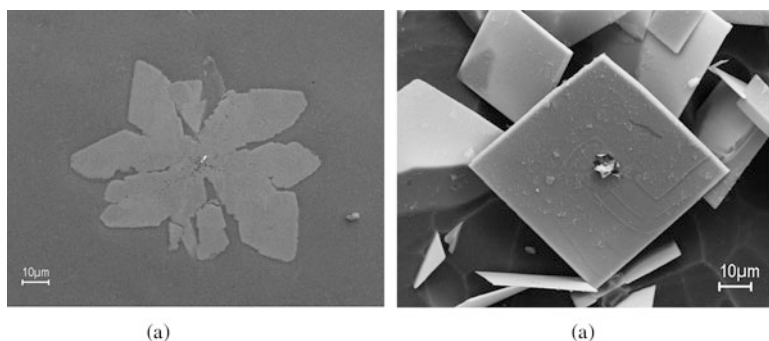
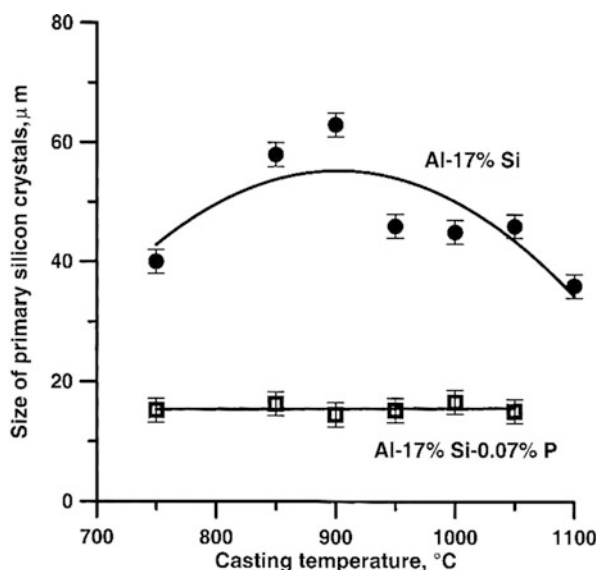


**Fig. 8.26** Nucleation of primary particles on aluminum oxide (particles in the center): (a)  $\text{Al}_3\text{Ti}$  under conventional solidification conditions and (b)  $\text{Al}_3\text{Zr}$  after ultrasonic melt processing (Courtesy of F. Wang)

**Fig. 8.27** Effect of casting temperature on the size of primary Si in an Al-17% Si alloy with and without P addition (after [75])



Actually, the activation of nonmetallic impurities may facilitate nucleation and refine any primary phase that solidifies in the alloy [90]. Figure 8.26 shows examples of intermetallic nucleation on oxide particles in aluminum [91].

In the case of Al-Si alloys (Fig. 8.27), melt overheating causes initial coarsening and following refinement of primary Si crystals. The introduction of phosphorus, which is a powerful silicon refiner and is very stable at high temperatures, results in complete suppression of primary silicon growth on melt superheating. Refinement of primary phase in Al-Si and Al-Fe hypereutectic alloys upon melt overheating was reported also elsewhere, although the authors did not observe the coarsening stage [5, 92].

In magnesium alloys, melt superheating is one of the first patented techniques of grain refinement, more specifically in Mg–Al alloys [93]. Depending on the alloy composition, the recommended melt superheating is 150° to 260° above the liquidus followed by relatively rapid cooling to the pouring temperature. There were several hypotheses to explain the effect of magnesium melt superheating through different mechanisms. The formation of  $\text{Al}_8(\text{MgFe})_5$ ,  $\tau(\text{Al}_4\text{Mg})$  or their metastable modifications and their role as substrates for magnesium were suggested [94, 95]. Another mechanism involved nucleation of magnesium on  $\text{Al}_4\text{C}_3$  particles. It is interesting that the superheating seems to work even if no special additions of carbon or carbide have been made. This phenomenon is called “native grain refinement” and occurs only in Mg–Al alloys. It is noteworthy that this effect is more pronounced in high-purity alloys where the concentration of iron and manganese (that can interact with aluminum and carbide degrading the nucleation potency of  $\text{Al}_4\text{C}_3$ ) is kept as low as possible [96]. It is attributed to the natural uptake of carbon from the crucible, tools, or protective atmosphere at high temperatures.

A similar effect has been reported for an M963 Ni-based superalloy in which high overheating facilitates the reaction between Ti and dissolved nitrogen producing TiN [97]. The nitride particles act as nucleation sites for the MC carbide that is a grain refiner in this type of alloy.

Interesting effect can be achieved in Al–Zr alloys where rapid cooling of the melt from high temperature produces metastable cubic  $L1_2$   $\text{Al}_3\text{Zr}$  phase with the crystal structure similar to that of aluminum (Fig. 8.28). In this case, the melt superheating deactivates all available substrates for heterogeneous nucleation of the solid solution and equilibrium intermetallics. As a result, deeper undercooling can be achieved for the primary solidifying phase, deep enough to trigger the formation of a metastable phase. As this phase has very good crystallographic match with aluminum, it acts as a substrate nucleating aluminum grains and refining the structure.

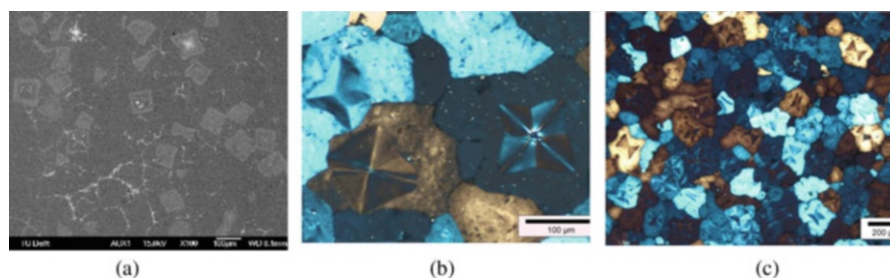


**Fig. 8.28** Formation of the metastable  $L1_2$   $\text{Al}_3\text{Zr}$  phase in an Al–1% Zr alloy cast from 930 °C: (a) primary metastable crystals; (b, c) primary crystals in the centers of aluminum grains (courtesy T. Atamanenko)

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# Index

## A

Absorption coefficient, 31, 291, 295, 296  
 Absorption contrast imaging, 32, 34  
 Acoustic attenuation, 160, 161  
 Acoustic energy, 154  
 Acoustic impedance, 157, 158  
 Acoustic power, 158–160, 167, 180, 182–185  
 Acoustic pressure, 153, 160–162, 164, 170, 177  
 Alloys  
   binary, 65, 187, 210, 287–290, 292–301  
   ferrous, 305–308  
   nonferrous, 302–305  
   ternary, 38, 40, 290, 300–301  
 Alternating magnetic fields, 15, 120, 125–127, 142, 146  
 Aluminum electrolysis, 75, 77, 78, 81  
 Arc processes, 76, 78, 84, 85, 178  
 Atomic clusters, 254, 278, 283–286, 290, 301  
 Atomic number density, 30  
 Atomic structure, 25, 42, 46, 205, 279, 287–290

## C

Casting, Refining, ElectroMagnetic (CREM) process, 145–147  
 Cavitation, 6, 7, 15, 110, 111, 113–115, 133, 141, 144, 153–156, 158–160, 162, 163, 165–167, 169–182, 186–188, 251–253, 309, 310  
 Cavitation bubble, 153, 162, 163  
   implosion, 171, 173  
   oscillation, 153, 155, 158, 163, 172, 179

## radius

critical, 162, 163  
 resonance, 153, 162, 163  
 Cavitation threshold, 144, 153, 158, 162, 163, 167, 176, 253  
 Cavitation zone, 154, 162, 165, 177, 180  
 Columnar-to-equiaxed transition (CET), 5, 140, 227  
 Composite, 1, 15, 32, 66, 67, 155, 171, 187, 188, 209  
 Contactless stirring, 110–112  
 Continuous casting, 15, 78, 141, 155, 180, 195, 230–233  
 Crystal growth, 15, 195, 209, 213, 220–222, 230, 233–235, 253  
 Crystal orientation, 196, 206, 210–216

## D

DC casting, 128–130, 132, 133, 135–140, 142, 144–148, 156, 176, 181–185, 188, 189  
 DC magnetic field, 96, 98–100, 103–105, 195, 196, 200, 201, 224, 226, 230–235  
 Deagglomeration, 175, 177, 187–189  
 Degassing, 110, 154–156, 167–171, 180–183  
 Dendritic grains, 37, 49–56, 143  
 Dendritic structures, 36, 60, 61, 68, 94, 251  
 Density, 5–7, 31, 36, 52, 64, 76, 77, 80, 86, 90, 91, 94, 96, 100, 120, 122, 127, 130, 134, 141, 142, 157, 162, 163, 176, 177, 180, 183, 196–198, 202–204, 224, 225, 244, 248, 249, 251, 259, 260, 278, 280, 290, 291, 293–297, 299–302, 305–308



**D**

neutron, 281–283, 287, 288

x-ray, 33, 34, 37–46, 281–283, 288–290

Diffusion, 2, 4, 5, 47, 50, 53, 77, 78, 92, 93, 103, 144, 155, 162, 164, 169, 200, 254, 293, 304

**E**

Electric current density, 86, 96, 196, 197, 198, 200, 251

Electromagnetic damping, 199, 210, 231, 232

Electromagnetic flow control, 76, 78

Electromagnetic force, 15, 83, 84, 90, 95, 97, 101, 103–105, 120, 121, 125, 129, 141, 142, 146–148, 195, 196, 199, 200, 232, 234, 243, 251, 252, 257

Electromagnetic levitation, 38, 75, 78, 207

Electromagnetic Processing of Materials (EPM), 76, 195, 243, 244

Electromagnetic stirring, 7–9, 13, 15, 101, 119–148

Electromagnetic vibration, 119–148, 244, 245, 250–253

Electromagnetic Vibration Casting (EVC) process, 147, 148

Emulsification, 154, 178, 179

**F**

Feeble magnetic materials, 195, 197, 204–209

Fragmentation, 5–7, 9, 10, 12, 36, 37, 49–56, 59, 65, 136, 137, 140, 154, 172–174, 178, 186, 227, 258, 265–267

Free electron laser, 21, 24, 67

**G**

Gamma-rays, 291, 293–295, 299, 300

Grain density, 5

Grain growth, 5, 37, 49–56, 139, 274

Grain refinement, 1, 4–7, 38, 137, 139, 141, 143, 146, 148, 156, 172, 177, 178, 183, 185, 186, 188, 244–264, 303, 304, 308, 310, 312

**Grains**

columnar, 5, 8, 9, 140, 255

equiaxed, 7, 9, 52, 53, 136, 137, 140, 144, 185, 224, 227, 256, 263, 304, 310

feathery, 1, 7, 9, 12

Grain size, 1, 3–5, 37, 137, 141, 175, 187, 252, 257, 258, 303, 310

Gravity force density, 203

Growth restriction, 4, 5

Growth-restriction factor, 4

**H**

Hartmann number, 200, 203, 221, 234

Heat flow, 7, 15, 59

Heat/mass transfer, 36, 121–127, 141, 142

High magnetic field, 15, 98, 99, 195–235

Homogenization, 185, 293, 300, 306

**I**

Impurities, 75, 105, 154, 174, 176, 233, 244, 277, 279, 287, 290, 303, 308–312

Inclusion, 1, 6, 84, 90, 92, 105, 137, 139, 162, 165, 167, 171, 172, 175, 176, 178, 181, 230, 302, 308–310

Induction current, 113

Induction melting, 38, 102, 113, 279, 297

Inhomogeneities, 283, 293, 298, 301, 303

In situ study, 19–71, 154, 265–273

Interfacial area density, 204

Intermetallic, 1, 6, 7, 51, 56, 58, 59, 61–67, 137, 172–174, 176–178, 213, 268, 269, 272, 308, 311, 312

Intermetallic phases, 37, 56, 58, 59, 61–67, 268, 272

**L****Levitation**

magnetic, 95, 98, 101, 206–208

technique, 98, 279, 280, 289, 294

Liquid density, 90, 91, 157, 163

Liquid metal flow, 36, 46–48, 243

Liquid-solid interface, 55, 140, 201, 221, 225, 226, 233, 235, 259–261, 264, 265, 274

Lorentz force, 75–78, 85, 86, 88–90, 92, 94, 95, 107, 110, 112, 121, 125–127, 130, 134, 135, 196–201, 218, 220, 257–259, 262, 263, 266, 268

Low Frequency Electromagnetic Casting (LFEC) process, 145–147

Low-frequency electromagnetic field, 147

Low Frequency Electromagnetic Vibration Casting (LFEVC) processes, 147, 148

**M**

Magnetic density, 96  
 Magnetic flux density, 77, 127, 130, 134, 135, 197, 200, 224, 244, 248, 251, 267, 268, 271  
 Magnetic fields and microstructure, 146, 223, 228, 252, 264, 270  
 Magnetic levitation, 95, 98, 101, 206–208  
 Magnetic phase separation, 207–209  
 Magnetic susceptibility, 96, 197, 204–206, 210, 211, 216, 217  
 Magnetization effect, 197, 204–209  
 Magnetization energy, 205, 206, 213  
 Magnetization force, 195–197, 204, 207, 208  
 Magnetohydrodynamics (MHD), 13, 120, 121, 196–204, 218, 219, 243  
 Maxwell equations, 141, 198  
 Metallic glass composite, 66  
 Metallic glasses, 42, 43, 66  
 Microstructure, 9, 11, 12, 40, 51, 54–56, 60, 61, 65, 66, 78, 85, 90, 92–95, 110, 134, 137, 139, 140, 144, 146, 221–223, 228, 245–248, 251, 252, 256, 264, 265, 267, 268, 279–287, 289, 301–312

**N**

Navier-Stokes equations, 76, 77, 92, 121, 199  
 Ni superalloys, 312  
 Nucleation, 1, 2, 5–8, 13, 35, 37–39, 41, 48, 51, 52, 62, 64, 93, 110, 134, 136, 138–140, 145, 172, 173, 176–178, 186, 188, 218, 244–246, 249–251, 253, 254, 256, 262, 264, 274, 301–303, 311, 312

**O**

Oxide, 6, 7, 36, 43, 46, 62, 80, 83, 171, 173, 175, 180, 187, 254, 308–311

**P**

Particle distribution function, 285, 286, 289  
 Phase alignment, 210–216  
 Phase contrast imaging, 33, 34  
 Phase field modeling, 8, 68  
 Physical properties, 157, 196, 198, 199, 202, 214, 278, 279, 290–301  
 Primary crystals, 154, 213, 302, 303, 310, 312  
 Propagation velocity, 157

Ptychography, 34

Pulse electric current, 244–262, 265–267, 274  
 Pulse magnetic field, 54, 244, 254, 261–264, 267–274

**R**

Real-time study, 267

**S**

Scattering  
   neutron, 282  
   small angle, 280–281, 283, 286  
   x-ray, 28, 41, 42, 188, 279, 286  
 Semisolid processing, 37, 46–48, 55, 251, 252  
 Skin depth, 78, 112, 126, 127, 130, 134, 142, 146, 148, 262  
 Solidification under DC magnetic field, 195, 201, 226  
 Solute transfer, 36  
 Sonocapillary effect, 170, 171, 176  
 Sonotrode, 56, 110–115, 155, 156, 158–161, 165, 166, 172, 180–184, 187  
 Sound pressure, 157, 162, 163  
   *See also* Acoustic pressure  
 Steel, 15, 75, 81, 82, 84, 154, 155, 187, 195, 202, 230–233, 250, 255, 256, 261, 262, 264, 305–308  
 Storage ring, 20, 21, 24  
 Streaming, 5, 154, 173, 174, 179, 182, 187  
 Structure factor, 39, 282, 283, 288  
 Structure fragmentation, 178  
 Synchrotron X-ray, 20–24, 32–34, 36–38, 41, 42, 47, 49, 52–54, 60, 67, 171, 265, 267, 268, 272  
 Synchrotron  
   x-ray radiography, 47, 52, 53, 171  
   x-ray tomography, 267, 268

**T**

Thermoelectric convection, 220, 234  
 Thermoelectric power, 201, 220, 224

**U**

Ultrasound, 36, 56, 96, 153–156, 159, 160, 163, 165, 167, 170, 171, 174, 178, 182, 252, 297–299, 301  
 Undercooling  
   constitutional, 2–5, 140, 260, 304  
   thermal, 254, 256, 264, 304

**V**

Vibration force, 141, 142

Viscosity, 36, 76, 77, 93, 97–100, 122,  
124, 160, 162, 163, 179, 197,  
202, 278, 279, 290–295, 298,  
300, 301, 305, 306, 308

**W**

Wetting (wettability), 2, 6, 13, 170–172,  
175, 176, 187, 310

**X**

X-ray, 25, 225–227, 266–268

diffraction, 33, 34, 37–46, 281–283, 288–290

diffraction imaging, 33, 34

interaction with matter, 25–32

radiography, 36, 46–56, 171

scattering, 28, 41, 188, 279, 286

synchrotron, 20–24, 32–34, 36–38, 41,  
42, 47, 49, 52–54, 60, 67, 171,

265, 267, 268, 272

tomography, 34, 56, 58, 59, 61–67, 268