1. Introduction

In solidification processing of metallic materials, the control of the solidification step (grain structure, growth microstructure, segregation of chemical species . . . ), which is key for the quality and the properties in use of the products, should be as precise as possible. The difficulty results from the fact that the formation of the solid material from the melt is complex to analyse and model correctly because coupled dynamical phenomena are simultaneously active (diffusion, fluid flow . . . ), whose length and time scales are widespread over several orders of magnitude.

During alloy solidification, the solid–liquid interface(s) exhibit a variety of shapes (cellular, dendritic . . . ) that develop from Mullins–Sekerka morphological instability and are governed by the local growth conditions. For metallic systems, the solid–liquid interface morphology is usually frozen by quenching or decanting, and its evolution with time analyzed post-mortem on a series of samples assumed equivalent. Since the pioneering work of Jackson and Hunt,1) direct optical observation of the phenomena has been carried out on transparent organic systems that freeze like metals.1) Nowadays, in situ and real-time characterization by synchrotron X-ray imaging (radiography, topography, tomography) has become the method of choice to unveil the dynamical formation of the solidification microstructure and grain structure in solidification processing of metallic alloys.2–6) Critical growth phenomena and stress-driven effects in dendritic solidification and equiaxed growth of Al-based alloys were observed and characterized using the experimental set-up combining Synchrotron X-Ray Radiography (SXRR) and Synchrotron White-Beam X-Ray Topography (SWBXRT) that we have developed at the European Synchrotron Radiation Facility (ESRF).7–9) This set-up and the experimental procedure we use are first briefly described. Then, selected typical observations of dynamical phenomena of major importance in microstructure formation or/and having significant effect on grain structure are shown. It is demonstrated that earth gravity manifests itself beyond fluid flow interaction, inducing stresses, de-
formation and fragmentation in dendritic columnar mush and equiaxed growth. Finally, solute segregation, which is responsible of solutal poisoning of the growth of equiaxed grains, is analyzed on the basis of quantitative analysis of the grey level in radiographs.

2. Experimental Apparatus and Protocol

Thin samples of Al-based alloys (40 mm long, 6 mm wide, 150 to 200 μm thick), adjusted in soft graphite crucibles mounted on a holder connected to a motorised translation device, are solidified (Fig. 1(a)) in a Bridgman furnace either by pulling the crucible down at velocity \( V_p \) (1.0 ≤ \( V_p \) ≤ 50 μm/s) in a thermal gradient \( G \) (15 ≤ \( G \) ≤ 30°C/cm), or by decreasing heater temperature at rate \( R \) (0.5–10°C/min) with sample in a fixed position (cooling down). Series of melting and solidification runs are carried out at the ID19 beamline of ESRF, which is long enough (150 m) to allow the wide field of view (6 × 15 mm²) that is essential to evidence the interaction between columnar dendrites or/and equiaxed grains.

Solidification processing is monitored by in situ and real-time synchrotron X-ray imaging. The FReLoN CCD camera is used to record videos of the solid–liquid interface evolution, i.e. the solidification front dynamics. For SXRR radiography, the incoming white X-ray beam, which is perpendicular to the main surface of the sample, is made monochromatic either before traversing the sample or after in combined mode (Fig. 1(b)) when white-beam X-ray topography is used to record Laue images from the various diffracted beams. In alloys, absorption contrast, function of the atomic number and concentration of the chemical species, results from the segregation of the components. X-ray radiography allows observation of the solid–liquid interface morphology while white-beam X-ray topography enables the investigation of the formation of strains and defects in the growing solid microstructure. In SWBXRT, stresses and strains are manifested by specific contrasts and breaking of the Laue images (Fig. 1(c)) into several pieces as it will be shown in the following. In all cases, raw images have to be magnified to analyze morphology, deformation and stresses.

3. Results and Discussion

3.1. Columnar Dendritic Growth, Columnar-to-Equiaxed Transition and Equiaxed Growth

In solidification processing, columnar dendritic microstructure usually form at the mould walls from the morphological instability of the smooth solid–liquid interface by the amplification of corrugations and subsequent side-branching of primary stems. Under dynamical interaction with gravity-driven or forced fluid flow, localization of dendritic mush often establishes, and coupled growth with eutectic pattern is frequent, with dendrites protruding ahead into the liquid.8) In casting, columnar dendrites are in practice in competition with the growth of equiaxed crystals. As on the one hand columnar dendrites with oriented mechanical properties are required, e.g. jet engine turbine blades operating at high temperature and, on the other hand, equiaxed grain structure is worth for homogeneous macroscopic behavior under mechanical stress, such as for car engine blocks, the control of the columnar-to-equiaxed transition (CET) is central in engineering.

In experiments dedicated to CET carried out on Al–3.5 wt%Ni alloys refined by adding TiB₂ particles, we first apply a low pulling rate to establish dendritic columnar microstructure. After that, the pulling rate is at reference time \( t_j \) jumped to a higher value to trigger CET. Rapidly, equiaxed grains become visible (size larger than SXRR spatial resolution, 15 μm) in the solute-rich boundary layer adjacent to the columnar structure where nucleation undercooling is exceeded (Fig. 2(a)). It should be stressed that under gravity the falling down of equiaxed grains, such as those encircled in Figs. 2(a)–2(c), is enhancing grain packing above the columnar dendrites and eutectic front. Live monitoring also shows that equiaxed grains may in addition rotate because of uneven lengthening of their dendrite arms. Columnar growth is thus stopped and equiaxed growth regime installs (Fig. 2(b)) and propagates (Figs. 2(c), 2(d)). That columnar front is blocked without effective contact.
with equiaxed grains comforts the solutal blocking scenario proposed for CET by Martorano and coworkers. 10) Eventually, equiaxed grains get trapped in the eutectic phase, as it happens for the first fallen grains in Fig. 2(d), giving the false impression of a mixed columnar–equiaxed structure. This sedimentation effect can obviously be misleading in post mortem analysis of the grain structure, as well as in the feedback to modeling of the solidification sequence. Eventually, equiaxed growth is self-sustaining, and a fully equiaxed mushy zone formed by closely packed equiaxed grains (Fig. 2(d)). Equiaxed growth proceeds by the propagation of the forefront of this mushy zone with the velocity of leading dendrite tips nearing the pulling rate. In the melt just above, new grains repeatedly nucleate and grow, screening the current leading grains. This operating cycle is maintained till the end of the sample. Several key parameters of interest for model validation can be measured as a function of time and solidification parameters, for instance, when increasing the pulling rate the equiaxed grain density is observed to first rapidly increase and finally approach an asymptotic value as refinement efficiency is reaching its limit. The asymptotic value in our experiments gives a density of active particles close to what is empirically used in numerical simulation.

3.2. Bending, Fragmentation and Sedimentation of Dendrite Arms

During columnar solidification, unforeseen deformation is evidenced in the dendritic microstructure, in response to the growth-induced mechanical constraint imposed on dendrite arms by bending moment increasing concomitantly with their growth. In particular, SXRR videos show secondary dendrite arms growing almost horizontally, and thus roughly perpendicular to the gravity vector, rotating either individually or one after the other from their initial position by a few degrees downwards. In the latter case, after rotation each secondary arm ends parallel to the arms below. Actually, a growing horizontal secondary arm is similar to a cantilever beam whose length, and thus weight, is increasing with time. Such a cantilever beam is prone to bending under gravity. Mechanical bending occurs at the thin neck attaching the secondary arm to the primary dendrite stem, where stress is concentrated because of much lower moment of inertia (proportional to the 4th power of the local arm radius). Furthermore, it happens that bending is assisted by equiaxed grain(s) incidentally settling on arm extremity, thus adding extra weight.

Frequently, remelting/dissolution of thin solid neck is observed to follow arm bending, which results in dendrite fragmentation as shown in Fig. 3, where equiaxed grains, mostly initiated by sedimenting detached dendrite arms (e.g. arrows in c), are growing in the liquid channel in between the columnar dendrites growing along the sides, which is similar to what is observed in ingot casting. Settling equiaxed grains and detached dendrite arms may drag each other or still-attached dendrite branches during their motion. Drag is further applying mechanical strain that may induce crystallographic disorientation. It should be stressed that image processing is used in Fig. 3 as there is no visible contrast in raw radiograph for Al–7 wt%Si alloy because silicon is next to aluminum in the periodic table of the elements. In image processing, the raw radiographs of a given experiment are divided by a reference image. Radiograph of molten state just before cooling down is the reference image for Figs. 3(a)–3(c). Radiograph at earlier time is the reference for Fig. 3(d) which results in a composite image: moving grains show up twice, at time $t$ in dark gray (liquid→solid which increases X-ray absorption, time in black) and at time $t$–Δ$t$ in light gray (solid→liquid which decreases X-ray absorption, time in white).
3.3. Stresses and Strains Induced by Microstructure Formation

Strains and stresses are common in solidified materials. Plenty of factors can be at their origin such as solid state phase transformations or mere cooling down to room temperature. It follows that those accompanying the very formation of the growth microstructure are blurred after complete processing, and then delicate to identify and characterize. SWBXRT is appropriate to investigate in situ the strains and stresses self generated in the development of inner grain microstructure and global grain structure. Clear evidence of phenomena is favored in topography by the fact that X-rays are only diffracted by the solid so that the solid–liquid interface(s) are naturally sharp in topographs (Fig. 4).14

Synchrotron X-ray radiography timely allows investigation on metallic samples representative of materials of industrial interest, with SXRR images of microstructure formation dynamics replacing those obtained with transparent organic analogs by optical microscopy.13 Complementary critical information on the mechanical effects and crystalline defects that make a solidifying system strikingly different from a fluid–fluid system is unveiled by SWBXRT imaging. Indeed, new insight starts with the periodic elastic strain perpendicular to the solidification front that is apparent (Fig. 4(a)) before visible corrugation of the solid–liquid interface (Fig. 4(b)). The nearer this strain in the Laue image the more parallel to growth direction (close to [001] in Fig. 4) the diffracting planes. Similar black and white contrasts running along the cell bodies are also a characteristic feature in cellular arrays (Fig. 4(c)), which makes their physical origin easy to understand. Actually, the concentration of solute, copper in the present case, in the solid at the interface is decreasing when going from the cell tip down into the liquid grooves on the sides. This copper microsegregation gives way to a transverse solute gradient in the cell body to which a gradient of crystal lattice spacing is associated, and thus strain. This strain is in first approximation symmetrical but “seen” in opposite ways, increasing on one half of the cell and decreasing on the other, by the X-ray beam, which leads to the succession of black and white stripes in the cell array in Fig. 4(c).

Topographs become much more complex to analyze as the solidification microstructure is evolving into dendrites, and later on interacting with eutectic growth of interdendritic melt. Clearer insight is then achieved by combining synchrotron X-ray radiography and topography (Fig. 5).35

The evolution of the solid–liquid interface morphology, from the birth of morphological instability to dendrite–eutectic coupled growth, is monitored by SXRR while a series of SWBXRT snapshots at selected instants provide in parallel topographs that follow the formation and evolution of mechanical features. In topographs, the image of the polycrystalline solid is broken into as many pieces as individual grains constituting the solid in the radiograph (each grain is diffracting at different Bragg angles except for common reflection in the case of twinning,15) as shown in Fig. 6). First, the solid–liquid interface morphology is similar on both images. From about 2 000 s of growth, strains have developed enough to split each Laue image of the top part of the dendrite growing into surrounding melt above eutectic temperature \( T_E \) into several pieces, mostly secondary dendrite arms spread around the image of the main dendrite stem (Fig. 5(c)). From eutectic temperature and below, it is convenient to consider first the topograph of a fully eutectic grain (Fig. 5(a)). In the image, the \( \alpha \)-Al lamellae that emerge from existing aluminum grain with the same crystallographic orientation appear as a tousled bundle diverging from the incipient Al grain. This indicates that the \( \alpha \)-Al lamellae are undergoing increasing strain. Actually, the \( \alpha \)-Al lamellae grow with \( \beta \)-lamellae of intermetallic Al\(_3\)Ni phase, which do not diffract at the same Bragg angle, and form together a directional eutectic metal-matrix composite (MMC).16) MMCs are long considered for their mechanical

![Fig. 4](image-url)  
(a) Oscillatory variation of the gray level in a scan parallel to the solid–liquid interface characteristic of periodic strain in the solid when the threshold of morphological instability is approached, \( t=1.059 \) s after beginning of pulling at \( V_p=4 \) mm/s; and (b) onset of visible interface corrugations at inception of morphological instability, \( t=2.420 \) s. (c) Alternation of black and white contrasts along deep cell bodies, \( V_p=8.3 \) mm/s. Al–0.73 wt%Cu, \( G=20^\circ \)C/cm. SWBXRT at LURE synchrotron, France.

![Fig. 5](image-url)  
Observation of growth-induced stress in solidifying microstructure by combined Synchrotron X-ray imaging: Radiograph of dendrite-eutectic coupled growth after 3 287 s of growth (b) together with topograph of the fully eutectic grain (encircled by full line in (b)) showing progressive disorientation of \( \alpha \)-Al lamellae (a) and topograph of the dendritic grain (encircled by dashed line in (b)) where the dendrite Laue image is split into pieces above eutectic temperature \( T_E \) and effected by eutectic-induced stress below (c). Al–3.5 wt%Ni, \( V_p=1 \) mm/s, \( G=30^\circ \)C/cm.
Twinned grains in $\beta$-Mg$_2$Al, Samson phase in thermal holding before directional solidification: (a) Common [101]-reflection, (b) twinning unveiled in specific [0-1-1]-reflection of T1 and undetermined reflections of T2 and T3, and (c) faceted growth of twins T1, T2, T3 and new twin T4 in solidification. (d) Metallograph showing grain structure in a polycrystalline Photowatt Si wafer cut in directionally solidified “metallurgical” silicon showing normal size columnar grains (1) and small equiaxed-like grains (2), or grits, that are defects for solar cell efficiency.

properties, and the deformation of eutectic composites during temperature changes is documented in literature, in particular for $\alpha$-Al–$\beta$-Al$_3$Ni$_7$. In summary, this eutectic composite is representative of a ductile metallic matrix, $\alpha$-Al, with fragile reinforcement, $\beta$-Al$_3$Ni, whose thermal expansion coefficient is comparatively low. It then follows that $\beta$-Al$_3$Ni lamellae are applying compressive stress on $\alpha$-Al lamellae in directional solidification in applied temperature gradient $G$. At the larger scale of the $\alpha$-Al dendrite, the $\alpha$-Al–$\beta$-Al$_3$Ni eutectic globally behaves as a single phase with intermediate thermal expansion coefficient applying stress on the dendrite at the origin of strong black contrasts in the lower part of dendrite image (Fig. 5(c)).

Twinning is recurrent in processing of metallic materials, especially in solid-state transformations giving intermetallic compounds. It may already happen for complex metallic alloys in the solidification step as observed at ESRF by in situ SWBXRT during directional solidification of the Samson phase $\beta$-Mg$_2$Al$_3$. Indeed, the topographs in Figs. 6(a), 6(b) show three twinned crystals in the initial state obtained after thermal stabilization of the solid–melt interface. The twins are $\Sigma 9$ with [221] coherent twin plane and twinned grains are disoriented by 38.94° around a common [110] axis. In Fig. 6(a), the images of the 3 twinned grains T1, T2, T3 are gathered because they correspond to the common [101]-reflection. Directional solidification by decrease of upper furnace temperature at 0.5°C/min induces faceted growth of these 3 twins (Fig. 6(c)). Furthermore, it should be noticed the formation of new twin T4 adjacent to T1, which diffraacts at a different Bragg angle and hence appears at a different place on the topograph. Repeated growth twinning on one facet of grain T1 leads to a T1/T4 sandwich. Besides its relevance for structural materials, growth twinning in solidification processing of functional materials will also benefit of combined X-ray synchrotron imaging after upgrading to high temperature. For instance, the exponential increase in last years of solar cell demand for clean energy production in response to global warming has made polycrystalline “metallurgical” silicon of photovoltaic grade the best example of functional materials produced by solidification. For solar cell efficiency, research effort is on understanding and preventing the transition to small-grain equiaxed-like growth and growth twinning (Fig. 6(d)), as grain and twin boundaries favor detrimental electron-hole recombination reducing the power output.

3.4. Growth of Equiaxed Grains and Solute Poisoning

It is repeatedly referred to the central role of solute micro- and macro-segregation in alloy solidification in preceding sections (e.g. morphological instability, dendrite formation and competition with eutectic . . . ), which strongly suggests that quantitative measurement of the evolution of solute distribution during microstructure formation should be sought for. Fortunately, this can be done by quantitative analysis of the grey level in radiographs, which is a function of local solute concentration for a sample of uniform thickness. Basically, for binary alloys such as the dilute Al–Cu alloys analyzed hereafter, solute concentration is deduced from the variation over the field of view of the ratio of the intensity $I(y, z)$, with $y$ and $z$ the horizontal and vertical directions respectively, of the transmitted monochromatic X-ray beam to the reference transmitted intensity $I_0(y, z)$ recorded in the initial state at the end of thermal stabilization, just before solidification is switched on, where the solute concentration in the liquid is assumed uniform and equal to the initial alloy concentration. Therefore, gray-level measurement is carried out after image division by the radiograph of this initial state. This procedure suppresses attenuation due to X-ray absorption by the crucible walls and windows of the UHV chamber as well as the local variations caused by imperfections in the path of the X-ray beam, which can be on crucible walls, scintillator, CCD camera . . .

Before considering equiaxed growth and solute poisoning effect, it is worth to validate and calibrate the approach by considering simpler situations. In the initial solidification transient, the building of the solute boundary layer with exponential profile is quantitatively measured (Fig. 7(e)) while the recoil of the solid–liquid interface from the liquidus isotherm to the solidus one (Fig. 7(f)) which is needed to approach steady-state planar growth, is monitored (Figs. 7(a)–7(c)). In contradistinction, the measurement of the solute profile in the narrow liquid channels on the sides of the dendritic mush (Fig. 7(d)) shows a linear variation (Fig. 7(f)) imposed by the condition of local thermodynamic
equilibrium along the solid–liquid interface which makes the vertical solute gradient proportional to the applied temperature gradient.

Then, growth and dynamical interaction of equiaxed grains in the formation of grain structure can be characterized, and slowing down of grain growth till final blockage related to poisoning by solute accumulation in between neighbors. A typical example of interaction of leading primary dendrite arms during growth of equiaxed grains in Al–10 wt%Cu alloy solidified by cooling down the sample at 0.5°C/min is shown in Fig. 8. The evolution of the growth of dendrite arms $L_1$ and $L_2$ is very representative (Fig. 8(b)). First, parallel lengthening of arms $L_1$ and $L_2$, which are about 7 mm apart, indicates on the one hand that growth undercooling is homogeneous or very close to over the sample and, on the other hand, that these primary dendrites are growing freely. Then, there is a transition from this regime of parallel growth to a second one where arm lengthening is slowing down till cessation. The fact that visible growth arrest is not simultaneous for $L_1$ and $L_2$ suggests seeking for interaction with growing neighbor dendrites that are approaching with time, which depends on local neighborhood.

Assuming that dendrite growth is slow enough relationship for isothermal free growth of alloy dendrite at constant solute undercooling can be applied using the instantaneous value of temperature, $T(t)$. These relationships can be transposed from the model of free dendrite growth at given thermal undercooling so that the growth velocity $V_{op}$ of a 3D-dendrite reads

$$V_{op} = \sigma^* D (\Delta \log D)^2 (2d_0)$$

where $\sigma^*$ is the selection parameter and $D$ the solute diffusion coefficient in the melt, $A$ is the solute undercooling

$$\Delta = [C_a - C_{op}(t)]/[C_{op}(t)k(k-1)]$$

and $d_0$ the capillary length

$$d_0 = \Gamma [(T(t) - T_M)(k-1)]$$

with $C_0$ and $C_{op}(t)$ the alloy and tip solute concentration respectively, $k$ the solute partition coefficient, $T_M$ the liquidus temperature for $C_{op}$, $T_M$ the solvent melting point and $\Gamma$ the Gibbs–Thomson coefficient.

Taking the parameters for Al–10 wt%Cu, $\sigma^*$ = 0.02, $D = 2500 \mu\text{m}^2/\text{s}$, $\Gamma = 0.24 \text{C} \cdot \mu\text{m}$, $T_M = 660 \text{C}$, $k = 0.14$ and $m = -2.6 \text{C} / \text{wt%}$, the tip velocity obtained from Eq. (1) can be plotted and compared to the experimental growth velocity (Fig. 8(c)). Agreement is satisfactory in the free growth regime where growth is accelerated by cooling down which makes undercooling higher with time. This driving force starts to get opposed by solute poisoning when copper rejection upon solidification starts to make the far-field solute concentration felt by the dendrite tip raising above $C_{op}$, which in other words means that in Eq. (2) both $T_1$ and $C_0$
become functions of time and should henceforth read $T(t)$ and $C_d(t)$. The magnitude of solute poisoning can be estimated by considering the time at which this effect is balancing thermal undercooling, which corresponds to the black dot in Fig. 8(c). This happens after 350 s when $T(t)=631^\circ C$ and $C_d(t)=11.1$ wt% Cu. This latter value is close to the concentration measured in between the growing dendrite tip and the facing grain (Fig. 8(d)).

4. Conclusion

Researchers and engineers are long seeking for model experiments capturing the essence of the phenomena to feed numerical simulation with clearer fundamentals of solidification microstructure and grain structure formation in process modeling. Work in these directions is currently in projects CETSOL and XRMON of European Space Agency and Aide à la Recherche from French Space Agency CNES is gratefully acknowledged. The authors are also indebted to ESRF for beamtime allocation and to the staff of ID19 beamline for technical assistance.

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