In situ investigation of the crystallization kinetics and the mechanism of grain refinement in aluminum alloys

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Abstract

The crystallization kinetics during the liquid to solid phase transformation of pure aluminum and various Al–Ti–B alloys is investigated using differential thermal analysis (DTA) and three-dimensional X-ray diffraction (3D XRD). A reduced undercooling required to activate nucleation of aluminum grains is observed, when both solute titanium and TiB2 particles are present in the liquid. The cooling rate dependence of the onset temperature \( T_o \), the crystallization peak temperature \( T_P \), and the latent heat \( \Delta H \) are evaluated and compared for all samples. The DTA curves for slow cooling of an Al–0.3Ti–0.02B (wt.%) alloy illustrate the formation of an aluminide phase (TiAl3) upon solidification. A comparison of the DTA curves during slow cooling of the hypoperitectic Al–0.1Ti–0.1TiB2 (wt.%) and the hyperperitectic Al–0.3Ti–0.02B (wt.%) alloys seem to exhibit a kinetic similarity at the onset of the solidification. In situ 3D XRD measurements clearly exhibit the formation of a metastable TiAl3 phase prior to solidification of both alloys. This explains the mechanism of grain refinement in the presence of solute titanium and TiB2 particles in the grain refined aluminum alloys. The influence of titanium diffusion, latent heat, and cooling rate on the growth behaviour of individual aluminum grains during the phase transformation is further quantified.

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1. Introduction

Grain refinement plays an important role in the liquid to solid phase transformation of aluminum alloys [1,2]. Generally Al–Ti–B master alloys are added to the aluminum alloys to refine the grain size of the solidified product. These alloys contain microscopic TiB2 and TiAl3 nucleating particles. Although various theories regarding the grain refining mechanisms are proposed [3–8] (e.g. the particle theory, the phase diagram theory, the duplex nucleation theory, and the peritectic hulk theory), the mechanism of grain refinement remains a problem of considerable controversy in the scientific literature. The nucleant effects, i.e. which particle nucleates \( \alpha \)-Al grains and what are its characteristics, has been the subject of intensive research. Lately, the solute effects, i.e. the effect of dissolved titanium on grain refinement, has come into the forefront of grain refinement research. Therefore, a great interest exists to determine the kinetics of the liquid to solid phase transformation of aluminum alloys in situ in order to determine the role of the microscopic grain refining particles and the solute titanium.

The present paper describes differential thermal analysis (DTA) and three-dimensional X-ray diffraction (3D XRD) measurements on high purity aluminum, Al–0.15TiB2, Al–0.1Ti, Al–0.1Ti–0.1TiB2 (wt.%) alloys, and a commercial purity Al–0.3Ti–0.02B (wt.%) alloy during solidification at different cooling rates. The aim of these experiments is to ascertain the mechanisms responsible for grain nucleation and growth and to separate the effects of nucleating particles from that of the solute titanium. Part of the 3D XRD results for the high-purity alloys has been presented previously [9]. These results are also included in the present paper to allow for a systematic comparison of the DTA and 3D XRD data for different cooling rates.
2. Sample preparation

The studied samples were laboratory prepared from high purity aluminum, titanium, and TiB₂ particles. The pure aluminum (99.999%) and titanium (99.99%) were purchased from Goodfellow. The TiB₂ (99.99%) powder with a particle size distribution ranging from 3 to 6 μm and a maximum around 4.4 μm was purchased from Advanced Ceramics.

The Al–0.15TiB₂ (wt.%) alloy was prepared by melting together aluminum lumps with a total mass of 35 g and the TiB₂ particles into an aluminum oxide crucible. The sample was heated to a temperature of \( T = 1023 \text{ K} \). After holding at this temperature for 30 min, the crucible was removed from the furnace and the liquid alloy was homogenized by stirring using an aluminum oxide rod. After solidification the sample was remelted and the above-mentioned process was repeated three times to ensure that the TiB₂ particles were homogeneously distributed in the Al–0.15TiB₂ (wt.%) alloy.

In order to prepare the Al–0.1Ti (wt.%) alloy, a different route was adopted. First, Al–1Ti (wt.%) master alloy samples, of 5 g each, were prepared by melting together the appropriate amounts of aluminum and titanium in an electric arc furnace in a high purity argon atmosphere. The molten samples were stirred by using the arc flame for homogenization. Then the samples were solidified, rotated by changing the top and bottom positions, and remelted. This process was repeated five times to ensure that titanium is homogeneously distributed in the sample. Having prepared the Al–1Ti (wt.%) master alloy, the Al–0.1Ti and Al–0.1Ti–0.1TiB₂ (wt.%) samples were prepared by melting the master alloy together with an appropriate amount of high purity aluminum and TiB₂ particles, by the method described for the Al–0.15TiB₂ sample. The chemical composition of these aluminum alloys was confirmed by X-ray fluorescence spectroscopy (XRF).

The Al–0.3Ti–0.02B (wt.%) alloy was prepared from an Al–5Ti–0.2B (wt.%) commercial master alloy (KBM AFFILIPS). The particle size distribution of TiB₂ particles in the Al–0.3Ti–0.02B alloy was determined by optical microscopy and showed a particle size distribution in the range from 0.6 to 2.2 μm with a maximum around 1.2 μm. The chemical composition of this commercial Al–0.3Ti–0.02B alloy was analyzed. It was observed that iron was the main impurity in this alloy with about 0.2 wt.% Fe.

3. Experimental methods

3.1. Differential thermal analysis (DTA)

A Perkin-Elmer DTA instrument was used for measuring the crystallization kinetics during continuous cooling and heating. The instrument was calibrated using high purity zinc and aluminum samples for each of the applied cooling rates used in the measurements. All measurements were carried out in a helium atmosphere. From all alloys, solid samples with a cubic shape about 0.2 mm × 2 mm × 2 mm were used. For the crystallization experiment, the samples were heated to 973 K and kept for 5 min at that temperature to ensure that the sample is completely molten. Then the samples were cooled at constant rates of 0.5, 1, 5, 10, and 20 K/min. The exothermic crystallization peak was recorded as a function of temperature. In order to investigate the corresponding melting behaviour, a sample of each material composition was also heated with a heating rate of 10 K/min. The corresponding endothermic peak was recorded as a function of temperature.

3.2. Three-dimensional X-ray diffraction (3D XRD)

In order to resolve the nucleation process from the subsequent grain growth, in situ X-ray diffraction measurements were performed on the three-dimensional X-ray diffraction (3D XRD) microscope at the ID11 beam line at the European synchrotron radiation facility (ESRF). A monochromatic beam of hard X-rays with an energy of 70 keV illuminated each sample. The samples were placed in a glassy carbon container with a height of 20 mm, an inner diameter of 5 mm, and a wall thickness of 1 mm. The sample container was then placed into a quartz tube that was part of the vacuum furnace. A small sample rotation around an axis perpendicular to the beam gives rise to a diffraction pattern on the two-dimensional detector that is placed behind the sample. For a small illuminated sample volume, the diffraction spots originating from solid aluminum grains in the liquid metal do not form continuous powder diffraction rings, but instead appear as distinct spots on the two-dimensional detector during solidification. The measuring procedure aimed to determine the nucleation rate by measuring the number of diffraction spots on the detector as a function of time during solidification. The intensity change of these diffraction spots is a measure of the grain volume. The solidification experiments involved continuous cooling of molten samples, held at 973 K for 30 min, at different cooling rates. The complete details of the experimental setup and measuring procedure are given elsewhere [10].

4. Results and discussion

4.1. DTA measurements

4.1.1. Crystallization behaviour

Fig. 1 shows the typical DTA curves obtained for pure aluminum, Al–0.15TiB₂, Al–0.1Ti, Al–0.1Ti–0.1TiB₂, and Al–0.3Ti–0.02B alloys during solidification at a constant cooling rate of 20 K/min. Two characteristic phenomena are resolved in the studied temperature range at this cooling rate. The first one corresponds to the variation in onset temperature of crystallization (\( T_s \)) and the second to the peak temperature of crystallization (\( T_p \)).

A complete set of DTA thermograms, measured for all sample compositions and at different cooling rates from 0.5 to 10 K/min is shown in Fig. 2. It is clear that the exothermic curves become wider and the characteristic temperatures shift to the lower values as the cooling rate increases. Table 1 summarizes the characteristic data of the crystallization exotherms for all the samples studied. The undercooling is maximum for pure aluminum. A relatively low undercooling is found to activate the nucleation of aluminum grains upon solidification when both...
Fig. 1. Crystallization curves of the liquid to solid phase transformation for pure aluminum, Al–0.15TiB₂, Al–0.1Ti, Al–0.1Ti–0.1TiB₂, and Al–0.3Ti–0.02B alloys at a cooling rate of 20 K/min (for clarity each curve is shifted from the previous one by adding eight).

The question of fundamental interest is how a small amount of titanium enhances the nucleation efficiency of the TiB₂ particles. From the curves shown in Fig. 2, it is apparent that the DTA exotherms for the Al–0.3Ti–0.02B (wt. %) sample exhibit distinct peaks upon freezing at a temperature above \( T > T_P \), and below \( T < T_P \) the crystallization peak temperature, with a size and shape that depends on the cooling rate. Calculations using the thermodynamic database MTDATA suggest that the two additional peaks observed in the commercial purity Al–0.3Ti–0.02B sample, predominantly at low cooling rates, correspond to the formation of TiAl₃ (for \( T > T_P \)) and Fe₄Al₁₃ (for \( T < T_P \)).

The formation of a TiAl₃ phase in the hyperperitectic Al–0.3Ti–0.02B alloy favours an enhanced nucleation in this sample. The experimental results of Mohanty and Gruzleski [11] and Schumacher and Greer [12] have suggested that TiAl₃ lay-

Fig. 2. Crystallization curves of the liquid to solid phase transformation at pure aluminum, Al–0.15TiB₂, Al–0.1Ti, Al–0.1Ti–0.1TiB₂, and Al–0.3Ti–0.02B alloys for cooling rates of 0.5, 1, 5, and 10 K/min (for clarity each curve for 0.5 and 1 K/min is shifted by adding three while for 5 and 10 K/min is shifted by adding five).
The value of latent heat reported for pure aluminum is 385 J/g [18].

The difference in crystallization kinetics for the different investigated samples during solidification can also be analysed by comparing the relative crystallinity as a function of temperature $X(T)$ deduced directly from the heat flow $\left(\frac{dH_c}{dT}\right)$ by using

$$X(T) = \int_{T_o}^{T} \left(\frac{dH_c}{dT}\right) dT \int_{T_o}^{T} \left(\frac{dH_c}{dT}\right) dT$$

where $T_o$ and $T_c$ represent the crystallization onset temperature and end temperature, respectively. $H_c$ is the enthalpy of crystallization. Fig. 3 shows the relative degree of crystallinity $X(T)$ as a function of temperature for all the high purity samples studied at various cooling rates. The crystallization curves exhibit the traditional sigmoidal shape for the liquid to solid phase transformation. The transition temperature and transition rate changes significantly with cooling rate and sample composition. Fig. 4 shows the evolution of the relative crystallinity $X(T)$ as a function of temperature during solidification for the commercial purity Al-0.1Ti-0.1TiB$_2$ alloy. The results indicate that for higher cooling rates, the crystallization curves are analogous to those in Fig. 3 but change a lot for slow cooling. During slow cooling of the Al-0.3Ti-0.02B alloy, the freezing behaviour is altered by the segregation of titanium and iron present in the melt.

The plots of the relative crystallinity as a function of time $X(t)$ for all the samples at a cooling rate of 10 K/min are illustrated in Fig. 5. It is clear from the plots that for the same cooling rate, the time evolution of the crystallization process during the liquid to solid phase transformation of pure aluminum and Al-0.1TiB$_2$ is almost identical. The nucleation starts earlier in time, at low undercooling, when both TiB$_2$ nucleating particles and the solute titanium is present as observed in the Al-0.1Ti-0.1TiB$_2$ and Al-0.3Ti-0.02B alloys. The addition of solute titanium, even at a hypereutectic composition, enhances the nucleation potential of TiB$_2$ grain refining particles as illustrated by the Al-0.1Ti-0.1TiB$_2$ crystallization curve.

4.1.2. Melting behaviour

In order to investigate the effects of grain refining particles on the melting behaviour of aluminum, the samples were also heated with a constant heating rate of 10 K/min. An example of the endothermic curves and the corresponding change in crystallization fraction with temperature is shown in Fig. 6. The temperature range was chosen to be sufficiently wide to ensure that the melting was complete. The values of the heat absorbed during melting are given in Table 2 for each sample. The experimental results, for the variation in crystal fraction with temperature, for pure aluminum and the TiB$_2$ particles of the DTA curves might be associated with the variation in nucleation behaviour caused by the release of latent heat. As the nucleation rate strongly increases with the melt undercooling, a slight decrease in melt undercooling, e.g. due to the release of latent heat, can abruptly cease the nucleation process. After the onset of the solidification the evolution of the solid fraction is controlled by both nucleation and growth. Soon after the nucleation starts, the release of latent heat stops the nucleation process. Finally, the solid fraction is controlled only by grain growth.
embedded in an Al matrix (Al–0.15TiB<sub>2</sub> alloy) indicate that the presence of TiB<sub>2</sub> impurities does not significantly change the melting kinetics in Al–0.15TiB<sub>2</sub> sample, compared to pure aluminum. The presence of solute titanium in aluminum, as observed in Al–0.1Ti alloy, is found to make a slight change compared to pure aluminum. The presence of Fe<sub>4</sub>Al<sub>13</sub> due to the iron impurities in the commercial purity Al–0.3Ti–0.02B alloy constitutes a needle-like second phase particles with a low melting point. By using optical microscopy, these particles were
found to be distributed along the grain boundaries, as shown in Fig. 7. The melting of Fe₄Al₁₃ starts earlier and hence results in a significant decrease in melting point of the investigated commercial purity sample, as observed in Fig. 6(b).

Fig. 8 illustrates a phenomenological symmetry during melting and freezing of the Al–0.3Ti–0.02B alloy. The melting/freezing transition exhibits a thermal hysteresis and confirms the first order character of phase transformation. The width $\Delta T_{1/2}$ of the transformed fraction $X(T)$ versus $T$ at $X(T) = 0.5$ is a useful quantitative measure of the thermal hysteresis. The corresponding values of $\Delta T_{1/2}$ for all the samples at a cooling/heating rate of 10 K/min are listed in Table 2 and decreases with the addition of grain refiners in aluminum. A comparison of the freezing curves with the equilibrium solidification temperature of aluminum (broken line at $T = 933$ K) in Fig. 9, clearly demonstrates the presence of significant undercooling during solidification of pure aluminum and Al–0.15TiB₂ alloys, while almost no undercooling is observed for Al–0.1Ti and Al–0.1Ti–0.1TiB₂ alloys.

### 4.2. Grain nucleation and growth studied by 3D XRD

In order to quantify the grain nucleation and growth behaviour of individual aluminum grains during solidification of these alloys, a 3D XRD study was conducted. The results showed that the addition of grain refiners significantly increased the number of nuclei formed during solidification, leading to a finer grain structure. The 3D XRD patterns also revealed that the growth rate of the grains was inversely proportional to the grain size, with smaller grains growing faster than larger ones. This behaviour is consistent with the theory of grain growth in solidification processes.

### Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\Delta T_{1/2}$ (K)</th>
<th>$\Delta H$ (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>19.1</td>
<td>339</td>
</tr>
<tr>
<td>Al–0.15TiB₂</td>
<td>18.8</td>
<td>361</td>
</tr>
<tr>
<td>Al–0.1Ti</td>
<td>18.3</td>
<td>380</td>
</tr>
<tr>
<td>Al–0.1Ti–0.1TiB₂</td>
<td>17.2</td>
<td>375</td>
</tr>
<tr>
<td>Al–0.3Ti–0.02B</td>
<td>16.1</td>
<td>317</td>
</tr>
</tbody>
</table>

Fig. 7. Optical microscopy image of the commercial purity Al–0.3Ti–0.02B (wt.%) alloy, at the room temperature. The needles like particles are observed at the grain boundary and correspond to the Fe₄Al₁₃ phase, formed during solidification.

Fig. 8. Temperature dependence of the relative crystallinity for the Al–0.3Ti–0.02B alloy as a function of temperature during cooling and heating for a rate of 10 K/min. (The broken lines indicate the onset of freezing at $T = 935.1$ K and melting at $T = 928.5$ K.)
Fig. 9. Temperature dependence of the relative crystallinity for pure aluminum, Al–0.15TiB₂, Al–0.1Ti and Al–0.1Ti–0.1TiB₂ alloys as a function of temperature during cooling and heating for a rate of 10 K/min. (The broken line indicates the solidification temperature of pure aluminum at \( T = 933 \) K.)

samples, three-dimensional X-ray diffraction measurements were performed. The experimental results describing the nucleation and growth of individual aluminum grains during solidification, with two different cooling rates at 1 and 10 K/min, of high purity grain refined Al–Ti–B alloys have been previously reported in [9]. The experimental findings with these model alloys have provided evidence for the formation of a long debated metastable TiAl₃ phase, responsible for grain refinement in hypoperitectic grain refined aluminium titanium alloy. This article presents a detailed study of 3D XRD measurements during solidification of model alloys and compares the results with a commercial purity sample with hypoperitectic composition. As expected [1,2], the formation of TiAl₃ phase, prior to nucleation of aluminium grains in the commercial purity hyperperitectic aluminium titanium alloy. As cooling rate constitutes an important parameter during solidification. Therefore in addition to the previously reported 3D XRD measurements for model alloys during solidification [9], the detailed results for cooling rates ranging from 1 to 40 K/min are presented. This elaborates the systematic variation of undercooling with cooling rate and consequently its effect on nucleation and grain growth process.

4.2.1. Grain nucleation

For illustration, raw images acquired during the liquid to solid phase transformation of Al–0.1Ti–0.1TiB₂ alloy with a cooling rate of 20 K/min are shown in Fig. 10. The illumination time for each displayed diffraction pattern is 1 s using a beam size of 300 μm × 300 μm and the real time interval between consecutive diffraction patterns is 14 s. The diffraction pattern from the molten sample (a) displays the two characteristic liquid rings associated with the short-range order in the molten aluminium. The inner most ring is due to the scattering from the glassy structure of the quartz tube. The amount of grain refiners present in the aluminum is found to be too small to make a significant change in the short-range order of the molten aluminum. The subsequent diffraction patterns during cooling comprises of diffraction spots from aluminium grains, which nucleate in the beginning and grow till virtually no intensity is left in the liquid rings, indicating that the phase transformation is complete.

The nucleation rate, the corresponding evolution of total number of aluminum grains along with the solid fraction \( f_S \), estimated from the normalized variation in the first liquid peak intensity, during solidification of Al–0.15TiB₂, Al–0.1Ti,
Al–0.1Ti–0.1TiB₂ and Al–0.3Ti–0.02B alloys at different cooling rates is presented in Figs. 11–14, respectively. Clearly the undercooling increases for increasing cooling rates. A quantitative comparison of the experimental curves shows that, the nucleation rate during solidification is enhanced only when both solute titanium and TiB₂ particles are present in the melt, as observed in the Al–0.1Ti–0.1TiB₂ and Al–0.3Ti–0.02B alloys. This illustrates the higher nucleation efficiency of TiB₂ particles during solidification, in the presence of solute titanium as predicted by grain refinement theories [1,2]. As reported earlier [9], the nucleation process for almost all the samples investigated, and the applied cooling rates, is always complete for the solid fraction \( f_s \approx 0.2 \). As shown for the DTA measurements, the growth of nucleated grains leads to a significant release of latent heat [5]. This limits the undercooling \( \Delta T \) required to activate further nucleation events as the transformation proceeds.

The overall nucleation rate is an exponential function of Gibbs free energy, \( \Delta G \), which is proportional to \( \Delta T \) [13]. This indicates that a decrease in undercooling caused by the release of latent heat can have striking effects to cease the nucleation process, as observed in Figs. 11–14.

4.2.2. Grain growth versus cooling rate

The growth behaviour of individual aluminum grains during solidification is determined by monitoring the intensity of the diffraction spots during solidification. Fig. 15 illustrates the overall growth kinetics of the individual aluminum grains, for the alloys containing solute titanium with and without added TiB₂ particles. The individual growth curves show a close resemblance to the behaviour of the solid fraction. The observed growth behavior of the individual grains is controlled by the diffusion of solute titanium from the liquid alloy into the solid...
Fig. 11. Nucleation rate, the number of α-aluminum grains (N) and the corresponding evolution of solid fraction (f_s) as a function of temperature during solidification in the Al-0.15TiB_2 (wt.%) alloys at different cooling rates.
Fig. 12. Nucleation rate, the number of α-aluminum grains ($N$) and the corresponding evolution of solid fraction ($f_s$) as a function of temperature during solidification in the Al–0.1Ti (wt.%) alloys at different cooling rates.
Fig. 13. The nucleation rate, the number of α-aluminum grains ($N$) and the corresponding evolution of solid fraction ($f_s$) as a function of temperature during solidification in the Al–0.1Ti–0.1TiB2 (wt.%) alloys at different cooling rates.
Fig. 14. Nucleation rate, the evolution of α-aluminum grains (N) and the corresponding solid fraction (fS) as a function of temperature during solidification in the Al-0.3Ti-0.02B (wt.%) alloys at different cooling rates.
For diffusion-controlled growth the grain radius $R$ as a function of time $t$ is given by [14]:

$$R(t) = \lambda_s \sqrt{D_s (t - t_s)},$$

(2)

where $\lambda_s$ is a parameter that is determined from the titanium solubility in the liquid and the solid phases, $D_s$ the diffusion constant of solute titanium in the liquid [15] and $t_s$ is the moment of nucleation of the grain. Eq. (2) only applies in the initial stage of the transformation where the interaction between growing grains can be neglected. This is shown in Fig. 15 where the individual growth curves overlap with the model prediction in the initial stage of the transformation. During the later stages the release of latent heat and the interaction of growing grains reduces the growth.

Fig. 16 shows the growth behaviour of several individual aluminum grains during solidification of the Al–0.1Ti–0.1TiB$_2$ alloy at cooling rates of 2.5, 5 and 10 K/min. The model prediction for diffusion controlled grain growth is also shown. The observed growth behaviour of individual aluminum grains is similar for all the cooling rates. Again, three different stages for grain growth can be distinguished. The model calculations are in reasonable agreement with the experimental data at slow cooling rates. For higher cooling rates, an increasing undercooling is observed before the nucleation starts. However, the initial growth behaviour exhibits a close resemblance with the model predictions even at higher cooling rates.

4.2.3 Evolution of metastable TiAl$_3$

A careful analysis of the measured diffraction patterns shows the presence of a limited number of weak diffraction spots, prior to the nucleation of aluminum grains, during slow cooling of the Al–0.1Ti–0.1TiB$_2$ and Al–0.3Ti–0.02B alloys. These diffraction spots cannot be indexed as aluminum grains. The crystallographic analysis indicates that the scattering angles corresponding to these diffraction spots fit to the TiAl$_3$ phase with two different crystallographic structures, tetragonal as well as cubic. Figs. 17 and 18 describe the evolution of these TiAl$_3$ grains during continuous cooling of the liquid Al–0.1Ti–0.1TiB$_2$ and Al–0.3Ti–0.02B alloys at slow cooling rates. It is interesting to see that these diffraction spots first appear roughly 10 K above the experimental solidification temperature of aluminum. At the nucleation temperature of the aluminum grains the intensity of the TiAl$_3$ reflections start to decrease, and finally vanish near the end of the transformation. The absence of these TiAl$_3$ reflections in the sample containing only solute titanium or only TiB$_2$ particles shows that the TiAl$_3$ phase plays an essential role in the enhanced nucleation process as revealed in Figs. 13 and 14, compared to that observed in Figs. 11 and 12. This formation of TiAl$_3$ phases prior to the nucleation of aluminum grains in Al–0.1Ti–0.1TiB$_2$ and Al–0.3Ti–0.02B alloys favours our interpretation of the crystallization process during the DTA measurements of these samples. Apparently, the nucleation of TiAl$_3$ on the TiB$_2$ substrate is substantially more effective than the nucleation of aluminum. From earlier measurements it is known that once TiAl$_3$ is formed it acts as an excellent nucleation site for aluminum [16]. Our present in situ study shows that the TiB$_2$ substrates stabilise a TiAl$_3$ phase in a limited temperature range above the solidification temperature of aluminum. This formation of a TiAl$_3$ phase in aluminum alloys with a titanium concentration below 0.15 wt.%, where it is considered unstable according to the Al–Ti phase diagram [17], has long been proposed but was so far not supported by experimental evidence due to the lack of in situ data [2,11].

While according to the Al–Ti phase diagram, the TiAl$_3$ is a stable phase in a hyperperitectic aluminum alloy, above the melting temperature. Our measurements indicate that upon nucleation of α-aluminum grains during continuous cooling, the TiAl$_3$ grains cease to grow and their radius decreases with a further decrease in temperature of both hyperperitectic and hypoperitectic grain refined aluminum alloys. No such observation of the evolution of a TiAl$_3$ phase within the melt has been reported earlier.

The role played by the TiAl$_3$ phase in the nucleation of α-aluminum during solidification of grain refined aluminum alloys has been a matter of speculations. The TiAl$_3$ substrate is con-

Fig. 15. Grain radius of individual aluminum grains (■) during solidification of Al–0.1Ti–0.1TiB$_2$ and Al–0.1Ti alloys, as a function of temperature, for continuous cooling at a cooling rate of 1 K/min. The solid lines indicate the model calculation for diffusion-controlled grain growth (from Ref. [9]).
Fig. 16. Grain radius of individual aluminum grains during solidification of Al–0.1Ti–0.1TiB₂ alloy, as a function of temperature, with continuous cooling at different cooling rates (a) 2.5 K/min, (b) 5 K/min, and (c) 10 K/min. The solid lines indicate the model calculation for diffusion-controlled grain growth.

Fig. 17. The grain radius of individual TiAl₃ grains in the aluminum alloy with solute titanium and added TiB₂ particles (a) and compared to the growth of an individual aluminum grain in (b). The TiAl₃ grains nucleate about 10 K above the experimental onset of nucleation for aluminum grains, and become unstable when solid aluminum has formed (from Ref. [9]).
Fig. 18. Evolution of the solid fraction $f_S$ of aluminum (□) and the radius of TiAl3 grains (●) during liquid to solid phase transformation of the Al-0.3Ti-0.02B alloy at a slow cooling rate of 1 and 2.5 K/min. The solid fraction of aluminum is deduced from the normalized variation in the intensity of the first liquid peak of aluminum.

sidered to be a better nucleation site for aluminum grains than the TiB2 particles, and hence, responsible for grain refinement. Previously Mohanty et al. have confirmed this mechanism and reported the existence of TiAl3 layer sandwiched between the TiB2 surface and the aluminum grains, in grain refined aluminum alloys. Our experimental observations support those reported by Mohanty et al. It suggests that the surface of TiB2 particles, nucleate TiAl3 grains prior to the solidification of aluminum. However these TiAl3 grains exhibit a metastable behavior. The TiAl3 grains dissolve upon solidification of aluminum and most probably responsible for the enhanced nucleation of aluminum grains.

5. Conclusions

We have performed DTA and 3D XRD measurements to study the crystallization kinetics and mechanism of grain nucleation and growth of individual grains during the liquid to solid phase transformation of grain refined aluminum alloys. The formation of a TiAl3 phase is observed to be responsible for enhanced nucleation in hyperperitectic, as well as hypoperitectic grain refined aluminum alloys. The growth behaviour of individual aluminium grains, just after nucleation, is controlled by titanium diffusion. However, afterwards the release of latent heat is also crucial in governing the growth kinetics during solidification.

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References