

Characterization Of Hypereutectic Al-19%Si Alloy Solidification Process Using In-Situ Neutron Diffraction

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Abstract

In-situ thermal analysis and neutron diffraction techniques were used simultaneously to evaluate the kinetics of the non-equilibrium solidification process of Al-19%Si binary alloy. Neutron diffraction patterns were collected in stepwise mode during solidification between 740 and 400°C. The variation of intensity of the diffraction peaks was analysed and compared to the results of a conventional cooling curve analysis. Neutron diffraction detected nucleation of the Si phase (primary and eutectic), as well as the Al phase during Al-Si eutectic nucleation. This illustrates the potential of neutron diffraction for high resolution melt analysis at near-liquidus temperatures, required for advanced studies of grain refining, eutectic modification, etc. The solid-to-liquid volume fraction was determined based on the change of intensity of neutron diffraction peaks over the solidification interval. Overall, the volume determined was in good agreement with the results of the cooling curve thermal analysis.

Neutron Diffraction during the Alloy Solidification Process

The hypereutectic Al-Si alloy (about 16-23% Si) is recognized as an excellent material for high performance automotive cast component applications. Important examples include linerless engine blocks for passenger vehicles, and motorcycle cylinder blocks produced by high pressure die casting (HPDC) and low pressure permanent mold (LPPM) casting processes [1-4]. Proper understanding of solidification kinetics will lead to optimization of casting technologies and improved microstructures of as-cast alloys.

The hypereutectic Al-19%Si alloy was used in the present "pilot" studies. The binary-alloy chemistry was selected, to minimize the effect of other alloying elements on neutron diffraction and thermal analysis data. Such an approach allows for better validation of the suitability of neutron diffraction techniques for solidification analysis [3,5,6].

Experimental Procedure

A novel solidification cell was designed and built to carry out controlled melting and solidification experiments under simultaneous exposure to neutron radiation. A stainless steel crucible containing the analysed alloy was placed inside an open titanium tubing filled with Argon, to prevent oxidation at higher temperatures. The solidifying sample was irradiated with monochromatic thermal neutrons of wavelength 0.237 nm using a {311} reflection of a Si monocrystal. Diffraction

patterns were collected isothermally at several temperatures starting from 740 and ending at 400°C. The measurements were taken in terms of scattered intensity vs. diffraction angle 2Θ (where Θ is the Bragg angle), using the C2 spectrometer of AECL's NRU reactor. The scattering angle ranged from 37 to 117 degrees for each run at each temperature.

Experimental Results

Figure 1 depicts diffraction patterns received throughout the experiments, as the Al-19%Si melt temperature was reduced in the stepwise mode from 740 to 695, 660, 630, 600, 570, 560, and finally, to 400°C. As expected, no new peaks were observed in the pattern received for the molten alloy at temperatures above liquidus at 740°C, but the diffraction intensity through the entire range of the scattering angle was increased due to diffuse scattering from the melt. The curved shape of the 740°C diffraction pattern (as compared, for example, to that of the 400°C pattern) suggests that it represents a pattern received for a liquid sample [6]. Other diffraction patterns in Figure 1 show peaks that represent diffraction by several crystallographic planes of the solid Al and/or Si crystals through the solidification interval. Integrated intensity of the peaks received at 400°C represents 100% fraction solid (FS).

3D Sequential Graph

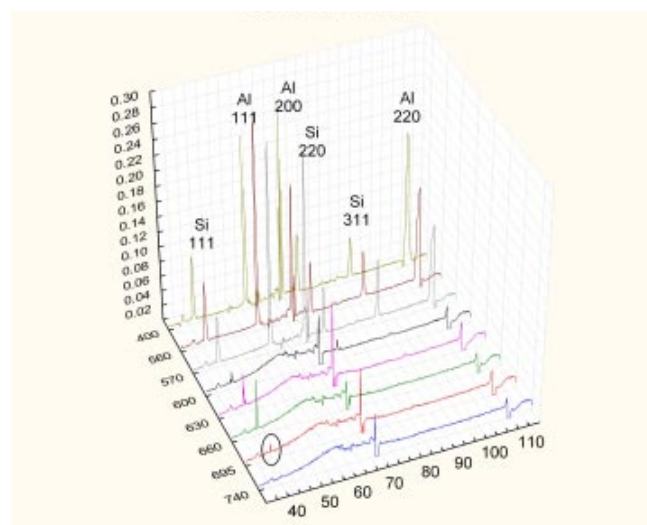


Fig. 1 Neutron diffraction pattern of the Al-19%Si binary alloy solidification process collected at various temperatures, ranging from 740°C (45°C above the equilibrium liquidus temperature) to 400°C (143°C below the solidus temperature).

The integral intensity of the diffraction peaks can be used as information that directly reflects the relative amount of solid phase that contributed to the neutron scattering. Analysis of the diffraction pattern for the Al-19%Si melt at 695°C showed that some solid Si existed in the melt. The diffraction peak (circled in Figure 1) that exists at about 44° 2 θ can only be attributed to the [111] reflection of Si. It is to be noted that 695°C is about 23°C higher than the liquidus temperature established from the thermal analysis experiments.

Correspondingly, by collecting the diffraction patterns for the semisolid alloy for various temperatures within the solidification interval, one can retrieve valuable information on the dynamics of non-equilibrium solidification; for example, FS of Al and FS of Si vs. temperature of the melt, as a result of direct measurement and calculation of the integrated intensity of the diffraction peaks.

Analysis of Fraction Liquid using Neutron Diffraction

The diffraction pattern of a semisolid sample is the sum of the scattering from the liquid and solid phases; therefore, the Bragg peaks from a solid appear to sit upon the broad, diffuse scattering from the liquid [6]. As with the study of [6], we make the approximation that the liquid structure (and hence diffuse scattering) does not change appreciably over the temperature range of interest; in addition, we assume changes in composition of the liquid as it evolves in the solidification interval can be ignored. With these assumptions, neutron diffraction is capable of simultaneously being an independent monitor of the proportions of both liquid melt and solid alloy inside the solidifying test sample.

Figure 2 represents the diffraction patterns received for the sample material at different temperatures. There is a clear difference in the intensity of the background signal for all between-the-peaks areas, which originates from the reduction in fraction liquid in a course of alloy solidification. This means that it is relatively simple to separate melt and solid scattering. This separation is done by performing a simple integration of scattering intensity over the range in which the change in the scattering pattern is only due to the change in the proportion of liquid; for equation (1):

$$(1) \quad FL(T) \sim \frac{\int_{2\theta=45}^{2\theta=59} \frac{dI(T)}{d\theta} d\theta}{\int_{2\theta=45}^{2\theta=59} \frac{dI}{d\theta} d\theta} \quad T=740^{\circ}\text{C}$$

where FL – fraction liquid at a given temperature, I – normalized scattering intensity, and θ – scattering angle.

The regions of the diffraction pattern immediately beyond the solid-alloy peaks can therefore be used as an indicator of liquid content in the sample volume. Three such regions were identified in Figure 2; namely, 45 – 59°, 77 – 91°, and 93.5 – 108° 2 θ . Normalization was done in such a way that the initial liquid content at 740°C was 100%, and the liquid content at 400°C was 0%. The weak, unlabelled peaks in the pattern are

from the container and furnace, and we make the approximation that these are of constant intensity in this temperature range.

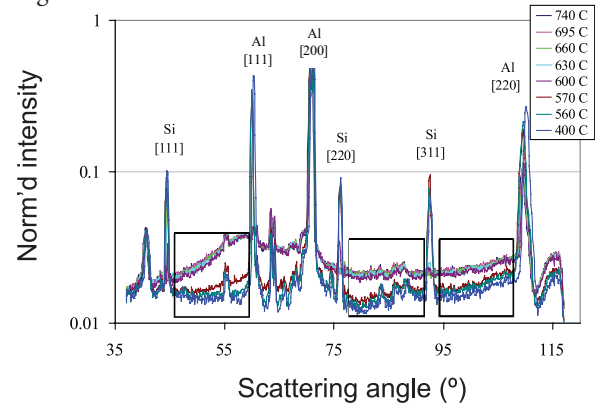


Fig. 2 Neutron diffraction pattern collected during the Al-19%Si binary alloy solidification process. Selected no-peak areas were used for the fraction liquid analysis.

The results of this analysis are shown in Figure 3, along with two lines that represent the non-equilibrium solidus and liquidus temperatures determined from the thermal analysis carried out during the Al-19%Si binary alloy solidification process. The fraction liquid is about 95% at about 10°C below the non-equilibrium liquidus temperature, and most of the solid phase evolves at the later stage of solidification (eutectic evolution). Each diffraction peak should have an individual evolution of intensity as a function of temperature, all related by the atomic displacement, or temperature, parameter; the higher angle peaks decreasing more quickly with increase in temperature. Figure 3 shows this effect to be negligible over the temperature range of interest, and within the statistics of our measurements. Therefore, we ignore this parameter, and any anisotropy in this analysis.

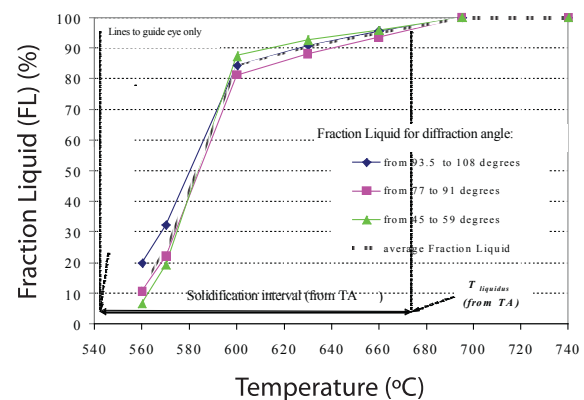


Fig. 3 Fraction liquid curve obtained from neutron diffraction analysis of the Al-19%Si binary alloy solidification process.

Analysis of Fraction Solid using Neutron Diffraction

Figures 4 (a) and (b) depict the Si [111] and Al [220] peak evolution over the solidification interval and further cooling to 400°C. The integral intensity of the diffraction peaks is clearly increasing as each peak becomes higher. The angular position

of the peaks also changes as the temperature decreases, which corresponds to thermal contraction of the solid metal (i.e., a reduction in the lattice plane spacing reflected by the shift in Bragg's peak position).

Similar to the liquid phase analysis, by performing a simple integration of the peak's normalized intensity over the angular range that covers the width of the peak, one can retrieve the relative FS for the selected temperatures within the solidification interval of the alloy. For example, the following integration over a two-degree interval was applied for the [111] reflection of Si. The assumption is made that the crystallographic texture of the solid is constant over the entire solidification range, e.g., that the shape of primary Al and Si are the same as those in phases formed below the eutectic.

$$(2) \quad FS(T)^{Si[111]} \sim \int_{\angle Si[111]-1^\circ}^{\angle Si[111]+1^\circ} \frac{dI(T)}{d\Theta} d\Theta / \int_{\angle Si[111]-1^\circ}^{\angle Si[111]+1^\circ} \frac{dI}{d\Theta} d\Theta \quad T \leq T_{solidus}$$

The results of separate calculations performed for Si [111] and Al [220] are presented in Figure 5. In addition to this, Figure 5 also contains a fraction-solid profile received from the bulk liquid analysis (earlier in this report) as $FS = 1 - FL$. The non-equilibrium solidification range and FS vs. temperature solidification profile determined by thermal analysis are also marked on the graph.

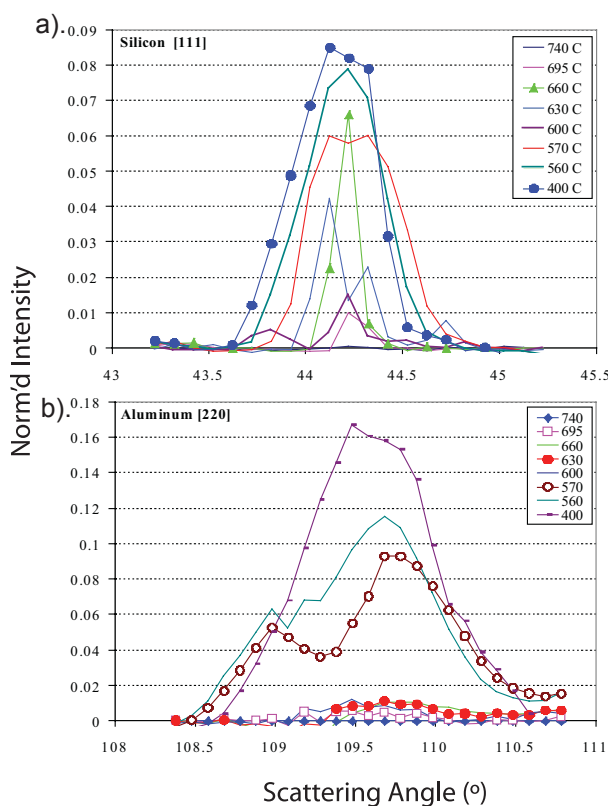


Fig. 4 Diffraction intensity change in the neutron diffraction experiments recorded during the Al-19%Si binary alloy solidification process between 740 and 400°C, for the following phases: a) Silicon [111], b) Aluminum [220].

An important observation from Figure 5 is that solid Si starts evolving in the melt much sooner than solid Al, which is in agreement with the solidification sequence for the studied alloy. The presence of Si crystals (or clusters of Si crystals) can be detected above the liquidus temperature (FSSi about 3%) and rapidly evolves in excess of 20% about 12 degrees below the liquidus temperature. On the other hand, solid Al evolves very slowly as the metal temperature decreases, but accelerates rapidly at temperatures below 600°C. This observation corresponds well with the earlier results of thermal analysis and liquid phase analysis, which indicated that most of the alloy solidifies as eutectic within the temperature range of 570–560°C (to 90~95% solid), with solidification completion at about 543°C. The “overall” solidification profile represented by the line that was derived from the liquid-phase analysis matches well with the results received for the solid Si and solid Al evolution, though lacks Al/Si-related specifics. The same is also true for the other line that represents the “overall” solidification profile based on the thermal analysis data.

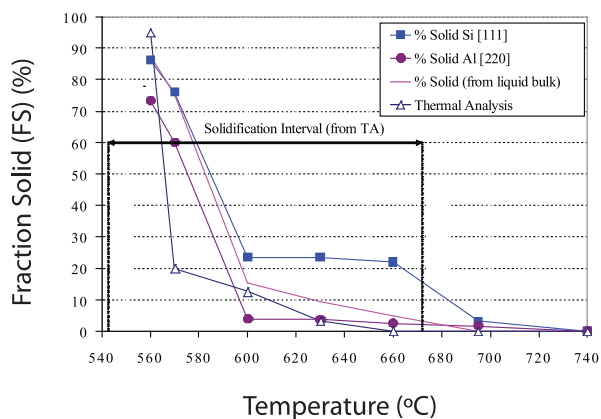


Fig. 5 Fraction solid evolution obtained during neutron diffraction analysis of the Al-19%Si binary alloy solidification process. Data were received from “liquid bulk” analysis and derived from Si [111] and Al [220] diffraction peaks.

Regardless of the “classical” use of neutron diffraction for studies of solid metals in metallurgical research, the results presented show the potential of applying neutron diffraction for high resolution analysis of liquid and semi-solid alloy. These studies will contribute to better understanding of the solidification behaviour of the Al-Si hypereutectic alloys during casting processes such as HPDC and LPPM.

Conclusions

Neutron diffraction was used for the first time in studies of non-equilibrium solidification of metal alloys. Several assumptions and approximations made in this first study, which will be tested and refined in future studies, but from which the following characteristics of solidification of the Al-19%Si binary alloy can be made:

- There is solid Si present in the diffraction pattern at temperatures above the non-equilibrium liquidus temperature of 672°C. The content of solid Si in the melt at 695°C exceeds 3%. Si phase evolution

above the liquidus temperature may indicate the agglomeration of clusters of primary Si.

- The presence of solid Al is first observed at 660°C, well below the liquidus temperature.
- There is an obvious difference in the solidification path of Al and Si, with the latter evolving at a much higher rate during the early stage of solidification of the alloy (primary Si).
- The intensity of neutron scattering from the liquid metal can be used as an independent indicator of fraction liquid in the melt.
- Accelerated solidification that can be observed in the solid-phase neutron diffraction experiments between 570°C and about 560°C matched well with the findings of the liquid-phase neutron diffraction analysis and the thermal analysis of the solidification process. This confirms that most of the FS evolves as eutectic at the end of solidification process.

References

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