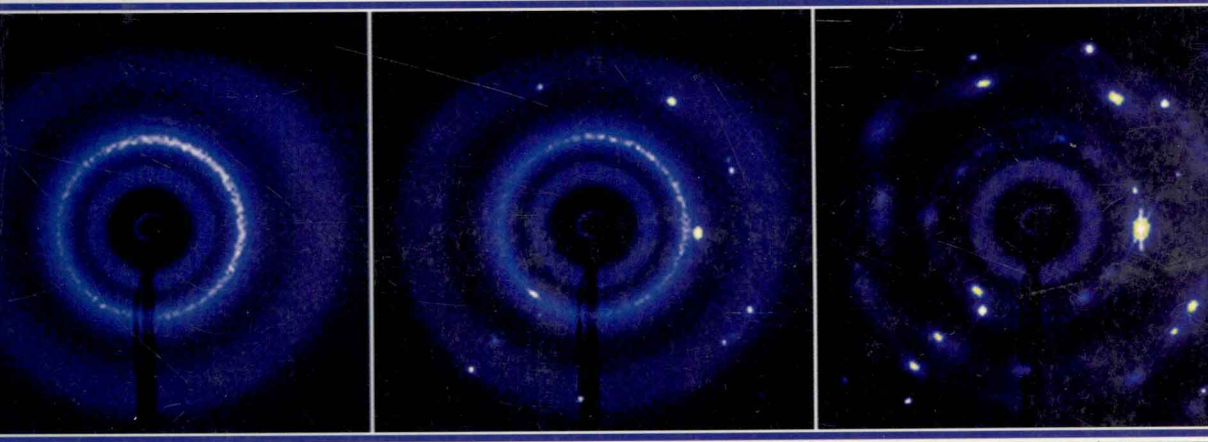
Solidification

Real –Time Investigation of Grain Nucleation and Growth During Liquid to Solid Phase Transformation of Aluminum Alloys



Naveed Iqbal

Department of Radiation, Radionuclides & Reactors

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Real-Time Investigation of Grain Nucleation and Growth
During Liquid to Solid Phase Transformation of Aluminum Alloys

PROEFSCHRIFT

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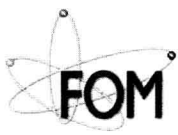

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PART I

Theory, Instruments and Methods

Contents

PART I: Theory, Instruments and Methods

PART II: Experimental Results and Discussion

Chapter 1

Introduction

Aluminum is widely used throughout the world economy, particularly in the transportation, packaging, and construction industries. As a lightweight, resistant to corrosion, high-strength, and recyclable structural metal, aluminum has and will continue to play an important role as applications extend to infrastructure, aerospace, and other High-Tec industries. The challenge for the aluminum industry is to improve the material properties so as to meet the growing needs for stronger and lighter materials. For instance, the auto industry is under pressure to reduce environmentally harmful emissions and improve gas mileage. Aluminum represents the best solution for developing lighter, stronger, and more fuel-efficient vehicles.

A statistical review of aluminum consumption by the leading aluminum consumers during the last decade (1992-2002) is presented in table 1.1 [1]. The "aluminum supply" comes from three basic sources: primary (domestic production from alumina); imports of ingot and semifabricated (mill) products; and recycled metal (from scrap, also known as secondary recovery). Subtracting a country's exports of ingot and mill products from its aluminum supply yields its "apparent aluminum consumption." Reflecting the worldwide trend toward greater use of aluminum, the change in world's primary aluminum production during the last decade is shown in figure 1.1 [1]. The statistics indicate that the worldwide primary aluminum production, over the period, increased at an annual rate of 2.9 percent—reaching 25.9 million metric tons in 2002. Other than North America, all of the aluminum-producing regions of the world Africa, Latin America, Asia, European Union, Other Europe, and Oceania, experienced at least modest average annual growth rates during the period.

Aluminum, when in the pure form, is generally polycrystalline with a large grain size of more than 1 mm, exhibiting poor mechanical strength, which is an important aspect of the performance in industrial applications. Strengthening of metals can be obtained in several ways, for example by solid solution hardening, work hardening, precipitation hardening or grain refinement. Grain refinement is technologically attractive because it generally does not adversely affect ductility and toughness, contrary to most other strengthening methods. The yield stress σ_y generally increases for a decreasing average grain size d, according to the Hall-Petch equation [2];

$$\sigma_y = \sigma_o + k/\sqrt{d} \qquad (1.1)$$

Table 1.1: Statistical review of aluminum consumption by different countries during the last decade (1992-2002) [1]. All the quantities are in thousands of metric tons.

Aluminum consumption (Thousands of Metric Tons)		
Country	1992	2002
United States	6952	8453
China	n/a	4288
Japan	3619	3561
Germany	2044	2493
Italy	1132	1645
France	989	1363
Canada	600	885
United Kingdom	800	868
Brazil	326	717
India	383	642
Netherlands	261	405

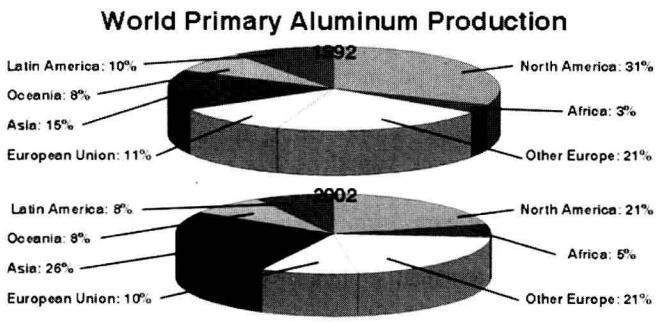

Figure 1.1: The statistical review of worldwide primary aluminum production over the last decade (1992-2002) [1].

Metals obey the Hall-Petch equation over several orders of magnitude in grain size. The average grain size changes with material and processing conditions and is estimated to be 200 μm for grain refined aluminum [3]. Figure 1.2 shows the microscopic grain structure of pure solid aluminum and a grained refined aluminum alloy. Note the drastic reduction in grain size and change in grain morphology, from columnar structure to equiaxed grains, after the addition of grain refiners.

Grain refinement is directly related to the nucleation and growth of aluminum grains during solidification. The nucleation process involves the ordering of groups of atoms in the liquid to form very small solid clusters. These fluctuations occur at temperatures both above and below the melting point T_m, but clusters formed above T_m always revert to the liquid since it is the most stable phase. However clusters formed below the melting temperature T_m can evolve to solid nuclei provided their size is sufficiently large to be stable against melting. Thermodynamically, the barrier for a nucleation event is associated to the relatively large surface energy of the solid-liquid interface with respect to the gain in energy between the solid and the liquid phase for a small cluster. This energy barrier for nucleation is of the order of

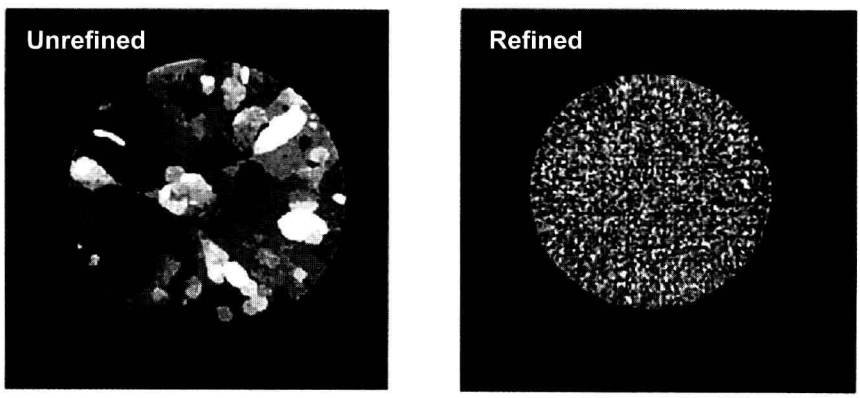

Figure 1.2: Grain structure of aluminum without and with grain refinement during solidification.

0.2 $k_B T_m$ for homogenous nucleation in pure metals [4]. The addition of foreign substrates in the melt provides nucleation sites with a reduced energy barrier for nucleation that enhances the nucleation rate. This process is known as heterogeneous nucleation. The stable nuclei formed on the foreign substrates then grow in size resulting into an equiaxed and finer grain structure. Figure 1.3 illustrates the mechanism of homogenous nucleation in pure aluminum and heterogeneous nucleation on a foreign substrate.

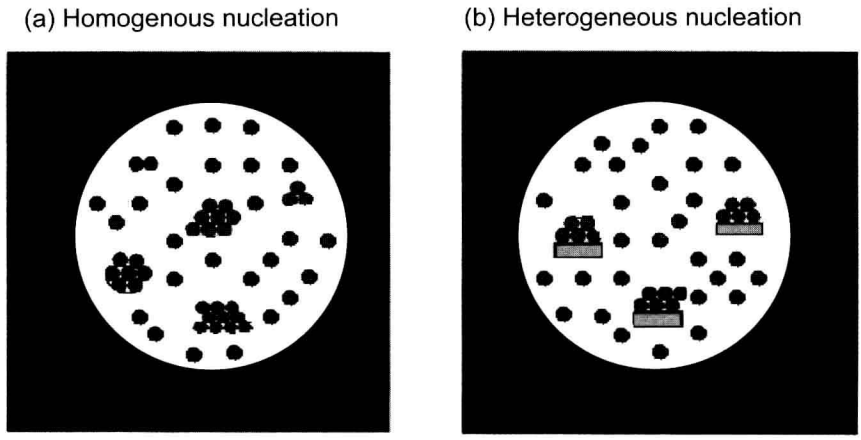

Figure 1.3: A schematic representation of (a) homogenous nucleation and (b) heterogeneous nucleation on foreign substrate during the liquid to solid phase transformation.

The use of grain refinement is widespread in the aluminum industry and is commonly achieved through the addition of small amounts of Al-Ti-B or Al-Ti-C master alloys [3, 5-7]. These alloys contain microscopic TiB_2, $TiAl_3$ and TiC particles which can act as substrates for heterogeneous nucleation of aluminum grains during solidification. The Al-Ti-B master alloys are most commonly used as they are easier to prepare [8] by the reaction of Ti and B-containing salts with molten aluminum primarily due to higher solubility of boron in molten aluminum and high stability and low solubility in molten aluminum of resulting TiB_2 particles. The carbon has low solubility in aluminum while the stability of TiC particles at low concentration of titanium in aluminum is also an issue. In this thesis grain refinement by Al-Ti-B master alloys is studied. The major issue in grain refinement of Al-Ti-B alloys is the role of TiB_2 and $TiAl_3$ particles during solidification. Numerous studies [9] have established that there are favourable epitaxial relationships between solid aluminum and the surface of $TiAl_3$ particles. For example, the {110} planes of $TiAl_3$ match well with the {112} planes of solid aluminum. The lattice disregistery between the two planes is less than two percent [3]. This means that the {110} planes of the titanium aluminide crystal seem almost like a piece of solid aluminum and so grain can nucleate very easily there. This epitaxial relationship makes the $TiAl_3$ surface a better nucleation site compared to that of TiB_2. However the stability of $TiAl_3$ particles in an aluminum alloy strongly depends on the concentration of solute titanium in the melt. During the production of aluminum alloys, the master alloy is added at levels, which result in solute titanium concentration below the peritectic composition (0.15 wt.% Ti). For these hypoperitectic aluminum compositions, $TiAl_3$ is not a stable phase [3] and apparently TiB_2 are the only nucleation sites available in the melt during solidification. Microscopic observations [10,11] for the grain refinement of pure aluminum in the presence of TiB_2 particles have however shown that the TiB_2 particles without solute titanium are poor nucleants for aluminum grains during solidification. Hence the question arises "how does the small amount of solute titanium enhances the nucleation on TiB_2 particles and improve the grain refinement process?" Figure 1.4 shows the variation in grain size of solidified aluminum for

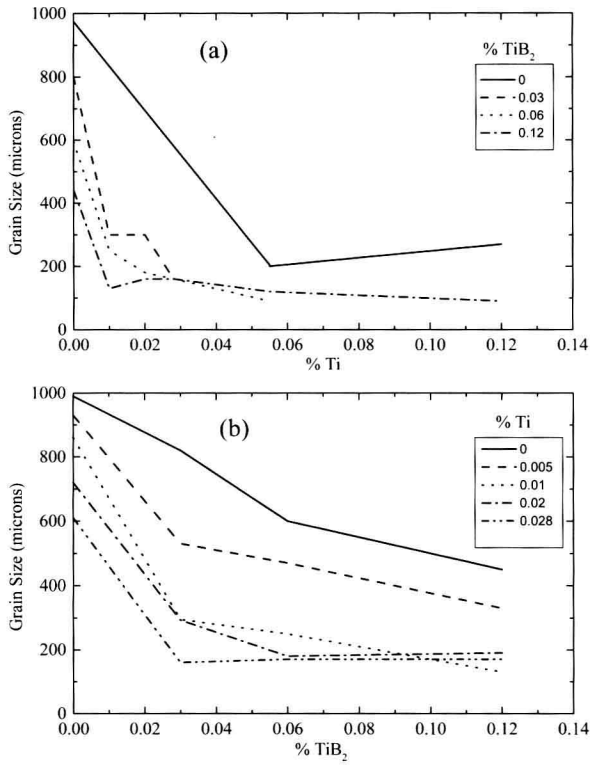

Figure 1.4: The variation in grain size of solidified aluminum for the addition of TiB_2 particles and solute Ti. (a) The effect of additional solute titanium at various TiB_2 concentrations. The insert shows the addition levels of TiB_2 (wt.%). (b) The effect of additional TiB_2 at various solute titanium concentrations. The insert shows the levels of added solute Ti (wt.%). The graphs are based on data from ref. [5].

different concentrations of TiB_2 particles and the solute titanium independently and both together. The grain size reduces significantly when solute titanium is added in the aluminum melt containing TiB_2 particles.

In order to obtain a complete understanding of the mechanism of grain refinement, detailed experimental observations of the evolving microstructure during solidification are crucial. Generally calorimetric techniques such as differential thermal analysis (DTA) probe the heat produced during solidification, which is a measure of the phase fraction transformed. This technique only provides information about the overall transformation, but does not help to give an independent determination of grain nucleation and growth. Since liquid and solid phases have different local structure, promising experimental techniques that can exploit this information to monitor the structure during solidification are neutron diffraction and synchrotron radiation. These types of radiation have the ability to penetrate several millimetres of aluminum and at the same time provide real-time information on the evolving microstructure during solidification at high temperature. For synchrotron radiation hard X-rays are needed to penetrate the bulk of the sample.

Time resolved neutron diffraction measurements during solidification of aluminum alloys provide instantaneous information about the evolution of liquid/solid fraction and the crystallization kinetics of evolving grains.

The only technique that can independently determine the nucleation rate, the growth rate of individual grains and the fraction transformed during solidification is the three dimensional X-ray diffraction technique [12]. This technique has successfully been applied for the determination of the nucleation and growth rate of individual grains during solid-state transformation in aluminum [13] and steel [14].

The research presented in this thesis aims to experimentally investigate the crystallization process during solidification of grain refined aluminum alloys and to compare these results with the physical models that describe grain nucleation and grain growth during the transformation. The investigated samples include high purity aluminum containing TiB_2 nucleating particles and solute titanium separately and both together so as to independently establish the role played by them during the grain refinement process. These alloys serve as model systems for studying the mechanism of grain nucleation and growth during the liquid to solid phase transformation. The results obtained are compared with another commercial purity grain refined aluminum alloy.

Chapter 2 reviews the theories that form the basis of the grain refinement mechanism and the physical models that explain the transformation kinetics during solidification.

The experimental techniques applied in this study are described in chapter 3. These experimental techniques involve differential thermal analysis (DTA), neutron diffraction, small angle neutron scattering and three-dimensional X-ray diffraction microscopy.

Chapter 4 presents a brief overview of the problem investigated in this thesis. It also reviews the analysis and conclusions of our experiments, which are described in detail in the upcoming chapters.

The results of differential thermal analysis (DTA) experiments, describing the over all transformation kinetics of aluminum alloys during solidification, are given in chapter 5.

In chapter 6 the experimental findings of in-situ neutron diffraction and small angle neutron scattering measurements during the crystallization of aluminum alloys are presented.

Chapter 7 presents the nucleation kinetics and the growth behaviour of individual grains during solidification, measured with the three-dimensional X-ray diffraction technique.

The thesis is finally summarised in the end.

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