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Nucleation kinetics of entrained eutectic Si in Al–5Si alloys

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Abstract

A series of high-purity Al–5 wt.% Si alloys with trace additions of Sr, Fe and P were prepared by using arc-melting and subsequent melt-spinning. The nucleation phenomenon incorporating the free growth criterion of eutectic Si was investigated by using the entrained droplet technique, atomic resolution scanning transmission electron microscopy and differential scanning calorimetry. It was found that Sr addition exerts no positive effect on the nucleation process; instead, an increased undercooling was observed. A combined addition of Sr and Fe further increased the undercooling, as compared with the addition of Sr only. Only trace P addition has a profound effect on the nucleation of Si by a proposed formation of AlP patches on primary Al. The estimated AlP patch size was found to be sufficient for the free growth of Si to occur inside the eutectic droplet. Nucleation kinetics was discussed on the basis of classical nucleation theory and the free growth model. For the first time, realistic and physically meaningful nucleation site values were obtained. The interactions between Sr and P were also highlighted. This investigation demonstrates strong experimental supports for the free growth nucleation kinetics and the well-accepted impurity-induced twinning growth mechanism, as well as the poisoning of the twin plane re-entrant edge growth mechanism.

Keywords: Al–Si alloys; Nucleation kinetics; Eutectic solidification; Free growth; Melt-spinning

1. Introduction

Al–Si-based alloys are important casting alloys, and constitute ~90% of all shape castings [1]. Primary Si, eutectic Si and other intermetallics, i.e. β-Al_5FeSi, are present in Al–Si-based alloys. The size and shape of eutectic Si in hypoeutectic Al–Si alloys play a major role in determining the final mechanical properties of the manufactured parts, in particular fracture elongation. The eutectic Si of these Al–Si alloys is usually modified by chemical additions of Sr or Na. The phenomenon of modification was first discovered by Pacz [2]. Since then, this scientific discovery is the subject of publications [3–23] to elucidate the physical metallurgical phenomena involved. Nevertheless, the nucleation and growth mechanisms during modification are still a matter of debate. Generally, higher undercoolings are observed for both nucleation and growth during thermal analysis, suggesting that nucleation is depressed and subsequent growth is also hindered [12].

Regarding the aspect of growth, early research [6] proposed that Na addition caused the obstruction of Si crystal growth by surface adsorption of Na on Si. Interestingly, it was postulated as early as 1950 that Si crystal growth may be obstructed via the presence of Na-rich [$NaAlSi_{1.25}$] or [$NaAlSi_{1.33}$] compounds [7]. Plumb and Lewis [8] suggested that the Na addition retarded the nucleation of Si through

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its adsorption on the nuclei interface, during eutectic solidification. Wagner [9] and Hamilton and Seidensticker [10] proposed a twin plane re-entrant edge (TPRE) growth mechanism in Ge dendrites. They proposed that growth occurred more readily at the re-entrant edges, which could play a key role in the modification of Ge crystals. Based on the observations of Wagner [9] and Hamilton and Seidensticker [10], as well as the concept of surface adsorption, Day and Hellawell proposed the poisoning of TPREs [3] in 1968. It was assumed that the modifier retarded Si growth by selectively adsorbing at the TPRE, and thus deactivating the growth advantage of the TPRE mechanism. Furthermore, in 1987, Hellawell [11] and Lu and Hellawell [12] developed a growth mechanism after conducting experiments with the additions of impurities, i.e. Na and Sr, and postulated that these impurities were adsorbed on the growing surfaces of Si and caused frequent twinning to occur, which they named as impurity-induced twinning (IIT). It should be noted that either the poisoning of the TPRE mechanism [3] or the IIT mechanism [12] can be attributed to the interfacial poisoning of Si at the growing interface, highlighting the importance of the adsorption of modifier atoms on the growing interface. The main difference is the interfacial poisoning position. For poisoning of the TPRE, interfacial poisoning was proposed to occur at the re-entrant edges, while for IIT, interfacial poisoning was proposed to take place at the ledges (i.e. step or kink sites) on the already growing atomic layers. Both IIT and poisoning of TPRE mechanisms have been experimentally investigated in the case of Sr [5,13–16], although micro X-ray fluorescence spectroscopy mapping [13,14] reveals that Sr is homogenously distributed within the eutectic Si, while energy-dispersive X-ray spectroscopy (EDX) mapping using scanning transmission electron microscope (STEM) and atom probe tomography (APT) [15] show that two types of Al–Si–Sr clusters are distributed at the re-entrant edges and Si growing plane, respectively. This difference may be due to the techniques and resolution used; however, the adsorption of Sr within eutectic Si indeed causes a fine fibrous morphology. A similar experimental observation using the electron probe microanalysis technique (EPMA) also shows that Sr resides mostly inside the Si in an A356 alloy [16]. However, it should be noted that most of these investigations are based on commercial purity Al–Si based alloys produced using conventional casting. It has been reported that there is an important impurity effect on the nucleation and growth of eutectic Si in Al–Si-based alloys [17]. The research on high purity Al–Si alloys is of great interest to elucidate the impurity effect on the nucleation and growth of Si, as suggested by Cho et al. [18]. It is of great necessity to reveal the atomic distribution of Sr within Si particles in extreme cases of high cooling, such as melt-spinning, and under controlled slow cooling in entrained droplets. However, the low Sr concentrations used and the interplay between Si twins and Sr solutes at the re-entrant edge make this observation very challenging.

With respect to nucleation, much more detailed research is required to elucidate the nucleation kinetics during modification. Crosley and Mondolfo [19] reported the poisoning effect of Na on P containing hypoeutectic Al–Si alloys. Na addition forces the nucleation of Si to larger undercoolings. This was attributed to the formation of Na_3P compounds which reduced the amount of the potent AlP phase. Furthermore, Crosley and Mondolfo [19] emphasized that nucleation has a major influence on the modification and AlP could be the nucleation site for eutectic Si due to its excellent match with Si [20–22]. Nogita et al. [20] found the evidence of centrally located AlP particles surrounded by a Si crystal in a hypoeutectic Al–Si alloy containing 40 ppm P. Similar results were also obtained by Ho and Cantor [17] in entrained droplet experiments. Flood and Hunt [23], using quench experiments, demonstrated that Na addition not only changed the growth morphology, but also prevented the nucleation ahead of the eutectic growth front. This produced higher undercoolings and therefore a finer eutectic lamellar spacing. Cho et al. [18] discussed the poisoning effect of Sr on the AlP compound. They proposed that the intermetallic compound Al_2Si_2Sr consumed the AlP, thus reducing the number of nucleated eutectic grains. Clearly, there is an important interaction between the modified elements (i.e. Na, Sr) and P.

If Na or Sr addition poisons the AlP, as proposed in the literature [18–23], an obvious question arises to the nature of the remaining nucleation sites to nucleate Si. Al_2O_3 and SiO_2 impurity particles [24], oxide bi-films [25] and the Al_4Sr phase [26] have been suggested to promote the nucleation of eutectic Si. In addition, the role of Fe-containing intermetallics as a nucleating agent for eutectic Si is also a particular matter of debate. Ho and Cantor [17,27] reported on Al–Si alloys prepared using high-purity materials containing only 50 ppm Fe and considered this amount of Fe as an insignificant impurity. However, Shankar et al. [28,29] proposed that small quantities of Fe (as small as 12 ppm) play an important role in the nucleation of eutectic Si. Khalifa et al. [30] and Yang et al. [31] also suggested that β-Al_5FeSi could be a nucleation site for eutectic Si in hypoeutectic Al–Si alloys. The main reason for the high number of potential types of the nucleation sites may be due to the fact that nucleation is notoriously difficult to study because of the inherent presence of impurities. It was Wang and Smith [32] who first suggested a novel entrained droplet technique to study heterogeneous nucleation. The potential of this technique was recognized and developed further by Cantor and co-workers [17,27,33,34], who employed rapid solidification to produce micrometer- to nanometer-size droplets, thereby improving the reproducibility of nucleation undercooling by up to 0.2 °C. Ho and Cantor [17] studied high-purity Al–Si alloys containing traces of P using the entrained droplet technique [32] and found that just 0.25–2 ppm P is sufficient to form AlP which could act as a nucleation site for eutectic Si, verifying the results of Crosley and Mondolfo [19] and