Scripta Materialia 110 (2016) 87–91

Contents lists available at ScienceDirect

Scripta Materialia

journal homepage: www.elsevier.com/locate/scriptamat

Pre-nucleation clusters mediated crystallization in Al–Si melts

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ARTICLE INFO

Article history:
Received 28 June 2015
Revised 5 August 2015
Accepted 9 August 2015
Available online 22 August 2015

Keywords:
Pre-nucleation clusters
Aluminum alloys
Solidification
Nucleation
Grain growth

ABSTRACT

Triggered by exogenous local ordering structures, pre-nucleation clusters appear in Al–Si melts and significantly alter the crystallization process. In absence of potent nucleating substrates (in high-purity melts), they delay silicon crystal nucleation, otherwise (in commercial-purity melts), they enhance nucleation and growth as well as change the growth mechanism of silicon. This makes the silicon grain size a competition result of nucleation and growth processes and some empirical rules of classical nucleation unreliable, e.g., easy nucleation no longer means grain-refined microstructures. These phenomena are further explained by characterizing the remains of these pre-nucleation clusters in solidified alloys.

Nucleation and growth are inevitable processes for crystals' formation from melts, and nucleation plays a dominant role in determining the size distribution of crystals in ingots. Therefore, a massive effort has been made to control the as-cast microstructures [1]. For more than one century [2], the classical nucleation theory has provided a well-accepted description of the formation process of a crystal within melts. However, all clusters are unstable relative to free atoms, before reaching a critical size, and the cluster concentration decreases exponentially with size [3]. Therefore, homogenous nucleation relying on inherent clustering tendency requires a high undercooling and is a rare phenomenon in experiments [4]. However, heterogeneous nucleation is a much easier pathway, because initiating on a nucleating substrate remarkably reduces the energy barrier and undercooling for nucleation. Usually, some impurities in commercial purity melts, e.g., AlP and γ-Al_2O_3 in Al–Si melts [5,6], can enhance heterogeneous nucleation and suppress homogenous nucleation.

Despite the prosperity of classical nucleation theory, the principles of classical nucleation theory have been called into question by an increasing number of reports about pre-nucleation clusters involved in nucleation and growth process in calcium carbonate [7], magnetite [8], proteins [9] and other materials [10]. Strong interactions among ions or molecules (monomers) play a key role on the formation of the pre-nucleation clusters [10]. Besides, solvent, e.g., H_2O, sometimes is also a crucial factor [11]. However, in metallic melts, both the strong interactions and the solvent effects lose to a large extent, and pre-nucleation clusters have seldom been found, except our recent reports on Al–Si melts [12–14]. In these reports, the added Al–10Si–2Fe master alloy decomposes and reserves only local ordering clusters which trigger the formation of pre-nucleation clusters, and this is totally different from most of inoculants acting by leaving intact crystalline particles and directly seeding a crystal owning to crystal structure matching [15]. To present, the reserved local ordering clusters are thought to resemble the structural units in α-Al_8Fe_2Si, and their persistence against complete dissolution within 2 h may be attributed to the inherent covalent bonds [13,16,17].

The participation of pre-nucleation clusters both changes nucleation and affects growth of protein crystals [9] and calcite crystals [18]. What will happen to the similar scenario occurring in melts in which the formation mechanism of pre-nucleation clusters is different from that in aqueous solutions? To answer this question, this study investigated the effects of pre-nucleation clusters on nucleation and growth in Al–Si melts.

Al–15 wt.% Si melts were prepared from commercial purity Al (99.7 wt.%) and Si (99.3 wt.%) or high purity Al (6 N) and Si (6 N) in a medium frequency induction furnace, respectively. Then the prepared melts were transferred to an electric resistance furnace for homogenization at 780 °C. Some melts were further inoculated with an Al–P master alloy (introducing 300 ppm P in the form of AlP into melts [6]) and an Al–10Si–2Fe master alloy (addition level: 1% of the melt weight) [12,13], respectively. With further 30 min holding, the melts were poured into a graphite mold (Φ27 mm * 30 mm). The cooling curves during solidification were separately measured using a K type thermocouple with a frequency of 10 Hz [12]. The commercial purity ingots were dissolved

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http://dx.doi.org/10.1016/j.scriptamat.2015.08.007
1359-6462/

in HCl solution, and silicon crystals were extracted by centrifugation. The morphologies of these extracted silicon crystals were characterized using a scanning electron microscope (SEM, Hitachi SU-70). Two special Al–10 wt.% Si alloys possessing only eutectic silicon grains (naturally always forming twins inside) and aluminum and not any primary silicon grains (not always forming twins insides) were prepared similarly, except solidifying in a copper mold (3 mm * 20 mm * 50 mm) after inoculation. These alloys can unambiguously demonstrate the effect of pre-nucleation clusters on crystal growth, e.g., extinguishing twins in eutectic silicon (discussed below), by excluding the reference from primary silicon. The above-mentioned alloys were characterized by a high-resolution transmission electron microscope (HRTEM, Tecnai G2 F30).

Fig. 1a shows the measured cooling curves of the commercial purity Al–15Si melts, where the first and secondary slope changes indicate the formation of primary silicon and eutectics, respectively. The melt inoculated with Al–Si–Fe shows the highest nucleation and growth temperatures for both primary and eutectic phases, indicating a reduction in undercooling for crystal nucleation and growth compared with that for the base alloy melt. However, in stark contrast to the cognition that AlP is a potent nucleating substrate for silicon phase, it remarkably increases the undercooling for primary silicon, though lowering the undercooling for eutectic reaction as expected. As shown in Fig. 1b–d, both Al–Si–Fe and AlP effectively increase the nucleation frequency of both primary and eutectic silicon particles. It is worth to note that primary silicon is simultaneously refined but eutectic silicon shows negligible changes in morphology for the AlP inoculated ingot. In the Al–Si–Fe inoculated ingot, the refinement of primary silicon is not very efficient, but the eutectic silicon becomes remarkably short (see Fig. 1 and S1). These anomalous changes for primary silicon relative to corresponding changes on cooling curves are entirely unexpected [1,19]. Therefore, though both Al–Si–Fe and AlP effectively enhance silicon phase nucleation in commercial purity Al–Si melts, the underlying mechanisms are significantly different.

Fig. 2 shows the typical microstructures and corresponding cooling curves of high purity Al–15Si alloys. The microstructure for high purity Al–15Si base alloy is different from those for the commercial purity alloys, with polyhedral primary silicon particles entirely replaced by dendritic ones. Further inoculation with Al–Si–Fe hardly affects this change, but inoculation with AlP regains a microstructure as that shown in Fig. 1. The dendritic silicon particles are caused by the deep undercooling that melts reach before nucleation commencement, as well as the fact that silicon can change from faceted to non-faceted growth over a relatively small range of undercooling due to an intermediate Jackson factor [20]. In the high purity base alloy melts, potent nucleating substrates are insufficient, which suppresses the heterogeneous nucleation of primary silicon and favors non-faceted growth of silicon at a high undercooling (at a temperature near the eutectic temperature). In contrast to the scenario in the commercial purity melt, inoculation with Al–Si–Fe here increases the nucleation undercooling of primary silicon. This is consistent with the corresponding microstructure and suggests that Al–Si–Fe inoculation cannot introduce nucleating substrates. While in the AlP inoculated melt, the introduced AlP acts as potent nucleating substrates for primary

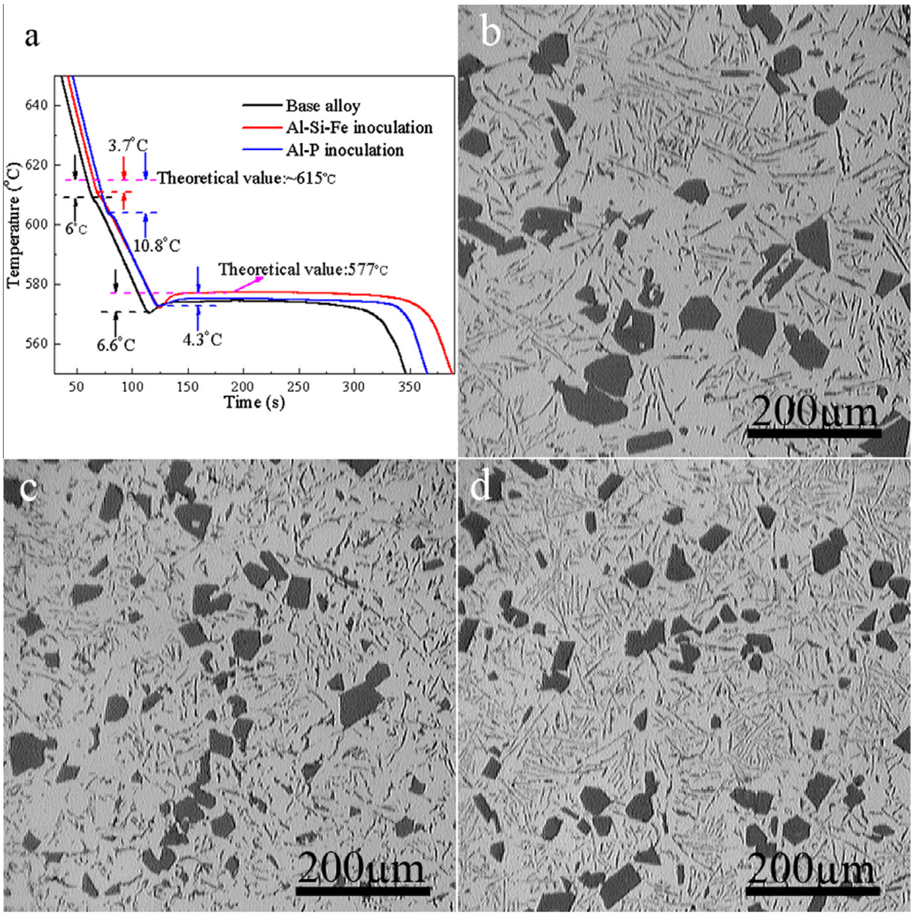

Fig. 1. (a) Cooling curves of commercial purity Al–15Si melts with different treatments, (b)–(d) typical microstructures of commercial purity Al–15Si alloys, (b) base alloy, (c) Al–Si–Fe inoculated alloy, (d) AlP inoculated alloy.