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Distribution of Fe-rich phases in eutectic grains of Sr-modified Al–10 wt.% Si–0.1 wt.% Fe casting alloy

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ABSTRACT

The addition of Sr to Al–Si-based alloys is known to modify the morphology of the eutectic Si phase and to influence the nucleation of eutectic grains. Understanding the distribution and the morphology of small constituent phases in eutectic grains such as Fe-rich intermetallic phases can further yield an insight into the cellular substructure of eutectic grains formed during solidification. The addition of 200 ppm Sr to an Al–10Si–0.1Fe alloy and its influence on the formation of Fe-rich phases was comprehensively studied by several microscopy techniques. Optical microscopy combined with scanning electron microscopy revealed the existence of two types of Fe-rich phases at cell boundaries of eutectic grains. The Fe-rich phases were identified as α-$Al_{14}Fe_3Si_2$ and δ-Al_4FeSi_2 by transmission electron microscopy. Both Fe-rich phases are located at distinct regions in the eutectic grain, namely in the transition region (region 2: α-phase) and the outer region (region 3: δ-phase) of the eutectic grain. The three-dimensional morphology of the eutectic Si phase and the Fe-rich phases at the eutectic cell boundaries was investigated by focused ion beam tomography. The Fe-rich α-phase was found to form concentrated networks with the 3D morphology of "sheets", whereas the Fe-rich δ-phases exist as thin platelets. The distribution of Fe-rich phases in the cellular substructure of eutectic grains are described on the basis of the evolution of the eutectic solidification front by a qualitative solidification model.

1. Introduction

The treatment of Al–Si alloy melts through addition of low amounts (100–200 ppm) of chemical modifiers such as Na [1,2], Sr [3,4], Ca, Ba and Eu [5] significantly influences the formation of the eutectic microstructure [6–8] and ultimately improves mechanical properties of Al–Si cast alloys [9,10]. The most striking feature of the eutectic modification is the transition of the Si morphology from coarse plates (unmodified eutectic) to fine fibres (modified eutectic) [11,12]. The plate-to-fibre transition is commonly attributed to the restriction of the anisotropic growth directions [13–15] of the eutectic Si phase, usually being the leading phase with respect to the eutectic Al matrix. The transition corresponds to a change from a typical irregular and ragged [16] (i.e. uncoupled) to a roughly spherical [17] (i.e. coupled) eutectic solidification front [2]. Both the eutectic Si phase (either grown as plates or fibres) and the eutectic Al matrix constitute the microstructure of the eutectic grains, i.e. the Al–Si eutectic that has grown from different nucleation sites in the melt. In Sr-modified Al–Si alloys it has also been observed that the eutectic Si phase can change its morphology from fibres to plates and back to fibres within an individual eutectic grain [18,19].

Comprehensive studies during the past decades have shed light not only on growth but also on nucleation of eutectic grains in modified Al–Si alloys [2,19–22]. For instance, it has been found that the addition of modifiers considerably decreases the nucleation frequency of eutectic grains [21,23] and thus leads to at least 10 times larger sizes of eutectic grains [19]. The restricted nucleation of eutectic grains [2] is attributed to a strong interaction of the modifiers with potential nucleation sites of eutectic Si phase [20,22,24,25].

Besides chemical modifiers, additional alloying and/or impurity elements also critically influence the formation of Al–Si eutectic. For instance, commercial Al–Si-based alloys always contain traces of Fe (0.1–0.2 wt.%) that cannot be removed from the melt in a cost efficient way. During growth, Fe segregates at the solidification front and forms complex intermetallic phases, either before (primary) or during final eutectic reactions (secondary). Several Fe-rich phases such as α-type with a so-called "Chinese script" morphology and β-/δ-type, which appear as needles/plates, respectively, have been identified in Al–Si casting alloys, strongly depending on the composition and cooling conditions of the alloy [26–28]. The formation of brittle Fe-rich plates can cause adverse

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effects on the castability and mechanical properties of an Al–Si alloy [26,29]. Fe-rich phases in Na- and Sr-modified Al–Si alloys have been extensively studied [30–36], but the influence of modifiers on the formation of Fe-rich phases in Al–Si alloys is still not completely understood [32,34,35]. For instance, the formation (type, size, distribution, 3D morphology) of small secondary Fe-rich phases in the eutectic grains with respect to the differences in nucleation and growth of eutectic grains in unmodified/modified alloys as mentioned above (Si plates/fibres, uncoupled/coupled solidification front, eutectic grain size) remains to be clarified.

In the present work, we investigated secondary Fe-rich phases in eutectic grains of a Sr-modified Al–10 wt.% Si–0.1 wt.% Fe using microscopy techniques over several orders of magnitude (mm–nm). The low amount of 0.1 wt.% Fe was chosen to avoid any formation of primary Fe-rich phases that would superimpose on the effect of the modifier on secondary Fe-rich phases. The distribution and location of secondary Fe-rich phases within eutectic grains was studied by optical microscopy and scanning electron microscopy (SEM). In order to understand the formation of the microstructure in three dimensions (3D), the use of tomographic techniques with sub-μm resolution has become indispensable [17,12,37,38]. Therefore, the 3D morphology of the Fe-rich phases and eutectic Si phase was visualised by site-specific focused ion beam (FIB) tomography. The crystal structure and the chemical composition of the Fe-rich phases were identified by transmission electron microscopy (TEM).

2. Experimental

2.1. Alloy preparation

Al–10Si (wt.%) alloys were manufactured by Rheinfelden Alloys GmbH (Rheinfelden, Germany). Approximately 50 kg of commercially pure Al and 5 kg of commercially pure Si (Si – 98.5; Fe – 0.35 in wt.%; 25 ppm P) were melted in an induction furnace at 760 °C. To remove any gases and oxides, the melt was degassed with a rotation impeller for 15 min using Ar and for further 5 min using Ar + Cl. For the eutectic modification, an Al–10Sr master alloy was added, after which the melt was held at 760 °C for 20 min to ensure complete dissolution. Chemical analysis was performed using an optical emission spectrometer. The chemical compositions of both the unmodified and the Sr-modified Al–10Si alloy are listed in Table 1.

The unmodified and the Sr-modified melts were cast into a cylindrical permanent mould (30 mm in diameter and 200 mm in height) where they solidified for about 40 s in the mould and, after removal of the mould, subsequently solidified in air. The cooling curve of the cylindrical mould was calculated with the simulation software WinCast® [39]. At the beginning of solidification (initial 40 s), the cooling rate of the cast alloys was estimated to be ~8 K/s in the centre of the mould.

2.2. Microstructural characterisation

The cast rods were metallographically prepared as described in a previous study [37]. All investigated specimens were extracted from the centres of the castings about 15 mm from the bottom of the ingot. Samples for optical microscopy were etched for 30 s at 20 °C in a mixture of 60 ml water, 10 g sodium hydroxide and 5 g potassium ferricyanide (modified Murakami's reagent) to reveal details of the cellular substructure of the eutectic grains [40,41].

For TEM analysis, the samples were prepared by mechanical polishing and Ar-ion beam thinning [37]. In order to find Fe-rich phases along electron-transparent regions, the TEM lamellae were first inspected in a SEM. TEM analysis of Fe-rich phases was then carried out using a Philips CM30 microscope operating at 300 kV and equipped with an EDAX Genesis energy dispersive X-ray spectroscopy (EDX) system. The chemical composition of the constituent phases was analysed by TEM-EDX with a minimum of five measurements for each Fe-rich phase. The crystal structures of the phases were determined by selected area electron diffraction (SAED).

A Zeiss 1540EsB CrossBeam® workstation was employed for a 3D characterisation of Fe-rich phases and the adjacent eutectic Si phase. Two distinct locations in a eutectic grain of the Sr-modified alloy were investigated by FIB tomography. FIB serial sectioning was performed using 30 keV Ga ions with an ion beam current of 200 and 1000 pA corresponding to a milling step in *z*-direction of 20 and 35 nm, respectively. A secondary electron (SE) In-lens detector was used for SEM imaging of 2D slices. Due to low acceleration voltage used for imaging (2 kV), the detected secondary electrons detected gave rise to a signal that is sensitive to the surface conductivity of the material [42] and yielded high-resolution images. Signal variations observed in the eutectic Al matrix are attributed to channelling contrast and thus correspond to slightly different crystallographic orientations of individual eutectic Al grains (polycrystalline Al matrix).

The software *ImageJ* with the plugin *stackreg* [43] was used to align the image stacks recursively. An observed gradual variation in signal intensity of each 2D slice was caused by shadowing which is due to the geometry of the FIB/SEM system [44]. 2D image filters were applied to eliminate such shadowing effects, to remove the background and to enhance the contrast between the eutectic phases. The 3D morphology of the eutectic Si phase and Fe-rich phases were visualised using the software *VGStudio MAX 2.1* after processing with a $5 \times 5 \times 5$ median filter to reduce noise. The application of global thresholds yields segments corresponding to the eutectic Si phase and Fe-rich phases. Volume fractions of both phases were determined in 3D.

3. Results

3.1. Microstructural features

The typical eutectic microstructure of the polished sample surface as it appears in the SEM is shown in Fig. 1a for the unmodified alloy and in Fig. 1b for the Sr-modified alloy. The unmodified Al–Si eutectic (Fig. 1a) consists of coarse Si plates (dark grey) embedded in the eutectic Al matrix. Fe-rich phases with so-called "Chinese script" morphology (white) are finely distributed throughout the eutectic grains. They are often located along Si plates, as marked by arrows in Fig. 1a, and they are typically <5 μm (as measured on sample surfaces).

The microstructure of the Sr-modified Al–Si eutectic is illustrated in Fig. 1b. It exhibits the typical fine fibrous morphology of the eutectic Si phase. In addition, the Al–Si eutectic shows a cellular substructure with Fe-rich phases of "Chinese script" morphology (in 2D) segregated at the eutectic cell boundaries (marked by arrows). Close to these cell boundaries the eutectic Si phase locally exhibits larger fibre spacings than does the fine Al–Si eutectic in the centre of the eutectic cells. Several Fe-rich phases are also observed to be adjacent to primary Al dendrites as indicated by the left arrows in Fig. 1b.

The Fe-rich phases and the cellular substructure of the eutectic grains in the Sr-modified alloy were optically enhanced by etching the sample surface and were subsequently imaged in the optical microscope by differential interference contrast (see Fig. 2). Many spherical features appear bright and these are surrounded by darker regions (see Fig. 2a). Beside the Al–Si eutectic, primary Al dendrites (white) are found to be uniformly distributed across the microstructure. The observed spherical features in the Al–Si eutectic can be attributed to the centres of eutectic grains as previously described by McDonald et al. [19].

The area marked by the rectangle in Fig. 2a has been investigated in more detail and is magnified in Fig. 2b. Three distinct

Table 1
Chemical composition of the unmodified and the Sr-modified Al–10Si–0.1Fe alloy with main elements Al, Si and Fe (in wt.%), and additional impurity levels (in ppm).

Alloy	Al	Si	Fe	Cu	Mn	Mg	Cr	Ti	Ni	Ga	V	P	Sr
	wt.%			ppm									
Unmodified	89.8	10.1	0.1 s	10	20	10	11	61	38	41	102	3	<1
Sr-modified	89.8	10.0	0.1	10	20	10	11	60	38	42	102	4	201