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Synchrotron radiation micro-beam analysis of the effect of strontium on primary silicon in Zn–27Al–3Si alloy

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ABSTRACT

The influence of Sr on two- and three-dimensional morphology of primary Si in Zn–27Al–3Si alloy was investigated. Distribution and crystalline structure of Sr were analyzed by using synchrotron radiation micro-beam. The results show that Sr could modify polygonal primary Si to nearly standard spherical shape. Modified primary Si enriched with Sr, which partially evolves as Al_2Si_2Sr, while partially presents as independent atoms. Sr promotes high-density paralleled and intersected {111}Si twins during the growth of primary Si. These observations thus provide experiment evidence to support the modification mechanisms based on impurity-induced twinning and poisoning of twin plane reentrant edge.

1. Introduction

Primary silicon phase possesses a useful combination of physical and mechanical properties, including high melting point (1414 °C), high elastic modulus (534 GPa), high hardness (HV 960) and outstanding wear resistance, thus widely used to enhance the wear resistance, heat resistance and dimensional stability of alloys [1,2]. However, the anisotropic and faceted growth mechanism determine that primary Si crystals have blocky morphology containing smooth plane, sharp corners and crystal defects [3,4], which impair mechanical properties of the alloys owing to inducing stress accumulation [5,6]. Therefore, to achieve desirable properties especially tensile properties, primary Si must be refined and modified. A review of open literature shows that modification of the primary silicon phase in hypereutectic alloys was carried out extensively [5,7–9], and phosphorus (P) is the commercial used modification for primary Si and could significantly refine primary Si particles by forming heterogeneous nucleus (AlP) for silicon crystal [7]. However, P has little influence on the morphology of primary Si and needs high melting temperature to get their best efficiency. Strontium (Sr) is a long acting and good remelting modifying element, and can change the eutectic Si from coarse needle-like morphology into fine fibrous-like structure and increase the strength and ductility of the final products [10,11]. Therefore, Sr is conventionally accepted as a commercial modifier for eutectic Si. However, until now there is still a disagreement about the influence of Sr on primary Si. Nogita et al. [12] and Yilimaz et al. [13] reported that primary Si with dendritic morphology was mainly formed in the hypereutectic Al–Si alloys treated with Sr. But Liu et al. found that the primary Si in Al–20 wt%Si alloys became smaller and rounder with the increasing Sr addition [8]. In this work, effects of Sr on the two- and three-dimension morphology of primary Si in Zn–27Al–3Si alloy, which possesses outstanding mechanical and wear resistance properties and has been analyzed by synchrotron microradiography in our previous work [14–16], were investigated to enrich the modification mechanisms of Si phase by Sr.

As directly related to the modification mechanisms, modifiers distribution in the modified alloys attracted much attention in recent years. Nogita et al. [17] utilized X-ray fluorescence to analyze Sr, Eu and Yb distribution in hypoeutectic Al–Si alloys and revealed Sr and Eu strongly segregates to the eutectic silicon. Recently, Timpel et al. [10] investigated Sr distribution in modified eutectic Si using atom probe tomography (APT) and revealed rod shaped Sr-containing intermetallic phase exists with Al rich locations inside

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the eutectic Si, owing to the limitation of APT, no exact crystalline structure information was obtained. However, until now few attempts to clarify the distribution and existence forms of the modifier element within primary Si phase have been reported. In this study, Sr-modified primary Si was investigated using high energy synchrotron micro-beam analysis technique, which perfectly combines micro X-ray fluorescence (μ-XRF) and micro X-Ray Diffraction (μ-XRD) analysis (the sensitivity of elemental and phase analysis up to ppb level and nanometer scale, respectively), additionally, the mechanisms of modification were also discussed based on the experimental observation.

2. Experimental procedures

Zn–27Al–3Si–xSr alloys (x = 0%, 0.06%, 0.1%, 0.2%) were prepared using commercial pure (99.7% purity) Al, pure Zn (99.995% purity), crystalline Si (99.3%), element Sr was added in the form of Al–10%Sr master alloy. The detail melting and casting process has been depicted in our previous work [15]. The samples for microstructure analysis were standardly grinded, polished and etched with Keller's reagent (1 ml HF + 1.5 ml HCl + 2.5 ml HNO_3 + 95 ml H_2O) and then investigated by a Zeiss supra 55 scanning electron microscope (SEM) operated at 15 kV. The samples were also deeply etched with a solution (15% HNO_3) to reveal the three-dimensional morphology of primary silicon. High resolution transmission electron microscope (HRTEM) analysis was carried out using a JEOL 2100 TEM (200 keV incident beam voltage) equipped with scanning TEM (STEM) detector.

The synchrotron radiation micro-beam analysis was carried out at beamline BL15U1 at Shanghai Synchrotron Radiation Facility (SSRF) equipped with an optical microscope, high-precision μ-XRF and μ-XRD. The selected beam energy was 18 keV with X-ray wavelength of 0.069 nm. To facilitate interesting field selection, slice samples cut from the casting ingots were grinded, and well-polished to a thickness of about 40 μm. The optical microscope and μ-XRF detector were used to identify the different phases and to obtain elemental map from the microstructure of the specimen, respectively. The μ-XRF elemental maps were obtained for an area of 35 × 40 pixel grids from 0.2%Sr modified sample, each pixel grid represented a $3 \times 2.5\ \mu m^2$ region. According to μ-XRF results, interesting micro-fields were selected and investigated using μ-XRD to identify the phase composition. The diffraction rings of the micro-fields were integrated and processed using FIT2D software to obtain the resultant spectrum (intensity versus 2θ), and subsequently analyzed by Jade 6.5 software.

3. Results and discussion

The morphology change of the primary Si particles as a function of Sr concentration was depicted in our previous work [15]. Fig. 1 shows the SEM micrographs of unmodified and 0.2%Sr-modified Zn–27Al–3Si alloys. It is obvious that there is a substantial difference between the morphology of primary Si crystal in the two alloys. In the unmodified alloy (Fig. 1a), primary Si crystals present in the form of irregular polygonal containing sharp angles, large smooth plane and pores, which would induce stress concentration and decrease the strength and ductility of the alloy. As shown in Fig. 1b, these polygonal primary Si crystals actually have triangle, plate-like, and octahedron three-dimensional morphology, confirming the faceted and anisotropic growth of them. It should be note that one or two natural growth twins frequently present on the edge of plate-like primary Si particles, conforming these particles grow by the natural “twin plane reentrant edge” (TPRE) mechanism, which postulates that the 141°external angle between {111} planes form self-perpetuating re-entrant edge that acts as favorable growth sites and enables Si crystal rapid growth along the <112> directions [10]. If TPRE is not disturbed during solidification, plate-like primary Si would eventually transform into triangle morphology [18] that shown Fig. 1b. As shown in Fig. 1c, with an addition of 0.2%Sr, the polygonal primary Si crystals are completely modified to the near-perfect sphere ones with an average roundness of 1.12 (roundness of perfect sphere is 1). Fig. 1d shows the three-dimensional morphology of the Sr-modified primary Si, which presents an actual spherical stereoscopic structure, indicating an isotropic growth manner. All this experimental observation provides strong evidence that Sr has a significant spheroidizing effect on the primary Si of Zn–27Al–3Si alloy.

μ-XRF and μ-XRD analysis for the spherical primary Si was carried out using high energy synchrotron radiation micro-beam source, the relevant results are shown in Fig. 2. The optical image shown in Fig. 2a was used to identify the spherical Si particles. Element distribution maps of Si and Sr obtained by using μ-XRF are shown in Fig. 2b and c, respectively, wherein different colors represent different fluorescence counts of the corresponding element in the location, and the purple to orange gradation of colors denote negligible to high concentration level. As can be seen, the distribution of Sr in the alloy is well consistent with that of Si, and Sr is of negligible concentration in the aluminium and zinc phases, providing experimental evidence that Sr is enriched in the spherical primary Si. It is notable that although enriched with elemental Sr, the distribution of Sr in the spherical silicon is not homogeneous, which is verified by the nonuniformly distributed colors. This is not similar to the results for Sr-modified Al-Si hypoeutectic alloy, wherein Sr segregated uniformly in the fiber-shape eutectic silicon [19]. An area of 7 × 7 pixel grids was investigated using μ-XRD according to the μ-XRF result, and “+” in Fig. 2c denotes the region (grid) where Sr-containing phase was detected. Fig. 2d shows a typical μ-XRD spectrums obtained from one of the grids marked with “+” in Fig. 2c, as can be seen, spherical primary Si is not single-phase material, apart from Si crystal, it contains a Sr-containing intermetallic phase, which was indexed as Al_2Si_2Sr with hexagonal close-packed (hcp) crystal structure (a = 4.187 nm, c = 7.427 nm). It is notable that all the grids marked by “+” in Fig. 2c, alike showed identical results as that depicted in Fig. 2d, except the relative peak intensity varies marginally among them, providing conclusive evidence that Al_2Si_2Sr forms during the solidification of spherical primary Si. Al_2Si_2Sr was reported to exist in the Sr-modified eutectic Si [20], but has scarcely discovered in primary Si in Zn–Al–Si alloys, especially in spherical Si. According to Manickaraj et al. Sr atoms are segregated to the regions enveloped by the tortuous eutectic Si, eutectic Al, and remaining eutectic liquid, wherein they nucleate as the Al_2Si_2Sr intermetallic phase along with the Al and Si [21]. However, our previous synchrotron radiation X-ray real-time imaging experiment revealed that, as the first-precipitated phase, spherical Si is surrounded only by liquid alloy and no such isolated regions formed during its main growth process [16]. Thus, this intermetallic phase identified in the present study is worth being further investigated with respect to its formation mechanism. It should be noted that the distribution of Al_2Si_2Sr is not uniform, this is similar to the situation in Sr-modified eutectic Si [21]. No XRD peaks related to Sr-containing phase can be detected in lots of locations in spherical Si, even in some locations with much higher Sr concentration (Fig. 2c), indicating apart from the formation of Al_2Si_2Sr, tremendous elemental Sr is also present as independent atoms (no crystal structure) in silicon lattice. This observation thus provides indirect support to the operation of the modification mechanisms that require the modifying atoms absorb onto the silicon growth steps, such as poisoning of TPRE mechanism and impurity-induced twinning (IIT) mechanism [22].

TEM micrographs of the modified primary Si are shown in Fig. 3.