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Grain boundary segregation of phosphorus and silicon in polycrystals and bicrystals of the Fe–2.6Si–0.055P alloy

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Abstract

Grain boundary segregation of phosphorus and silicon was investigated in polycrystals and bicrystals of an Fe–2.6Si–0.055P (wt.%) alloy after annealing at 600 or 800 °C by Auger electron spectroscopy. Lower segregation effects were revealed in bicrystals if compared with polycrystalline samples annealed at the same conditions. Intergranular fracture was found to be enhanced when the grain boundary concentration of phosphorus was increased.

Keywords: Iron-based alloy; Polycrystal; Bicrystal; Grain boundary segregation; Auger electron spectroscopy; Portion of intergranular fracture

1. Introduction

Technical polycrystalline materials are composed of grains (crystals) separated from each other by grain boundaries forming a three-dimensional network. Even if the volume fraction of this network is mostly negligible in comparison to the bulk, the structure and chemical composition of grain boundaries influence significantly mechanical, physical, and chemical properties, as well as the service reliability of materials [1–3]. Chemical changes at grain boundaries are mostly caused by segregation of surface-active elements in a sense of the total energy reduction [4]. The recent theoretical and experimental studies revealed that not all grain boundaries exhibit the same segregation behaviour. Special grain boundaries, characterised by compact structures (less different from the bulk) and lower excess energy show lower susceptibility to segregation than general grain boundaries with more complex structures and higher internal energies [5,6]. The structural-dependent variations in segregation behaviour of grain boundaries are represented by the segregation anisotropy [5].

The intention of this work is to compare segregation of phosphorus and silicon at different types of grain boundaries (special versus general) during annealing of the Fe–2.6Si–0.055P alloy at different temperatures.

2. Experimental

Both polycrystalline and bicrystalline samples were prepared from the Fe–2.6Si–0.055P alloy. In the case of polycrystals, the alloy was hot forged between 1100 and 800 °C, homogenised at 1050 °C for 1 h, and annealed at either 600 °C for 300 h or at 800 °C for 100 h. Average grain size of 350 μm was achieved for these samples. Bicrystals with the [1 0 0] twist boundary were prepared by melting the 10 mm long zone in the middle of the ⟨1 0 0⟩ single crystal with the length of 60 mm and the diameter of 13 mm, rotating one part relatively to the other in the molten zone by 45° and slow freezing. The composition heterogeneity arisen in the process of solidification was reduced by annealing of the bicrystal for 96 h at 1200 °C in argon [7]. Finally, the bicrystals were annealed at 800 °C for 100 h.

The composition of grain boundaries was studied by Auger electron spectroscopy (AES) using Microlab 310F VG-scientific

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facility equipped with a field emission gun. Notched cylindrical samples 5 mm diameter × 30 mm long were *in situ* impact fractured at about −120 °C and subsequently analysed in ultra high vacuum of 5×10^{-8} Pa. For analyses, a focussed electron beam (approximately 10 nm in diameter) of the kinetic energy of 10 keV and of the current of 10 nA was used. To determine the phosphorus and silicon grain boundary concentrations, 40–60 AES analyses per sample were done at several intergranular facets or bicrystal boundary. The Auger spectra were collected in the energy range 50–1650 eV. The composition of the grain boundary monolayer was determined from the derivative Auger peak-to-peak heights measured at the fracture surface according to the standardless method [8] taking into account the attenuation length of Auger electrons and the backscattering term.

Fracture surfaces of the samples were observed by JEOL JSM-650F scanning electron microscope (SEM); portions of intergranular fracture (PIF) were also determined.

3. Results

Typical fracture surfaces of polycrystalline samples and bicrystals are shown in Fig. 1. The former surface consists of many intergranular and transgranular facets corresponding to the positions of individual grains in the bulk (Fig. 1a). The preferential propagation of the transgranular crack along {1 0 0} planes and variations in the crystallographic orientation of individual grains resulted in embossed morphology of the surface. Details of intergranular and transgranular facets observed on fracture surfaces of the polycrystalline samples are apparent in Fig. 2a and b, respectively. The fracture surface of bicrystal is flat, except for two large steps near the surface periphery (Fig. 1b). The smoother areas were formed due to intergranular decohesion (Fig. 2c); the areas containing shallow bifurcated steps (so-called hackle structure) can be attributed to transgranular cleavage (Fig. 2d). AES analysis detected presence of iron, silicon and oxygen at the fracture surface. The traces of oxygen resulted from the surface contamination from the residual gas atmosphere in the apparatus. Besides these three elements, phosphorus was additionally detected on intergranular facets.

The PIF values and grain boundary concentrations of phosphorus and silicon (all determined experimentally) are given in Table 1. In Fig. 3, the phosphorus and silicon grain boundary concentrations are plotted in dependence on temperature. Besides the experimental values (points), the calculated equilibrium values (curves) are also presented. Theoretical values of the phosphorus and silicon grain boundary concentrations were

Table 1
Experimentally determined values of portion of intergranular fraction (PIF) and grain boundary concentrations of phosphorus (X_P^S) and silicon (X_{Si}^S)

Sample	Annealing conditions	PIF (%)	X_P^S (at.%)	X_{Si}^S (at.%)
Polycrystal	600 °C/300 h	3.8	13.6 ± 4.5	0.2 ± 0.1
Bicrystal	800 °C/100 h	17.1	8.9 ± 2.0	6.5 ± 0.7
Polycrystal	800 °C/100 h	23.8	15.9 ± 2.2	6.9 ± 0.9
Polycrystal	800 °C/100 h	25.0	18.2 ± 5.1	10.1 ± 1.2

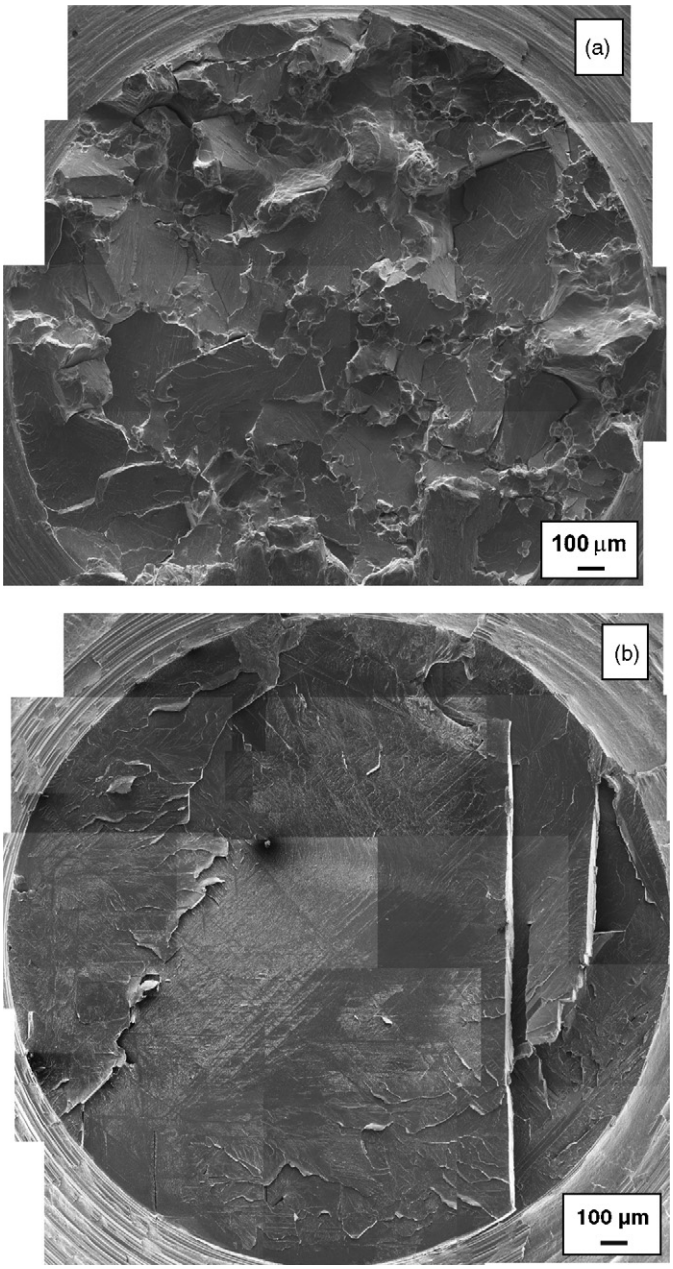

Fig. 1. Typical fracture surfaces: (a) polycrystalline sample; (b) bicrystal; both annealed at 800 °C for 100 h and impact fractured at about −120 °C. SEM, secondary electron image.

calculated according to equations [9,10]:

$$\frac{X_i^S}{1 - X_i^S - \sum_{j\neq i,m} X_j^S} = \frac{X_i^B}{1 - X_i^B - \sum_{j\neq i,m} X_j^B} \exp(-G_i/RT), \quad (1)$$

$$\Delta G_i = \Delta H_i^0 - T\Delta S_i^0 - 2\alpha_{im}(X_i^S - X_i^B) + \sum_{j\neq i,m} \alpha'_{ij}(X_j^S - X_j^B). \quad (2)$$