Effects of grain size and grain boundary segregation on fracture behaviour of a polycrystalline Fe-2.65Si-0.028P alloy

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Abstract

Grain boundary segregation of phosphorus and silicon was investigated in an Fe-2.65Si-0.028P alloy. Polycrystalline samples of various grain sizes and grain boundary compositions were fractured by impact in vacuum. Chemical compositions of grain boundaries were analysed by Auger electron spectroscopy. Scanning electron microscopy was used to observe fracture surfaces and to determine portions of intergranular fracture. The aim was to characterise the influence of the grain size and the grain boundary concentrations of phosphorus and silicon on the character of fracture surface. The portion of intergranular fracture was found to correlate positively with the grain size and the amount of grain boundary segregation.

Key words: iron alloys, interface segregation, intergranular brittleness, Auger electron spectroscopy, scanning electron microscopy

1. Introduction

Chemical composition of internal surfaces (grain boundaries) has decisive influence on mechanical, physical, and chemical properties of materials. Compositional changes at the grain boundaries result mostly from the segregation of surface-active elements, which is a process controlled by reduction of the system total energy [1, 2]. The role of the grain boundary segregation in influencing the properties of polycrystalline materials can be characterised in different ways. For instance, Seah [3, 4] has used a theoretical approach for prediction of links between the chemistry and the cohesion of grain boundaries. He calculated sublimation enthalpies of individual elements using the modified layer-by-layer model for ideal binary solid solution. Consequently, the values of sublimation enthalpy were exerted to predict the behaviour of two arbitrary elements in their binary systems: if the sublimation enthalpy of a solute element is lower than that of the solvent element, the solute element will reduce the grain boundary cohesion. In agreement with the theoretical predictions, many experimental studies were done to quantify the relationships between the concentration of segregated elements and the cohesion of grain boundaries. It is difficult to determine exact experimental values of the grain boundary cohesion [5, 6]. The semi-empirical transition temperature was therefore used to characterise the "embrittling" potency instead of the exact values of the cohesion energy [7–9]. Cianelli et al. [8] compared effects of antimony, tin, and phosphorus on the shift of the transition temperature in Ni-Cr low alloy steels. According to the above criterion, antimony and tin were found to be much stronger embrittling factors than phosphorus. Yu and McMahon Jr. [9] characterised the influence of the microstructure parameters (size of prior austenitic grains and hardness) on the shift of the transition temperature in a 2.25Cr-1Mo steel with two levels of phosphorus bulk concentration. The results can be summarised as follows: the transition temperature increases (i.e. the

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*Corresponding author: tel.: +421 033 55 11 033; fax: +421 033 55 11 758; e-mail address: jozef.janovec@stuba.sk steel becomes more brittle) with increasing the average size of prior austenitic grains and/or the hardness. This tendency was stronger in the steel with higher bulk phosphorus content.

Theoretical approaches are often combined with experimental measurements of grain boundary segregation. Guttmann [10] proposed the most general theory of equilibrium segregation in regular solid solution. In this theory based on generalised Langmuir-McLean isotherm [11] there are considered: the binary (Fowler type) and ternary interactions, the site-competition effect, the formation of stable clusters consisting of two atoms (quasimolecules), and the precipitation of two-dimensional compounds. Structural aspects of the grain boundary segregation (so-called segregation anisotropy) were characterised by Lejček and Hofmann [12] who investigated equilibrium segregation at individual grain boundaries in bicrystals of Fe-Si-P base systems. Watanabe [13] proposed the concept of grain boundary engineering reflecting the novel findings on segregation anisotropy. Last but not least, Grabke and co-workers [14, 15] contributed to precision of the segregation theories through exact experimental measurements, specification of grain boundary segregation in steels, and determination of many thermodynamic parameters.

The main intention of this work is to characterise the link between fracture behaviour on one hand and the average grain size and the grain boundary concentrations of phosphorus and silicon in the Fe-2.65Si-0.028P alloy on the other hand. The Fe-2.65Si-0.028P alloy was selected as a suitable experimental material for segregation studies, because of microstructure stability and absence of phase transformations during the post-solidification cooling [16–19].

2. Experimental procedures

Table 1. Chemical composition of the Fe-2.65Si-0.028P alloy. Mass contents of elements are given in %

Element	Si	P	C	N	Al	Fe
Content	2.650	0.028	0.009	0.004	0.004	bal.

The Fe-2.65Si-0.028P alloy (Table 1) was melted in a vacuum furnace and hot forged between 1100 and 800 ℃ under protective atmosphere. The samples placed into the evacuated silica capsules were then homogenised (to control both the average size and the dimensional homogeneity of grains) and annealed (to evoke compositional changes at the grain boundaries). The parameters of homogenisation and annealing are given in Table 2.

Grain boundary segregation was measured by Auger electron spectroscopy (AES) using a *Microlab 310F VG – scientific* facility equipped with a field emission gun. Notched cylindrical samples of dimensions ø 5 × 30 mm were *in-situ* impact fractured at about −120 ℃ 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. The Auger spectra were collected for the energy range of 50–1650 eV. 40–60 AES measurements were performed per condition at several intergranular (grain boundary) and transgranular (volume) facets.

Light microscopy (LM) was used to characterise the microstructure of the alloy and to determine the values of average grain size. The polished samples were etched in 2% nital. Fracture surfaces of the samples fractured by impact in *Microlab* were observed in *JEOL JSM – 650F* scanning electron microscope (SEM). The values of the portion of intergranular fracture (*PIF*) were simultaneously determined.

3. Results

Typical microstructure of the alloy is illustrated in Fig. 1. It is formed by regular ferrite grains free of

Table 2. Data characterising experimental conditions of the Fe-2.65Si-0.028P alloy: designation of particular conditions, parameters of homogenisation, parameters of annealing, average grain size, portion of intergranular fracture – *PIF*, experimental values of grain boundary concentrations of phosphorus and silicon

Parameter	Condition				
	A	B	C	D	E
Homogenisation (℃/h)	1050/0.25	1050/1	1050/8	1050/8	1050/8
Annealing (℃/h)	800/100	800/100	800/100	600/300	450/300
Grain size (μm)	105 ± 14	230 ± 38	484 ± 70	521 ± 64	496 ± 72
PIF (%)	3.5	13.9	61.2	12.2	8.5
Grain boundary concentration of P (at.%)	7.5 ± 2.2	8.8 ± 0.6	10.1 ± 2.1	8.3 ± 2.7	3.0 ± 0.1
Grain boundary concentration of Si (at.%)	4.3 ± 0.9	0.15 ± 0.02	15.5 ± 2.2	1.7 ± 0.2	0.1 ± 0.01

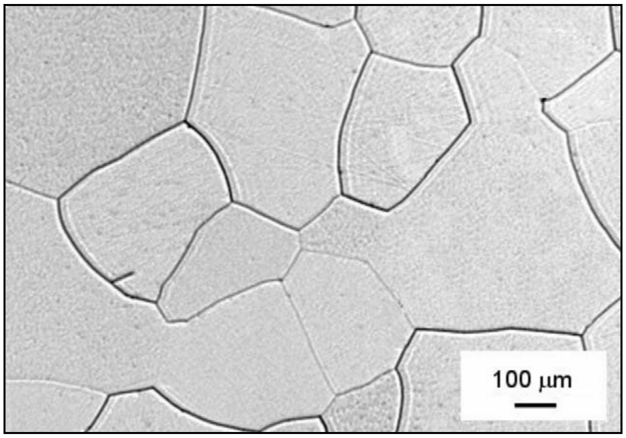

Fig. 1. Micrograph showing typical microstructure of the alloy containing regular ferrite grains free of precipitates. Condition E, etched in 2% nital.

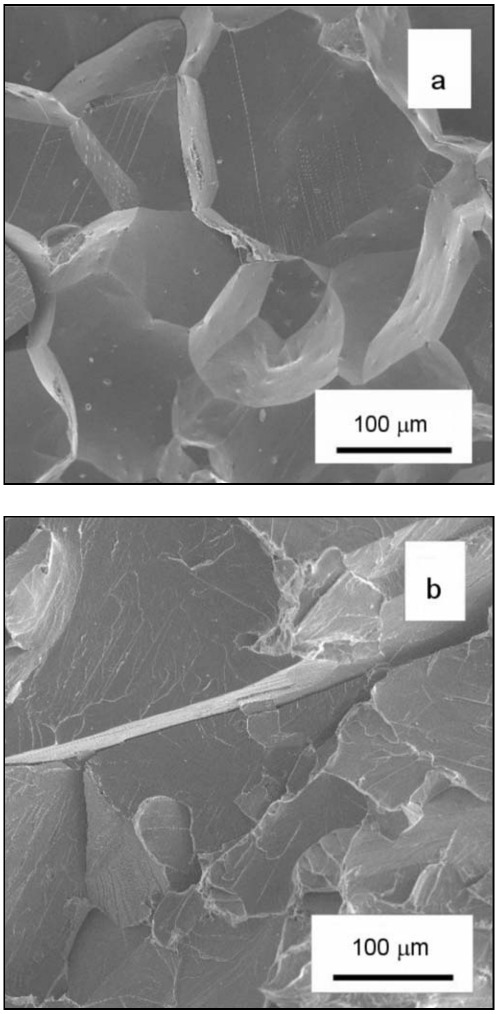

Fig. 2. SEM images showing typical fracture surfaces of samples fractured by impact of (a) intergranular facets (condition C), (b) transgranular facets (condition D).

precipitates. The values of the average grain size vary between 105 and 521 μm in dependence on the homogenisation parameters (Table 2). Fracture surfaces of all samples consist of intergranular and transgranular facets (Fig. 2). The smooth areas correspond to intergranular facets (Fig. 2a) and the areas containing shallow bifurcated steps (so-called hackle structure) are attributed to transgranular cleavage (Fig. 2b). The *PIF* values for all conditions are given in Table 2.

Typical Auger spectra corresponding to transgranular and intergranular facets are illustrated in Figs. 3a and 3b, respectively. The analysed localities are marked by white stars on illustration fractographs in the lower right corners of spectra. On transgranular facets, iron, silicon, and oxygen (due to the contamination) were identified. Besides the above elements, phosphorus was also detected on intergranular facets.

The transformation of the experimentally determined peak-to-peak heights of Si (96 eV), P (123 eV), and Fe (705 eV) was performed according to the procedure [16]:

$$X_i^{\mathrm{S}} = N_i^{\mathrm{S}} \left(\sum_j N_j^{\mathrm{S}} \right)^{-1}, \tag{1}$$

with

$$N_i^{\mathrm{S}} = \frac{N_i^* \lambda^{\mathrm{st}}(E_i, \phi) R^{\mathrm{st}}(E_i, \alpha)}{S_i \lambda(E_i, \phi) R(E_i, \alpha)} \cdot \cdot [2K_i - K_i(d) \cdot (1 + \mathrm{e}^{\frac{-d}{\lambda(E_i, \phi)}})] \cdot [1 - \mathrm{e}^{\frac{-d}{\lambda(E_i, \phi)}}]^{-1}. \tag{2}$$

In Eqs. (1) and (2), K_i and S_i are the derivative Auger peak-to-peak heights measured at the grain boundary and the relative Auger sensitivity, respectively; N_i^* is the atomic density of pure element i, d is the thickness of the segregated layer, and $K_i(d)$ is the derivative Auger peak-to-peak height measured in volume. The attenuation length of Auger electrons, $\lambda(E_i, \phi)$, can be written:

$$\lambda(E_i, \phi) = \lambda(E_i) \cdot \cos\phi, \tag{3}$$

where E_i is the energy of the Auger electron emitted from the fracture surface under the angle ϕ related to the surface normal. The backscattering term, $R(E_i, \alpha)$, is defined as

$$R(E_i, \alpha) = 1 + r(E_i, \alpha), \tag{4}$$

where $r(E_i, \alpha)$ depends on the character of the matrix, E_i, and the angle α between the primary electron beam and surface normal. The superscript st refers to the standard state. It was supposed that the segregated species are equally distributed between both

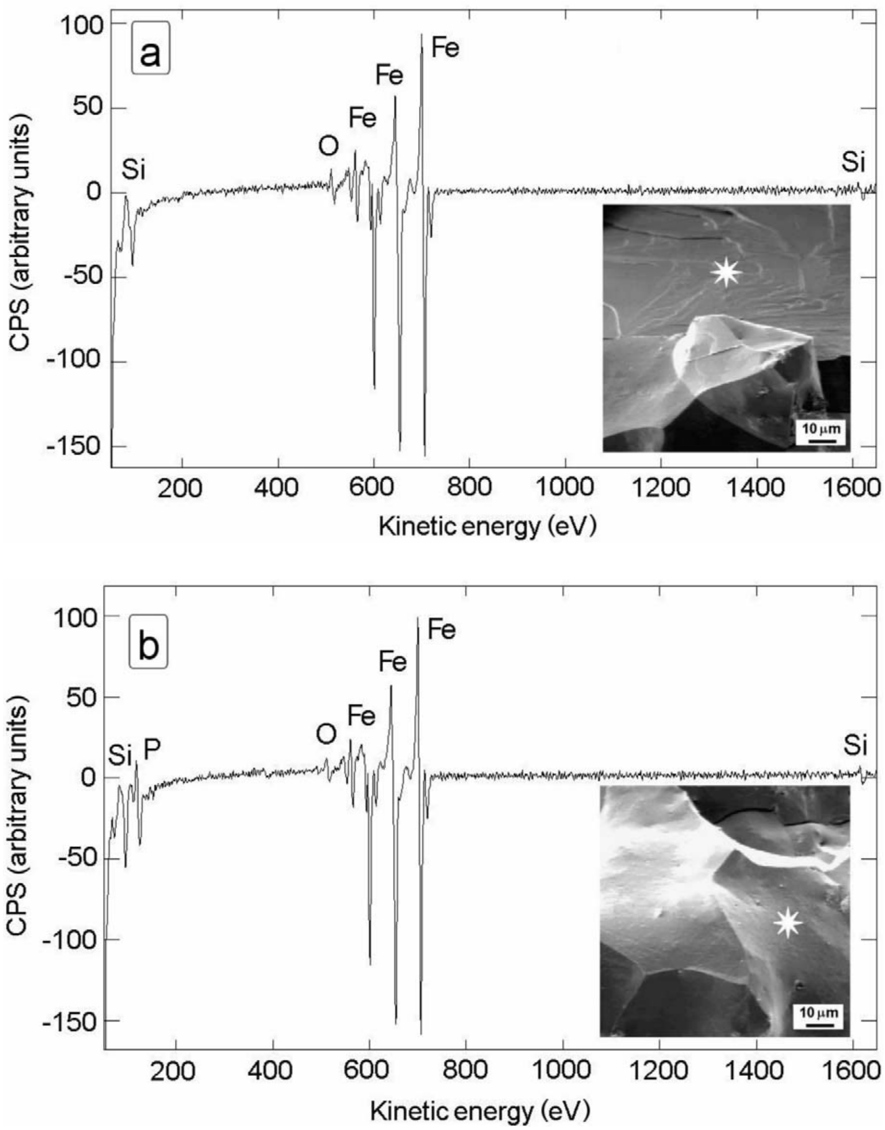

Fig. 3. Typical Auger spectra corresponding to (a) transgranular facet, (b) intergranular facet. The analysed localities are marked by white stars on fractographs localised in the lower right corner of the spectra.

parts of the intergranularly fractured sample and that the segregation effects are localised in one atomic layer parallel to the grain boundary.

4. Discussion

The present experiments were planned with the intention to obtain reliable data for considering the links between the grain boundary concentrations of segregated elements and the grain size on one hand, and *PIF* on the other hand. In the following sections, individual items are discussed in more detail.

4.1. Grain boundary composition

According to the segregation theory, equilibrium concentration of a solute at the grain boundaries in a binary system decreases with increasing temperature. In a multicomponent system with site competition or mutual repulsive interaction of segregating elements, the temperature dependence of chemical composition is more complex. Usually, this dependence for the more surface-active element follows similar tendency as in a binary alloy. However, the less surface-active element is depleted from the grain boundaries at low temperatures. At moderate temperatures, its concentration increases accordingly to reduced concentration of the strongly segregating element. Eventually, it decreases with increasing temperature at high temperatures to approach approximately the bulk composition [20]. In the case of the pre-equilibrium states, the kinetics of interface segregation in an actual state is decisive. When taking into account all these effects, the chemical composition of the grain boundaries in a large range of concentrations can be obtained. These values may differ substantially from those expected from the theory of equilibrium segregation. In this work, substantially different chemical composition was established via heat treatment in different samples to enable an assessment of the effect of segregation on the fracture behaviour. Due to the above-described complexity of the process, the experimental values of the grain boundary concentrations of both segregating elements apparently increase with increasing temperature. It suggests that equilibrium was not achieved in the experiment.

The grain boundary concentrations of silicon exhibit "qualitative" differences. After annealing at 450 and 600 ℃ (conditions E and D, Table 2), they were found to be lower than the bulk silicon content. The silicon depletion at the grain boundaries was also observed for the fine-grained samples annealed at 800 ℃ (conditions A and B). It can be caused by a strong repulsion between phosphorus and silicon atoms ($\alpha'_{\mathrm{PSi}} = 92.0\ \mathrm{kJ \cdot mol^{-1}}$ [21], where α'_{PSi} is the ternary P-Si interaction coefficient) and a higher segregation tendency of phosphorus ($\Delta H^{\circ}_{\mathrm{P}} = -22.9\ \mathrm{kJ \cdot mol^{-1}}$ [22]) in comparison to silicon ($\Delta H^{\circ}_{\mathrm{Si}} = -17.0\ \mathrm{kJ \cdot mol^{-1}}$ [23]). On the other hand, the grain boundary concentration of silicon annealed under condition C is about three times higher than the bulk silicon content (Table 2). The silicon depletion was also reported previously for an Fe-6at.%Si-P-S alloy annealed at 600 ℃ [24–26].

4.2. Grain size

According to the theory of equilibrium segregation [10, 11] and the concept of grain boundary engineering [13], there are three main factors influencing the equilibrium grain boundary concentration of segregated elements: annealing temperature, bulk chemical composition of the alloy, and type of the grain boundary (general, vicinal, special). Microstructural factors including grain size may play an important role in affecting segregation kinetics, but they cannot influence the equilibrium state [25], e.g. the equilibrium interfacial concentration of segregated elements. Only in the case of nanosized grains with enormously enhanced volume of the grain boundaries and/or very low bulk concentration of the solute [27], the interfacial segregation can be significantly reduced due to the substantial exhaustion of the bulk from the solute. When the polycrystalline samples varying in grain size exhibit the different grain boundary concentrations of an element after annealing at the same conditions (e.g. phosphorus after annealing at 800 ℃ for 100 h, Fig. 4), it is an anomaly which can be explained in two ways: (1) equilibrium was not established and the microstructure factors (e.g. grain size) influence the phosphorus segregation; (2) equilibrium was achieved and differences in the phosphorus grain boundary concentration result from the segregation anisotropy. It is hard to find any dependence of grain boundary segregation on grain size from the present results. It might seem that grain boundary concentration of phosphorus slightly increases with increasing grain size (Fig. 4). However, the data on silicon grain boundary concentration are heavily scattered. Taking this scatter into account together with the error of measured data on phosphorus segregation, we have to conclude that solute segregation is not affected by the grain size. This conclusion is fully compatible with the calculations of Ishida [27].

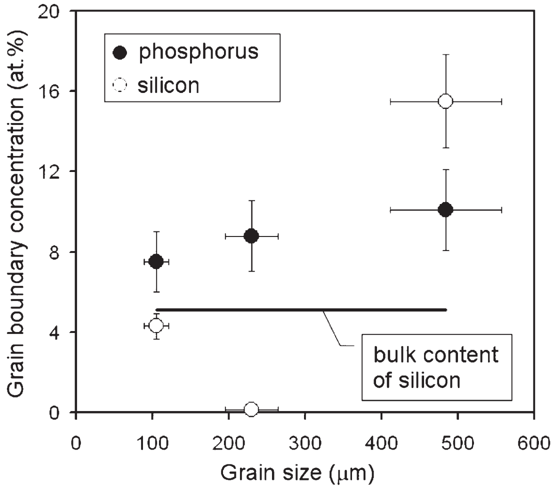

Fig. 4. Dependence of phosphorus and silicon grain boundary concentrations on grain size. The bulk silicon content (5.13 at.%) is also illustrated. The samples were annealed at 800 ℃ for 100 h (conditions A, B, C).

4.3. Links between *PIF*, grain size and grain boundary segregation

Despite of a limited extent of the experiment, there are clear trends of increasing *PIF* with increasing both the grain boundary segregation and the grain size (Figs. 5 and 6). Previously reported positive correlations between the phosphorus grain boundary concentration and *PIF* (transition temperature) [7–9, 28] were also confirmed in this work (see solid circles and the corresponding trend line in Fig. 5). This finding is in agreement with the theoretical predictions of Seah [3, 4], because phosphorus possessing lower value of the sublimation enthalpy than iron should contribute to the grain boundary embrittlement of Fe-base materials. The clear proof of this trend is somehow complicated by presence of silicon, which is also the embrittling element in iron [1]. In the present experiment, however, the points related to low grain boundary concentrations of silicon are irregularly distributed in the plot (see empty circles in Fig. 5) that makes impossible to do a more exact characterisation. On the

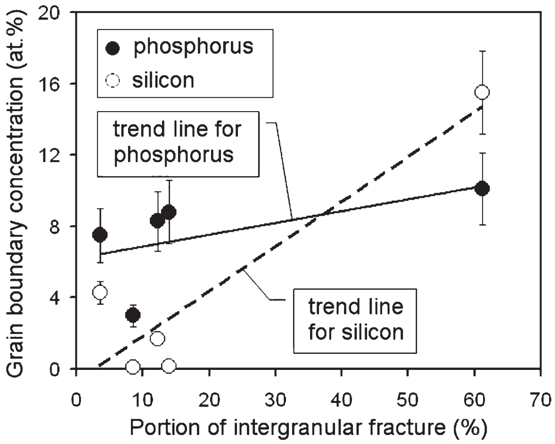

Fig. 5. Dependence of phosphorus (solid trend line) and silicon (dashed trend line) grain boundary concentrations on *PIF*.

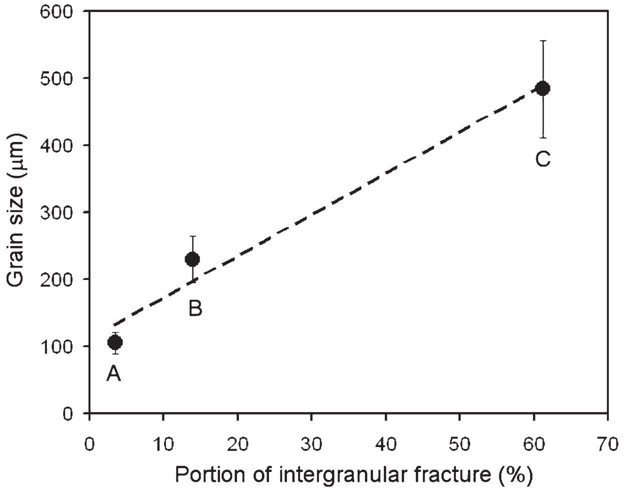

Fig. 6. Dependence of the portion of intergranular fraction (*PIF*) on grain size of the samples annealed at 800 ℃ for 100 h (conditions A, B, C).

other hand, the comparison of the *PIF* values for the high grain boundary concentrations with those corresponding to the average value in the low-silicon region supports the idea of increasing embrittlement with increasing content of silicon. However – as was mentioned above – the situation is complicated due to the presence of two embrittling elements in the system and their possibly different effects on the embrittlement of the material.

The increase of *PIF* values with increasing grain size apparent from Fig. 6 can be understood in terms of both the crack branching process and the grain-boundary dislocation pile-ups. The propagation of a brittle crack is controlled by a balance between the crack driving force and the crack growth resistance. In metallic materials, the transgranular resistance is comparable with that of grain boundaries (for [001] cleavage in bcc metals might be even lower). In our case, however, the resistance of intergranular facets becomes much lower due to segregation of impurities. By assuming equal trans- and intergranular crack driving forces, it means that the crack would grow rather intergranularly. When the crack front approaches a triple point, however, branching (forking) of the crack front can take place. This process causes a significant decrease in the crack driving force (anti-shielding). Moreover, the crack growth resistance becomes much higher since new fracture surfaces are to be created in both branches [5, 29]. Consequently, the crack front might prefer transgranular propagation. As a result, the probability of finding transgranular facets must be higher in fine-grained materials containing higher triple-point concentrations. On the other hand, stress concentrations ahead of dislocation pile-ups produce a selective anti-shielding effect along grain boundaries in the process zone. These stresses are higher in larger grains due to longer pile-ups so that much easier intergranular crack propagation can be expected in coarser microstructures. Thus, both discussed micromechanisms lead to a higher percentage of intergranular facets in coarse-grained materials.

5. Conclusions

The study of the grain boundary segregation in the polycrystalline Fe-2.65Si-0.028P alloy and the tendency to embrittlement in differently thermally treated samples revealed the following facts:

1. The combined transgranular/intergranular morphology was observed on impact fractured surfaces of the investigated samples.

2. Iron, silicon, and oxygen (due to the contamination) were identified on transgranular facets. Besides the above elements, phosphorus was also detected on intergranular facets.

3. An apparent increase of grain boundary concentration of phosphorus with increasing temperature suggests that equilibrium was not achieved in the experiment.

4. The depletion of the grain boundaries by silicon was observed under all conditions except for the samples annealed at 800 ℃ for 100 h with the highest grain size. It is the consequence of the pre-equilibrium stages of segregation.

5. Grain boundary concentrations of phosphorus and silicon were found to be independent on the grain size of polycrystalline samples annealed at 800 ℃ for 100 h.

6. A positive correlation was found between the portion of intergranular fracture and the amount of grain boundary segregation.

7. It was confirmed a positive correlation between the portion of intergranular fracture and the grain size for the samples annealed at 800 ℃ for 100 h.

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