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► To cite this version:  
<10.1051/jphyscol:1990127>. <jpa-00230285>

HAL Id: jpa-00230285  
https://hal.archives-ouvertes.fr/jpa-00230285  
Submitted on 1 Jan 1990

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SEGREGATION AT SPECIAL GRAIN BOUNDARIES IN Fe-Si ALLOY BICRYSTALS

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Résumé - La ségrégation du silicium était étudiée avec la spectrométrie Auger aux joints de grains symétriques Σ=3, {112} et Σ=5, {013} dans des échantillons bicristallins d'un alliage Fe-12.9 at% Si qu'étaient équilibrés dans la région 773 - 1173 K. L'enthalpie de ségrégation, ΔH = -8.1 ± 0.5 kJ/mol, et l'entropie, ΔS = -6.9 ± 0.4 J/(mol K) étaient déterminées pour le joint de grain {013} aux températures 973 - 1173 K. Pour le joint de grain {112}, les valeurs correspondantes ΔH = -4 ± 3 kJ/mol et ΔS = -4 ± 3 J/(mol K) étaient obtenues. Aux deux joints, une diminution de la ségrégation du Si était observé à 773 K. De plus une distribution à profondeur élongée de l'enrichissement du Si était observée malgré les hautes températures et malgré les longs temps du chauffage. Ces deux phénomènes sont probablement causés par des effets de l'ordre dans cet alliage. L'addition du phosphore à cet alliage est la cause d'une diminution du content du Si au joint de grain {112}.

Abstract - The segregation of silicon to the Σ=3, {112} and Σ=5, {013} symmetrical grain boundaries was studied in well-defined bicrystals of an Fe-12.9 at% Si alloy annealed in the range 773 - 1173 K using Auger electron spectroscopy. The segregation enthalpy, ΔH = -8.1 ± 0.5 kJ/mol, and entropy, ΔS = -6.9 ± 0.4 J/(mol K), were determined for the {013} grain boundary in the temperature range 973 - 1173 K. For the {112} boundary the corresponding values ΔH = -4 ± 3 kJ/mol and ΔS = -4 ± 3 J/(mol K) were obtained. At both these boundaries, a decrease of the segregation of Si was observed at 773 K. In addition, a wide in-depth distribution of silicon enrichment was observed away from the boundaries in spite of relatively high annealing temperatures and times. Both effects are probably due to the ordering effects in this alloy. Addition of phosphorus to this alloy caused a depletion of silicon at the {112} grain boundary.

1 - INTRODUCTION

Strong interest in understanding the effects of grain boundaries on material properties is still growing and some attempts have been made to modify these properties by controlling the character and arrangement of the grain boundaries. Several years ago a concept of "Grain Boundary Design" was suggested /1/, based on an idea of the selection of certain types and positions of grain boundaries in polycrystalline materials to obtain the best properties for the required purpose. In general, special grain boundaries seem to play an important role in this concept because their physical and mechanical properties differ substantially from those of random boundaries.

Some attempts have been made to study the segregation behaviour at different grain boundaries in Fe-Si alloys. Watanabe et al. found some differences in the values of relative peak heights of silicon at high-angle tilt grain boundaries of an Fe-3 mass% Si alloy /2/. Qualitatively, a different behaviour of silicon was reported at the Σ=3, {112} and the Σ=5, {013} grain boundaries (segregation and depletion, respectively) in a similar alloy containing traces of phosphorus /3/. However, both these studies were performed on samples in a nonequilibrium state. In the present work, the equilibrium segregation of Si is determined at the {112} and {013} symmetrical boundaries in standard annealed bicrystals of an Fe-12.9 at% Si alloy. The effect of phosphorus doping on the segregation behaviour of silicon is also reported.

2 - EXPERIMENTAL

For the study of grain boundary chemistry, bicrystalline samples of an Fe-12.9 at% Si alloy were used having {112} (Σ=3, 70.5° [110]) and {013} (Σ=5, 37° [100]) symmetrical grain boundaries. The bulk bicrystals of the alloy containing 25 atppm P, 87 atppm C and 23 atppm O were grown by the floating-zone technique /4/. From these bicrystals the samples (diameter of 3.1 mm, length of 12 mm) were cut perpendicular to the grain boundary and notched there. Prepared samples were annealed at temperatures in the range 773 - 1173 K for different times under vacuum and then water quenched. The annealing temperatures and times are presented in Table I. For a comparative experiment, one sample with a {112} grain boundary was doped with phosphorus (0.54 at%), homogenized 30 days at 1423 K and then similarly

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treated as the other samples at 873 K (96 h).

Table I: Annealing conditions of bicrystalline samples.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>1173</th>
<th>1073</th>
<th>973</th>
<th>873</th>
<th>773</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time, t (h)</td>
<td>24</td>
<td>24</td>
<td>48</td>
<td>96</td>
<td>120</td>
</tr>
<tr>
<td>r(DSi) (μm)</td>
<td>89</td>
<td>34</td>
<td>15</td>
<td>6</td>
<td>1</td>
</tr>
</tbody>
</table>

The annealed samples were fractured by impact bending in-situ after cooling with liquid nitrogen in an ultra-high-vacuum chamber (5 x 10^-8 Pa) of a Scanning Auger Microprobe (PHI 600 Multiprobe), and the fracture surfaces were analyzed immediately after fracture. AES was performed at a primary beam voltage of 10 kV, an electron beam current of 350 nA and a beam diameter of 1 μm. To obtain information about the depth distribution of the elements, Ar+ ion sputtering was used with an ion beam of 3 keV energy, rastered over an area of about 3 x 3 mm². The analyzed spot was about 7 x 7 μm² and the sputtering rate was 0.27 nm/min for Ta2O5, as calibrated by means of reference samples of known thickness.

3 - RESULTS

From the derivative Auger spectra the peak-to-peak heights of individual elements were recorded and normalized to the Fe 703 eV peak-to-peak heights. The temperature dependencies of these relative peak-to-peak heights, r(i), of Si, C and O for both types of the grain boundaries are shown in Fig. 1. Only Si segregation is observed at both grain boundaries in the phosphorus-free alloy. Carbon appears at high temperatures at the {013} grain boundary only, whereas its content at the {112} boundary was not higher than that found at an transcristalline (TK) fracture surface. The values of r(O) found at both grain boundaries were comparable with those measured at the transcristalline fracture surface. For each element, the value of r(i) for a sample with phosphorus doping is also displayed.

The depth distribution of elements involved has shown that the r(Si) values increase during sputtering, pass through a maximum and then decrease slowly to a saturation value (Fig. 2). These changes occur in a relatively thick subboundary layer (about 10 atomic layers). A long-range increase of r(Fe 47 eV) also exists. On the other hand, r(O) decreases from the beginning of sputtering and reaches a constant level after

**Fig. 1** - Temperature dependencies of the Auger peak-to-peak height (APPH) ratios of element i to that of Fe (703 eV), r(i), (i = Si (92 eV), O (510 eV) and C (273 eV)), as measured at fracture surfaces of {013} grain boundaries (c), and {112} grain boundaries (Δ). ▲ ... values of r(i) measured at the {112} grain boundary in the sample doped with 0.54 at% P. Values of TK(i) denote the level of a particular element found at a transcristalline fracture surface. The dashed-dotted line represents the most probable course of temperature dependence of r(Si).
about 2 min. of sputtering. A "depletion" of Si was observed also at the transcrystalline fracture surface (one atomic layer) which is connected with the oxygen contamination of the surface. The long-range changes in the silicon depth profiles seem to indicate a nonequilibrium segregation state. However, as shown in Fig. 3, prolonged annealing times (Table I) did not reveal changes of r(Si) even after annealing of the samples at 773 K for 2 months. The character of the depth profiles remains also similar to those shown in Fig. 2. In bicrystals of an Fe-4 at% Si alloy, the same times were found to be sufficient to reach equilibrium segregation /6/.

In the sample doped with phosphorus, segregation of phosphorus and depletion of silicon was observed at 873 K. In the depth distribution of elements, not only r(Si) varies over a distance of several monolayers but also r(P) decreases constantly to deeper layers. Neither an application of another ion gun nor an increase of the sputtering rate by a factor 10 were sufficient for reaching a saturation value of the phosphorus peak-to-peak height.

From the measured data, the atomic concentrations of silicon were calculated by means of the method described in /7/ assuming the same distribution of segregating element onto both boundary halves during fracture. The temperature dependence of the silicon concentration is shown in Fig. 4. Applying the usual McLean equation for equilibrium segregation in a binary system /8/, the segregation enthalpies and entropies of Si were determined as ΔH = -8.1 ± 0.5 kJ/mol and ΔS = -6.9 ± 0.4 J/(mol K) for the {013} grain boundary (973 K - 1173 K) and ΔH = -4 ± 3 kJ/mol and ΔS = -4 ± 3 J/(mol K) for the {112} one (873 K - 1173 K). The full drawn lines in Fig. 4 correspond to these values.

4 - DISCUSSION

As it is seen from Figs. 1 and 4, the amount of silicon increases with decreasing temperature for both grain boundaries, passes through a maximum near 900 K and then decreases again. As expected, the segregation behaviour of silicon at higher temperatures can be characterized by small negative values of the segregation enthalpy. The decrease of Si concentration at 773 K seems to contradict this result. At first instance it may be argued that the annealing time (7 days) was insufficient for obtaining equilibrium segregation of silicon, and a similar conclusion would apply for the sputtering depth profile. However, a prolonged annealing for 2 months led to the same value of the r(Si) (Fig. 3) and to a similar depth distribution of Si (Fig. 2). In addition, experiments with grain boundary segregation of Si and P in an Fe-4 at% Si alloy revealed the equilibrium segregation of both elements in the temperature range of 773 - 1173 K for the same annealing times as used here /6/. No dependence of the thickness of the segregation layer was found either on the annealing temperature or on the diffusion length or - as mentioned above - on the annealing time. It seems that this behaviour is intrinsic to this material due to the ordering of the alloy. Under the applied annealing conditions, the Fe-12.9 at% Si alloy is ordered into the α2 phase (B2 structure) at 1073 K and 973 K, into the α1 phase (DO3 structure) at 773 K and into a mixture of α1 + α2 phases at 873 K. At 1173 K, the alloy is a disordered α solid-solution /9,10/. Previously, the "multilayer" surface segregation was observed, e.g. in Au-Cu (11), Ni-Pt (12) and Fe-Cr (13) binary alloys, where ordering takes place. Sanchez and Morán-López theoretically analyzed the chemical composition of surface and subsurface layers of a Cu-Pt alloy and deduced the influence of ordering on the segregation behaviour /14/. Because of resemblance of surfaces and
grain boundaries as planar defects of a crystal lattice, a behaviour similar to surfaces should be expected also for grain boundaries. The decrease of silicon concentration at 773 K observed at both the \{013\} and the \{112\} symmetrical grain boundaries (Fig. 1) can therefore also be explained by ordering of the alloy: The more ordered $\alpha_1$ phase at 773 K (as compared with the mixture of $\alpha_1 + \alpha_2$ phases at 873 K) should tend to stabilize perfectly ordered boundary layers and, therefore, to suppress segregation.

A "depletion" of silicon found at the intercrystalline fracture surfaces (Fig. 2) can be explained by slow continuous contamination of the exposed surface with oxygen during measurement of segregation at individual points. The same effect was observed at the transcrystalline fracture surface. To reach a constant depth distribution of silicon in the case of the transcrystalline fracture surface, the oxygen coverage at this fracture surface was estimated to be 0.55 monolayer at the starting time of sputtering 29 minutes, after exposing an internal surface to the residual gas of the vacuum chamber.

The content of oxygen at fracture surfaces along both types of grain boundaries is comparable with the contamination level of the transcrystalline fracture surface (Fig. 1). Therefore, we can attribute the presence of oxygen at the boundary to adsorption from the residual gas atmosphere and not to grain boundary segregation. The differences in the course of both "temperature dependencies" can serve as a measure of the different abilities of the \{112\} and the \{013\} surfaces to the adsorption of oxygen.

Carbon seems to segregate to a \{013\} grain boundary at higher temperatures. This behaviour suggests a mutual replacement of carbon and silicon due to site competition between these elements, similar to observation of de Rugy and Viefhaus at the low-index surfaces of an Fe-3 mass% Si alloy. However, in this case the less surface active silicon prevails at higher temperatures. Therefore, it is more probable that the observed carbon increase is caused by contamination after fracture. Due to mutual site competition, carbon atoms may preferentially adsorb at surfaces with a low level of Si segregation, which therefore leads to the observed apparent temperature dependence of its amount at the boundary. Similarly to oxygen, the ability of the \{112\} surface to carbon adsorption is low, as compared with the transcrystalline fracture surface (Fig. 1). A quick carbon contamination of the transcrystalline fracture surface after its exposure to the residual gas atmosphere and a slow increase of $r(C)$ with the time of measurement were also detected.

Some quantitative differences exist in the temperature dependences of the concentration of Si found at both types of grain boundaries (Fig. 4). As expected, the silicon segregation to the $\Sigma=3, \{112\}$ grain boundary is higher than that to the "more special" $\Sigma=5, \{013\}$ grain boundary. A higher absolute value of the segregation enthalpy for the \{013\} grain boundary was found as compared with the \{112\} one. These results are compatible with the models of grain boundary structure in b.c.c. metals, as obtained by means of computer simulations /e.g. 16,17/. The structure of the \{112\} coherent twin boundary exhibits a very dense atomic arrangement with very small free volume /16/. However, even this small free volume is sufficient for certain segregation of silicon to this boundary. On the other hand, the excess volume in capped trigonal prisms which form the structural units of the \{013\} grain boundary /17/ offers more low-energy sites for the solute segregation. Unfortunately, no quantitative data of the grain boundary segregation of silicon in iron were found in the literature. As expected, the absolute value of the enthalpy of the silicon segregation to the (100) free surface in an Fe-3 wt% Si alloy, 48 kJ/mol /15/ is much higher than values 4 and 8.1 kJ/mol measured in the present work. The absolute value of the entropy of silicon segregation to the same surface, 15 J/(mol K), is also higher than those found for the \{112\} and \{013\} grain boundaries. The low absolute values of segregation entropy for the latter, 4 and 6.9 J/(mol K), respectively, seem to reflect the symmetry of the atomic arrangement of the special grain boundaries studied in the present work.

![Fig. 4 - Temperature dependence of the concentration of silicon, $X_b(Si)$, at the \{013\} (o) and \{112\} (A) grain boundaries.](image1)

![Fig. 5 - Dependencies of values of $r(Si)$ and $r(C)$ on \{013\} are found at various regions of the intercrystalline fracture surface along the \{112\} grain boundary doped with phosphorus.](image2)
Because of an inherent brittleness of the alloy /9/ probably enhanced by the silicon segregation, the Σ=5 bicrystals annealed at lower temperatures were prone to fracture even when cautiously handled during sample preparation. Therefore, no measurement of the composition of the {013} grain boundary annealed at 873 K was accomplished and only limited data were obtained for the annealing at 773 K. However, based on the measured data we can suppose the course of the temperature dependence as indicated by the dashed line in Fig. 1.

Doping of samples with phosphorus (0.54 at%) fundamentally changes the segregation behaviour of silicon at the {112} grain boundary. The high amount of phosphorus segregating to this boundary at 873 K (11.45 at%) removes silicon from the boundary layer to such an extent that silicon depletion occurs there (Fig. 1). This behaviour is result of a repulsive interaction of silicon and phosphorus /18/. The repulsive interaction between Si and P atoms is also seen from the measurement of r(i) in individual regions. It is seen from Fig. 5 that higher values of r(P) were found in regions with lower values of r(Si). A similar behaviour was earlier observed in the case of the {013} grain boundary /19,20/ in an Fe-6 at% Si alloy in a nonequilibrium state and explained on the basis of effects of defects at the fracture surface on the AES measurements /20/. Similar effects of this repulsive interaction were also found in the study of an equilibrium segregation of P and Si to the {112} grain boundary in an Fe-4 at% Si containing traces of phosphorus /6/. Although equilibrium segregation of phosphorus was probably not reached in the present sample, the tendency of phosphorus to segregate to the {112} grain boundary is obvious, thus removing silicon from this boundary. This observation is of considerable importance for the grain boundary design concept /1/.

The content of carbon at the {112} grain boundary of the P-doped sample is higher than the level found at the transcrystalline fracture surface but the oxygen content is below the value of TK(O) (Fig. 1). The presence of carbon in this case is also a consequence of a contamination of the fracture surface after fracture. Comparison of the values of r(P) with those of r(C) measured in individual regions of the P-segregated grain boundary (Fig. 5) discloses practically a mutual independence. The spectra were recorded from various regions of the fracture surface where some defects (introduced by fracturing) were also present. Therefore, not only the composition of a pure grain boundary but also subboundary layers laid free contributed to the measurements in these regions, as explained recently /20/. If carbon would segregate at a grain boundary, this contribution of subboundary layers would have the same effect as in the case of segregating phosphorus and a positive dependence between r(P) and r(C) in contrast to Fig. 5 should be found.

5 - CONCLUSIONS

The chemical composition of the {013} and the {112} symmetrical grain boundaries in the Σ=5, 37° [100] and the Σ=3, 70.5° [110] bicrystals in an Fe-12.9 at% Si alloy was studied by Auger electron spectroscopy, in the temperature range between 773 to 1173 K. From the data obtained the following conclusion can be made.

1) The temperature dependencies of silicon segregation to both grain boundaries exhibit a maximum near 900 K.

2) Both the decrease of silicon segregation at 773 K and a relatively wide in-depth range of the silicon enrichment at all temperatures independent of the values of diffusion length estimates, are found for both grain boundaries. This behaviour is attributed to ordering tendencies in this alloy.

3) The temperature dependence of the Si enrichment above 850 K allows the determination of the segregation enthalpy (∆H) and entropy of segregation (∆S). The obtained values are ∆H = -8.1 ± 0.5 kJ/mol and ∆S = -6.9 ± 0.4 J/(mol K) for the {013} grain boundary, and ∆H = -4 ± 3 kJ/mol and ∆S = -4 ± 3 J/(mol K), for the {112} boundary. The difference in the segregation enthalpies can be explained by the more dense structure of the {112} twin boundary as compared with the {013} boundary.

4) Oxygen and carbon do not segregate to these grain boundaries. An apparent segregation of carbon to the {013} grain boundary is shown to be a result of a contamination of the fracture surface after exposure to the residual gas atmosphere.

5) Doping of the {112} grain boundary with phosphorus leads to a qualitative change of the segregation behaviour of silicon: Whereas Si segregates to the {112} boundary in a pure binary Fe-Si alloy, its depletion is observed in the presence of phosphorus. It is shown that this change of the segregation behaviour is a result of repulsive interaction between P and Si atoms at the grain boundary.
ACKNOWLEDGEMENT

The authors gratefully acknowledge the support by the Alexander von Humboldt Stiftung during the stay of P. Lejček at the Max-Planck-Institut für Metallforschung, Institut für Werkstoffwissenschaft, Stuttgart.

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