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ORIENTATION–DEPENDENT ANTIMONY SEGREGATION ON FeSi ALLOY SURFACES

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The antimony surface segregation was investigated on surfaces of a polycrystalline Fe–Si alloy with 0.05 wt. % Sb, under UHV conditions, in the temperature range from 450 to 950 °C. The grain boundary segregation in experimental alloys was negligible. It was concluded that the texture formation results from orientation–dependent effects of antimony on the surface energy and through them on grain boundaries. Controlled surface segregation promotes the selective grain growth.

1. Introduction

It is well known that many processes which start at the surfaces, such as catalysis, surface diffusion and recrystallization, are determined by the atomic composition of surfaces of metals [1,2]. The atomic composition of grain boundaries is also very important because it affects the physical properties as well as corrosion behaviour of metals and alloys. For materials used at high temperatures, the composition of interfaces may be drastically changed by segregation and by the enrichment of dissolved surface active atoms diffusing on the surface or grain boundaries.

It has been experimentally confirmed that antimony in FeSi alloy (silicon steel) can affect the magnetic properties simply by enrichment at the free surfaces, i.e. surfaces and grain boundaries [2–12]. Such enrichment affects recrystallization, producing an increase in the number of ferrite grains with soft magnetic lattice and in this way improves the magnetic properties. Our investigations show a strong correlation between the antimony surface segregation and the orientation of the grains emerging at the sheet surface [6–10].

2. *Experimental*

The experimental FeSi 2.0 Sb 0.05 alloy, with the chemical composition Fe, 2% Si, 0.3% Al, 0.003% C, 0.001% P, 0.001% S and 0.05% Sb, was prepared from pure base material in laboratory. Ingots were hot rolled to a 2.5 mm thick strip, decarburized and descaled, and cold rolled to the final thickness of 0.15 mm.

The surface segregation phenomena were investigated "in situ" by Auger electron spectroscopy (AES) at a basic vacuum of 4×10^{-10} mbar in the temperature range from 450 to 950 °C. The sample surface was metalographically polished before the AES measurements.

The antimony enrichment of the surface was determined by following the peak–to–height ratio (PHR) of amplitudes of the dominant $Sb(M_5N_{4,5}N_{4,5})$ and $Fe(LM_{2,3})$ Auger transitions at kinetic energies of 454 and 650 eV, respectively. The Auger spectrometer was additionally equipped with thermal desorption spectrometry (TDS) for in situ measurements of desorption.

Grain boundary segregation was also investigated by AES. Cylindrical fracture specimens were prepared from the hot rolled strips of thickness 4 mm. The specimens were evacuated to about 10^{-6} mbar and encapsulated in quartz tubes, normalized at 1000 °C, cooled in air and aged at 550 °C for 200 and 500 hours, than introduced into the UHV system of the Auger spectrometer at a basic vacuum 4×10^{-10} mbar and, after cooling to approximately –120 °C, "in situ" impact fractured. The AES analyses were made for as many intergranular fractures as possible.

The recrystallization of the experimental and comparison steel prepared from the same base material but without antimony, was studied in the temperature range from 550 to 950 °C. Both steels were decarburized before the recrystallization process. The microstructure was examined and the average grain size was estimated.

The grain orientation was determined by the etch pit method and by X–ray difractometry with Mo Kα radiation.

3. *Results*

The highest antimony surface segregation was established at 700 °C. Antimony enrichment, caused by segregation phenomena, can be measured only at elevated temperature with the AES method. The mole fraction of Sb, 0.05%, is in the range of solubility at all temperatures investigated, but below the detection limit of AES in the temperature range from 20 to about 550 °C. AES measurements showed different thicknesses of segregated antimony layers on different grains.

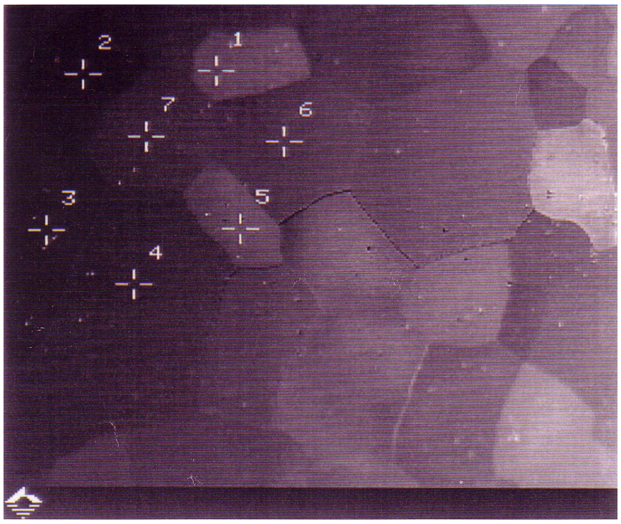


Fig. 1. Scanning electron microscopy image of corresponding points on different grains of measured AES spectra of antimony surface segregation.

TABLE 1.
The antimony/iron peak–hight ratio (Sb454/Fe650) *for all recorded AES spectra measured on different grains.*

Grain	PHR Sb454/Fe650
1	0.325
2	0.436
3	0.400
4	0.421
5	0.329
6	0.457
7	0.379

The antimony/iron PHR Sb454 /Fe650 for all recorded AES spectra measured on different grains is shown in Table 1. The PHR Sb454/Fe650 varied between 0.325 and 0.436. Correlation between the PHR and the intensity within the Sb (SAM) image, Fig. 2, is not very good. This is probably due to a channelling effect of the primary electron beam, since the intensity, especially of the iron Auger signal, depends on the angle of incidence of the primary electron beam with respect to the crystallographic orientation of the grain [13] (Fig. 2).

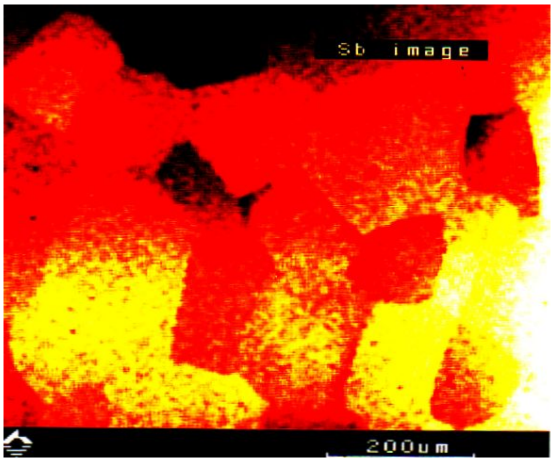


Fig. 2. SAM image demonstrating the differences in PHR (Sb/Fe) *for antimony in* FeSiSb0.05 *alloy.*

If the influence of a possible channelling effect is neglected, it is possible to estimate the Sb surface concentration by comparison with the results on Sb surface segregation on single–crystal surfaces of Fe–4% Sb of defined orientation. For the same primary energy of exciting electrons, the following saturation PHR were measured for single–crystal surfaces of (100), (110) and (111) orientation: Sb/Fe650: 0.42 for the (111) oriented surface, Sb/Fe650: 0.58 for the (110) oriented surface and Sb/Fe650: 0.40 for the (100) oriented surface. For (100) oriented surface, saturation coverage is half of a monolayer corresponding to a (LEED) c(2x2) overlay pattern [14]. For the other surface orientation, no well defined ordered structure of surface coverage was observed. The PHR are of the same order as in polycrystalline specimens. The saturation PHR for the (100) surface was used for calibration. The saturation surface concentrations for polycrystalline specimens were in range of 0.2 to 0.6 of a monolayer.

The kinetics of surface antimony segregation was also measured by AES at the constant temperatures 700, 750, 800 and 850 °C. Figure 3 shows the time dependence of PHR at 700 and 800 °C. At elevated temperatures ($T > 700$ °C), the antimony surface segregation rate decreased.

There are two possible explanations for this effect: simultaneous Sb and S segregation and competition for sites available on the surface, and/or desorption from the segregated layer.

Competitive surface segregation of antimony and sulphur can be described by the following equations:

$$\frac{\Theta_{\mathrm{Sb}}}{1-\Theta_{\mathrm{Sb}}-\Theta_{\mathrm{S}}} = \chi_{\mathrm{Sb}} \exp(-\Delta G_{\mathrm{Sb}}/RT), \tag{1}$$

$$\frac{\Theta_S}{1-\Theta_S-\Theta_{Sb}} = \chi_S \exp(-\Delta G_S/RT), \tag{2}$$

where Θ_{Sb} and Θ_S are the saturation coverages, χ_{Sb} and χ_S are mole fractions, and ΔG_{Sb} and ΔG_S are free energies of Sb and S surface segregation, respectively, R is the specific gas constant and T absolute temperature [13–15].

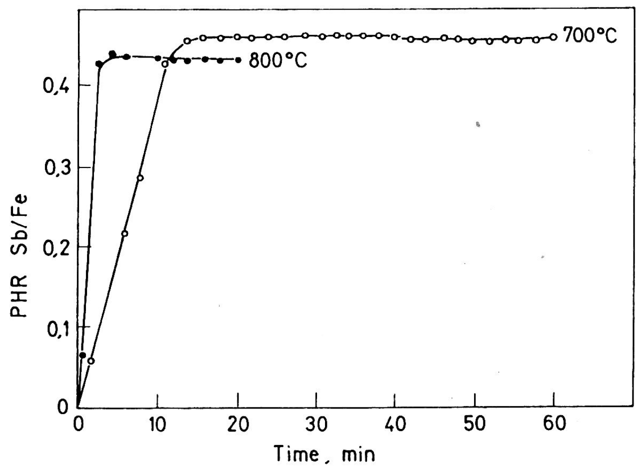


Fig. 3. Kinetics of surface antimony segregation measured by AES, at constant temperatures of 700 and 800 °C on the surface of FeSiSb0.05 *alloy.*

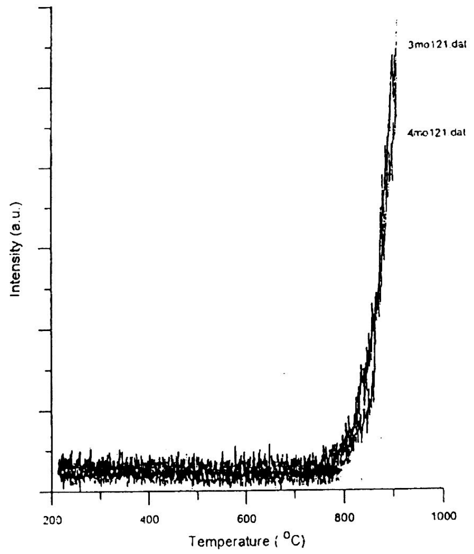


Fig. 4. TDS plot demonstrating Sb *desorption from the surface segregated layer at* $T > 750$ °C.

Strong interaction and co–segregation of Ni and Sb was observed at the grain boundaries, but in the investigated steel, the content of Ni is very low, and it is not to be expected in our investigation [18,19].

Antimony desorption from segregated layer was established by (TDS) at $T >$ 750 °C (Fig. 4).

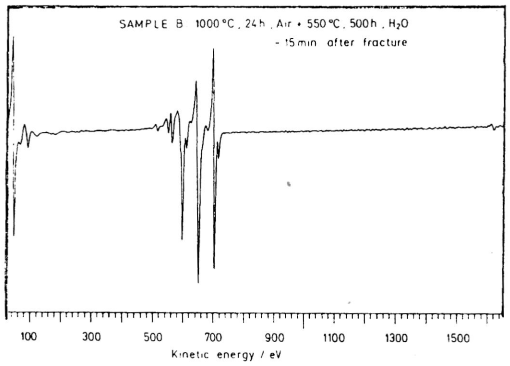
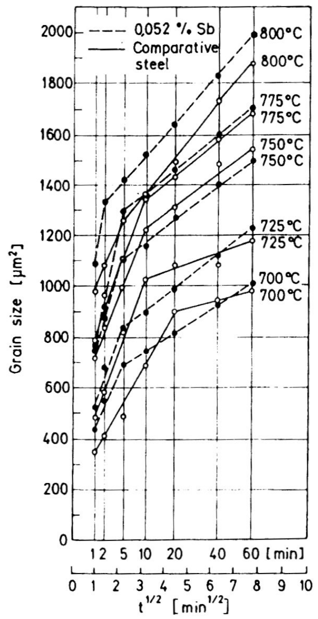


Fig. 5. AES spectra taken at intergranular facet of FeSiSb0.05 *alloy.*



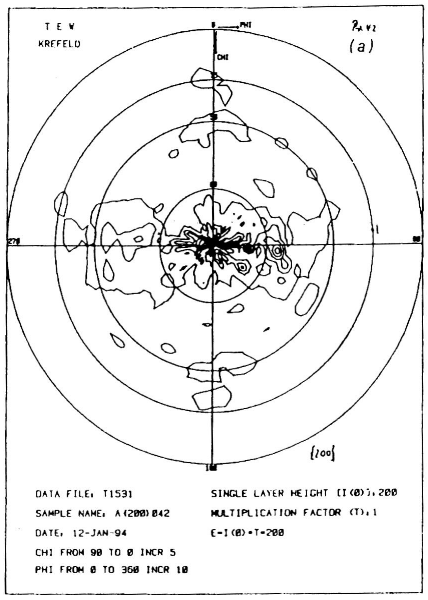


Fig. 6. The dependence of grain size on the annealing time for FeSiSb0.05 *alloy and a comparison* FeSi *alloy.*

Fig. 7. Pole figures of FeSiSb0.05 *alloy. Small share of grains with texture (100)(001) was obtained (right).*

Grain boundaries of FeSi steel alloyed with 0.05 and 0.1% Sb were also analyzed by AES after ageing for 200 and 500 hours at 550 °C. The fracture facets were almost completely transgranular and only on some areas intergranular decohesion was noticed. In the investigated alloys, there was no indication of antimony grain boundary segregation (Fig. 5). Only negligible grain boundary segregation of other solute elements, such as silicon and aluminium, was found.

The influence of antimony on recrystallization and grain growth was studied in FeSiSb0.05 alloy and in a comparison alloy. The kinetics of grain growth and grain size were determined in the temperature range from 700 to 800 °C. There was no significant effect of Sb on the rate of recrystallization, but it was found that after the recrystallization was finished at a temperature 750 °C, the grains were coarser in the FeSiSb0.05 alloy (Fig. 6).

The grain orientation for alloy with antimony and comparison alloy was determined by X-ray diffractometry. The pole figure, obtained in Fig. 7, showed that only a small proportion of grains with the texture (100)(001) was found in the FeSiSb0.05 alloy.

4. *Conclusion*

During the annealing process of the FeSi Sb0.05 alloy, antimony segregated on the surface at temperatures $T > 550$ °C, and in the temperature range from 600 to 700 °C only Sb segregation was found. The maximum equilibrium antimony surface segregation was 0.6 monolayer. It was established at 700 °C on the grains with (111) surface orientation. A strong correlation between the surface segregation of antimony and the orientation of the grains at the sheet surface was established.

Antimony surface segregation decreased the surface energy of the grains with (100) surface orientation, and these grains grow on the account of grains with other surface crystallographic orientations, such as (110) and (111). Only a certain level of surface segregation promoted selective grain growth. At excessive segregated surface coverage, the surface energy of all orientations is strongly decreased and no preferential grain growth is obtained.

Grain boundary segregation of antimony and other solute elements, such as C, Al, S and P, were negligible in the investigated alloys.

The results of the present investigation support the hypothesis that the texture formation results from orientation dependent effects of antimony on the surface energy and not from effects on grain boundary stability and mobility.

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SMJEROVNA OVISNOST IZDVAJANJA ANTIMONA NA POVRŠINAMA LEGURA FeSi

Proučavano je površinsko izdvajanje antimona na površinama polikristalne legure FeSi sa 0.05 tež.%, u ultravakuumu i na temperaturama od 450 do 950 °C. Izdvajanje na granicama zrna je zanemarivo. Ustanovljeno je da je nastajanje teksture posljedica smjerovno–ovisnih učinaka antimona na površinsku energiju pa stoga i na granice zrna. Upravljavano površinsko izdvajanje potiče poseban rast zrna.