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Surface Activated Recrystallization of Antimony Alloyed Non-Oriented Electrical Steel Sheet

Površinsko aktivirana rekristalizacija silicijevih elektro jekel, legiranih z antimonom

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In the present paper the effect of antimony on recrystallization texture of non oriented steel sheets is discussed. The antimony surface and grain boundary segregation were investigated. Since the grain boundary segregation was negligible one can conclude that the texture formation results from orientation dependent effects of Sb on the surface energy and through them on grain boundaries.
Key words: non oriented steel sheet, recrystallization, grain growth, adsorption, surface and grain boundary segregation.

Raziskali smo vpliv antimona na teksturo rekristalizacije neorientirane elektro pločevine, kot tudi segregacijo antimona na površini in na mejah zrn. Segregacija antimona po mejah zrn preiskovanih jekel je zanemarljiva. Predpostavljamo, da se zaradi vpliva antimona na površini pločevine površinska energija zrn z orientacijo (100) zmanjša in vpliva na oblikovanje ugodne teksture.
Ključne besede: neorientirana elektro pločevina, rekristalizacija, rast zrn, adsorbcija, površinska segregacija, segregacija po mejah zrn.

1. Introduction

Low loss and high permeability non oriented silicon steels are needed for efficient electrical power generation and transformation, which is one of the conditions for energy conservation and environmental amelioration[1-5]. To attain the full potential of this highly developed material its recrystallization texture must be improved[10].

It has been found that small additions of certain elements (Sb,Sn,Se,Te) especially antimony, into the steel for non oriented electrical sheets, affect the recrystallization and lead to an increase of the number of ferrite grains with favorable orientation[6-9]. The effect on grain growth and orientation can be caused by surface and/or grain boundary segregation of Sb or else. The surface segregation, its kinetics and equilibrium were measured using Auger Electron Spectroscopy and Thermal Desorption Spectroscopy on and in steel doped with Sb.

2. Experimental

Experimental steels of the composition given in **Table 1**, were prepared in laboratory from the same base material. The specimens for the surface segregation studies, of dimensions 6 mm in diameter and thickness of 0.15 mm were mounted into the UHV system. The samples were heated up to 900°C for 10 minutes and then sputter clean, annealed in the temperature range from 450 to 950°C and investigated 'in situ' by AES. The antimony enrichment of the surface was determined by following the peak height ratio (PHR) of amplitudes between the dominant $Sb(M_5N_{4,5}N_{4,5})$ and $Fe(LM_{2,3}V)$. Auger transitions at kinetic energies of 454 and 650 eV, respectively[6,7,11-13].

Table 1: Chemical composition in mass contents in % of the experimental steels:

Steel	C	Mn	Si	S	Al	Sb
1	0.005	0.18	1.85	0.001	0.19	0.05
2	0.004	0.20	1.94	0.001	0.11	0.1
3	0.004	0.20	2.12	0.001	0.19	–

Cylindrical specimens for grain boundary segregation measurements were prepared from the ingots of the same base material, notched, encapsulated in quartz tubes evacuated to approximately 10^{-6} mbar, normalized for 24 hours at 1000°C, cooled and aged at 850, 700 and 550°C for different times, from 1 to 500 hours.

Also the grain boundary segregation was investigated by AES method. Cylindrical specimens were introduced into UHV system of AES spectrometer at basic vacuum $4x10^{-10}$ mbar and after cooling to approximately -120°C were impact fractured 'in situ'. The AES analysis were taken from as many intergranular fracture facets as possible[11,12,14-16].

The antimony desorption from the surface segregated layer was investigated by performing Thermal desorption

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Spectrometry - TDS. The specimen was introduced in the UHV system of AES spectrometer additionally equipped with TDS and heated several times up to 950°C[18].

The grain orientation was determined by X-ray difractometry with Mo Kα radiation.

3. Results and discussion

The highest antimony surface segregation was established at 700°C until no further increase in Sb concentration could be observed and the sulfur concentration was acceptable low, **figure 1**.

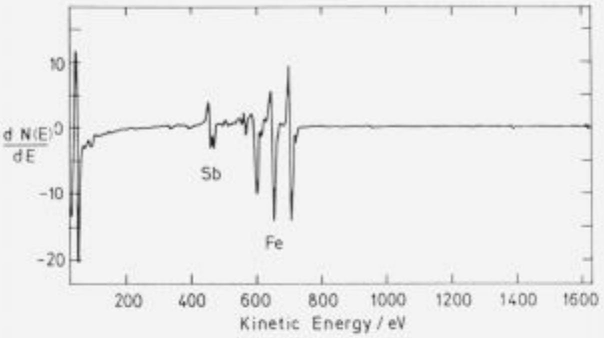


Figure 1: AES spectra of maximum equilibrium antimony segregation obtained at 700°C for steel with 0.05% Sb.

Slika 1: AES spekter maksimalne ravnotežne segregacije antimona dosežene pri 700°C za jeklo legirano z 0.05% Sb.

Table 2: Antimony to iron peak height ratios for all recordered AES spectra of Sb surface segregation measured on the different grains, shown in **figure 2**.

Grain	PHR (Sb/Fe650eV)
1	0.32
2	0.39
3	0.28
4	0.44
5	0.43
6	0.37
7	0.38
8	0.42

Table 2 shows antimony to iron peak height ratios for all recordered Auger spectra. The corresponding points on the different grains are noted on the SEM images, **figure 2**. The Sb/Fe650 eV peak height ratio varies between 0.28 and 0.44. There is not always a correlation of the peak height ratios and the intensity within the Sb SAM images and this may be due to a channeling effect of the primary electron beam. The intensity, especially of the iron Auger signal, depends on the angle of incidence for the primary electron beam with respect to the crystallographic orientation of the grains[11]. If we neglect this influence of possible channeling effects we can estimate the Sb surface concentration by comparison with the results on Sb surface segregation on single crystal surfaces of defined orientation. For the same primary energy of exciting electrons the following saturation peak height ratios were measured for single crystal surfaces of (100), (110) and (111) orientation:

Sb/Fe 650 eV = 0.42 for the (111) oriented surface
Sb/Fe 650 eV = 0.58 for the (110) oriented surface
Sb/Fe 650 eV = 0.40 for the (100) oriented surface

For the (100) oriented surface saturation coverage is half of a monolayer corresponding to a LEED c(2x2) overlayer pattern. For the other surface orientations no well defined ordered structure of surface coverage was observed[11]. But the peak height ratios are in the same order as for the polycristalline samples. The peak height ratio at saturation for the (100) surface was used as a calibration and the surface concentration for the polycrystalline samples at saturation were in the range of 0.2 to 0.6 of a monolayer.

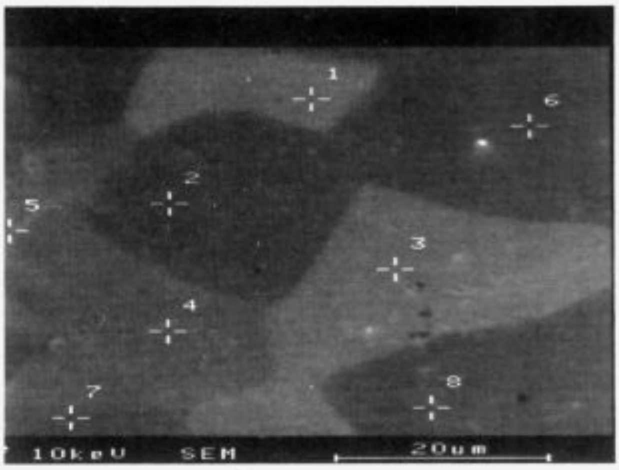


Figure 2: AES measurements of Sb surface segregation on the different grains. Antimony to iron peak height ratios for all recordered spectra are given in Table 2.

Slika 2: AES meritve površinske segregacije Sb na različnih zrnih. Razmerja vrhov antimona napram železu za posnete spektre so podana v tabeli 2.

It was found that even in one grain the antimony segregation layer is not uniform, close by grain boundary the segregated layer was thicker, **figure 3**.

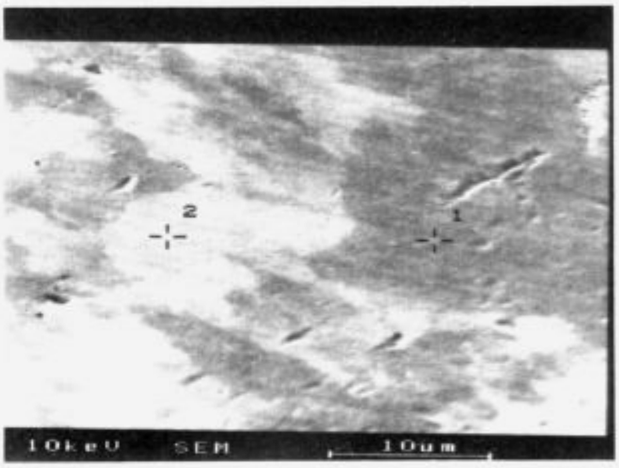


Figure 3: SEM image of the grain with segregated antimony layer. Close to grain boundary the segregated layer was found thicker.

Slika 3: SEM posnetek zrn s segregirano plastjo Sb. Ob meji zrna je bila segregirana plast Sb debelejša.

The kinetics of surface antimony segregation measured by AES at 700 and 800°C is shown in **figure 4**. It was found that at elevated temperatures T > 750°C, antimony surface segregation rate decreases. There are two possible explanation for this effect;

simultaneously antimony and sulfur segregation and/or Sb desorption from segregated layer.

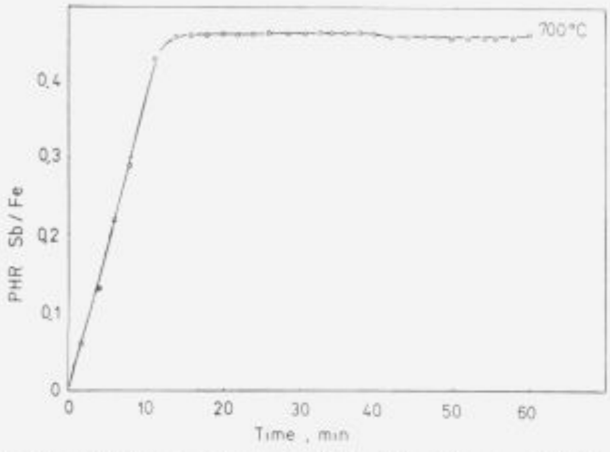


Figure 4: Kinetics of maximum equilibrium Sb surface segregation of steel alloyed with 0.05% Sb, obtained at 700°C.

Slika 4: Kinetika maksimalne ravnotežne površinske segregacije antimona za jeklo z 0.05% Sb, dobljena pri konstantnem žarjenju na temperaturi 700°C.

Sb desorption from the segregated layer was investigated by Thermal Desorption Spectrometry in temperature range from 20 to 950°C. In **figure 4** the results of TDS investigation are shown. Sb as well as S desorption from the segregated layer was established at T > 750°C.

Thus one can conclude that the effect of decrease of antimony segregation rate at elevated temperature T > 750°C is the result of both phenomena: antimony desorption and simultaneously segregation of Sb and S as we proposed in our earlier paper.[10]

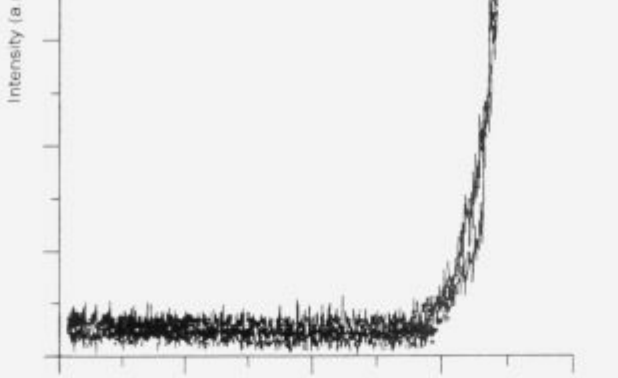


Figure 5: The antimony desorption from the segregated layer was established at T > 750°C, by Thermal Desorption Spectrometry.

Slika 5: Odparevanje antimona iz segregirane plasti smo izmerili z metodo TDS pri temperaturah T > 750°C.

Also grain boundaries of the material were analyzed by AES after annealing at 850, 700, 600 and 550°C for 1 to 500 hours. We found that the grain boundary segregation of antimony and also of other solute elements was negligible[8] which is not in agreement with our earlier findings[5]. However the Sb grain boundary segregation was established in a crack open to the surface of cylindrical specimen. It is therefore possible that in the earlier work the surface antimony segregation and not grain boundary segregation was measured. Strong interaction and cosegregation of Ni and Sb was observed at the grain boundaries[14-17] but in our investigation it is not to be expected because of very low Ni content. Bryant[16] and Gas[17] reported that they found grain boundary segregation of antimony in pure Fe-Sb alloy after 200 and 500 hours of annealing in vacuum at 550°C. After the same thermal treatment of the investigated steels, the present investigation revealed that grain boundary segregation of antimony and also of other solute elements was negligible.

The influence of antimony on recrystallization and grain growth was studied on steel alloyed with 0.05% Sb and on comparative steel. The kinetics of grain growth and the final grain size was determined in the temperature range from 700 to 800°C, there was no clear effect of Sb on the rate of the grain growth, while the recrystallization was slow in the antimony alloyed steel, **figure 5**.

The grain orientation for both steel alloyed with Sb and comparative steel was determined with X-ray difractometry,

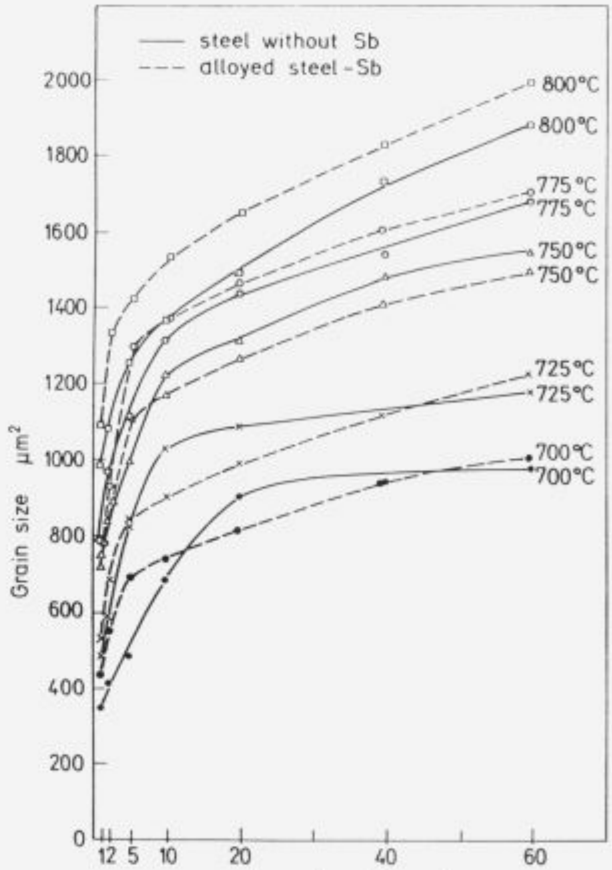
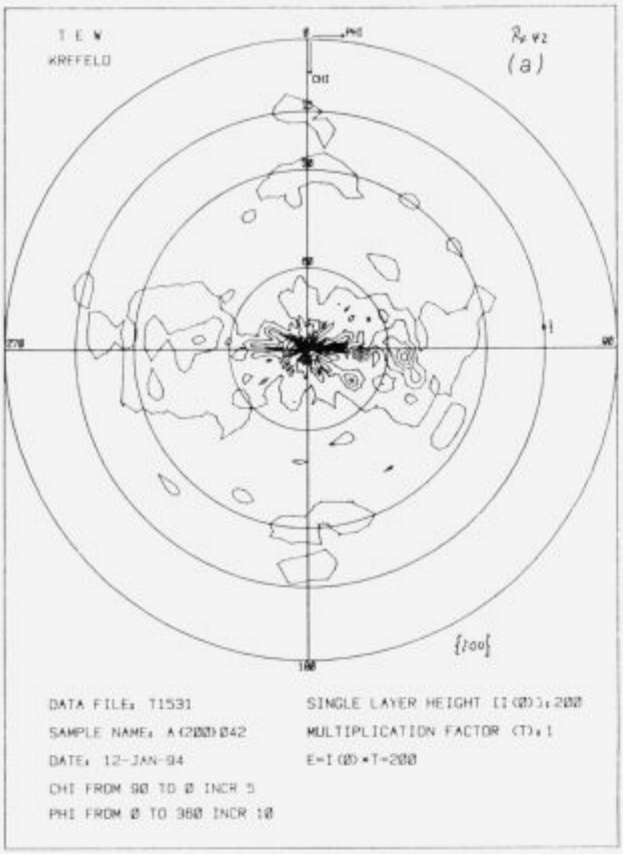
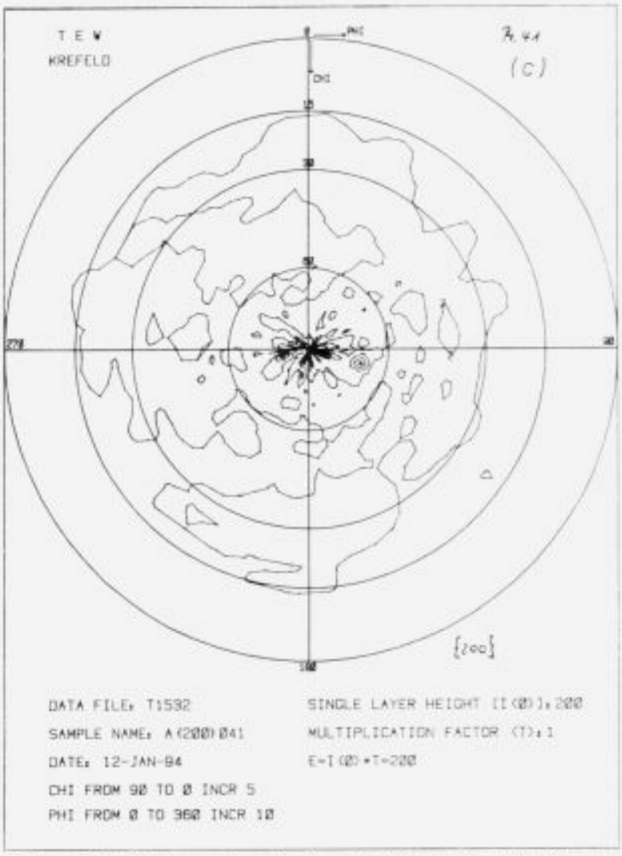


Figure 6: Grain size in dependence of annealing time for steels with 0.05% Sb and without Sb10.

Slika 6: Velikost zrn v odvisnosti od časa žarjenja za jeklo z 0.05% Sb in primerjalno jeklo brez Sb10.





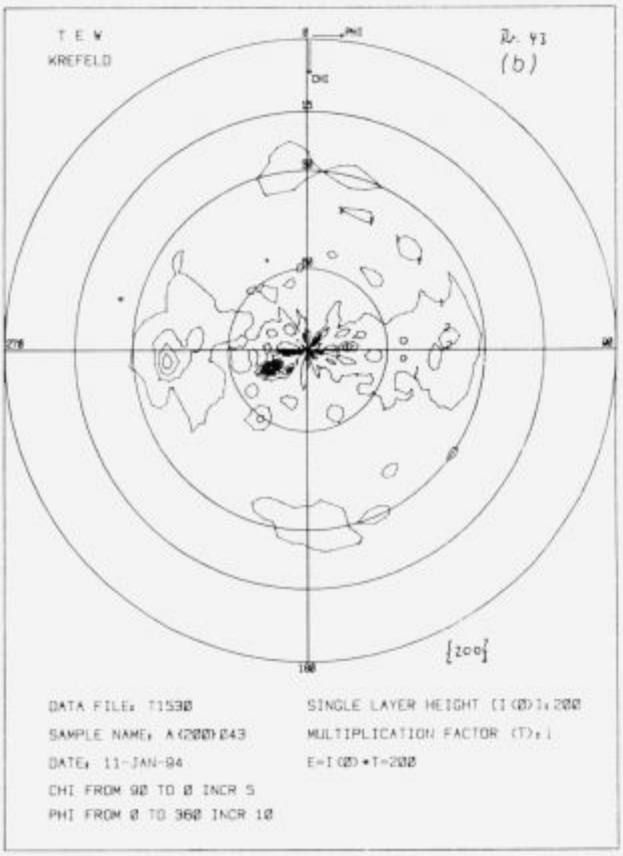


Figure 7: Pole figures of steels alloyed with 0.05% Sb, 0.1% Sb and comparative steel established by X-ray difractometry, using Mo-Kα radiation. Small share of grains with the texture (100)(001) was obtained in 0.05% Sb steel(a), for 0.1% Sb steel a weak texture with (111)(001) orientation was established.

Slika 7: Polove figure jekel legiranih z 0.05% Sb, 0.1% Sb in za primerjalno jeklo brez Sb smo določili z metodo rentgenskega uklona z uporabo Mo Kα sevanja. V jeklu z 0.05% Sb je bil ugotovljen manjši delež zrn z orientacijo (100)(001) (a); za jeklo z 0.1% Sb pa je bila določena šibka tekstura (111)(110), (b).

using Mo Kα radiation. Ordered pole figures are shown in **figure 6**, for comparative steel. For both steels alloyed with antimony a week orientation is estimated. Small share of grains with the texture (100) (001) was obtained in steel with 0.05% Sb, while for the steel alloyed with 0.1% Sb a weak texture of (111) (110) orientation was established. Similar results of grain orientation were obtained by performing an etch pits method, as reported already[8].

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

4. Conclusions

The antimony surface segregation depends on grain orientation. The maximum antimony surface segregation coverage at saturation was found at 700°C by AES.

The Sb surface segregation depends on grain orientation. The peak height ratio at saturation for the (100) single crystal surface was used as a calibration and the maximal surface concentration for the polycrystalline samples at saturation was 0.6 of a monolayer.

Grain boundary segregation of antimony and of other solute elements e.g., S, C, P, Si, Al, in the experimental steels were negligible.

The desorption of antimony and sulfur was established at T > 750°C, by TDS method. Thus one can conclude that the decrease in antimony segregation rate at elevated temperature is the result of simultaneously segregation of antimony and sulfur as well as of antimony and sulfur desorption.

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