Influence of Antimony on the Texture and Properties of 2% Si, 0.3% Al Steel for Non-Oriented Sheet

M. Jenko, F. Vodopivec, H.J. Grabke*, H. Viehhaus*, M. Godec and D. Steiner Petrovic

Institute of Metals and Technology, Lepi pot 11, P.O. Box 431, 61000 Ljubljana, Slovenija

** Max-Planck-Institut für Eisenforschung, Max-Planck Strasse 1, Düsseldorf, Germany*

Abstract. The effect of additions of antimony (0.05% Sb) to silicon steel on the improvement of the electrical properties of non-oriented steel sheet was investigated. Measurements of surface segregation of Sb were performed under UHV conditions in the temperature range from 450 to 900 °C, using AES and TDS. Maximum equilibrium surface segregation of antimony was determined at 700 °C. At higher temperatures, $T > 800^\circ\text{C}$, the desorption of antimony from the surface was measured. The grain boundary segregation was negligible and we can conclude that the texture formation, rich in (100) grains, results from the effect of the orientation dependent surface segregation of Sb. This segregation causes differences in surface energies and the stability of different grains. Controlled surface segregation promotes selective grain growth improving the electrical properties of non-oriented steel sheet.

1. INTRODUCTION

It has been experimentally confirmed by several authors that the addition of about 100 ppm of antimony can affect the magnetic properties of silicon steel, simply by enrichment at surfaces and/or grain boundaries (1-10). This enrichment affects recrystallization, producing an increase in the number of ferrite grains with soft magnetic lattice space orientation in the sheet plane and in this way improves the magnetic properties. Our investigations show a strong correlation between the surface segregation of antimony and the orientation of the grains emerging at the sheet surface.

2. EXPERIMENTAL

The experimental steel of composition Fe, 2.0 % Si, 0.3 % Al, 0.030 % C, 0.001% P, 0.001% S and 0.05% Sb was prepared in the laboratory. Ingots were hot rolled to strip of thickness 2.5 mm, decarburized, descaled and after intermediate annealing and cold rolling, cold rolled to the final thickness of 0.5mm and 0.15mm with a final deformation of 60%. The specimen was mounted in the UHV system, and heated up to 900 °C for 10 minutes and then sputter cleaned, annealed in the temperature range from 450 to 900°C and investigated in situ by AES and TDS.

The antimony enrichment of the surface was determined by following the peak height ratio (PHR) of amplitudes between the dominant $\text{Sb}(\text{M}_{5}\text{N}_{4,5}\text{N}_{4,5})$ and $\text{Fe}(\text{LM}_{2,3})$ Auger transitions at kinetic energies of 454 eV and 650/703 eV respectively (16,17,20). The AES spectrometer was additionally equipped with Thermal Desorption Spectrometry - TDS for "in situ" investigation of antimony desorption.

Grain boundary segregation was also investigated by AES. Cylindrical fracture specimens were prepared from the hot rolled strip of thickness 4 mm. The specimens were encapsulated in quartz tubes, evacuated to about 10^{-6} mbar, normalized for 24 hours at 1000°C, cooled in air and aged at 550°C for 200 and 500 hours, then introduced into the UHV system of the Auger spectrometer at basic vacuum 4×10^{-10} mbar and after cooling to approximately -120°C "in situ" impact fractured. The AES analyses were taken from as many intergranular fractures as possible.

The recrystallization of experimental and comparison steel prepared from the same base material without antimony was studied in the temperature range from 550 to 850° C. Both steels were decarburized before the recrystallization process and annealed in a lead bath for different times from 1 to 60 minutes. The microstructure was examined and the average grain size was assessed.

The grain orientation was determined by the etch pit method and by X-ray diffractometry with Mo K α radiation.

3.RESULTS AND DISCUSSION

Antimony enrichment, caused by equilibrium segregation on the surface, can only be measured at elevated temperatures 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 the AES method.

The highest antimony surface enrichment was established at 700° C ; above this temperature, no further increase in Sb concentration was observed (figure 1).

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

Table 1 shows antimony to iron peak height ratios for all recorded Auger spectra. The point enrichment ratios in different grains are noted on the SEM images in figure 2. The Sb/Fe 650 eV peak height ratio varies between 0.232 and 0.585. There is not always a correlation between the peak height ratios and the intensity within the Sb SAM images and 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), figure 3.

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 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 and 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 (13). The peak height ratios are in the same order as in polycrystalline specimens. The saturation peak height ratio for the (100) surface was used as a calibration. The saturation surface concentrations for the polycrystalline samples were in the range of 0.2 to 0.6 of a monolayer.

Table 1: PHR Sb/Fe of recorded AES spectra on different grains

<i>spectrum</i>	<i>Sb/Fe650</i>	<i>Sb/Fe703</i>
SBJ101 1/7	0.325	0.274
SBJ101 2/7	0.436	0.386
SBJ101 3/7	0.400	0.341
SBJ101 4/7	0.421	0.356
SBJ101 5/7	0.329	0.277
SBJ101 6/7	0.457	0.381
SBJ101 7/7	0.379	0.327

Figure 2: SEM image of corresponding points on different grains of recorded AES spectra of Sb surface segregation

Figure 3: Scanning AES image demonstrating the differences in PHR for antimony in steel alloyed with 0.05%Sb.

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, where $T > 750^\circ\text{C}$, the antimony surface segregation rate decreases.

Figure 4: Kinetics of maximum equilibrium Sb surface segregation of investigated steel at 700°C and at 800°C.

Figure 5 : TDS spectrum showing that Sb evaporates from the segregated layer at $T > 750^\circ\text{C}$.

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

In steels other solute elements, such as C, S and P are present, and two or more elements can simultaneously segregate to the surface. There is generally competition for the site available. The relative amount of segregated elements on the surface depends on their free energy of segregation and the

concentration in the bulk(14,15). Strong interaction and co-segregation of Ni and Sb was observed at the grain boundaries(17-19), but in the steel investigated the content of Ni is very low and it is not to be expected in our investigation.

Antimony desorption from the segregated layer was established by Thermal Desorption Spectrometry at $T > 750^{\circ}\text{C}$, figure 5.

Grain boundaries of the material were also analyzed by AES after annealing at 850, 700, 600 and 550°C for 1 to 500 hours and only negligible grain boundary segregation of antimony and other solute elements was established.

Bryant (18), Gas and Guttman (19) established 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, the present investigation revealed only negligible grain boundary segregation of antimony and of other solute elements in the steels investigated, as already reported (11).

The influence of antimony on recrystallization and grain growth was studied in steel with 0.05 % Sb and in a comparison steel. The kinetics of grain growth and the final grain size were determined in the temperature range from 700 to 800°C . There was no significant effect of Sb grain growth rate, but it was found that at recrystallization finished in the temperature range 700 - 800°C the grains were coarser in the antimony steel (figure 6).

The grain orientation for steel alloyed with Sb and comparison steel was determined by X-ray diffractometry, using Mo $K\alpha$ radiation. The pole figures obtained are shown in figure 7: only a small proportion of grains with the texture (100)(001) was found in steel with 0.05% Sb.

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

Figure 7: Pole figures of Sb alloyed and comparison steel. Small share of grains with texture (100)(001) was obtained in 0.05%Sb steel.

Similar grain orientation results were obtained by the etch pit method (11).

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 grain boundary stability and mobility.

4. CONCLUSIONS

The results of this investigation proved that antimony additions in silicon steel affect recrystallization by producing an increase in the number of ferrite grains with soft magnetic lattice space orientation in the sheet plane, and in this way improves the magnetic properties.

Antimony addition becomes effective simply by enrichment on the surface, which is measured on the surface at elevated temperatures by the AES method. The maximum surface segregation of antimony was 0.6 of a monolayer and it was established at 700 °C.

A strong correlation between the surface segregation of antimony and the orientation of grains emerging at the sheet surface was established.

Antimony decreases the surface energy of grains with (100) orientation in the sheet plane, and these grains grow on account of grains with other space orientations in the sheet plane. Only a certain level of surface segregation promotes selective grain growth. With excessive surface coverage, the surface energy of all orientations is strongly decreased and no preferential grain growth is obtained.

References

1. G. Lyudkovski, P.K.Rastogi and M.Bala, *Journal of Metals*, 1(1986) 18
2. G. Lyudkovski, P.K.Rastogi, *Metall. Trans. A*, 15A (1984) 257.
3. H. Shimanaka, T.Irie, K. Matsumura and K. Nakamura, *J.Magn. Magn. Mat.* 19(1980) 63
4. P.Marko, A.Šolyom, V.Frič, *J.Magn.Magn.Mat.* 41 (1984)
5. F.Vodopivec, F.Marinšek, D.Gnidovec, B.Praček, M.Jenko, *J. Magn. Magn.Mat.* 97, (1991) 281.
6. F.Kovač, Š.Nížnik, *Metallography* 95, *Proceed.*, Slovakia, April 1995, Paper 14, p.84-87
7. M.Jenko, F.Vodopivec, B.Praček, *App. Surf. Sci.* 70/71 (1993) 118
8. M.Jenko, F.Vodopivec, B.Praček, M.Godec and D.Steiner, *J.Mag.Mag.Mat.* 133(1994) 229.
9. G. Lyudkovski, *IEEE Trans.Magnetics* mag. 22 (1986)5, 508
10. G. Lyudkovski, A.G.Preban, J.M.Shapiro, *J.Appl.Phys.* 5 (1982) 3, 2419
11. M.Jenko, F.Vodopivec, H.J. Grabke, H.Viefhaus, B.Praček, M.Lucas, M.Godec, *Steel research* 65 11,(1994) 500.
12. M.Jenko, H.Viefhaus, M.Lucas, F.Vodopivec, M.Godec, D.Steiner Petrovič, M.Milun, T.Valla, *Metals, Alloys, Technologies*, 28,4, (1994) 561-565
13. V. Rutenberg, H. Viefhaus, *Surf.Sci.* 172 (1986) 615
14. H.J.Grabke, *Iron and Steels*, *ISIJ int.* Vol.29 (1989) 529
15. H.J.Grabke, *Kovine, zlitine, tehnologije* 1/2(1993)9.
16. C.Lea, M.P.Seah, *Phil.Mag.*35, 1 (1977) 213
17. E.D.Hondros, M.P.Seah, *Metal Trans.* 8A (1977)1363
18. C.L.Briant, M.Ritter, *Acta metall.* 32(1984)2031
19. P.Gas, M.Guttman, J.Bernardini, *Acta metall.* 30(1982)1309
20. D.P.Woodruff, T.A.Delchar, *Modern Techniques of Surface Science*, Cambridge University Press, 1994