Sn Segregation and Its Influence on Electrical Steel Texture Development

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During the recrystallization microalloyed Sn in non-oriented electrical steel segregates to the surface and on grain boundary and affects the texture development. In spite of the fact that the grain boundary segregation is much smaller compared to surface segregation, both have an influence on recrystallization and on texture development in electrical steel. Auger electron spectroscopy (AES) was used to measure the grain boundary and surface segregation of Sn in non-oriented electrical steels alloyed with different Sn weight contents (0.025, 0.05 and 0.1 %). The grain boundary segregation of the specimens, which were previously aged at 530°C for various times and were fractured under UHV conditions, was measured. The surface segregation temperature dependence and its kinetics were followed in polycrystalline specimens in the temperature range from 400 to 900°C on the grains of known crystallographic orientations: (100), (111) and (110). The textures were measured by X-ray texture goniometer and the results were presented as orientation distribution functions (ODF). By controlled surface and grain boundary segregation it is possible to achieve the selective grain growth which improves the electrical properties of non-oriented electrical steel. The best results were obtained by alloying it with 0.05 wt% Sn.

KEY WORDS: non-oriented electrical steel; tin; surface and grain boundary segregation; recrystallization; texture.

1. Introduction

In this century an immense progress has been made in grain oriented electrical steel production with highly defined Goss texture ({110}⟨100⟩), but less is known about non-oriented electrical steel. Due to the fact that non-oriented electrical steel is mostly applied in small motors, its anisotropy should be assured. The ideal texture of non-oriented electrical steel would be a cubic fibre texture at which most of the grains have {100} plane parallel to the steel sheet plane, while azimuthal orientation of grains is totally random. Such a texture has on the average the highest number of magnetic favourable ⟨100⟩ directions.

Recrystallization of electrical steel is decisively dependent on chemical composition and structure of surface[1,2)] and grain boundary.[3,4)] The chemical composition of surfaces and grain boundary are drastically changed during heat treatment of steels due to the well-known phenomenon called segregation. Some of the alloying elements and also some of the tramp elements in ppm level from IV A to VI A group enrich surface and grain boundary. An equilibrium segregation is reached by the interaction of free bonds on the surface with the segregating elements. This decreases the surface energy and releases the elastic energy of the lattice.[5)]

By alloying non-oriented electrical steels with small additions of surface active elements such as Sn, Sb, Te and Se, the texture can be significantly improved.[6–9)] Sn, when added in the range of a 0.02–0.1 wt%, can improve magnetic properties,[10)] though it is steel parasite and not desirable in structural steels. During the recrystallization process, Sn segregates at the grain boundary and on the surface. The thickness and structure of the segregated layer depend on the crystallographic orientation.[11)] Thus, by segregation, the surface energy decreases selectively, and so the difference in the total energy of the grain, which is the driving force for its growth during recrystallization. It is logical to expect a selective effect on grain growth with a different spatial orientation.

The aim of the present work was to find out the correlation of segregation and the texture development. Surface and grain boundary segregation of Sn in non-oriented electrical steel alloyed with 2 wt% Si and 1 wt% Al and different contents of Sn (0.025, 0.05 and 0.1 wt%) were determined. The temperature dependence and the kinetics of surface segregation were studied with an emphasis on the orientation dependence. The correlation between Sn segregation and texture development was ascertained. The segregation of Sn during the recrystallization increased the grain growth of (100) grains lying in the plane of the sheet and at the same time decreased the growth of (111) grains.

Table 1. Chemical composition of steels in wt%.

Steel	C	Mn	Si	S	Al	Sn
A	0.0015	0.24	2.2	0.0005	1.10	0.000
B	0.0025	0.26	2.01	0.0028	1.10	0.027
C	0.0015	0.23	2.02	0.0005	0.95	0.048
D	0.0015	0.23	2.08	0.0004	0.95	0.097

2. Experimental

The four experimental non-oriented electrical sheets were produced from the same basic material. The compositions of vacuum melted and cast steels are listed in **Table 1**.

The resulting ingots of about 15 kg weights were hot rolled, at a starting temperature of 1 200°C, to the final strip thicknesses of 6 mm and 2.5 mm. The strips were descaled and decarburized in a wet hydrogen (dew point 25°C) for 2 hr at 840°C.

Segregation was studied "*in situ*" using Auger Electron Spectroscopy—AES. The Sn enrichment on the surface was determined by following the peak height ratio (PHR) of amplitudes between the dominant $Sn(M_5N_{45}N_{45})$ and the $Fe(L_3M_{23}M_{54})$ Auger transitions, located at the 430 and 651 eV kinetic electron energies, respectively.

For grain boundary segregation the notched cylindrical specimens of 3.7 mm and 5 mm in diameter and of 3 mm length, were prepared from a 6 mm thick hot rolled strip. The specimens were encapsulated in quartz tubes and were evacuated to 10^{-6} mbar. After they had been normalised for 24 hr at 1000°C, they were aged from 5 to 500 hr at 550°C. The cylindrical notched specimens were introduced into a UHV chamber of the spectrometer, being cooled to about −120°C, the specimens were fractured by impact. The newly-formed surface was imaged by a scanning electron microscope (SEM). The Auger spectra were taken from as many intergranular fractures as possible and the results were averaged.[12]

The specimens for surface segregation were prepared from a hot rolled strip of 2.5 mm, descaled, decarburized and, after intermediate annealing (900°C, 1 hr, dry hydrogen), cold rolled to the final thickness of 0.5, 0.2, and 0.1 mm with a cold deformation of 60%. Specimens were recrystallized *in-situ* during AES measurements in UHV (4×10^{-10} mbar), as well as in a tube furnace in an argon atmosphere.

The grain orientation was determined by the etch pitting method.[13,14] The specimens with known orientation were heated to 900°C for 10 min and cooled down to room temperature. These were then sputter-cleaned and annealed in a temperature range of 450 to 1 000°C. The temperature was increased in steps of 50°C every 15 min and the AES spectra were recorded *in-situ* every 3.5 min. For the kinetics studies, the specimens were heated to a certain temperature, sputtered to a clean surface and exposed to the same temperature for different periods of time.

The X-ray diffraction method was used for texture measurements. A goniometer using MoKα radiation was applied and the (200), (110) and (211) pole figures were performed. Additionally, orientation distribution functions (ODF) were calculated and texture fibres were plotted. The textures were measured on the surface and

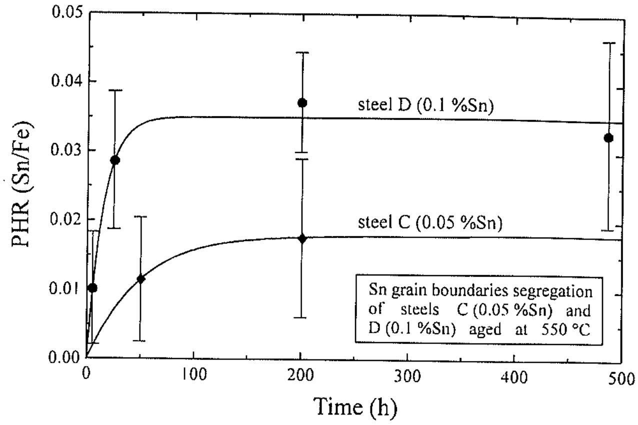
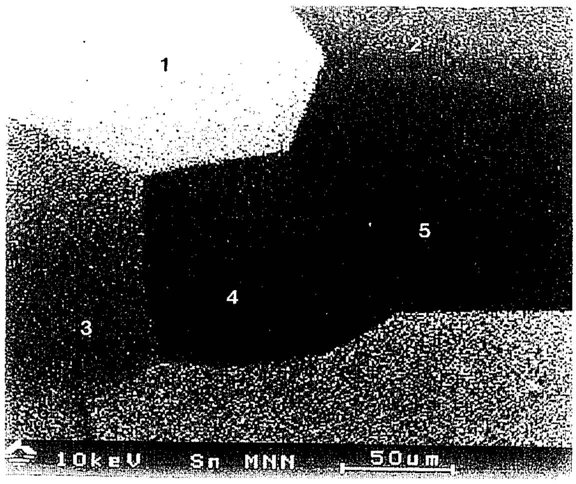


Fig. 1. Peak height ratio (PHR) between the dominant $Sn(M_5N_{45}N_{45})$ and the $Fe(L_3M_{23}M_{54})$ Auger transitions at the kinetic electron energy of 430 eV and 651 eV, respectively, in dependence of different ageing times.



Grain	1	2	3	4	5	6
PHR Sn/Fe	0.40	0.23	0.29	0.30	0.31	0.40
Orientation	(344)	(144)	(118)	(133)	(025)	(236)

Fig. 2. Scanning Auger micrograph (SAM) of Sn $(M_5N_{45}N_{45})$ Auger transition with a legend of grain orientation and appertaining PHRs Sn/Fe.

in the middle plane of a 0.5 mm thick cold rolled steel sheet after had been recrystallized at 840°C for 35 min in argon.

3. Results and Discussion

Sn added into experimental steels was in the range of solubility in α-Fe at all examined temperatures but it was below the detection limit of AES. After the specimens were exposed to a higher temperature, Sn enriched the surface, grain boundary and interfaces due to equilibrium segregation and its segregation were detectable by AES. All the AES spectra were normalised to $Fe(L_3M_{23}M_{54})$ Auger transition at the 651 eV kinetic energy.[11]

The equilibrium grain boundary segregation of Sn was attained after annealing the specimen alloyed with 0.1 and 0.05% Sn for approximately 100 hr at 550°C (**Fig. 1**). The scattering of results was rather large due to the strong dependence of Sn segregation on grain boundary character.[15] Steel alloyed with 0.05% Sn had much less

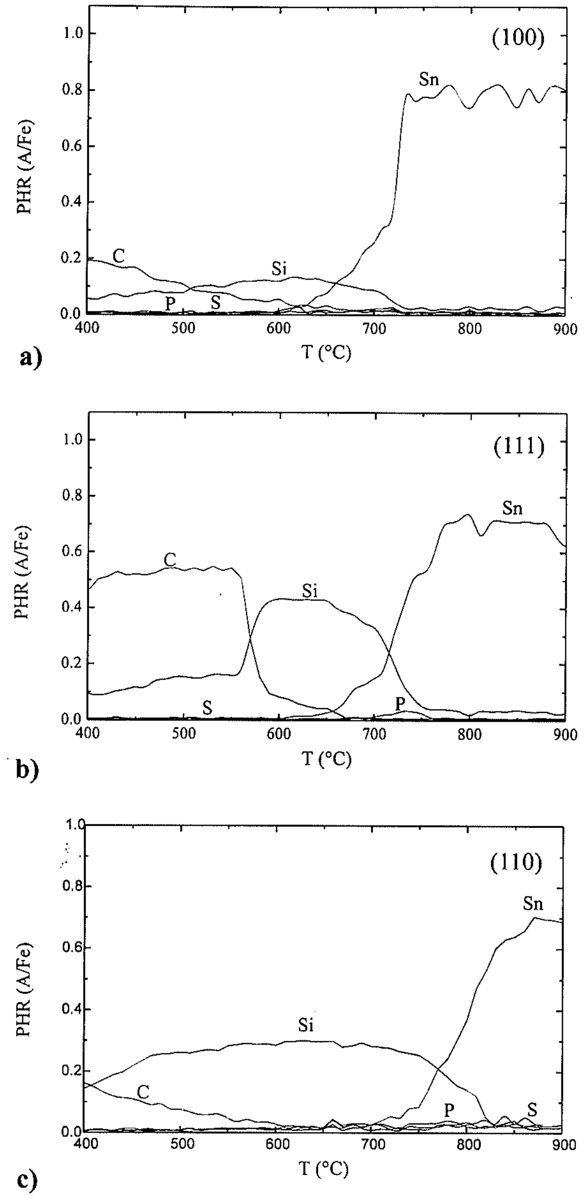


Fig. 3. Temperature dependence of surface segregation of C, Si, P, S and Sn of electrical steels alloyed with 0.05% Sn recorded on (a) (100), (b) (111) and (c) (110) oriented grain.

intergranular facets.

Figure 2 shows a SAM image of electrical steel surface heated to 800°C for 10 min. A different amount of segregating Sn on different crystallographically oriented grains can be noticed. A different grain orientation provided different sites for segregated Sn atoms. By comparing PHRs Sn/Fe among different specimens one should take care of the so called channelling effect especially due to the fact that Auger iron signal is very sensitive to the angle of sample surface and analyser axis.[16]

The temperature dependence of surface segregation of alloying and tramp elements was studied on a non-oriented electrical steel alloyed with 0.05% Sn on different grain orientations—(100), (111) and (110)—respectively; **Figures 3(a)**, **3(b)** and **3(c)**. To understand the temperature dependence behaviour of surface segregation, the results obtained on binary alloys should be considered.[17] At lower temperatures (~400°C), C segregated to the surface due to very high diffusion coefficient in comparison to Si and P, although the bulk concentration was at very low 15 ppm. At higher temperatures, C atoms were displaced by Si atoms.[18] The P and S atoms displaced the silicon at higher temperatures.[17] Their bulk diffusion coefficient was rather low, but their segregation enthalpy was very high, so Sn started segregating significantly above 600°C. The explanation of shift of Sn segregation curve to lower temperature on (100) oriented grain compared to (111) and (110) oriented grain might occur due to differences in C and Si segregation. On the (100) oriented grain, half of the monolayer of carbon atoms coverage was approached while on the (111) orientation a graphite was detected by AES measurement. Grabke *et al.*[19] observed the same behaviour of C segregation on these different orientations. Also the difference in thicknesses of silicon layers among grains with low lattice index might define the temperature dependence of Sn segregation.

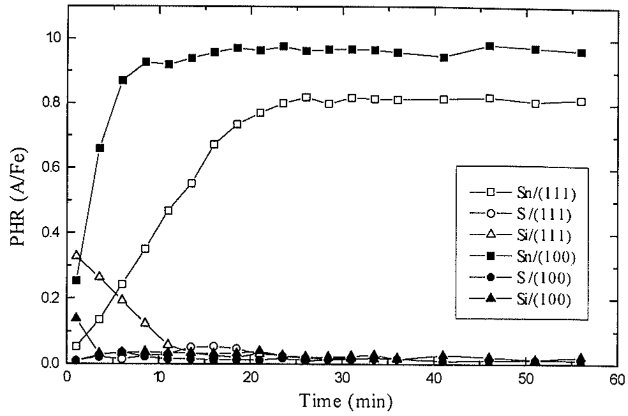


Fig. 4. Sn, Si and S surface segregation kinetics for non-oriented electrical steel alloyed with 0.1% Sn measured on (100) and (111) oriented grains.

The kinetics study confirmed the orientation dependence of Sn surface segregation as well as thickness of segregated layer. **Figure 4** shows the kinetics of Sn, Si and S surface segregation of non-oriented electrical steel alloyed with 0.1% Sn. Our measurements show that Sn surface coverage depends on Sn bulk concentration and Θ value approached one for (100) and (111) orientation. Θ is the ratio between the surface concentration and saturation coverage of segregating elements.

The textures of 0.5 mm thick electrical steels with 0.05 wt% Sn and without Sn were measured on the surface and in the middle plane after the half of the steel sheet thickness was removed. This was done in order to find out the influence of surface and grain boundaries segregated Sn on texture development. The orientation distribution functions (ODF) $f(g)$ were calculated from the (200), (110) and (211) pole figures. From the pole figures (200) (**Fig. 5**) which represent the texture information on $\{001\}$ intensity it was shown that most of the grains have an orientation close to cube texture $\{001\}\langle 100\rangle$ with the deviation angle of 10 degrees. Therefore the textures were presented as α, γ and η fibres. The η fibre represents $\langle 100\rangle$ direction parallel to the

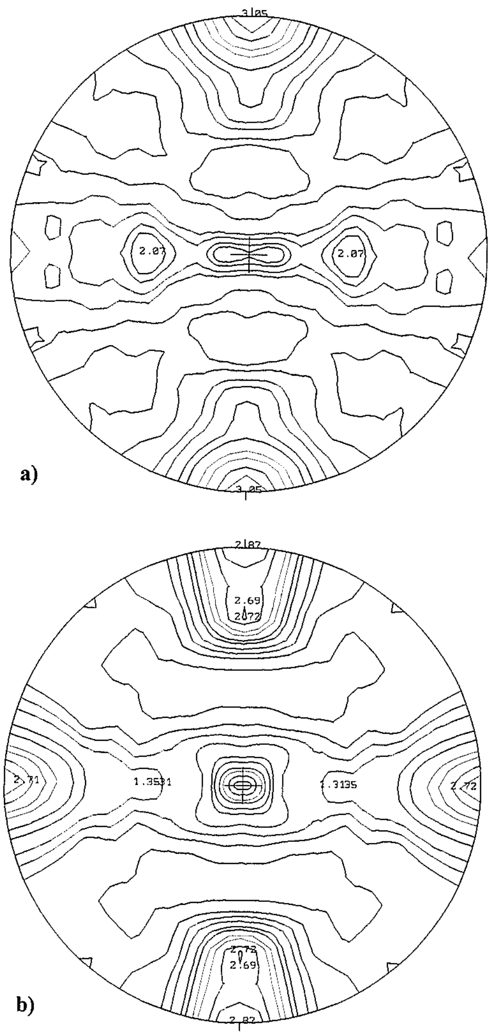


Fig. 5. Computed pole figure (200) of recrystallized texture for electrical steels measure on the surface (a) without Sn and (b) alloyed with 0.05% Sn.

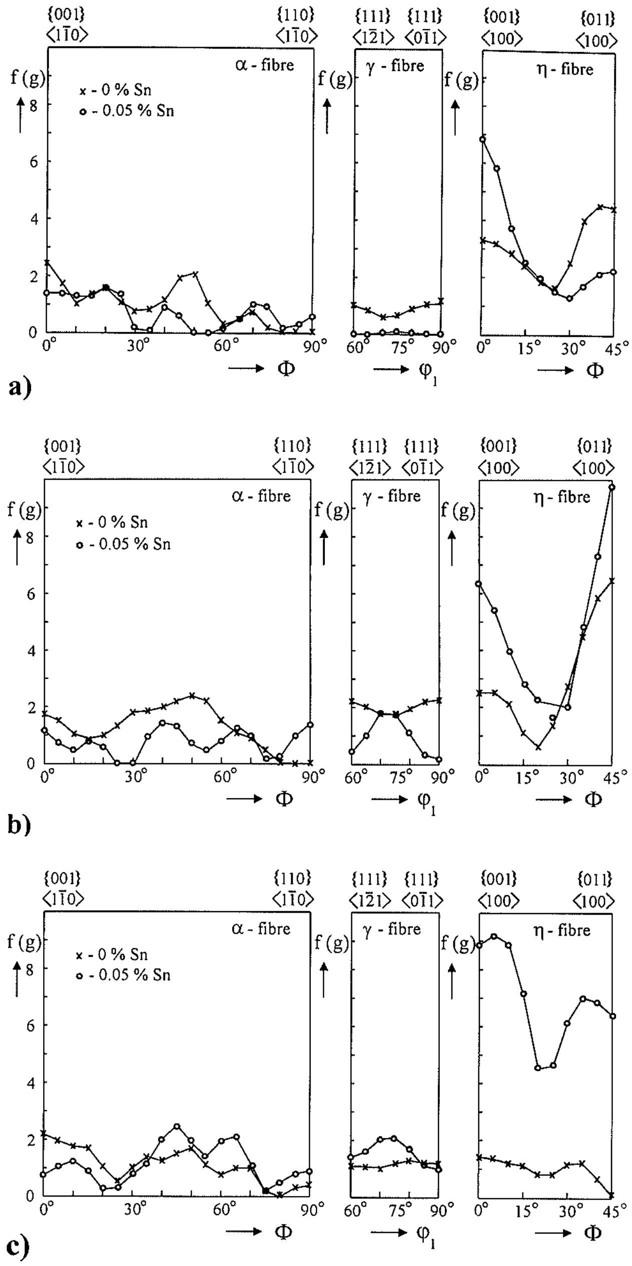


Fig. 6. Fibre diagram of recrystallized texture for electrical steels measured (a) on the surface and (b) in the middle plane and (c) in the middle plane after the specimens has previously been aged for 25 hr at 530°C.

rolling direction with {001}⟨100⟩–{011}⟨100⟩. When Euler angle Θ is zero intensity $f(g)$ of η fibre is proportional to the volume fraction of {001} grains with ⟨100⟩ direction parallel to the rolling direction. On the surface (**Fig. 6(a)**) an increase of {001}⟨100⟩ texture in the steel with 0.05% Sn was observed compared to steel without Sn, partly due to the {011}⟨100⟩ texture. At the same time {111} component of the texture was diminished nearly to zero. The similar results were obtained in the middle plane of the steel sheet (Fig. **6(b)**). Presence of Sn in the steel increase {001}⟨100⟩ and {011}⟨100⟩ textures, but the diminution of {111} texture component is slightly less pronounced. In Fig. **6(c)** texture fibres in the middle plane of steel sheet is shown after it had previously been aged for 25 hr at 530°C to increase the grain boundary segregation. The Sn grain boundary enrichment had an influence on texture development. η fibre (Fig. 6(c)) shows a strong increase of {001}⟨100⟩ and {011}⟨100⟩ textures. At the other hand the ageing of electrical steel without Sn at the temperature of 530°C has the consequence of reduction of {001}⟨100⟩ texture and the diminution of {011}⟨100⟩ texture nearly to zero. Texture measurements show an increase of Goss and cubic-{011}⟨100⟩ textures of steel alloyed with 0.05% Sn in the part of orientations described by α, γ and η fibres. The study of whole volume fraction of {001}⟨uvw⟩ texture is in progress and will be presented in the separate paper.

Sn surface segregation advantageously promotes growth of (100) oriented grains by a selective diminution of the surface energy. At the same time, Sn grain boundary segregation selectively changes grain boundary mobility of certain grain boundary type[20] by which the texture of material is determined.[21]

4. Conclusions

The grain boundary and surface segregation of Sn in non-oriented electrical steels were determined. Maximum equilibrium segregation on the surface for steel alloyed with 0.05% Sn was reached at 800°C and approached for majority of orientations the one monolayer. The Sn grain boundary segregation was found. An equilibrium grain boundary segregation was reached after the specimens were aged above 100 hr at 550°C. The tendency for Sn surface segregation was much higher compared to the grain boundary segregation.

During the recrystallization Sn atoms segregated on the surface and also at the grain boundary and so decreased the surface energy of crystal grains selectively and also selectively increased the mobility of some grain boundaries. By alloying the electrical steel with 0.05% Sn, a positive effect on the texture development has been achieved.

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