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Sn Influence on the Recrystallization of Non-Oriented Electrical Sheet

Vpliv Sn na rekristalizacijo neorientirane elektro pločevine

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During the recrystallization microalloyed tin in non-oriented silicon steel segregates to the surface and grain boundary and as a surface active element selectively decreases the surface energy of grains, planes of which (100) lie parallel to the surface sheet. This phenomenon can be used to achieve non-oriented electrical steel with improved electromagnetic properties. Auger electron spectroscopy was used to measure the grain boundary and surface segregation of tin in non-oriented electrical steels. The grain boundary segregation of the specimens, which were previously aged at 550°C for different times and were fractured in UHV conditions, was measured. The segregation temperature dependence and its kinetics were followed in polycrystalline specimens in the temperature range from 400°C to 900°C on the grains of known orientations: (100), (111) and (110). In spite of fact that the grain boundary segregation is much smaller compared with surface segregation, both might have an influence on recrystallization and on texture development in electrical steel. The textures of electrical steels were measured by X-ray texture goniometer. The results were presented as orientation distribution functions. The selective grain growth can be achieved by controlled surface segregation by which the electrical properties of non-oriented electrical steel are improved. The best results were obtained by alloying it with 0.05 wt.% Sn.

Key words: non-oriented silicon steel, tin, surface and grain boundary segregation, recrystallization, texture

Kositer, mikrolegiran v neorientirani elektro pločevini, pri rekristalizaciji segregira na površino in meje zrn in kot površinsko aktivni element selektivno zmanjša površinsko energijo zrn, katerih ravnine (100) ležijo vzporedno s površino pločevine. Ta pojav lahko izkoristimo za izdelavo neorientirane elektro pločevine z izboljšanimi elektromagnetnimi lastnostmi. S spektroskopijo Augerjevih elektronov smo zasledovali segregacijo po mejah zrn in na površini neorientirane elektropločevine. Segregacijo po mejah zrn smo merili na vzorcih, ki so bili predhodno starani na temperaturi 550°C različno dolgo in prelomljeni v pogojih UVV. Tudi temperaturno odvisnost segregacije in njeno kinetiko smo zasledovali na polikristalnih vzorcih, v temperaturnem območju od 400°C do 900°C, na zrnih znanih orientacij: (100), (111) in (110). Kljub temu, da je segregacija po mejah zrn veliko manjša od segregacije na površini, pa imata verjetno obe vpliv na rekristalizacijo in tako na razvoj teksture elektro pločevine. Teksturiranost elektro pločevin smo določili z rentgenskim goniometrom. Rezultati so predstavljeni z orientacijskimi porazdelitvenimi funkcijami. S kontrolirano površinsko segregacijo dosežemo selektivno rast zrn, kar izboljša električne lastnosti neorientirane elektro pločevine. Najboljše rezultate smo dosegli pri legiranju z 0.05 mas.% Sn.

Ključne besede: neorientirana elektro pločevina, kositer, površinska segregacija in segregacija po mejah zrn, rekristalizacija, tekstura

1 Introduction

Recrystallization, corrosion, adsorption, catalysis, surface diffusion, adhesion, sintering and some other processes are decisively depended of chemical composition and structure of surface. On the other hand the mechanical properties and the corrosion resistivity of metals and alloys are greatly influenced by the atomic composition of grain boundaries and interfaces[1].

The chemical composition of surfaces and grain boundaries 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 boundaries. 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[2].

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[3-9]. Tin, when added in the range of a 0.02-0.1 wt%, can improve magnetic properties, though it is not desirable in steel[10]. During the recrystallization process, tin segregates at the grain boundaries 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 space 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 tin in non-oriented electrical steel alloyed with 2 wt.% Si and 1 wt.% Al and different contents of tin (0.025, 0.05 and 0.1.wt.%) were determined. The temperature dependence and the kinetics of surface segregation were studied with the emphasis on orientation dependence. The correlation

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between tin segregation and texture development was ascertained. The segregation of tin during the recrystallization increased the grain growth of (100) grains lying in the plane of the sheet and in the same time decreased the growth of (111) grains.

2 Experimental

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**.

Table 1: Chemical composition of steels in wt.%
Tabela 1: Kemijska sestava preiskovanih jekel v mas.%

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

The resulting ingots of about 15 kg weights were hot rolled, at a starting temperature of 1200°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 two hours at 840°C.

Segregation was studied "in situ" using Auger Electron Spectroscopy - AES. The tin 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.

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 hours at 1000°C, they were aged from 5 to 1000 hours 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[12-13].

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 hour, 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 secondary recrystallized in-situ during AES measurements in UHV (10^{-10} mbar), as well as in a tube furnace in an argon atmosphere.

The grain orientation was determined by the etch pitting method[14,15]. The specimens with known orientation were heated to 900°C for 10 minutes and cooled down to room temperature. These were then sputter cleaned and annealed in a temperature range of 450°C to 1000°C. The temperature was increased in steps of 50°C every 15 minutes and the AES spectra were recorded in-situ every 3.5 minutes. 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.

3 Results and discussion

Tin 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 higher temperature tin enriched the surface, grain boundaries and interfaces due to equilibrium segregation and its segregation were detectable by AES. All AES spectra were normalised to $Fe(L_3M_{23}M_{54})$ Auger transition at the 651 eV kinetic energy[11].

3.1 Grain boundary segregation

The equilibrium segregation of tin was attained after annealing the specimen alloyed with 0.1% Sn for 200 hours at 550°C (**figure 1**). Considering that tin is equal distributed on both fractured sides, it was estimated a 7% tin monolayer at grain boundaries. The scattering of results was rather large due to the strong dependence of tin segregation to grain boundary orientation[12,16]. Steel alloyed with 0.05% Sn had much less intergranular facets. Evaluated equilibrium segregation was smaller than in steel alloyed with 0.1% Sn. Detailed AES analyses of

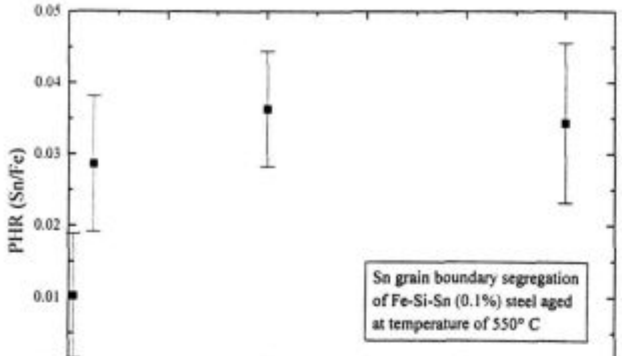
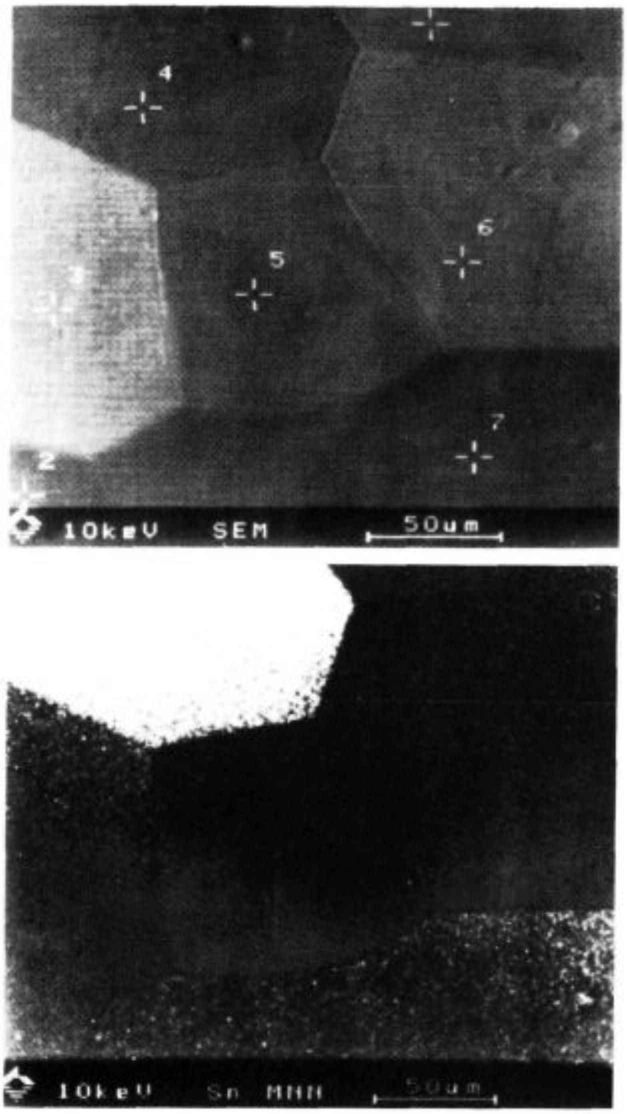


Figure 1: Peak height ratio (PHR) between the dominant $Sn(M_5N_{45}N_{45})$ and the $Fe(L_3M_{23}M_{54})$ Auger transitions at the kinetic electron energy of 430 eV and 651, respectively, in dependence of different ageing time
Slika 1: Razmerje višine vrhov (RVV) med $Sn(M_5N_{45}N_{45})$ in $Fe(L_3M_{23}M_{54})$ Augerjevimi prehodi pri kinetični energiji elektronov 430 eV in 651 eV v odvisnosti od časa staranja

free surfaces between inclusion (AlN, Al_2O_3) and matrix clearly indicated that the considerable tin segregation occurs at the interface. The degree of tin segregation at the interface is five times larger than at the grain boundaries.

3.2 Surface segregation

Scanning Auger image (SAM) of non-oriented electrical steel heated to 800°C for 10 minutes was taken. The orientation of individual grains was determined by the method described in our previous publication[15]. **Figure 2** shows SEM and SAM images of surface. A different surface tin segregation on different grains was noticed. Different grain orientation provided different sites for segregated tin atoms. By comparing PHRs Sn/Fe among different specimens one should take care of 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[13].



Grain	1	2	3	4	5	7
PHR Sn/Fe	0.23	0.31	0.29	0.40	0.30	0.40
Orientation	(144)	(025)	(118)	(111)	(5913)	(236)

Figure 2: a) SEM image of 0.2 mm thick non-oriented electrical steel alloyed with 0.1% Sn, **b)** a SAM image Sn-MNN transition recorded on a same area, **c)** table shows a relation between grain orientation and Sn PHR

Slika 2: a) SEM posnetek površine neorientirane elektro pločevine legirane z 0.1% Sn, **b)** SAM posnetek Sn MNN prehoda posnet na istem mestu, **c)** tabela podaja zvezo med orientacijami zrn in RVV

Figure 3 shows the temperature dependence of surface segregation of alloying and tramp elements of non-oriented electrical steel alloyed with 0.05% Sn on different grain orientations - (001) and (111) - respectively. Electrical steel is a multicomponent system and so very complicated to understand the temperature dependence behaviour of surface segregation, therefore the results obtained on binary alloys should be considered[17]. The relations of the surface segregation enthalpies and volume diffusivities are as follows: $\Delta H^0_{Si} < \Delta H^0_C < \Delta H^0_P$ and $D^C_V >> D^{Si}_V > D^P_V$[17].

At lower temperatures (~300°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 co-

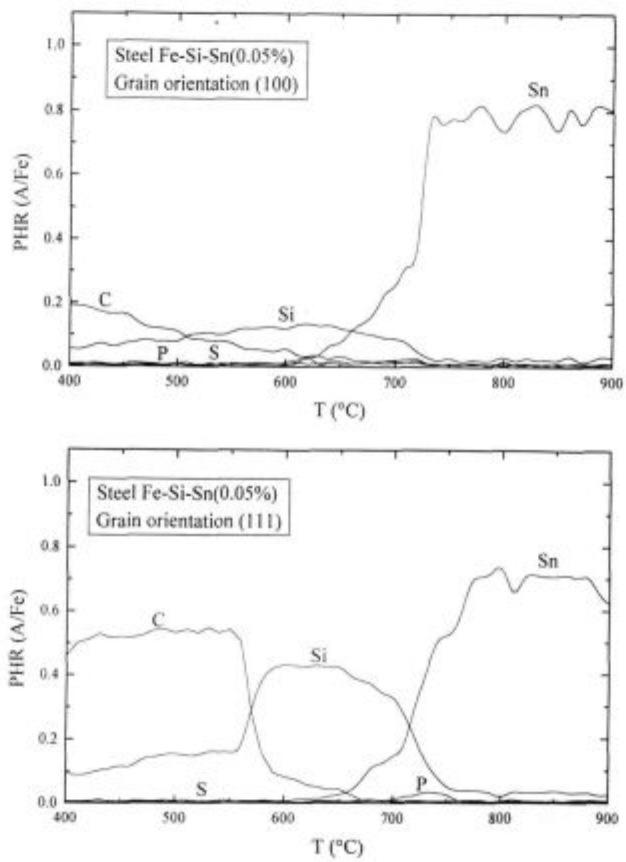


Figure 3: Temperature dependence of surface segregation of C, Si, P, S and Sn of electrical steels alloyed with 0.05% Sn **a)** (100) oriented grain and **b)** (111) oriented grain

Slika 3: Temperaturna odvisnost površinske segregacije C, Si, P, S in Sn za elektro pločevino legirano s 0.05% Sn **a)** zrno (100) orientacije in **b)** zrno (111) orientacije efficient was rather low, but their segregation enthalpy was very high, so tin started segregating significantly above 600°C. The kinetics study confirmed the orientation dependence of tin surface segregation as well as thickness of segregated layer.

It was ascertained[11] that on (100) and (111) faces, the segregation of tin was beyond one monolayer, due to the strong decrease of surface energy. On a surface with a (111) orientation FeSn intermetallic compound of one unit cell thickness was found. Our measurements showed that tin surface coverage dependence on tin bulk concentration and Θ value approached one for (100) and (111) orientation.

3.3 Texture measurements

The textures of 0.5 mm thick electrical steels were measured on the surface and in the middle plane after the half of the sheet thickness were removed. Taking into account that approximately six crystal grains constitute the 0.5 mm thick cross-section steel sheet and the fact that penetration depths of x-rays were less than 0.1 mm one might conclude that there were analysed some grains whose growth was not affected by the surface segregated tin. Nevertheless, there were not more than 10% of such grains.

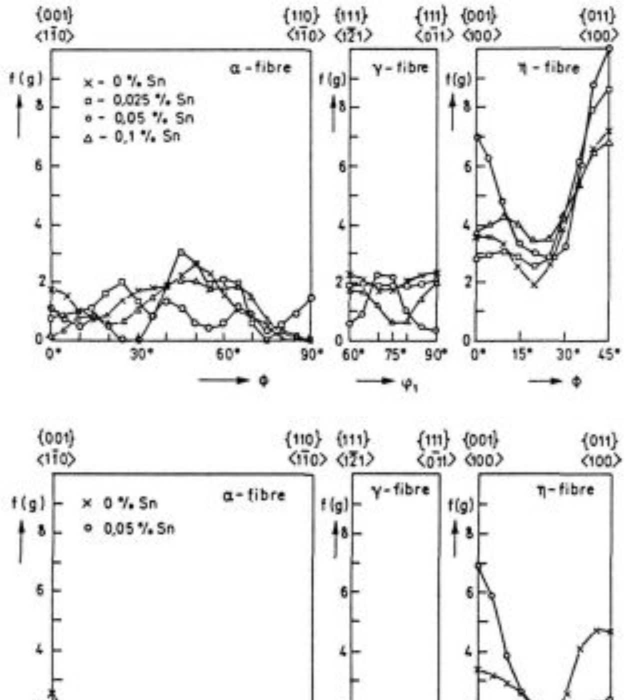


Figure 4: Fibre diagram of recrystallized texture for electrical steels measured **a)** in the middle plane and **b)** on the surface

Slika 4: Diagram vlaken rekristalizacijske teksture za elektro pločevine merjen **a)** v sredini in **b)** na površini

The orientation distribution functions (ODF) f (g) were calculated from the (200), (110) and (211) pole figures. The textures were presented as α, γ and η fibres. **Figure 4** shows texture fibres in the middle plane (a) and on the surface (b) of electrical steels alloyed with and without tin. The volume fraction of grains with the (100) planes measured on the surface and in the middle plane increased to the order of two compared the steel without tin with the steel alloyed with 0.05% tin. Less hard magnetic orientations were found on the surface. Texture development during the recrystallization was. Steel alloyed with 0.05% Sn, which had previously been aged 25 hours at 550°C, compared to the steel without tin, showed an increase of (100) planes parallel to the rolling direction to the order of three.

4 Conclusions

Grain boundary and surface segregation of tin in non-oriented electrical steels were determined. Maximum equilibrium segregation on the surface were reached at 750°C and approached for majority of orientations one monolayer. One iron atom on the surface corresponds to one segregating tin atom. It was proved that thickness of tin segregating layer depended of tin bulk concentration. Tin segregation was controlled by bulk diffusion; thus, the equilibrium enrichment of tin on the surface was slightly faster for a specimen with higher tin contents. The tendency for tin surface segregation was much higher compared to grain boundary segregation. At equilibrium grain boundary segregation only 7 and 3% of tin atoms were found on a grain boundary for steel alloyed with 0.1 and 0.05% Sn, respectively.

Different crystallographic orientations can provide different sites for segregating tin atoms. During the recrystallization tin atoms segregated on the surface and also at the grain boundary and so decreased the surface energy of crystal grains selectively.

The obtained results confirmed our supposition. Tin segregation took place during the recrystallization and decreased the surface energy of crystal grains with (100) and (110) plains parallel to the sheet surface. Textures represented as sections through three-dimensional orientation distribution space in fixed directions showed that volume fraction of magnetically soft grains increased for two times compared to steel without tin. Slightly better textures were obtained near the surface than in the middle plane of 0.5 mm thick steel sheet. The best results were obtained for steel alloyed with 0.05% Sn. We suppose that only a certain level of segregation promotes desired selective grain growth.

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