

## NANOSCALE PHASES ON SURFACE FE-6SI MAGNETIC SHEETS

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### Abstract

Analysis of the nanoscale phases which appear on the surface Fe-6Si samples were carried out after the various treatments - grinding and etching, annealing, and water jet abrasion. The basic information on structure, chemical and phase composition was obtained by X-Ray Powder Diffraction (XRD), Scanning Electron Microscopy with EDX, Glow Discharge Optical Emission Spectrometry (GDOES), Mössbauer Spectroscopy and X-ray Photoelectron Spectrometry (XPS). The results show high stability of the surface phase composition after the mechanical and heat treatments. Results obtained from the surface analysis in micrometer depth (XRD, EDX, GDOES) do not show any changes after the different treatments. Iron oxides were detected in XPS and conversion electron Mössbauer spectra (CEMS) which analyze the surface composition in a nanometer scale. In addition to, fine changes in atomic ordering on the surface can be observed after mechanical and heat treatments in the CEMS spectra.

**Keywords:** Fe-Si alloy, surface modification, nanostructure

## 1. INTRODUCTION

Silicon steel is widely used in electrical industry as soft magnetic materials in several applications like core transformers, engines, motors, etc. The increasing content of Si improves magnetic properties, but on the other hand is also reason of poor workability of these materials [1]. Consequently, many different methods of preparation have been developed e.g., a special thermochemical routing [2], hot dipping process followed by diffusion annealing [3], chemical vapor deposition [4] or mechanical alloying [5, 6].

Our samples were prepared as conventional preparing method (polishing, etching, annealing) so unorthodox method by pulsating water jet, where materials is disturb by individual drops of water with high kinetic energy [7, 8]. The aim of this work was to investigate changes in surfaces of the samples of Fe-Si alloy (6 wt% of Si) after different treatments.

## 2. EXPERIMENTAL DETAILS

### 2.1. Materials

The samples 10 x 10 x 3 mm<sup>2</sup> and 30 x 30 x 3 mm<sup>2</sup> were cut from sheet of hot-rolled Fe-Si alloy [9] using spark erosion. Surface of all samples were ground on SiC paper to 2500 grid and polish by colloidal silica. Sample No. 1 was etched in 2% Nital. Sample No. 2 was annealed at vacuum (10<sup>-3</sup> Pa) at 700°C for 70 hours. The surface of the sample No. 3 was prepared by high-speed water jet with the water jet type Hammelmann flat (nozzle diameter 2 mm and spraying angle 10°), the pulse rate 20.4 kHz, and working pressure 40 MPa. The stand off distance was 55 mm, traverse speed 2 mm/s, and with 10 transitions.

## 2.2. Methods

The surfaces of the samples were investigated by optical microscope (Neophot 32 by Carl Zeiss Jena) and scanning electron microscope Tescan LYRA 3 XMU FEG/SEMxFIB equipped with X-Max80 EDS detector for X-ray microanalysis and EBSD detector Nordlys by Oxford Instruments with Aztec control system.

The X-ray powder patterns were collected on X'Pert diffractometer and  $\text{CoK}\alpha$  radiation with qualitative analysis by HighScore® software and the JCPDS PDF-4 database. For a quantitative analysis HighScore plus® with Rietveld structural models based on the ICSD database was applied.

Depth profiling analysis were done by method Glow discharge optical emission spectrometry (GDOES) using GD-Profilier 2 instrument with the Quantum™ XP software (Horiba Jobin Yvon, France) operating in radio frequency at 13.56MHz.

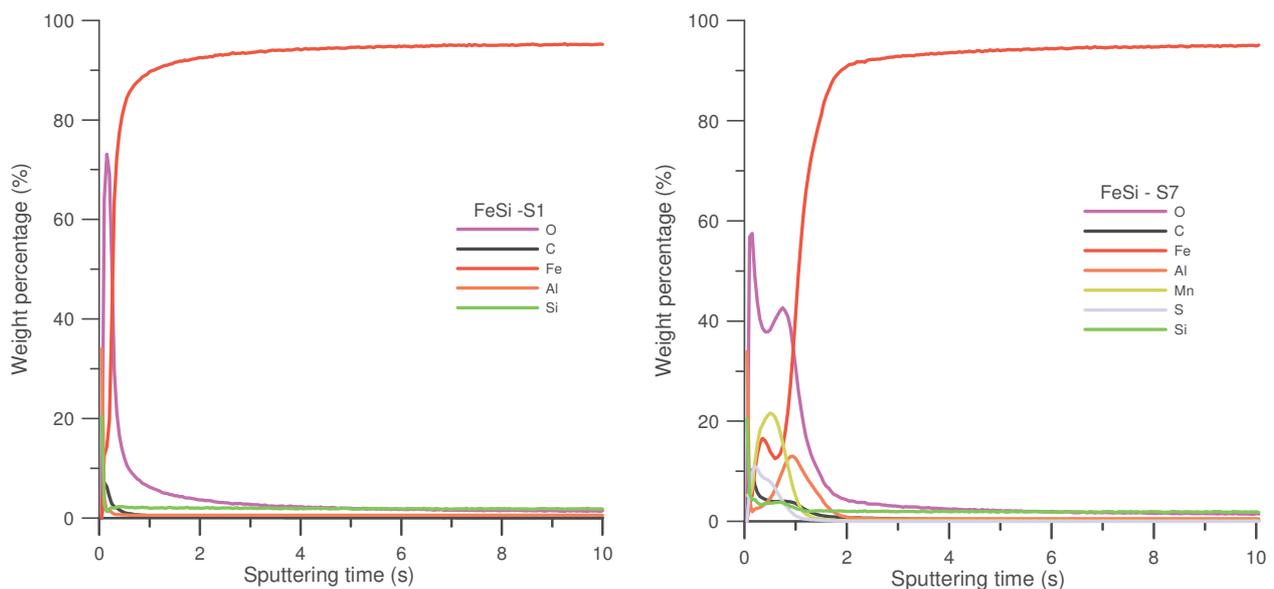
$^{57}\text{Fe}$  Mössbauer spectroscopy was carried out in scattering geometry with detection of 14.4 keV gamma radiation (MS) and conversion electrons (CEMS). The spectra were measured at room temperature and calibrated against  $\alpha\text{-Fe}$ . The computer processing of the spectra was done using CONFIT program package [10].

X-ray Photoelectron Spectroscopy (XPS) measurements were performed using monochromatic and non-monochromatic X-ray sources Al K-alpha. CasaXPS software was used for spectra processing and evaluation. Peak components fitting was performed using symmetric Gaussian (70%)-Lorentzian(30%) peaks and Shirley background.

## 3. RESULTS AND DISCUSSION

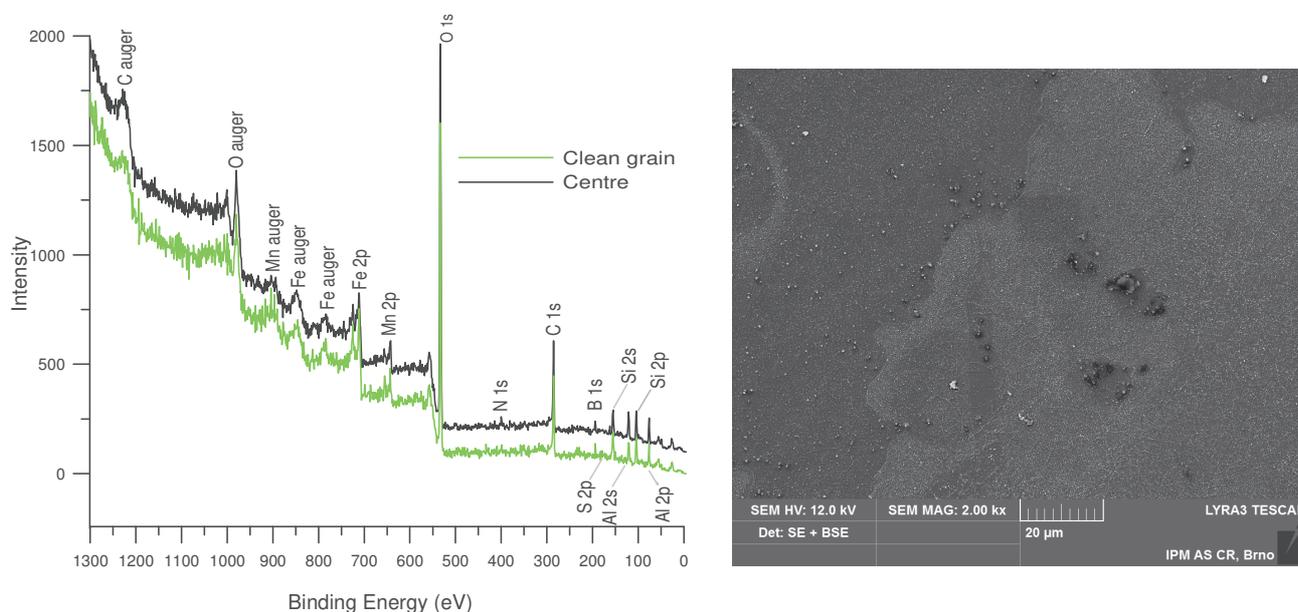
Chemical composition primary material was determined as 93.8 wt% Fe and 6.1 wt % Si by SEM/EDX observation. Small amounts of Al, Mn, and S were detected by GDOES and EDX analyses. They affected surface of the sample No. 2 annealed in vacuum. These impurities originated from the production of the original material sheet. Their detection was mentioned already in [9].

XRD analysis of the sample No. 2 show only  $\alpha\text{-Fe}$  phase and small amount MnS,  $\alpha\text{-Fe}$  only was observed in the samples No.1 and 3.



**Figure 1** Depth profiles made by GDOES for sample No.1 (left) and No. 2 (right)

An increasing in the contents of Mn, Al, and S in the surface layer of the sample No. 2 were also noted during GDOES profile analysis (**Figure 1**). The detailed EDX analysis confirms presence of Al and Mn in sample No. 2. The concentrations of the elements differ at different places but the places with the same structure have also very similar chemical composition.



**Figure 2** XPS spectra for two different place of the surface layer sample No. 2 (left). SEM image with two different structures observed on sample No. 2 (right).

Sample No. 2 and 3 were investigated by X-ray Photoelectron Spectroscopy (XPS). Sample No. 2 was degassed at 333°C for 10 min before analysis. This sample was inspecting with photoelectron microscope and two points on the sample were selected for measurements - labeled as “centre” and “clean grain”. The surface of the sample No. 3 was cleaned by Ar<sup>+</sup> at room temperature.

The comparison of the spectra for two different places on the sample No. 2 is shown in **Figure 2**. The peaks of iron, oxygen, carbon, aluminium, silicon, manganese, nitrogen, sulfur and boron were detected there.

According to the peak position of ionic states of Fe shows to the presence of species Fe<sup>0</sup> and Fe<sup>3+</sup>. The peak Fe at position 707.5eV is connected with Fe metal states. The Fe 2p<sub>3/2</sub> and Fe 2p<sub>1/2</sub> photoelectron peaks are observed around 710.9 and 724.24eV, which correspond to peaks for Fe<sup>3+</sup> [12, 13].

The O1s peak is move to higher binding energy (533 eV) that shows to presence metal oxide that was identified as Fe<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> according to position Si2p, B1s and Al2p peaks [14].

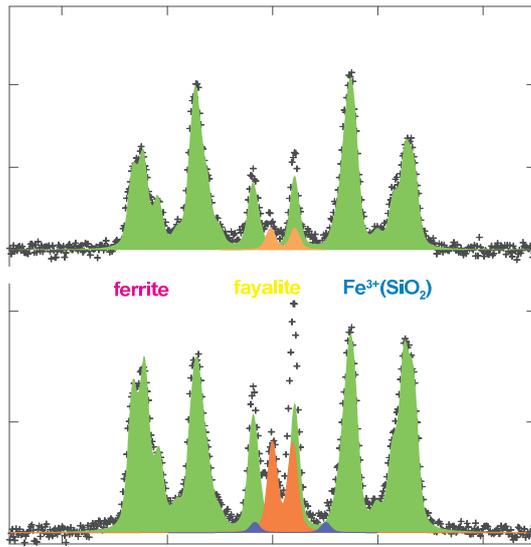
The Mn2p spectrum can be probably evaluated as MnS spectra, but XPS results for MnS are mentions rarely in literature [15]. This explanation has been supported by position of S2p peak at 161.9eV, which can be interpreted as sulfide.

The spectrum for the sample No. 3 has a lower quality in comparison with spectra for sample No. 2. Only peak for iron, oxygen, carbon and silicon were observed. The Fe 2p has maximum around 711.2eV and together with Fe3p correspond with Fe<sub>2</sub>O<sub>3</sub>. The Si2s peak has maximum around 153 eV and probably not correspond with oxide but could be identify as Fe<sub>2</sub>SiO<sub>4</sub> (153 eV) by NIST database [14].

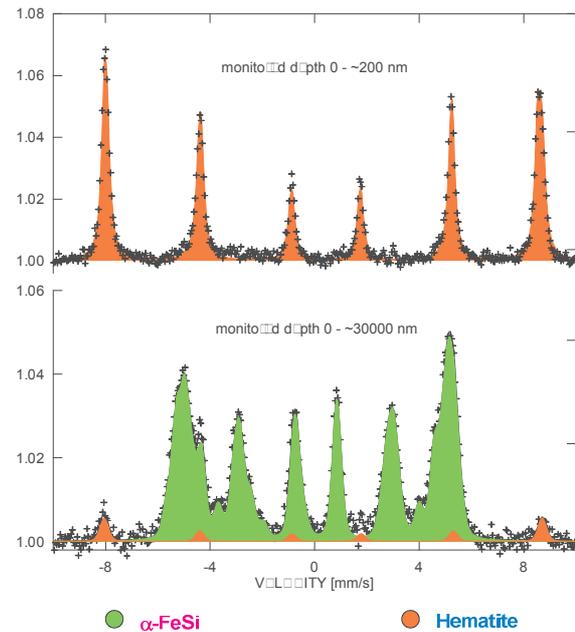
Basic information on surface phase composition (200nm in depth) was obtained from Mössbauer spectra taken by detection of conversion electrons (CEMS). Examples are shown in **Figure 3**. The thicker surface layer was investigated by Mössbauer spectra taken in scattering geometry with detection of 14.4 keV gamma rays

(MSBS) which scans a layer approximately 30 micrometer in depth. Comparison of the CEMS and MSBS spectra taken on the sample after the annealing at 700°C for 70 hrs in air is shown in **Figure 4**. Surface oxidation accompanied by formation of hematite with increasing its amount in the direction to free surface can be observed there.

From the data yielded from the CEMS spectra (**Table 1**) we can analyze the changes in the surface layer after annealing or abrasion by water jet. Following components of the spectra were obtained by the fitting procedure: (i) sextets representing bcc phase of Fe-Si and (ii) doublets representing iron ions in SiO<sub>2</sub> and fayalite



**Figure 3** CEMS spectra of the sample No. 1 with polished and etched surface (above) and the sample No.3 after abrasion by water jet



**Figure 4** Comparison of the CEMS and MSBS spectra of the sample No. 2 after the annealing at 700°C for 70 hrs in air

The components are characterized by their intensities (in atomic fraction of Fe) and hyperfine parameters - isomer shift (IS), quadrupole splitting/shift (QS) and hyperfine induction  $B_{hf}$  [16]. The phase analysis show that very low amount of the Fe<sup>3+</sup> in SiO<sub>2</sub> (represented by doublet with IS=0.39±0.02 mm/s) is present in the original and annealed sample surfaces. After abrasion by water jet its amount increases approximately two times and small amount (~0.01 a.f.) of fayalite appeared, which is represented by the doublet with IS=0.7±0.1 mm/s and QS=2.7±0.2 mm/s.

Distribution of the sextet intensities and the mean hyperfine induction  $\langle B_{hf} \rangle$  reflects amount and atomic ordering of Si atoms in the bcc  $\alpha$ -FeSi phase. It shows fine changes due to treatments of the samples. In comparison with random solid solution model we can estimate that a fine decrease in Si content in the surfaces occurs due to the annealing at 700°C for 70 hrs in vacuum and after the abrasion by water jet.

The ratio of the of the second to the first line intensities (areas) in sextets (R 2/1) refers to the mutual orientations of propagating gamma rays and orientations of magnetic moments [16]. The annealing at 700°C for 70 hrs in vacuum induced orientation of closing domains more parallel with surface. The abrasion by water jet causes a randomizing of orientation of magnetic moments at surface which can be caused by two factors - by the induced mechanical stresses and by the increase in the amount of oxide phases.

**Table 1** The results of the analyses of CEMS spectra (c = content for the component in atomic fraction a.f., R2/1 = ration of the second to first line areas in sextets, IS = isomer shift relative to pure  $\alpha$ -Fe, QS = quadrupole splitting/shift,  $B_{hf}$  = hyperfine induction,  $\langle B_{hf} \rangle$  = mean hyperfine induction)

Spectrum	c	R 2/1	IS [mm/s]	QS	$B_{hf}$	$\langle B_{hf} \rangle$
Sample No. 1: polished and etched surface						
S 1	0.32	1.12	-0.007	0.01	33.09	
S 2	0.39	1.12	0.023	0.03	30.67	
S 3	0.20	1.12	0.061	0.00	27.76	
S 4	0.07	1.12	0.106	0.24	23.45	
$\Sigma$ (S <sub>1</sub> ;S <sub>4</sub> )	0.98					30.38
D 1	0.02		0.268	1.11		
Sample No. 2: polished, etched, and annealed at 700°C for 70 hrs in vacuum ( $10^{-3}$ Pa)						
S 1	0.32	1.21	0.030	-0.01	33.21	
S 2	0.39	1.21	0.049	0.03	30.92	
S 3	0.20	1.21	0.108	0.02	27.80	
S 4	0.05	1.21	0.173	0.01	23.63	
$\Sigma$ (S <sub>1</sub> ;S <sub>4</sub> )	0.96					30.63
D 1	0.04		0.387	0.92		
Sample No. 3: polished, etched surface + abrasion by water jet						
S 1	0.31	0.74	0.024	-0.01	33.16	
S 2	0.38	0.74	0.059	0.01	30.62	
S 3	0.16	0.74	0.111	0.02	27.53	
S 4	0.04	0.74	0.165	-0.03	23.62	
$\Sigma$ (S <sub>1</sub> ;S <sub>4</sub> )	0.89					30.62
D 1	0.01		0.672	2.70		
D 2	0.10		0.380	0.77		
$\Sigma$ (D <sub>1</sub> ;D <sub>2</sub> )	0.11					

#### 4. CONCLUSION

The experimental results show differences in chemical, phase, and structure (atomic ordering) in the nanometer depth of the sample surfaces. After the grinding and etching a low amount of the  $Fe^{3+}$  in  $SiO_2$  was observed. After the annealing at 700°C for 70 hrs in vacuum presence of Mn, Al, and S based impurities (MnS,  $Al_2O_3$ ) together with  $Fe_2O_3$ ,  $SiO_2$  was detected. An important increase in the concentration of  $Fe^{3+}$  in  $SiO_2$  and small amount of fayalite was register on the surface treated by the water jet abrasion.

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