HRAES AND XPS STUDIES OF OXIDE LAYER FORMED ON ELECTRICAL STEEL

PREISKAVE OKSIDNE PLASTI NA ELEKTRO PLOČEVINI Z VISOKOLOČLJIVO SPEKTROSKOPIJO AUGERJEVIH ELEKTRONOV IN RENTGENSKO FOTOELEKTRONSKO SPEKTROSKOPIJO

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HRAES and XPS were used to investigate the electrical steel sample after a decarburization treatment. An oxide layer was found on the surface of the sample whose constituents as well as their chemical states were determined. Profile AES analysis of the sample's cross-section showed that composition of the oxide layer changed with depth. Elements present in electrical steel in minute concentrations were shown to form compounds in the oxide layer.

Keywords: HRAES, XPS, surface analysis, oxide layers, electrical steel

Vzorec elektropločevine po razogljičenju smo analizirali s pomočjo visokoločljive spektroskopije Augerjevih elektronov in rentgenske fotoelektronske spektroskopije. Ugotovili smo, da se na površini vzorca tvori oksidna plast in ji določili sestavo. Profilna analiza preseka vzorca je pokazala, da se sestava oksidne plasti spreminja z globino. Ugotovili smo, da elementi, ki so v osnovnem materialu prisotni le v sledeh, tvorijo spojine v oksidni plasti.

Ključne besede: HRAES, XPS, površinske analitske metode, oksidne plasti, elektro pločevina

1 INTRODUCTION

Oxide layer composition on the surface of the electrical steels is very important from the technological point of view. Normally, its composition reflects the manufacturing process. Non-oriented electrical steels may be alloyed by Si and Al in order to increase their electrical resistivity. Also, traces of elements, such as Cu and S (so called "tramp elements") and their compounds may be found in the final product due to the fact that electrical steels are manufactured from the scrap steel.

In the course of the manufacturing process electrical steel is hot rolled, then cold rolled and finally decarburized and recrystallized in a gas mixture of N_2 + H_2 + $(H_2O)_g$. During the decarburization process a surface oxide layer is formed. This layer, apart from its principal components, often contains trace elements in various forms.

So far surface spectroscopies have been frequently used to study oxide layers on metal surfaces (e.g. [1], [2], [3]). In this work the results of the X-ray photoemission spectroscopy (XPS) investigation of the results combined with the Auger electron spectroscopy (AES) and scanning electron microscopy (SEM) are presented. This combination of techniques enables one to obtain information about the oxide layer, morphology and chemical constituents, across the layer and perpendicular to the surface. In present study subsurface layers were probed only by performing AES analysis of the sample's cross-section. A more detailed study with full depth pro-file analysis of the oxide layers is currently underway and will be published separately.

2 EXPERIMENTAL

In the course of the manufacturing process the electrical steel, used for preparing the samples, was alloyed with 2% of Si and 1% of Al and subsequently hot and cold rolled to produce sheets of 0.5 mm thickness. These were cut into platelets of approx. 50 mm × 15 mm. Decarburization and recrystallization was carried out under laboratory conditions by annealing the samples in a gaseous mixture of N_2 + H_2 + $(H_2O)_g$ with N_2 : H_2 ratio 75 : 25. Annealing was performed for 3 minutes at 840 °C, for 1 minute at 970 °C and without $(H_2O)_g$ in the mixture for 1 minute at 1040 °C. After this thermal treatment smaller platelets of approx. 10 mm × 15 mm were cut out to be introduced into the SEM/AES/XPS apparatus. Also, sample for AES analysis of the cross section was prepared by polishing lateral surface of one of the platelets.

VG Microlab 310F apparatus with base vacuum during the analysis below 10^{-9} mbar was used to image the surface of the samples as well as to record the AES and XPS spectra. The Auger spectra of the samples showed very intense carbon and oxygen peaks and Fe peaks of very low intensity. Therefore, prior to further analysis, the surface of the sample was cleaned by argon sputtering at 3 keV ion energy, 1 µAcm^{-2} current density, for 15 minutes in order to remove layers of adsorbed impurities
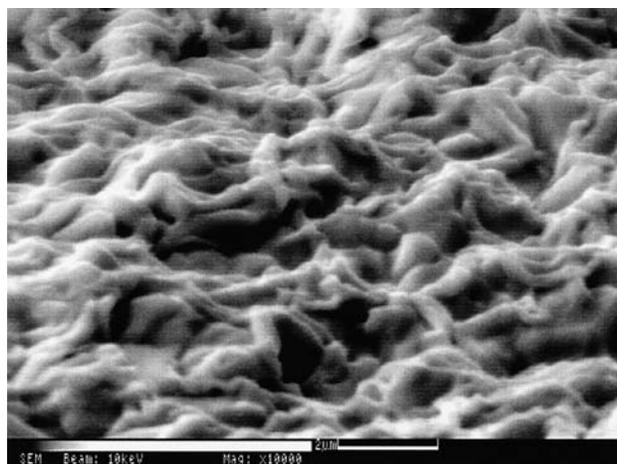
Figure 1: SEM image of the surface oxide layer
Slika 1: SEM posnetek površinske oksidne plasti
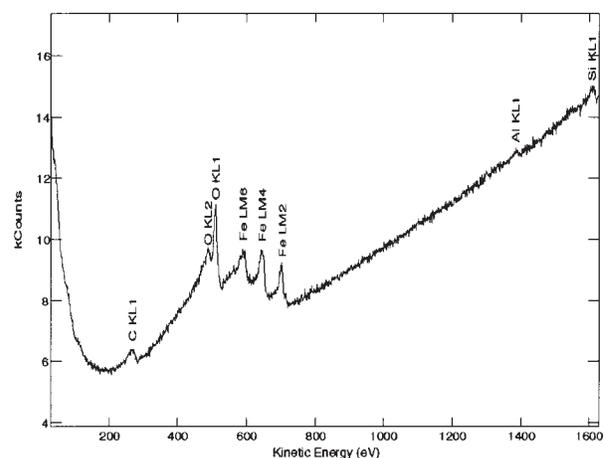
Figure 2: Survey AES spectrum of the area shown in Fig. 1
Slika 2: Pregledni AES spekter območja s slike 1

and to expose bare oxide layer that had been produced during the sample preparation process. AES measurements were performed at electron beam energy of 5 keV. Beam spot size in all modes of AES measurements was of the order of 50 nm. Al K_α at 1486.6 eV and Mg K_α at 1253.6 eV were used for XPS. Illuminated area during the measurement was about 3mm². Carbon contamination C 1s at 284.7 eV as measured on cleaned metallic sample was used for energy scale calibration. SEM images as well as AES and XPS spectra were processed by Eclipse Data System v2.1 software package. Linear combination of Gaussian and Lorentzian peak shapes with
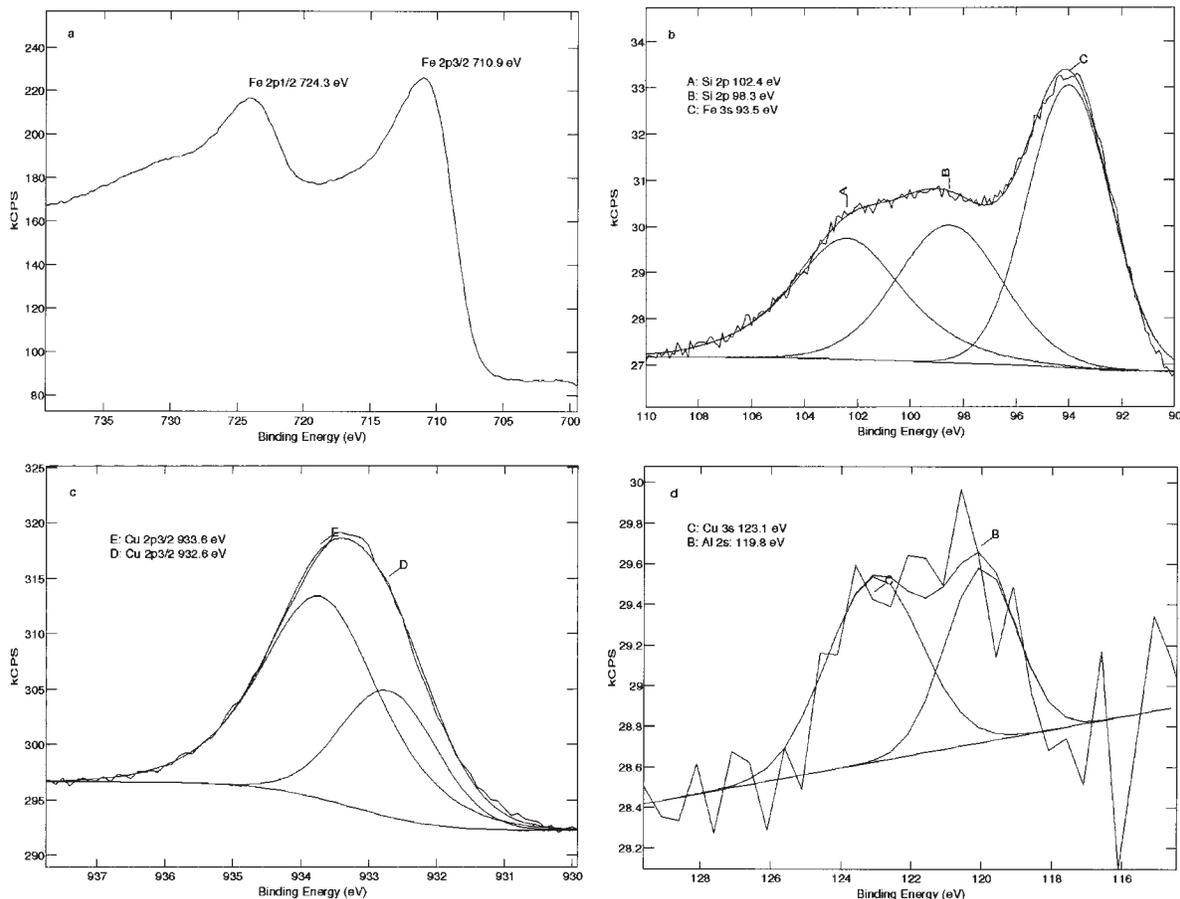
Figure 3: XPS spectra of the oxide layer surface; Fe 2p (a), Si 2p (b), Cu $2p_{3/2}$ (c), Al 2s (d)
Slika 3: XPS spektri oksidne plasti; Fe 2p (a), Si 2p (b), Cu $2p_{3/2}$ (c), Al 2s (d)

Shirley background subtraction was used for fitting peaks in XPS spectra. The only constraint was imposed on number of components if leaving it free resulted in unrealistically bad fit.

3 RESULTS AND DISCUSSION

A typical SEM image of the sample is shown in **Figure 1**. On the micrometer scale the surface is highly corrugated. Its chemical composition does not change significantly across the large area of the sample surface. A representative Auger spectrum shown in **Figure 2** shows clearly that an iron oxide is a dominant component of the layer. Note also a presence of the small peaks of C, Al and Si Auger electrons. XPS analysis of the layer enables us to determine which of several possible iron oxides has been formed during the sample preparation. In addition, it offers a possibility, to determine the chemical state of the alloying elements, Al and Si and trace elements, Cu in our case.

Figures 3a - 3d show the spectra for Fe, Si, Cu and Al. Where needed, spectra were fitted with peak components and they are also shown in Fig. 3. Al 2s was chosen for the analysis over more usually used Al 2p in order to avoid problems with overlapping Al 2p and Cu $3p_{3/2}$ peaks.

From the positions of the peaks in **Figures 3a - 3d** compared to the reference values [4, 5] it is clear that the oxide layer predominantly consists of Fe_2O_3. It is not likely to be an artifact caused by exposition of the sample to the air, since surface of the sample was cleaned by argon sputtering prior to the analysis. The Si 2p peak at 102.4 eV strongly indicates that layer also contains a small amount of Fe_2SiO_4. Also a shift of Fe $2p_{3/2}$ of only 0.1 - 0.2 eV towards lower binding energies with respect to its position if the oxide layer were pure Fe_2O_3 indicates low concentration of Fe_2SiO_4 in the oxide layer. This compound is expected in the oxide layer on the surface of the electrical steel alloyed with 2% of Si [6, 7, 8]. Its low content is somewhat surprising. It may be due to non-standard parameters of the decarburization thermal treatment [9]. There is also a component of Si 2p at 98.3 eV which can be most probably attributed to some silicide. Due to relatively small amount of data about energy values of Si 2p transitions in different silicides in reference databases some additional measurements will be required to clarify this point. Cu $2p_{3/2}$ had two components at 933.6 eV and 932.6 eV, respectively which was consistent with two Cu oxides. Al 2s was shifted approximately 1.5 eV towards higher binding energies with respect to elemental Al which was consistent with Al in Al_2O_3. Presence of Al_2O_3 in the oxide layer is additional indication of Fe_2O_3 being the main component of the layer, since studies of several binary Fe-Al systems with Al concentrations and thermal treatment parameters roughly comparable to ones used in this study, indicate that Al_2O_3 remains stable in case of Fe_2O_3, while in case
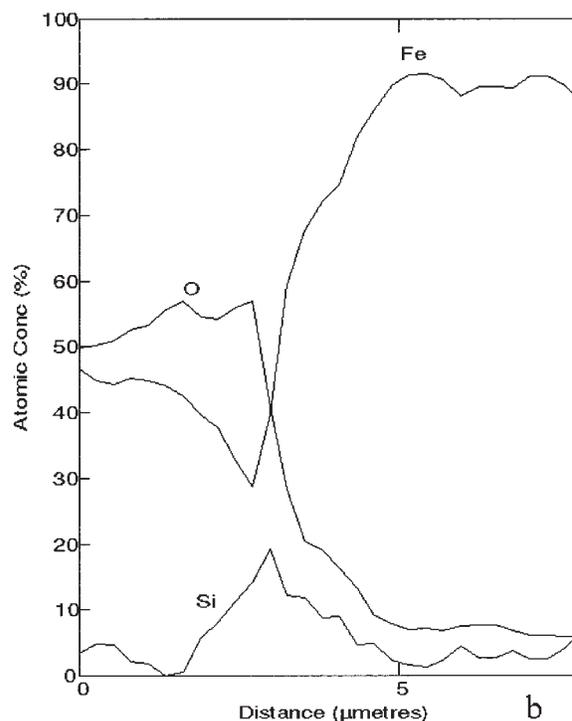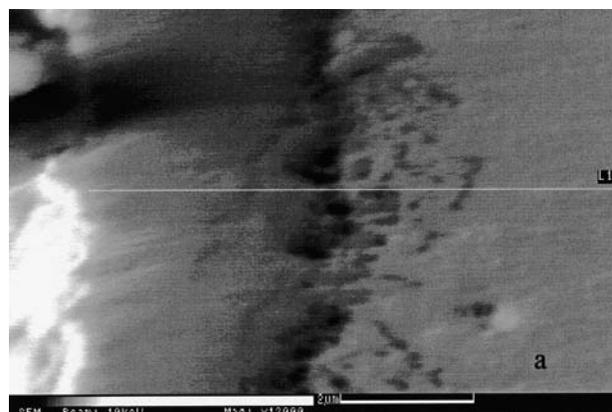
Figure 4: SEM image of the cross-section of the oxide layer - metal interface (a); Fe, Si and O atomic concentrations along the line L1 (b)
Slika 4: SEM posnetek stika med oksidno plastjo in kovino v prerezu (a); koncentracije Fe, Si in O vzdolž črte L1 (b)

of other ferrous oxides, ternary Fe-Al-O compounds are frequently formed [8, 10] .

AES linescan was performed by measuring Auger spectra at 30 points along line L1 (**Figures 4a, b**) on the cross-section of the sample. The concentration profiles for Fe, O and Si calculated from these spectra showed that Si concentration was highest in depth near the oxide layer - metal interface which suggested that also Fe_2SiO_4 concentration was much higher in that region than on the surface. This is consistent with the low surface Fe_2SiO_4 concentration measured by XPS.

4 CONCLUSIONS

SEM, AES, XPS and cross-sectional AES analysis of the electrical steel sample with an oxide layer formed during the decarburization process was performed. SEM image showed highly corrugated surface, while survey AES analysis showed this surface to be of an oxide character. XPS spectra over the characteristic binding energy ranges of the several elements as well as cross-sectional AES analysis showed that the oxide layer predominantly consisted of Fe_2O_3 with small amount of Fe_2SiO_4, CuO and Cu_2O. There was also a minute amount of Al_2O_3. Fe_2SiO_4 concentration increased towards the oxide layer - metal interface.

As already mentioned, this is a preliminary study of oxide layers formed onto electrical steel under laboratory conditions. A more comprehensive study is currently underway. It includes number of samples prepared using different thermal treatments. An attempt will be made to corelate parameters of the thermal treatments to the compositions of the oxide layers. Depth profiling techniques will be used to obtain data about concentration profiles of different compounds inside oxide layers.

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