

STUDY OF INSULATION LAYER FORMATION ON ELECTRICAL STEEL SURFACES BY X-RAY PHOTOELECTRON SPECTROSCOPY AND ELECTRON MICROPROBE ANALYSIS

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1. Introduction

The crystallographic orientation of grains (so-called Goss texture) in electrical steel sheets, which are made from an iron-silicon alloy (3 wt.-% Si), is essential for their ferromagnetic properties [1]. For applications an electrical insulating coating system consisting of a glass layer and a phosphate layer on both sides of the sheets is necessary to reduce the eddy current losses. Furthermore, the tension stress induced in the core material by the coating reduces the magnetostriction. The coating system is developed by a three step annealing process. For a reproducible and defect-free development of the layers, it is necessary to keep the process parameters extremely constant [1 - 4]. To control the process, it is important to know the mechanisms of the layer formation in detail. Therefore, the analysis of the final product only is not sufficient and the structure of the composition of layers after different process steps were analyzed.

The oxide layer and the interface metal/metaloxide were investigated by X-ray photoelectron spectroscopy (XPS) combined with Ar ion sputtering, the glass film and the phosphate coating by electron microprobe analysis (EMA).

2. Experimental

2.1. Production process

The processing steps responsible for building up an optimal insulation layer consist of three different thermal treatments: At first the steel sheet (coiled strip, thickness ≈ 0.3 mm) is decarburized at 850°C in an atmosphere of $\text{H}_2\text{O}/\text{H}_2/\text{N}_2$ with controlled composition. During this annealing step the surface of the steel sheets is oxidized and enriched with SiO_2 . After decarburization the strip is coated with a slurry of MgO dispersed in water. During the subsequent box annealing step (maximum temperature 1200°C) both the crystallographic orientation and the glass film are developed. In this process the MgO has two functions: first it prevents the coil laps from sticking to each other and second it reacts with the SiO_2 in the surface to form the glass film. Then the strip is coated with a dispersion of magnesiumphosphate. The following stress relief annealing is performed at 800°C , sufficient to form a solid phosphate layer.

2.2. Investigated samples

Electrical steel sheets surfaces (in the following A and B) were investigated in two different but unknown decarburization states (after decarburization and after stress relief annealing) and compared to an untreated reference sample.

2.3. Applied methods

For the XPS measurements an equipment of Leybold-Heraeus (LHS 10) was used. The specimens (size $8 \times 8 \text{ mm}^2$; measured area $3 \times 8 \text{ mm}^2$) were cleaned before the measurement in acetone, methanol and ethanol. They were irradiated with Al K_{α} or Mg K_{α} X-rays and the energies as well as the counting rates of the emitted photoelectrons were determined. The energies are typical of the specific elements and their chemical shift against a standard sample is typical of their chemical surrounding (oxidation state) [5]. To investigate elemental concentration profiles and the thickness of the oxide layer the surface was analyzed stepwise each time after removing thin layers by Ar ion (energy 4 keV) sputtering. 1000 s of Ar ion sputtering removed a surface layer of 50 nm. The investigated elements were Si (analyzed photoelectron: $2s \ 1/2$), Mg ($1s \ 1/2$), O ($1s \ 1/2$), Fe ($2p \ 3/2$) or ($2p \ 1/2$) and C ($1s \ 1/2$).

An electron microprobe from Cameca (Cameca Microbeam) with a spatial resolution of 2 - 3 μm was used to investigate the concentration profiles of the elements in the final products. The specimens were embedded in synthetic resin and cut perpendicular to the sheet surface. The cross section was polished and the electron beam (15 keV, 30 nA) was scanned at the sheet surface stepwise in lines parallel to the surface with a length of 60 μm and a stepwidth of 1 μm . In the bulk of the steel sheet, where the concentrations remained constant, a larger stepwidth was applied. The following elements were determined quantitatively: Si, Fe, Mg, O und P.

3. Results

3.1. Untreated reference sample

XPS of the untreated reference sample shows an oxidized surface layer of 15 to 20 nm in depth. The interface metal/metaloxide was located by the chemical shift of the XPS signal of Fe.

3.2. After decarburization

Fig. 1 shows the electron spectra of the analyzed surfaces with the iron peaks after different Ar ion sputtering times t . One finds that A and B are different with respect to their oxidized surface zone. For both surfaces the peak areas are increasing with the sputtering time, but at a different rate. The reason why it takes 800 s of Ar ion sputtering to measure a distinct Fe signal is not yet clear. The behaviour of the chemical shift is also different: in A it shifts to lower energies (for about

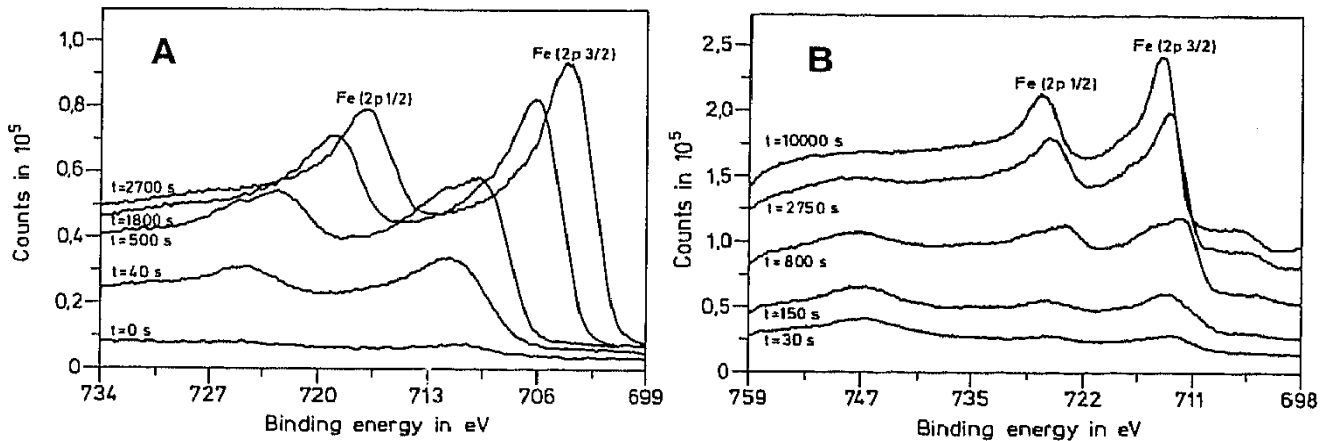


Fig. 1: XPS spectra (as measured) of decarburized steel sheet surfaces showing the Fe 2p 1/2 and Fe 2p 3/2 peaks after different Ar ion sputtering times t

5 - 6 eV) after a sputtering time of 1800 s (about 90 nm depth). In B no shift of the iron peaks was observed with increasing sputtering time. The reason for the observed chemical shift in A is the change in the oxidation state of the Fe, possibly from Fe²⁺ to Fe⁰ (whether Fe³⁺ is present or not cannot be stated). The metallic state of Fe and Si is proved by the large decrease of the oxygen signal (not shown here) in the XPS spectra measured in the bulk of the steel sheets. The standard value reported for the difference of the binding energy of the 2p 3/2 electron of Fe between metallic iron and FeO or Fe₂O₃ is 3 - 4 eV [6]. The slight difference to the reported value is possibly due to effects of electrical charging, which depend on the actual surface conductivity. These charging effects may also cause shifts of the absolute values of the electron energies between separate measurement series (as can be seen by comparing the measured binding energies (peak maxima) in Fig. 1). For a direct comparison of the results for A and B, the binding energies measured in the bulk of A and B have been chosen as standard state (chemical shift = 0 eV). The result is demonstrated in Fig. 2, where the chemical shifts of the XPS signals (related to the above defined standard states) of Fe, O, and Si, measured on both surfaces (same samples as in Fig. 1), as a function of the Ar ion sputtering time are shown. In A all three signals showed a chemical shift after a sputtering time of 1800 s. The behaviour of the Si and O signals confirms the findings for the Fe signal. On this basis it is possible to locate the interface metal/metaloxide at a depth of about 90 nm. The intensity of the XPS signal of O decreased also strongly after 1800 s of sputtering time. In B only minor chemical shifts were observed within the measured range (up to 10000 s sputtering time) and the intensity of the O signal was very low. By EMA the above findings were confirmed. They showed

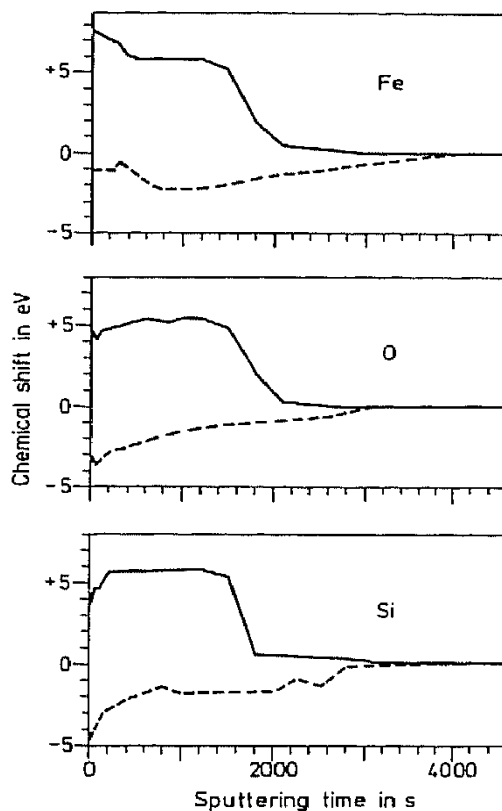


Fig. 2: Chemical shift of the XPS signals of Fe ($2p\ 3/2$), Si ($2p\ 1/2$) and O ($1s\ 1/2$) as a function of the Ar ion sputtering time measured in A (—) and B (---)

a higher oxygen content in the surface zone of A. However, due to the low spatial resolution of EMA (compared with the thickness of the oxidized zone) the EMA results are in this case only of limited value.

The comparison of the results obtained for steel sheets before and after decarburization reveals that during the decarburization process distinct differences in the oxidation degrees between A and B were induced. This observation can only be explained by assuming that the oxidation conditions were not identical for both.

3.3. Final products

To investigate the insulation layers of the final products EMA was applied. The concentrations of Fe, Si, Mg, P and additionally of O were measured. Again (Fig. 3) differences were found between both decarburization states A and B: the Mg and Si concentrations in A were higher than in B.

On the other hand, the P concentration is almost the same for both. The maximum of the P concentration was found about $2\ \mu\text{m}$ apart from the Mg and Si concentration maxima, thus allowing to estimate a thickness of the glass film of about $2\ \mu\text{m}$. The differences between A and B can be explained in the following way:

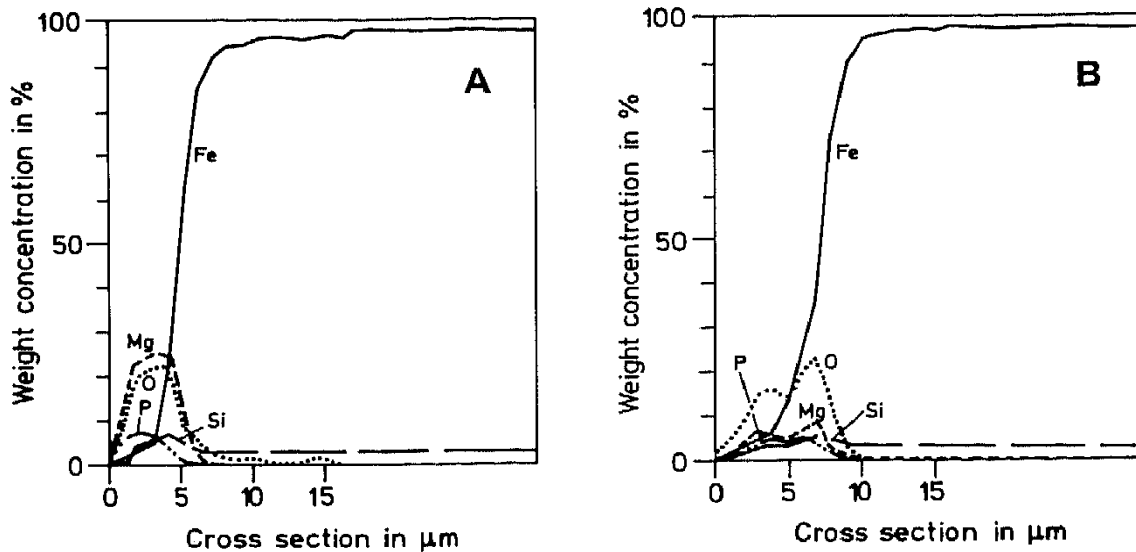


Fig. 3: Concentrations of Fe, Si, P, O and Mg (wt.-%) in cross sections of grain-oriented steel sheets (final product).

As a result of the decarburization process larger amounts of silicon and iron oxides, probably in the form of fayalite, were available in A. The phase diagram [7] of fayalite (Fe_2SiO_4) and forsterite (Mg_2SiO_4) reveals that an enrichment of fayalite in the oxide zone is favorable for the formation of the glass film by lowering the reaction temperature. As a result a thicker glass film is developed at A. The building up of the phosphate coating is independent of the decarburization state.

4. Summary

The investigation showed the influence of the decarburization process on the glass layer formation: an exact control of the oxidation conditions during decarburization is necessary to obtain good insulation layers.

The application of XPS and EMA measurements were proven to be helpful for the detection and interpretation of differences in the formation of the insulation layers on grain oriented steel sheets. Especially the measurement of the chemical shift with XPS allows to locate the interface between the oxidized zone and the metal.

5. Acknowledgement

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6. References

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