

Separation and Quantification of AlN and Al₂O₃ Precipitates in Oriented Electrotechnical Steels

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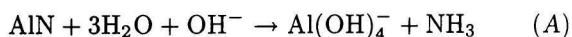
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Received 18 November 1996

The precipitates in Fe—3 % Si steels have been investigated in their states after hot rolling, cold rolling, decarburization annealing, and in the final states. The secondary microphases were obtained by electrochemical and chemical methods of separation. Using chemical analysis it has been found that the precipitate fraction from hot to final stage has a decreasing character, but the content of the particle-forming elements Al, Mn, and Ti increases. The MnS particles in the final stage of Fe—3 % Si steel are approximately two times more abundant than the precipitates on the Al base. After Al separation, we have obtained more AlN isolated particles than Al₂O₃ ones.

It is possible to obtain MnS, SiO₂, Fe₃C, 3Al₂O₃, SiO₂, TiN, FeO·Al₂O₃, AlN, and FeTi₂S₄ microphases from electrotechnical steels using chemical, electrochemical and esterhalogen separations [1, 2]. Those isolation methods differ by action of different reagents (acid for chemical, electrolyte for electrochemical, and bromomethyl acetate for esterhalogen separations). On the other hand, it is necessary (desirable) to minimize the fraction of these particles in the final state of the steel. The particle refinement takes place in the final stage of recrystallization annealing. For this reason, the quantification of particle fraction is important. MnS, α-Al₂O₃, and TiO₂ are extracted together by electrochemical way. MnO is practically not precipitated by electrochemical way. Very fine oxide microphases of Si and Al are dissolved on electrolysis. For extraction of AlN, the esterhalogen method is more effective than the chemical one [1]. Losses of fine and small particles may occur during phase separation. The precipitates of AlN, Al₂O₃, and MnS are accompanied with FeO, FeS or Fe₃C. In addition to stable Al₂O₃, SiO₂, and Cr₂O₃, other oxides may be present. Aluminium is present in steel in the form of metal (in solid solution) and bound in compounds (AlN, Al₂O₃). The first chemical paper related to compounds of nitrogen with aluminium appeared in 1862. However, up to the present, we can find different opinions on stability of AlN in acids such as HCl, H₂SO₄, HNO₃ and in water [3]. Under the constant conditions (apparatus, temperature, time of dissolving, and chemical purity), AlN is less stable in the alkali media. The dissociation rate of an AlN covalent nitride in NaOH solution is, in average, by two or three orders higher than in HCl solution and increases with the increasing concentration

of hydroxide and temperature of the reaction [3]



The goal of our work was to analyze the portion of precipitates in the process of production of oriented electrotechnical steels. Particles were obtained by chemical and electrochemical separations in four states of Fe—3 % Si steel (after hot rolling, cold rolling, decarburization annealing, and in the final state). We separated the precipitates on aluminium base (AlN from Al₂O₃) with a large quantity of MnS microphases.

EXPERIMENTAL

Separation and analysis of microphases have been carried out on samples from silicon electrotechnical steels with the chemical composition in hot strip given in Table 1. Four states have been used (after hot rolling, cold rolling, decarburization, and the final state — H, C, D, F, respectively). Separation of particles has been carried out by two methods [4]:

Electrochemical isolation (EI) performed on samples of dimensions $a = 45$ mm and $b = 20$ mm. The Pt screen was the cathode, the sample represented the anode, and the solution (500 cm³) consisting of 5 % sodium citrate, 1.2 % KBr, 0.5 % ascorbic acid, and H₂O (pH = 5.6—5.8) represented the electrolyte. The sample was anodically dissolved under the conditions of $i = 20$ mA cm⁻², $\theta = 25^\circ\text{C}$, $t = 5$ h.

Chemical isolation (CHI) where 5 g of the sample in the form of sawdust were dissolved in 200 cm³ of 1 M-H₂SO₄ under the conditions of $\theta = 64^\circ\text{C}$, $t = 2$ h in a thermostat.

Table 1. Chemical Composition of the Steels (*w*%)

Specimen	C	Mn	Si	P	S	Al	Cu	Ni	Cr	N
21997/4K	0.06	0.24	3.02	0.009	0.011	0.023	0.011	0.005	0.013	0.008
7422/K	0.06	0.24	3.02	0.009	0.011	0.026	0.011	0.005	0.013	0.008

After completion of both separation methods, the insoluble portion (precipitates) has been separated from the soluble one by filtration using a SYNPOR filter (0.23 μm). The precipitates together with the filter were subjected to chemical microanalysis after their drying and weighing. This was carried out by dissolving the particles according to the procedures described in [4–6]. Fe, Si, Mn, Al, and Ti were analyzed in the precipitate solutions using atomic absorption spectroscopy (AAS) and the spectrophotometric method. The Zeiss atomic absorption spectrometer, model 30, and the Hitachi spectrometer, model U-1100, have been used. The procedure of Al_N and Al₂O₃ separation was carried out by dissolving the particles together with the filter in 60 cm³ of 1.25 M-NaOH under the constant conditions of θ = 65 °C, t = 1.5 h in a thermostat [7]. The insoluble portion (Al₂O₃ and the other precipitates) was separated from the soluble one (Al_N) by filtration. Then, nitride aluminium (Al_N), forming Al_N, has been determined by the spectrophotometric method in the soluble portion, whereas, oxide aluminium (Al_O), forming Al₂O₃ in the insoluble one. The last step of analysis is connected with evaluation of element concentrations in the analyzed solutions using the standard solutions, which contain the same quantities of chemicals as the solutions in blank tests. As a result, four calibration curves have been plotted for *w*(Al) values from the measured absorptivity for Al (soluble, insoluble, nitride, oxide), namely *w_s*(Al), *w_i*(Al), *w_N*(Al), and *w_O*(Al).

RESULTS AND DISCUSSION

After both electrochemical and chemical separations of particles, the soluble (metallic) and insoluble portions have been obtained from four states (H, C, D, F) of the Fe–3 % Si steel. The insoluble portion (precipitates), remaining on the filter in the form of black (states H, C) or brown (states D, F) powder amounted from 0.5 g to 2.0 g. The portion of precipitates *w*(P) represented the difference between the loaded and the empty filters. The individual separations and chemical analysis of solutions, both of the soluble particles and precipitate solutions (determination of Al, Mn, Ti, Si, and Fe) were repeated several times with the same samples (21997/4K) for comparison of the individual methods and for checking of statistical errors. The results are given in mass % and in mass ppm.

Fig. 1 documents the decreasing share of precipitates *w*(P) from the hot state up to the final one for both methods of separation. Fig. 2 illustrates in the

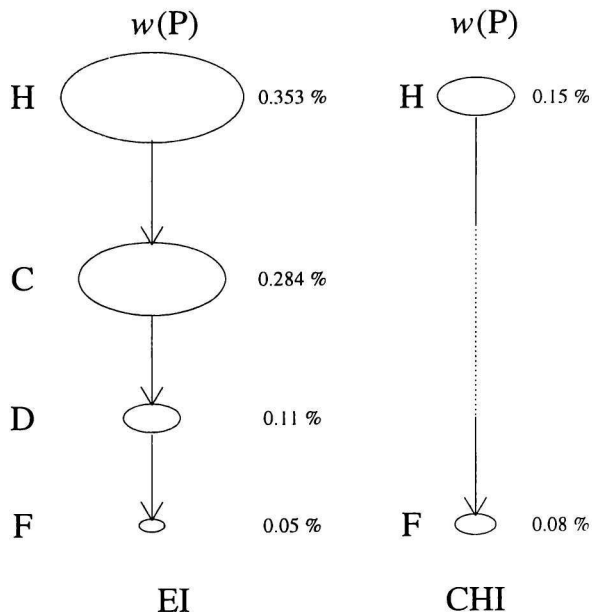


Fig. 1. Portion of precipitates, *w*(P), in mass % in the H, C, D, and F states obtained by the electrochemical (EI) and chemical isolation (CHI) methods.

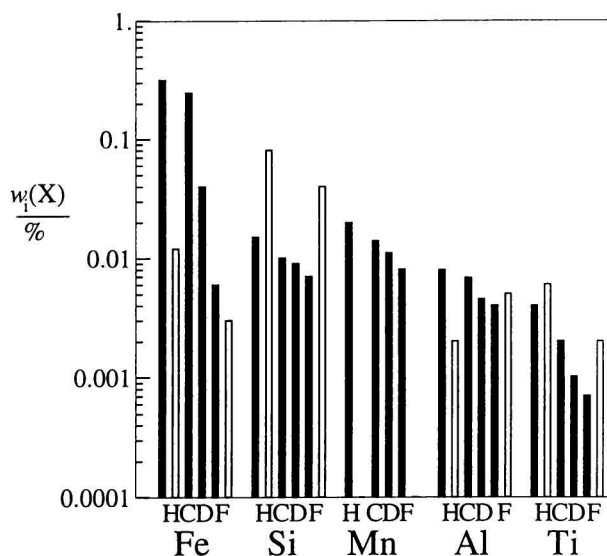


Fig. 2. Insoluble portion of *w_i*(X) elements in mass % after EI (full bars) and CHI (empty bars) methods.

logarithmic scale the dependence of *w_i*(P) from the hot state up to the final one, revealing the decrease of *w_i*(Mn) from 0.02 % to 0.008 % and of *w_i*(Al) from 0.008 % to 0.004 %. During CHI, MnS and partially

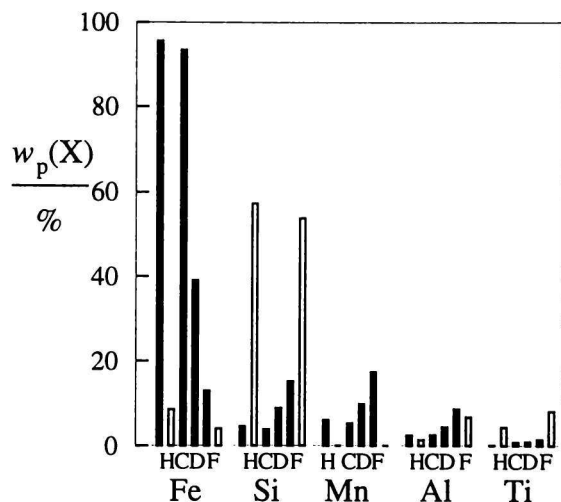


Fig. 3. Portion of elements in precipitates, $w_p(X)$, in mass % in the H, C, D, and F states after EI (full bars) and CHI (empty bars) methods.

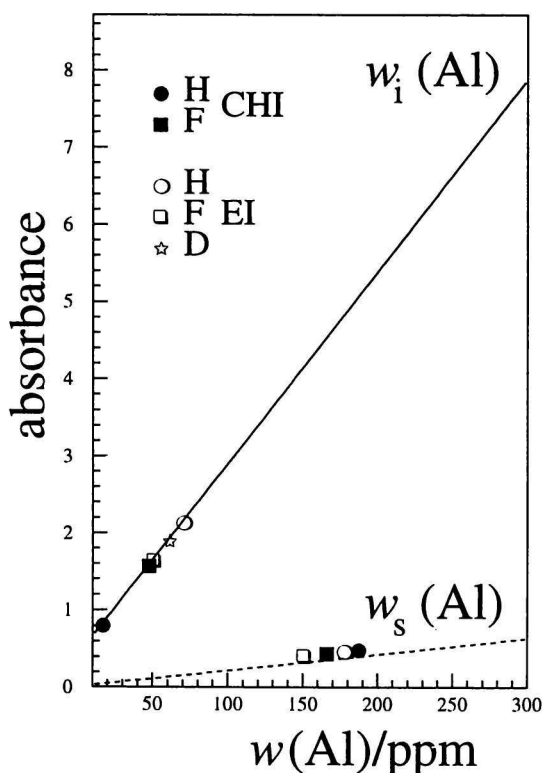


Fig. 4. Values of $w_i(\text{Al})$ and $w_s(\text{Al})$ in ppm for the H, D, and F states after EI (empty markers) and CHI (full markers) methods. The solid curve (dashed curve) represents the fit of absorbance as a function of $w_i(\text{Al})$ ($w_s(\text{Al})$).

also AlN are dissolved. Fig. 3 records the portion of elements in precipitates, $w_p(X)$. The content of Al, Mn, Si, and Ti increases in precipitates from the hot state to the final one, while the content of Fe decreases (from 90 % to 16 % on EI).

Microphases of AlN, Al_2O_3 , MnS, Fe_3C , TiN

were obtained by electrochemical separation. The high content of Fe is a disadvantage. Microphases of AlN, Al_2O_3 , Si_3N_4 , SiO_2 , TiN were obtained by chemical separation. The presence of a higher content of Si is a disadvantage.

We were interested in Al_t (total), Al_s (soluble), and Al_i (insoluble), *i.e.* free and bound aluminium in samples of the four states of Fe—3 % Si steel. The insoluble aluminium, Al_i , has been separated into two parts, nitride aluminium, Al_N and oxide one, Al_O . The sample 7422/K was used for individual separations and separation of microphases on the Al base. In general, the following relations are valid for aluminium in steel [7]

$$w_t(\text{Al}) = w_s(\text{Al}) + w_i(\text{Al}) \quad (1)$$

$$w_i(\text{Al}) = w_N(\text{Al}) + w_O(\text{Al}) \quad (2)$$

where $w_t(\text{Al})$, $w_s(\text{Al})$, and $w_i(\text{Al})$ represent the total, soluble, and insoluble amount of aluminium in electrochemical steel, respectively. Calibration curves for $w_i(\text{Al})$ and $w_s(\text{Al})$ from the H, D, and F states are depicted in Fig. 4 on the basis of measured absorptions in solutions of different Al concentrations. Decreasing values of $w_i(\text{Al})$ in ppm from the H state up to the F state are given in Fig. 5. We can compare the values of $w_N(\text{Al})$ and $w_O(\text{Al})$ (within $w_i(\text{Al})$, which decreases from 80 ppm to 40 ppm on EI). We have ascertained using the spectrographical method that the value of $w_N(\text{Al})$ (AlN phase) is higher than the value of $w_O(\text{Al})$ (Al_2O_3 phase) in precipitates. Fig. 6 gives the graphical records of the change in $w_i(\text{Mn})$ and $w_i(\text{Al})$ (as $w_N(\text{Al})$ and $w_O(\text{Al})$) for the hot, decarburated, and final states, respectively, for the EI method. The value of $w_i(\text{Mn})$ decreases from the H state up to the F state from 200 ppm to 80 ppm and that of $w_i(\text{Al})$ from 80 ppm to only 40 ppm. The decrease in $w_i(\text{Al})$ in the F state is not so distinct in comparison with the D state due to the presence of the stable Al_2O_3 particles. The change in the content of N and S in the AlN and MnS precipitates has been analyzed in [3] on similar steel. *i.e.* as in our case, using mass spectrometry both before and after isothermal annealing. On the basis of their analysis we observed the decrease in the content of MnS in the state before and after isothermal annealing and the increase in the content of AlN. Particles of AlN and MnS participate in the process of secondary recrystallization as inhibitors. The formation of the dispersion sulfidic phase of MnS starts in the process of hot milling. The particles should have the smallest dimensions possible [8]. The concentration of Mn, S, and C is important. Precipitation of the AlN precipitates takes place on cooling the steel during the process of hot milling or after its completion. After the final thermal treatment, dissolution of AlN and MnS particles and forced refining of S and Al take place by the effect of H_2 atmosphere. At to-

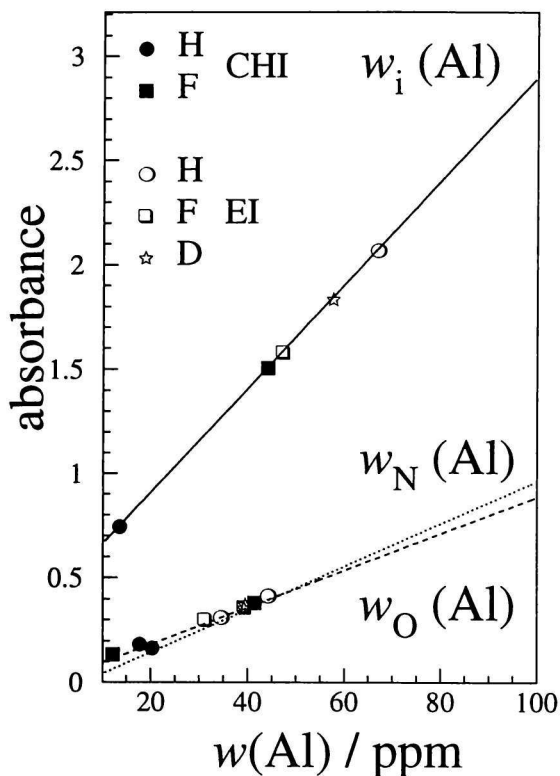


Fig. 5. Values of $w_i(\text{Al})$, $w_N(\text{Al})$, and $w_O(\text{Al})$ in ppm for the H, D, and F states after EI (empty markers) and CHI (full markers) methods. The solid, dashed, and dotted curves represent the fit of absorbance as a function of $w_i(\text{Al})$, $w_O(\text{Al})$, and $w_N(\text{Al})$, respectively.

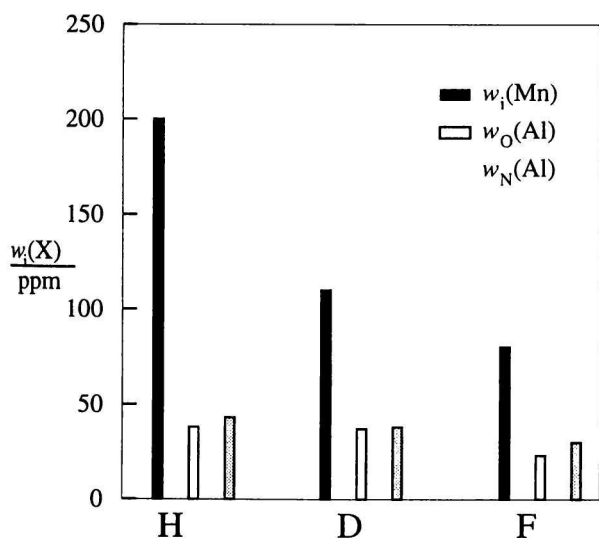


Fig. 6. Values of $w_i(\text{Mn})/\text{ppm}$ (full bars), $w_O(\text{Al})/\text{ppm}$ (empty bars), and $w_N(\text{Al})/\text{ppm}$ (hatched bars) for the H, D, and F states after the EI method.

tal concentration of Al in precipitates it is important to subtract Al, which forms Al_2O_3 , because the stable Al_2O_3 particles deteriorate electromagnetic properties in the final state.

CONCLUSION

The goal of the presented paper was to point out the changes in the participation of secondary phases and their chemical composition in the process of the production of transformer steels. The particles were obtained by chemical and electrochemical extraction.

The following facts have been ascertained by analysis of the results of separation of particles from the Fe—3 % Si steels:

The portion of precipitates in four states, formed by both methods of separation, decreases from the hot state, through the cold and decarburized ones to the final state.

When we compare spectrophotometrical and AAS analyses, the insoluble quantity of $w_i(\text{Al})$, $w_i(\text{Ti})$, $w_i(\text{Mn})$, $w_i(\text{Si})$, and $w_i(\text{Fe})$ decreases from the hot state to the final one, but the content of Al, Ti, and Mn in the particles increases.

The decrease in the portion of $w_i(\text{Mn})$ in the final state in comparison with the decarburized state indicates the effective refining of the MnS particles during high-temperature annealing.

In the final state, after division of insoluble Al into nitride aluminium (Al_N) and oxide one (Al_O), we have determined more precipitates of Al_N than of Al_2O_3 within double quantity of the MnS microphases using the spectrophotometric method.

The decrease in $w_i(\text{Al})$ in the final state in comparison with the decarburized state is not sufficient. This is caused by the fact that the relative high content of Al is bound to the stable particles of Al_2O_3 .

Acknowledgements. This work was supported by the Slovak Academy of Sciences under Grant No. 2/1107.

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Translated by M. Mižíková