EVOLUTION OF SULPHIDES IN Cu - BEARING GOES DURING INDUSTRIAL PRODUCTION PROCESS

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Abstract

Grain oriented electrical steels (GOES) produced by the AlN + Cu technology usually contain ca 0.5 wt. % of Cu. Evolution of microstructure during the final high temperature annealing of GOES is strongly affected by microstructural changes during the individual steps of industrial production process. Inhibition phases, AlN and sulphides, are expected to play an important role in the formation of the final Goss texture.

This paper deals with TEM characterization of sulphides in Cu - bearing GOES after basic steps of industrial production process: hot rolling, decarburization annealing (DCA) and high temperature annealing (HTA). In specimens after hot rolling only sulphides of manganese and complex sulphides of manganese containing, a small fraction of copper were identified. Typical size of these sulphides reached several hundreds of nanometres. These results prove a low solvus temperature of Cu rich sulphides in GOES. Re-precipitation of copper-rich sulphides was observed after decarburization annealing. Due to low temperature of precipitation, typical size of these sulphides reached only several tens of nanometres. Apart from complex sulphides of copper and manganese, fine Cu_2S particles were detected. In the paper the effect of Cu - bearing sulphides precipitation on the formation of other minor phases is discussed. Heterogeneous nucleation of AlN particles on fine sulphides was often observed. During high temperature annealing all sulphides gradually dissolved.

Keywords: GOES, precipitation processes, sulphides

1. INTRODUCTION

Magnetic properties (easy magnetisation, low eddy current losses, low hysteresis loss) of GOES depend heavily on the sharpness of the Goss texture ({110} <001>). The perfection of Goss texture in final GOES sheets is closely affected by structure evolution during the whole production process as it is agreed [1]. Factors considered for very important for the formation of the Goss texture during high temperature annealing, include the size of the initial grains with the Goss orientation, their orientation with respect to the other grains and the role of minor phases in grain boundary pinning [1]. The necessary conditions for abnormal Goss grain growth are controlled by microstructural parameters. Inhibitor phase particles (MnS or AlN depending on the production technology) restrict ferritic grain growth during uniform grain growth after the primary recrystallization. The role of copper addition to GOES has not been fully understood yet. The following mechanisms have been proposed:

- stabilization of austenite during hot rolling in two phase $\alpha + \gamma$ region,
- precipitation of ε - Cu,
- dissolution and re-precipitation of Cu_2S or complex Mn + Cu sulphides,
- segregation of copper at grain boundaries,
- support of deformation by twinning and shear.

In the case of AlN + Cu GOES manufacturing technology the most important type of precipitates is aluminium nitride, sulphides are credited with much less importance. In this case, sulphides can serve as a place for heterogeneous nucleation of nitrides [1]. The aim of the paper is to analyse the evolution of sulphides after basic steps of industrial production process of GOES.

2. EXPERIMENTAL MATERIALS AND PROCEDURES

The following production steps of the AlN + Cu industrial processing technology were studied: hot rolling of slabs (specimen A - HR), the 1st cold rolling + decarburization annealing (specimen A - DCA) and the 2nd cold rolling, which was followed by the high temperature annealing (specimen A - HTA). **Table 1** shows investigated chemical composition of the hot strip. Hot rolling was carried out at 1250 °C to the thickness of 2.00 mm. After pickling, the 1st cold rolling to mid-thickness of 0.6 mm was applied and it was followed by continuous DCA at the temperature of 820 °C in the atmosphere containing N_2 + 20 % H_2. During DCA, carbon content in the steel was reduced to 0.003 wt. %. After the 2nd cold rolling the sheet thickness was about 0.28 mm. Specimens for investigations were cut out from identical positions in the sheets. Analysis of precipitation was carried out using a transmission electron microscope JEM 2100 (TEM) for each step of processing. Identification of minor phases on carbon extraction replicas was carried out using electron diffraction and EDX techniques.

Table 1 Chemical composition of the hot strip (wt. %)

C	Mn	Si	S	Cr	Cu	$Al_{tot.}$	Ti	N
0.03	0.25	3.16	0.004	0.024	0.50	0.014	0.004	0.009

3. RESULTS

3.1. Specimen A - HR

Hot rolling of slabs took place in the two - phase (α + γ) region. Copper additions increase the stability and the volume fraction of austenite during hot rolling. Redistribution of elements, especially of interstitial elements, between ferrite and austenite is to be expected [1]. In the hot rolled strip, ferrite grain boundaries by Fe_3C particles were decorated which formed after coiling at ca 570 °C, **Figure 1a**. Inside grains low number density of particles was observed. **Figure 1b**. Following minor phases of MnS, complex sulphides of manganese and copper, rarely of TiN and AlN, were identified.

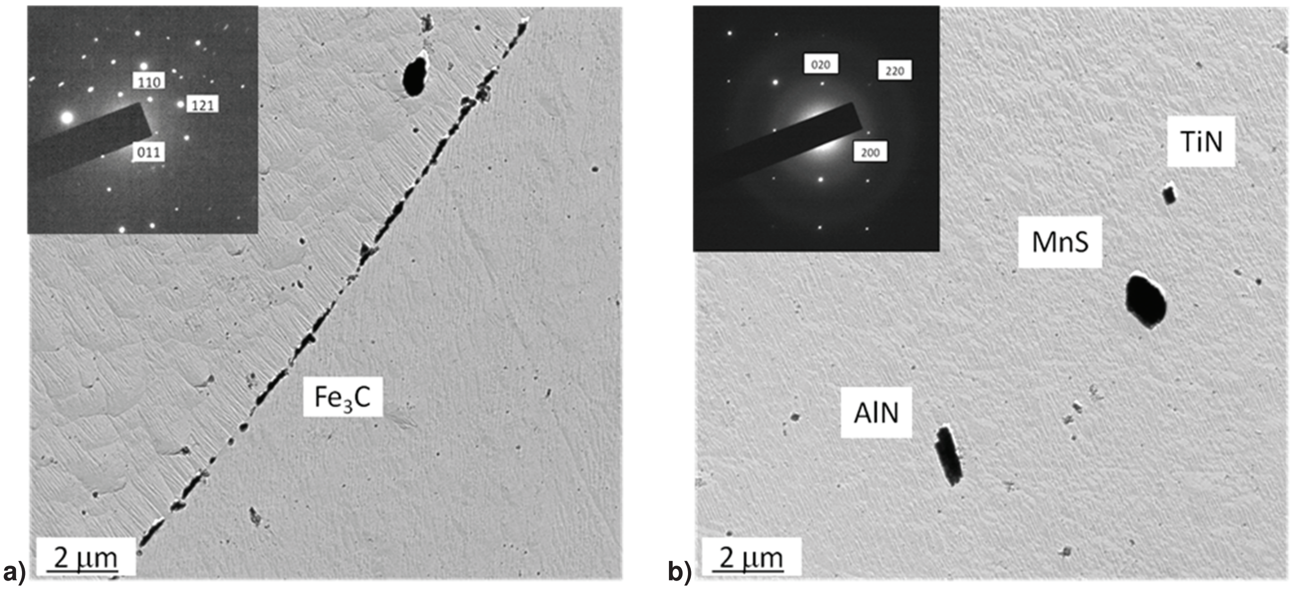

Figure 1 a Precipitation of Fe_3C along grain boundary, insert: zone axis [-11-1] of Fe_3C,
b intragranular particles of AlN, MnS and TiN, insert: zone axis [001] of TiN, specimen A - HR

Chemical composition of sulphides in the specimen A - HR determined by EDX **Table 2** shows. The A - HR specimen mostly contained manganese sulphides and complex Mn + Cu sulphides with a low content of copper. The copper content in individual particles of complex sulphides was lower than 15 at. %. Thermal stability of complex sulphides decreases with increasing content of copper as is related to the fact. Solution temperature of MnS is about 1300 °C, but copper sulphides dissolve at temperatures close to 950 °C [2]. MnS particles in the specimen A - HR after the hot rolling reached the typical size of about 350 nm. **Figure 2** defines the dependence of size of complex sulphides on at. % of manganese, shows that the typical size of complex sulphides is generally less than 300 nm.

Table 2 Results of semi-quantitative EDX analysis of sulphides, specimen A - HR (at. %)

No.	S	Mn	Cu	No.	S	Mn	Cu
1	47.59	46.91	5.49	**9**	48.58	51.42	0
2	47.29	48.72	3.98	**10**	46.8	45.28	7.92
3	45.38	40.31	14.31	**11**	42.78	57.22	-
4	49.8	50.2	-	**12**	47.4	47.76	4.84
5	49.76	43.3	6.93	**13**	47.68	52.32	-
6	49.87	48.97	1.16	**14**	48.83	51.17	-
7	49.29	49.21	1.5	**15**	50.01	48.28	1.7
8	47.95	52.05	-				

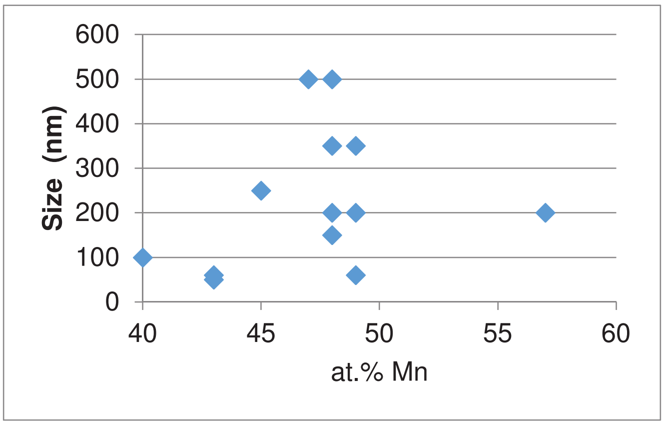

Figure 2 Dependence of the size of complex Mn + Cu sulphides on manganese content, specimen A - HR

3.2. Specimen A - DCA

Experimental investigations proved that decarburization annealing at 820 °C was accompanied by very intensive precipitation of sulphides and nitrides. Chemical composition of sulphides, as determined by EDX, is summarized in **Table 3**. Copper rich sulphides corresponded to Cu_2S phase. However, most sulphides contained both manganese and copper (complex Mn + Cu sulphides). In many cases heterogeneous nucleation of nitrides on the surface of sulphides was observed. The content of copper in complex sulphide particles was generally much higher than that in the specimen A-HR, which was cut out from the hot strip. This fact proved that during the decarburization annealing additional precipitation of complex sulphides occurred. The size of most copper rich sulphides was less than 100 nm, **Figure 3**.

Two nitrogen-bearing minor phases along ferrite grain boundaries were identified: Si_3N_4 and AlN, **Figure 4a.** Si_3N_4 nitride represents a metastable phase in GOES, which is gradually replaced by AlN phase in the temperature interval of ca 700 - 900 °C. Intragranular precipitation of AlN was very intensive and heterogeneous. Local differences in the number density of nitrides are probably a consequence of hot rolling in the two - phase region where some enrichment of austenite in carbon and nitrogen took place. In many cases heterogeneous nucleation of nitrides on the surface of sulphides was observed. The typical size of intragranular nitrides was 20 - 30 nm, **Figure 4b**. During DCA Fe_3C particles in the ferrite dissolved and the solid solution was decarburized to 0.003 wt. % C. TiN particles were not affected by DCA.

Table 3 Results of semi-quantitative EDX analysis of sulphides, specimen A - DCA (at. %)

No.	S	Mn	Cu	No.	S	Mn	Cu
1	38.6	4.9	56.5	**9**	36.5	2.8	60.7
2	39.5	6.1	54.4	**10**	34.7	-	65.3
3	36.6	4	59.4	**11**	37.7	7	55.2
4	50.5	49.5	-	**12**	32.7	6.2	61.1
5	48.5	51.5	-	**13**	42.1	22.7	35.2
6	34.8	-	65.2	**14**	39.5	20.4	40.1
7	35.2	14	50.8	**15**	33.9	7.4	58.7
8	38.4	7.9	53.7				

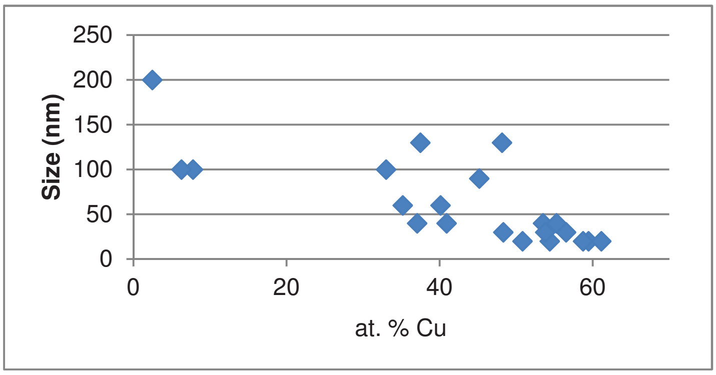

Figure 3 Dependence of the size of sulphide particles on the copper content, specimen A - DCA

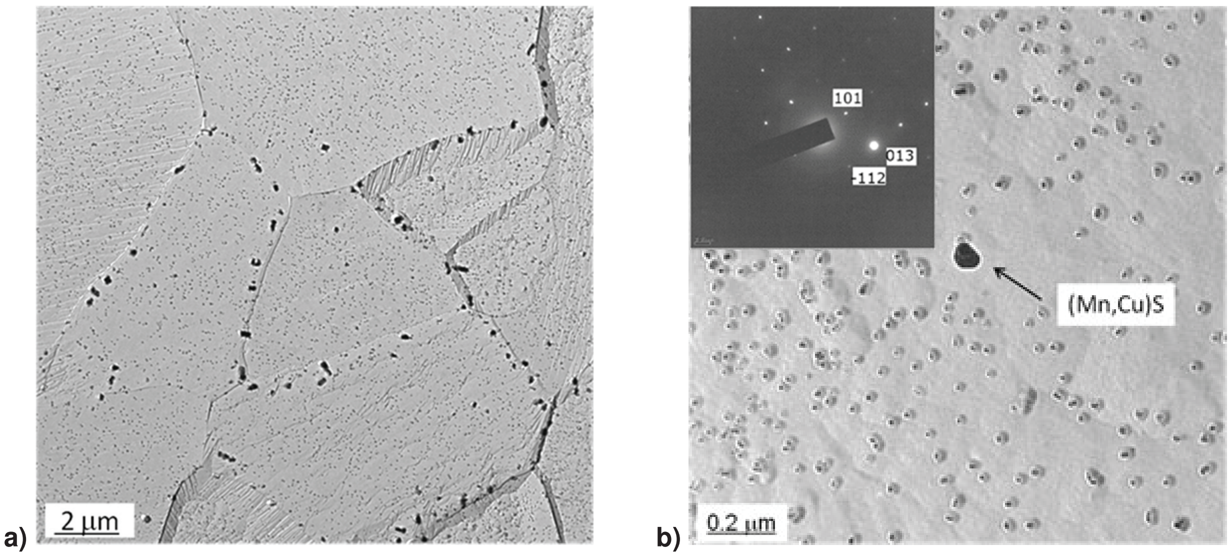

Figure 4 a) Precipitation of AlN and Si_3N_4 nitrides along grain boundaries, **b)** intragranular precipitation of AlN particles, insert: zone axis: [13-1] of AlN, and complex Mn + Cu sulphide particles

Quantitative parameters of the precipitates in the specimen A - DCA after decarburization annealing were analysed using the automated image analysis (software Image Pro 6.2).

The following parameters were determined:

- average particle diameter d_{av} = 37.2 ± 15 nm,
- minimum particle diameter d_{min} = 25.4 ± 14 nm,
- maximum particle diameter d_{max} = 51.4 ± 21 nm,
- ratio d_{max} / d_{min} = 2.02.

In accordance with published data it was found out, that the mean size of precipitates after decarburization annealing was several tens of nanometres [3]. Such precipitate dimensions are considered suitable for inhibiting the grain growth after the primary recrystallization. The number density of the precipitates in the specimen A-DCA was of the order of 10^7 particles / mm^2.

3.3. Specimen A - HTA

In the specimen after the high temperature annealing (after secondary recrystallization), it was found out that all sulphides and nitrides were dissolved with the exception of TiN particles. Titanium nitrides have high thermal stability and their effective dissolution is is expected at temperatures above 1300 °C. Undissolved TiN particles in the specimen A - HTA are documented in **Figure 5a**. In the **Figure 5b** is indicated EDX spectrum of a TiN particle.

a) **b)**

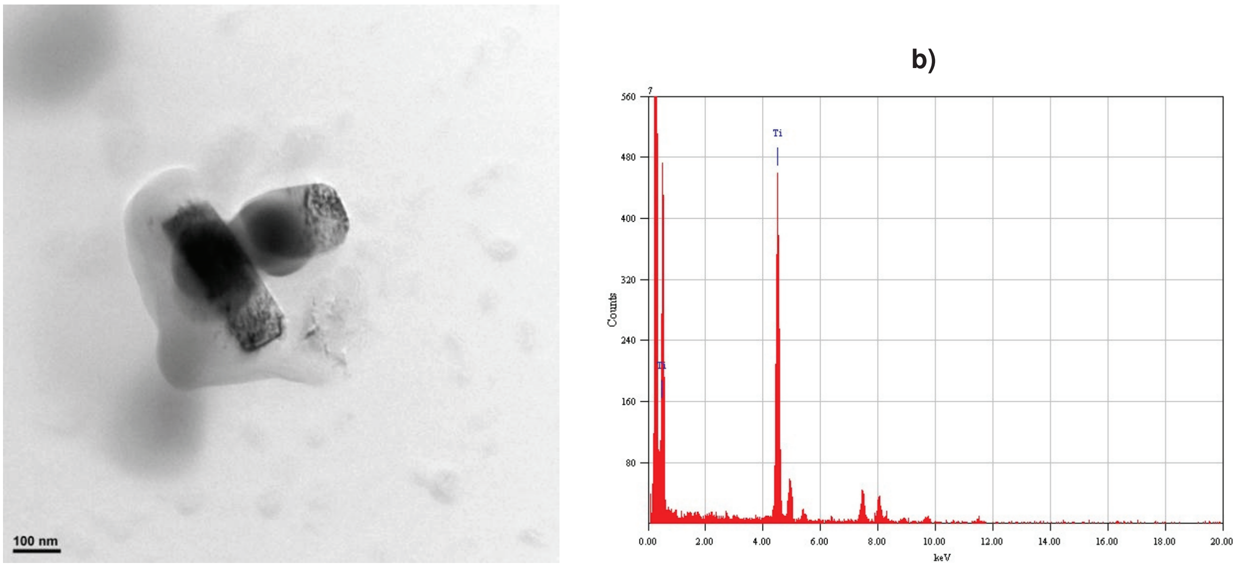

Figure 5 a) Undissolved TiN particles, **b)** EDX spectrum of TiN

4. CONCLUSION

- Grain boundaries in the hot rolled strip were decorated by thin films of cementite, which formed during cooling of coils. Inside ferritic grains a small number density of TiN, complex sulphides of manganese and copper and rarely AlN particles were found out. Based on the results of semi-quantitative EDX analysis it is possible to state that sulphides after hot rolling correspond to manganese sulphides and complex Mn + Cu sulphides with a low content of copper. The typical size of complex sulphides was less than 300 nm.
- During decarburization annealing at 820 °C an intensive precipitation of Si_3N_4 and AlN particles took place. Apart from nitrides, sulphide particles with a variable ratio of Mn and Cu and Cu_2S particles re-precipitated in the ferritic matrix. The size of most copper rich sulphides was less than 100 nm. In many cases heterogeneous nucleation of nitrides on the surface of sulphides was observed.

- After HTA all nitrides and sulphides were dissolved, except for TiN.

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