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FRACTIONAL GAS ANALYSIS PROCEDURE FOR DETERMINING THE CONTENTS OF OXIDE AND NITRIDE PHASES IN ALNICO ALLOYS

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Preliminary note – Prethodno priopćenje

Fractional gas analysis procedure for estimating the contents of oxide and nitride inclusions in Alnico alloys produced from wastes of production is developed. The effect of the temperature and time of melt holding before pouring on the content of impurity oxide and nitride inclusions is considered. The content of SiO_2 inclusions in Alnico mainly depends on the holding time before pouring and decreases with increasing holding time, whereas the content of Al_2O_3 inclusions decreases with increasing both temperature and time of holding. The content of TiN inclusions decreases with increasing holding time. As the holding temperature increases, the content of nitride inclusions decreases only with increasing holding time.

Key words: Alnico, fractional gas analysis, oxide inclusions, nitride inclusions; hard magnetic materials

Primjena frakcijske plinske analize za određivanje sadržaja oksidnih i dušičnih faza u ALNICO legurama. Razrađena je metoda frakcijske plinske analize za vrednovanje oksidnih i dušičnih uključaka u ALNICO legurama, dobijenih iz gospodarskih otpada. Posmatran je utjecaj temperature i vremena zadržavanja kupke prije lijevanja. Sadržaj uključaka SiO_2 uglavnom ovisi od vremena zadrške prije lijevanja i snižava se povećanjem tog vremena, istodobno se sadržaj uključaka Al_2O_3 smanjuje s povećavanjem i temperature i vremena zadrške. Sadržaj uključaka TiN smanjuje se povećavanjem vremena zadrške. S povećanjem temperature sadržaj dušičnih uključaka smanjuje se samo pri povećanju vremena zadrške prije lijevanja.

Ključne riječi: ALNICO legure, frakcionalna plinska analiza, oksidni uključci, dušični uključci, magnetno tvrdi materijali

INTRODUCTION

Production technology of Fe-Al-Ni-Co-Ti alloys (intended for Alnico permanent magnets) must provide given compositions and maximum length of dendrites (columnar crystals) that is determined by the minimum content of impurities, in particular, nonmetallic inclusions refining the macrostructure of magnets [1, 2]. It should be noted that the Fe-Al-Ni-Co-Ti alloys solidify with the formation of single-phase solid solutions; the process is nonequilibrium [3]. The reaching required composition of columnar crystals is determined by the distribution of principal components during the directional solidification, i.e., segregation processes, which are related to the distribution coefficients of the components and cooling rate of the alloys in the temperature range of solidification [4]. The length of columnar crystals is also determined by optimum contents of modifying alloying elements, such as S, C, Si, and minimum content of impurities [5, 6].

At present, the existing problems, such as the resource economy and decrease in high costs of hard magnetic materials, determine the necessary use of wastes of production. In this work, we study magnets prepared from Alnico wastes rather than from pure charge materials (this allows the prime cost of the final product to be decreased substantially) and, thus, analyze the structure of such magnets in order to reveal regularities of the effect of temperature and holding time of Alnico melts before pouring on the content of oxide and nitride impurity inclusions in ingots. The aim of this study is to develop an analytical procedure, namely, fractional gas analysis (FGA) technique, which allows the effect of impurity nonmetallic elements on the formation of columnar structure in the Alnico alloys to be revealed.

Earlier, we have elaborated the fractional gas analysis procedure that allows the content of oxygen (in the form of oxides Nd_2O_3 and $Nd_xFe_yO_z$) in Nd-Fe-B magnets [7] to be determined. Existing procedures for the determination and identification of nitride inclusions,

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such as optical and electron microscopy, X-ray diffraction and electron probe analyses, high-temperature hydrogen extraction, and methods assuming the separation of nitrogen-containing compounds from the alloys, are labor-consuming and do give inadequate accuracy. The fractional gas analysis shows promise for determining the content of nitride phases as well.

Inclusions SiO_2 are the most harmful for the Alnico alloys since the thermal expansion coefficient of the inclusions is higher than that of the metallic matrix. This leads to the formation of pores in finish products. Moreover, TiN inclusions hinder the grain growth. That is why the determination of oxygen and nitrogen species in hard-magnetic materials is effective for controlling and predicting the properties of permanent magnets.

EXPERIMENTAL PROCEDURE

The preparation procedure for Alnico alloys is described in detail in [8]. The initial alloy (Alnico wastes) was melted under a calcic-aluminous slag using an open induction furnace. Metals, such as Ti, Co, Nb, and Al, were made a part of the melt that was subsequently cast in a metallic mold. Thus, we obtain a common categorized furnace charge (CCFC). For the investigation, samples of the alloy were prepared as follows. The CCFC was melted and heated to temperatures of 1650, 1700, and 1750 °C, held at these temperatures for 30 s (melt 1) and 120 s (melt 3), tapped to a ladle lined with fused corundum, and poured in an acid lining mold heated to 1300 °C mounted on a cooler. To prevent the crystallization of the high-temperature γ phase, the cooling rate of the ingots after crystallization was no less than 100 K/min.

Table 1 shows the chemical composition of Alnico samples under study.

Table 1. **Chemical composition of Alnico samples (Fe – balance)**

Content of components / mas. %						
Al	Si	Ti	Co	Ni	Cu	Nb
6,8	0,16	4,9	34,9	13,4	2,9	0,98

The segregation of alloy components was studied by electron microprobe analysis using Camebax and MS-46 Cameca setups. The substantial segregation of titanium and niobium and slight segregation of copper at dendrite boundaries were found. Moreover, the dendrite boundaries were found to be depleted of aluminum. All other elements are characterized by uniform distribution in the alloy microstructure. The variations in the content of Fe, Co, Ni, Cu, Nb, Al, and Ti in the center and at boundaries of dendritic cells were found to be 33,8-35,7; 34,8-35,3; 13-14,4; 3,2-2,3; 7,91-0,75; 2,3-8,6; and 6,1-4,65 mas. %, respectively.

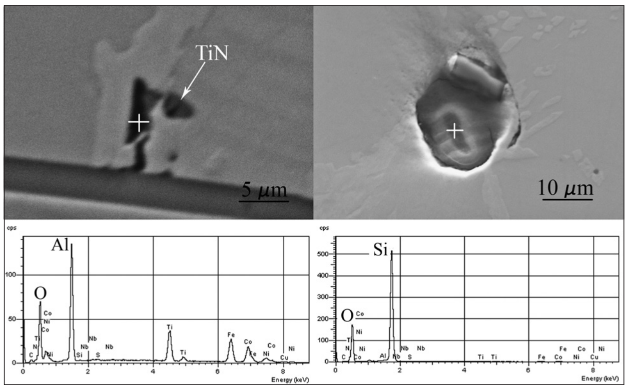

Figure 1. Micrographs and typical X-ray spectra of Al_2O_3 and SiO_2 oxide and TiN inclusions in the Alnico alloys under study

Using a Carl Zeiss scanning electron microscope equipped with a LEO 430i energy dispersive X-ray microanalyzer, two principal types of oxide inclusions and a nitride phase were found in the samples under study; these are Al_2O_3 and SiO_2 and TiN, respectively (Figure 1).

Along with fine precipitates of aluminum and silicon oxides and titanium nitride, slag drosses mainly consisting of aluminum oxides and Mg-containing calcium aluminosilicates were found in the Alnico samples.

The FGA of Alnico samples was performed on a TC-600 LECO gas-analyzer.

Fractional gas analysis is a modified reducing-melting procedure realized in a graphite crucible in a carrier-gas flow at a fixed linear heating rate [9]. The analysis is based on the difference in the thermodynamic stability of oxides (nitrides) upon heating that are principal species of oxygen (nitrogen) present in a metal. Thus, we present conditions of monotonic heating of a sample in a graphite crucible of an analyzer and obtain gas-evolution curves (evalogram) for oxygen and nitrogen in the form of CO and N_2, respectively. An evalogram is a system of maxima; each peak of the curve be related to one or other kind of inclusions and has a characteristic temperature, which corresponds to the onset and maximum of reduction (dissociation) and allows the associated compound to be identified. Principles of thermodynamic calculations of characteristic temperatures of oxide inclusions in Fe-based melts are given in [10].

The calculation of the temperature of titanium nitride dissociation is based on the following concept. During the FGA of Alnico samples, TiN inclusions dissociate with the formation of TiC:

$$TiN_{(s)} + C_{(gr)} = TiC_{(s)} + \tfrac{1}{2} N_{2(g)} \qquad (1)$$

The equilibrium constant of the reaction is

$$K_{(1)} = \frac{a_{TiC} \cdot \sqrt{p_{N_2}}}{a_{TiN} \cdot a_c}, \qquad (2)$$

where a is the activities of corresponding substances and p_{N_2} is the nitrogen partial pressure in the gas-analyzer furnace. Since the activities of substances in the standard state are equal to unity, the equilibrium temperature of dissociation reaction (the temperature of the onset of dissociation during FGA) of TiN with the formation of TiC is determined by only the pressure p_{N_2} equal to 1,875 bar:

$$T_{beg(1)} = \frac{\Delta H^{O}_{(1)}}{\Delta S^{O}_{(1)} - R \cdot \ln\sqrt{p_{N_2}}} \qquad (3)$$

where $\Delta H^{O}_{(1)}$ is the change of standard enthalpy for reaction (1), $\Delta S^{O}_{(1)}$ is the change of standard entropy for reaction (1); and R is the universal gas constant.

Using tabulated data [11], we have calculated the temperature of the onset of dissociation of titanium nitride; it is 2061 K.

RESULTS AND DISCUSSION

Figure 2 shows a typical curve of the oxygen extraction (obtained during FGA) in the form of CO for an Alnico sample. The curve is characterized by two gas-evolution peaks that indicate the presence of oxygen in the sample in the form of two compounds, such as SiO_2 (peak 1) and Al_2O_3 (peak 2).

Figure 3 shows the typical curve of the nitrogen extraction during the FGA of the Alnico sample. As is seen, the evolution of nitrogen occurs at the high temperature; the existence of the single peak indicates the presence of the single kind of nitrogen-containing inclusions.

We calculated the temperature of the onset of TiN dissociation and compared it with the experimental temperatures of the onset of nitrogen evolution. The average experimental magnitude is higher than the calculated value by –80 K. This difference can be explained by the fact that the tabulated data were obtained without the allowance for the kinetics of dissociation of the nitride in this type of alloys.

Figure 4 shows the effect of temperature and time of holding of the Fe-Al-Ni-Co-Ti melts before the pouring on the total oxygen content. As is seen, the total oxygen content decreases, as the temperature and time of holding increase. In this case, the melt becomes more homogeneous with respect to the oxygen inclusion content. This occurs at the expense of the removal of slag drosses from the metal and possible decrease of the oxygen solubility with increasing melt temperature.

Using the FGA results, we determined changes in the oxygen content (in the form oxides) as functions of the temperature and time of holding of the Fe-Al-Ni-Co-Ti melt before pouring. These dependences are shown in Figure 5. As is seen, the content of SiO_2 inclusions in the

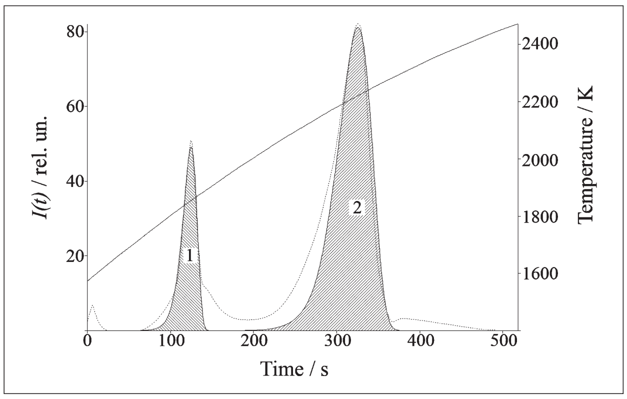

Figure 2. Curve of oxygen (in the form of CO) extraction from Alnico alloys during FGA performed at a heating rate of 2,1 K/s; *I(t)* is the intensity (relative units) of CO extraction on TC-600 (LECO) setup.

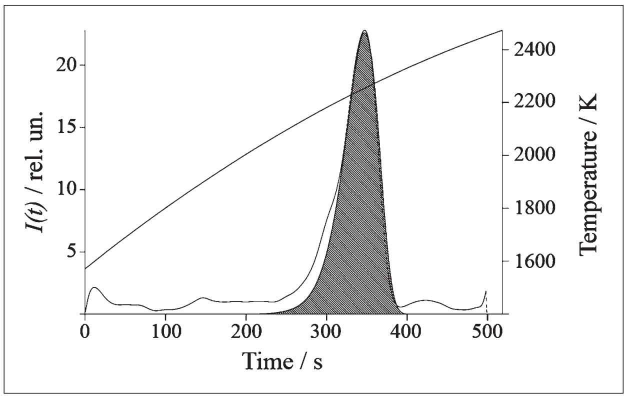

Figure 3. Curve of nitrogen extraction from Alnico alloys during FGA; *I(t)* is the intensity (relative units) of N_2 extraction.

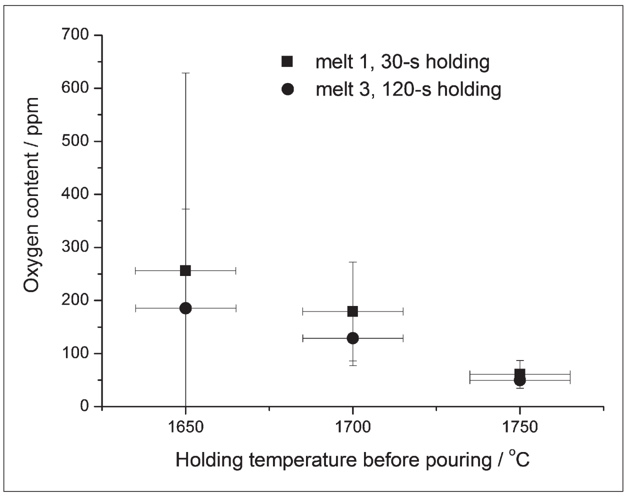

Figure 4. Effect of the temperature and time of holding of the Alnico melt before casting on the total oxygen content

Alnico samples mainly depends on the melt temperature and is almost independent on the holding time. In this case, the content of Al_2O_3 inclusions decreases with increasing both melt temperature and holding time.

According to the FGA results, the total oxygen content in the Alnico samples obtained after 30-s holding of the melt at 1750 °C is 60,8 ± 26,1 ppm; the oxygen contents in the form of SiO_2 and Al_2O_3 are 17,5 ± 13,0 and 40,7 ± 14,1 ppm, respectively. After 120-s holding of the melt at the same temperature, the total oxygen content in the Alnico samples is 49,7 ± 4,8 ppm; the oxygen contents in the form of SiO_2 and Al_2O_3 are 17,7 ± 0,4 and

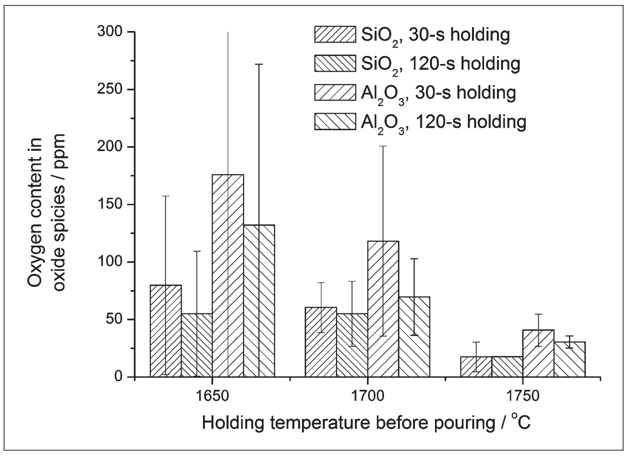

Figure 5. Effect of the temperature and time of holding of the Alnico melt before casting on the oxygen content in the form of oxides

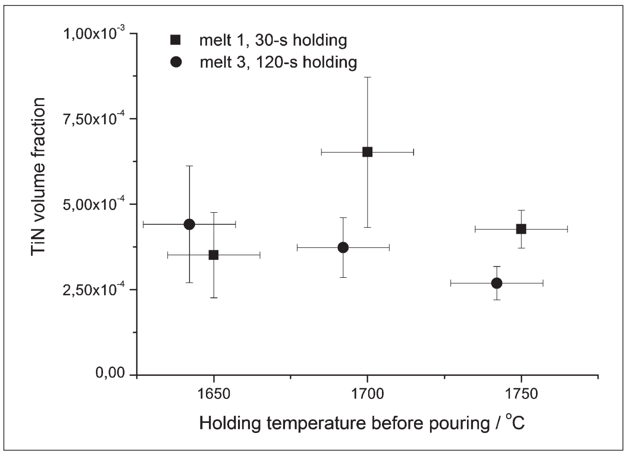

Figure 6. Effect of the temperature and time of holding of the Alnico melt before casting on the volume fraction of TiN

30,4 ± 5,3 ppm, respectively. Thus, the prolonged holding before the pouring allows the oxygen content in the alloys to be decreased at the expense of its removal from the melt in the form of Al_2O_3 inclusions.

The volume fractions of oxides in the samples can be calculated using data on the oxygen content and equation

$$V_{\text{oxide}} = \frac{O_{\text{oxide}} M_{\text{oxide}} \rho_{\text{matrix}}}{\rho_{\text{oxide}} y A_O} \qquad (4)$$

where ρ_{oxide} is the density of oxide of the given composition; ρ_{matrix} is the density of metallic matrix (7,2 g/cm^3 for the Alnico alloys); A_O is the atomic mass of oxygen; M_{oxide} is the molar mass of oxide; y is the oxygen index in the oxide formula; O_{oxide} is the oxygen mass fraction in the form of this oxide determined by FGA.

According to the literature data [12], ρ_{SiO_2} and $\rho_{Al_2O_2}$ are 2,8 and 4,1 g/cm^3, respectively. The calculated volume fractions of oxides in the Alnico alloys solidified after 120-s holding at 1750 °C are = 8,55 × 10^{-5} ± 1,93 × 10^{-6} and = 1,13 × 10^{-4} ± 1,98 × 10^{-5}.

The volume fraction of titanium nitrides in the alloy can be calculated using equation

$$V_{\text{TiN}} = \frac{N_{\text{TiN}} M_{\text{TiN}} \rho_{\text{matrix}}}{\rho_{\text{TiN}} y A_N} \qquad (5)$$

where ρ_{TiN} is the density of TiN; A_N is the atomic mass of nitrogen; M_{TiN} is the molar mass of TiN; N_{TiN} is the nitrogen mass fraction in the form of TiN determined by FGA. The density of TiN is 5,4 g/cm^3 [12].

Figure 6 shows the effect of the time and temperature of holding of the melt before pouring on the volume fraction of TiN in the Alnico samples.

As the holding time increases, the volume fraction of nitrides decreases. This is reached at the expense of the melt mixing and removal of TiN inclusions. As the holding temperature increases, the decrease in the TiN content takes place only during the prolonged holding. In this case, the melt becomes more uniform with respect to the nitrogen content. This can be related to a decrease in the nitrogen solubility with increasing melt temperature.

CONCLUSIONS

The structure of Alnico alloys (prepared from wastes of production) and the segregation of the principal components in them have been studied.

The procedure of fractional gas analysis, which is based on the difference in the thermodynamic stability of oxides, has been developed for Alnico alloys. Compounds SiO_2 and Al_2O_3 were found to be principal oxide inclusion present in these alloys.

As the temperature and time of holding of the Fe-Al-Ni-Co-Ti melt before the pouring increase, the total oxygen content decreases. In this case, the distribution of oxide inclusions becomes more uniform.

The results of the FGA show that the content of SiO_2 inclusions in the Alnico samples mainly depends on the holding time before pouring and decreases with increasing holding time, whereas the content of Al_2O_3 inclusions decreases with increasing both temperature and time of holding.

Nitrogen is shown to be present in the alloys in the form of TiN inclusions. The FGA procedure for the determination of nitride inclusions in the Alnico alloys has been developed. It was shown that the content of TiN inclusions in the Alnico alloys decreases with increasing holding time. As the holding temperature increases, the content of nitride inclusions decreases only with increasing holding time.

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Note: The responsible translator for English Language is N. Kolchugina.