

The Influence of Protective Atmosphere on the Oxidation of Sintered SmCo₅ Magnetic Materials

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Abstract: The possibility of using low and medium vacuum (10^{-3} - 10^{-4} bar), as a protective atmosphere, in the sintering and heat treatment of SmCo₅ magnets was explored. The influence of the used protective atmosphere on structural changes in SmCo₅ magnets was investigated, for different temperature and time intervals, but for a constant temperature and time of heat treatment. The presence of oxides, or any other inclusions, was not proved in any part of the sintered SmCo₅ sample, except in the surface layer. The width of the oxide layer was measured by Scanning Electron Microscopy (SEM), using the Texture Analysis System (TAS+). A regression model was established, showing that the width of the oxide layer grows with the square of the sintering temperature, and linearly with sintering time, for defined heat treatment conditions.

Keywords: SmCo₅ Magnet; Sintering; Protective Atmosphere; Oxidation.

Резюме: Истражена је могућност коришћења вакуума на границе између ниског и високог (10^{-3} - 10^{-4} бар) као заштитне атмосфере у процесима спекања и термичке обраде SmCo₅ магнета. Истражено је утицај заштитне атмосфере на структурне промене SmCo₅ магнета при различитим температурним и временским интервалима спекања, и при константној температури и трајању термичке обраде. Присуство оксидних и других укљученија у печеним примерцима SmCo₅ не је установљено. При помоћи скенирајућег електронског микроскопа са коришћењем система текстуалног анализа извршено је мерење дебљине оксидне зоне. Установљена је регресиона модел, према којој при одређеној температури термичке обраде дебљина оксидне зоне расте са квадратом температуре спекања и линеарно са временом спекања.

Кључеве слова: SmCo₅ магнит; Спекание; Заштитна атмосфера; Окисление.

Садржај: Истражена је могућност коришћења вакуума на граници између ниског и високог (10^{-3} - 10^{-4} bar) као заштитне атмосфере у фазама синтеровања и термичке обраде SmCo₅ магнета. Испитан је утицај заштитне атмосфере на структурне промене SmCo₅ магнета за различите температурне и временске интервале синтеровања, а за константну температуру и време термичке обраде. Присуство оксидних и других инклузија у било ком делу синтерованих SmCo₅ узорака, осим у површинском слоју, није доказано. Скенирајућом електронском микроскопијом (SEM), коришћењем Texture Analysis System-а (TAS+) мерена је дебљина оксидне зоне. Утврђен је регресиони модел према коме дебљина оксидне зоне расте са

квадратом температуре синтеровања, а линеарно са временом синтеровања, за дефинисану температуру термичке обраде.

Кључне речи: SmCo₅ магнет; Синтеровање; Заштитна атмосфера; Оксидација.

Introduction

The reactivity of materials used for the production of rare earth based magnetic materials is considerable and grows with increasing temperature. All the heat operations must occur in an atmosphere of inert gas, reductive atmosphere or vacuum [1,2]. The final sintered SmCo₅ magnet, of good quality, should consist of at least 95mass.% SmCo₅ hard intermetallic phase, and up to 5 mass.% of a phase richer in Sm, usually this is Sm₂Co₇. The presence of phases that have less of the rare earth component is allowed only in traces. [1-3]

Keeping in mind that SmCo₅ is a carrier of magnetic properties, and knowing the fact that oxygen most usually decreases the amount of the SmCo₅ phase, in that way lowering the magnetic properties, the concept of this paper was to examine the influence of protective atmosphere by observing the content of SmCo₅.

The great majority of authors most commonly suggest argon of high purity, then the combination of hydrogen and helium, as a protective atmosphere for sintering and heat treatment [2,3]. High vacuum is only occasionally mentioned as a possible working atmosphere, and even then, only in combination with some inert gas.

For the purpose of designing the working atmosphere during sintering and heat treatment, the possibility of using low and medium vacuum (10^{-3} - 10^{-4} bar) as a protective atmosphere, was investigated in this study for different temperature and time intervals of sintering, but for a constant time and temperature of heat treatment.

Experimental

In this paper part of the results investigating the possibility of using low vacuum as a protective atmosphere during sintering and heat treatment [4] are presented. As a protective atmosphere vacuum of 10^{-3} - 10^{-4} bar was applied. The investigated temperatures of sintering were 1100, 1120, 1140, 1160 and 1180°C, and for each investigated temperature sintering lasted 30, 45 or 60 minutes.

The temperature of heat treatment was 900°C. The heat treatment lasted 90 minutes for all investigated sintering conditions. Using continuous X-Ray analysis structural changes of the SmCo₅ phase, were investigated in all sintered and annealed samples. The investigation was carried out for the inner structure of the sample as well as for the surface layer. The presence of the oxide layer was proved by X-Ray and SEM analysis only in the surface layer, and the width of this layer was measured by SEM, using TAS+.

The experimental data obtained by measuring the width of the oxide layer were evaluated by means of a mathematical - statistical method. The approach was to use regression analysis to establish the influence of the sintering process parameters: time and temperature on the width of the oxide layer, for the given temperature of heat treatment of 900°C in the applied protective atmosphere.

Results and Discussion

Fig.1. presents representative diffractograms of sintered and heat-treated samples of SmCo_5 without a surface layer. Fig. 2. shows one randomly chosen diffractogram of the surface layer of a sintered and heat - treated SmCo_5 sample.

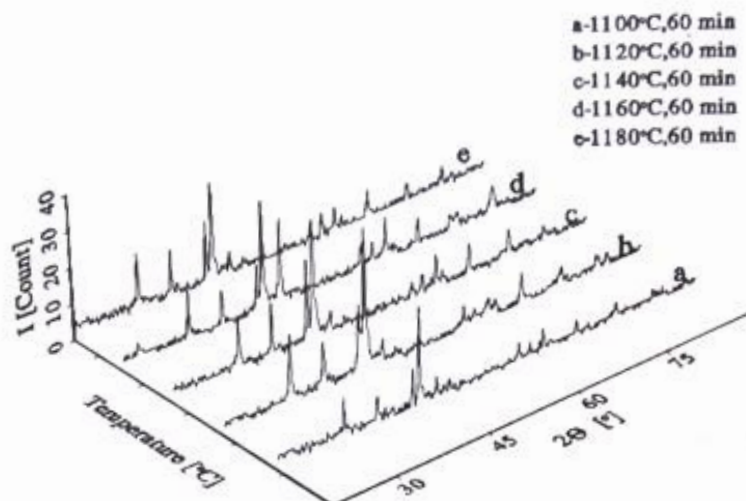


Fig.1 X-Ray diffractograms of SmCo_5 samples sintered at different temperatures; Heat treatment :900°C, 90 minutes, the surface layer has been removed

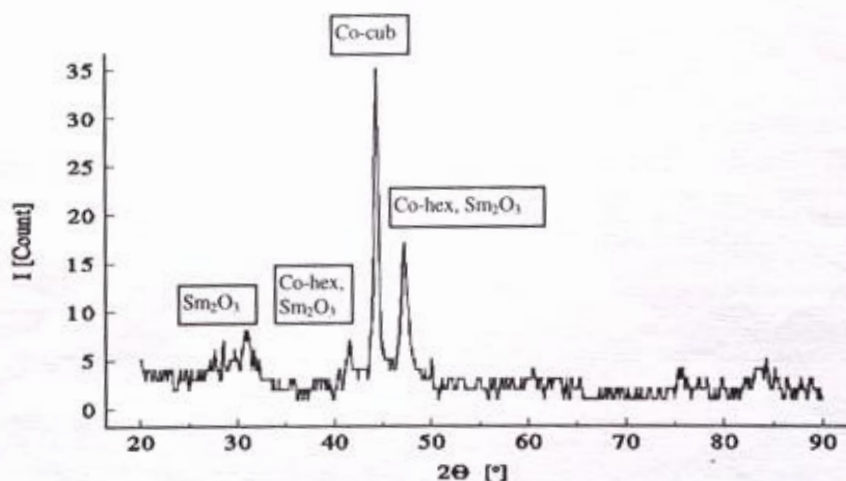


Fig.2 X-Ray diffractogram of the surface layer of a SmCo_5 sample sintered at 1160°C, 60 minutes; Heat treatment:900°C, 90 minutes

Identification of the diffractograms of the cross-section of all the investigated samples (Fig. 1.), without any doubt prove the existence of minimum 95mass.% of the SmCo_5 phase. The presence of less magnetic phases, oxides, or any other inclusions, was not proved in any part of the sintered SmCo_5 sample, except in the surface layer. By X-Ray

analysis of the surface layer for all the examined samples, the following phases were identified: Hexagonal Co, Cubic Co and Sm_2O_3 , the B type (Fig. 2.) [5]. On the surface of the sintered SmCo_5 samples during cooling, after the heat treatment is over, the surface layer becomes oxidized. It must be presumed that the oxidation is caused by a solid state reaction with oxygen which was present in the initial powder, rather than with oxygen adsorbed during pressing, as well with the oxygen present in small amounts in the used protective atmosphere [4].

The explanation for the formation of the oxide layer can be found in the crystal structure of SmCo_5 . The intermetallic SmCo_5 compound consists of two groups of atoms of significantly different dimensions, having a CaCu_5 type of structure. The structure of SmCo_5 may be described as an alternate stacking of layers, one formed by cobalt atoms and the other having one atom of samarium on every two cobalt atoms (Co_2Sm) [1,6]. If samarium is to fit easily into the Co_2Sm layer, then the samarium/cobalt ratio should not exceed 1.31. On the other hand, if it is to fill the hole in the adjacent cobalt layers this ratio should be 1.58. The actual Sm/Co radius ratio is 1.44. [6].

According to all this, samarium is too large to fit easily into the Co_2Sm layer and too small to be in contact with its 12 cobalt atoms in the adjacent layers. The ease with which samarium atoms can be detached from SmCo_5 and then quickly oxidized is thus readily understood. The presented interpretation could be the explanation for the appearance of the oxide layer that was observed on the investigated sintered and heat-treated SmCo_5 magnetic materials.

Figs.3a and 3b with microphotographs of the cross-section of the surface layer of sintered SmCo_5 samples illustrate the growth of the width of the oxide layer with the increase of the temperature and time of sintering .

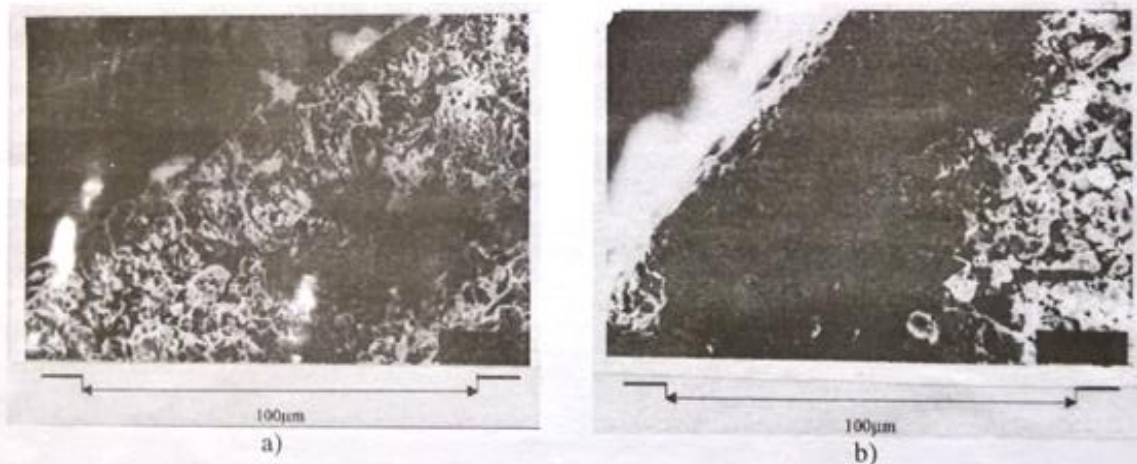


Fig.3 Scanning electron micrograph of sintered SmCo_5 ; temp.of heat treat.900°C, time 90 min. a) temp. sint. 1120°C, time 30min; x750 b) temp.sint.1180°C, time 60min; x750

By observing the microstructure of the cross-section of the surface layers of all investigated samples (Fig.3.a,b), the presence of the oxide layer is evident. The width of the oxide layer grows with increase of temperature and time of sintering corresponding to the experimental data obtained by measuring the oxide layer. The maximal measured average width of the oxide layer did not exceed $45\mu\text{m}$ and was measured for the highest temperature and the longest sintering time :1180°C, 60 minutes.

Fig.4. graphically presents the experimental data obtained by measuring the oxide layer as a function of temperature and time of sintering, evaluated by regression analysis together with a graphical presentation of the regression function itself for the investigated interval of temperature and time of sintering.

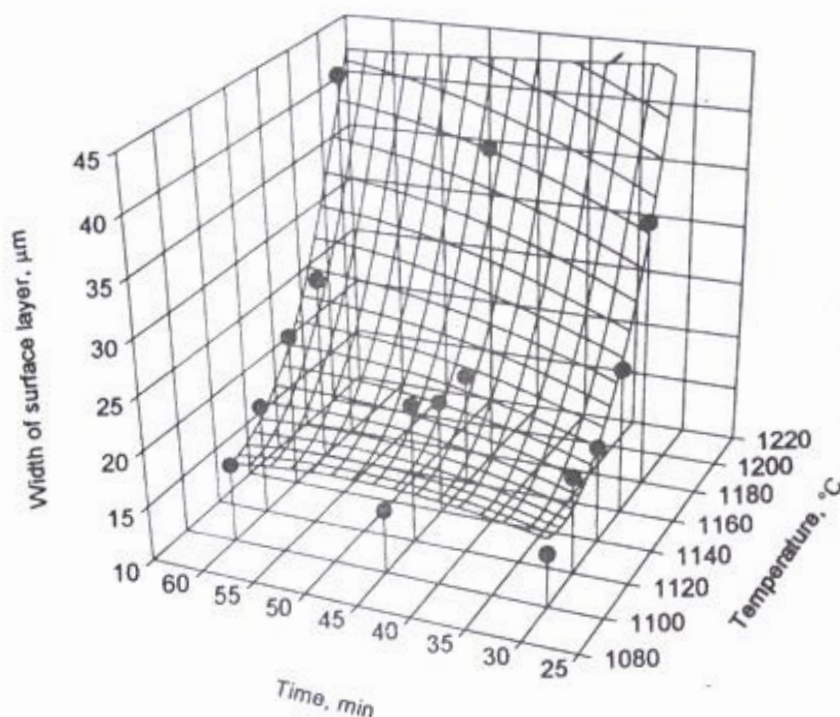


Fig. 4 Graphical representation the dependence of the width of the oxide layer on the temperature and time of sintering

Different regression functions were investigated [4], and the regression model with the highest value of the square of the coefficient of correlation (0.94) was chosen. The regression equation for the established model is:

$$\Delta = 7019.55 - 10.0519T - 3.54198\tau + 0.00360005 T^2 - 0.00548588 \tau + 0.00296862\tau T$$

The meaning of the symbols is as follows:

- Δ the width of oxide layer [μm]
- T temperature [K]
- τ time [min.]

From the graph (Fig. 4.), good agreement of the experimental data to the regression model is evident. It can be stated that the influence of sintering temperature on the width of the oxide layer is much more significant than the influence of the sintering time. The width of the oxide layer grows with the square of the sintering temperature and linearly with the sintering time, for a heat treatment temperature of 900°C.

We may draw the following conclusions:

- A. The possibility of using low and medium vacuum (10^{-3} - 10^{-4} bar), as a protective atmosphere, in the sintering and heat treatment of SmCo_5 magnet was confirmed.

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- B. Using the continued X-Ray analysis of sintered and heat - treated SmCo_5 samples, only the SmCo_5 phase was identified in the amount of a minimum of 95mass.% for all the investigated conditions of sintering and heat treatment.
- C. The presence of oxides, or any other inclusions, was not proved in any part of the sintered SmCo_5 sample, except in the surface layer.
- D. By X-Ray analysis of the surface layer, for all the examined samples, the following phases were identified: Hexagonal Co, Cubic Co and Sm_2O_3 , the B type.
- E. By SEM analysis of the microstructure of the surface layer of the sintered and heat treated SmCo_5 samples, the existence of an oxide layer was confirmed. The maximal width of the oxide layer, for all investigated cycles of sintering and heat treatment, was 45 μm .
- F. It was established that the width of the oxide layer grows with the square of sintering temperature, and linearly with the sintering time.
- G. It is possible to remove the oxide layer during machining, a common phase in the technological procedure of under the production of sintered SmCo_5 magnets. Therefore, we state that the measured width of the oxide layer, at the investigated conditions, can not affect the magnetic properties of the final magnet.

References

1. V. V. Sergeev, T. I. Bulygina, *Magnitoverdye Materialy*, Energiya, Moskva (1980)
2. J. Ormerod, *J. Less-Common Met.*, **111** (1985), 49-69
3. Brambilla, *Metal Powder Report*, **37**(1) (1982), 24-26
4. N. Talijan, *Ph.D. Thesis*, Faculty of Technology and Metallurgy, Belgrade University, 1995.
5. Powder diffraction file, Joint Committee on Powder Diffraction Standards (JCPDS) 1990.
6. D. M. Nicholas, P. Barnfield, J. Mendham, *J. Mater. Sci. Lett.* **7** (1988) 304-306