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The Characterization of Sintered $SmCo_5$ Magnets*

N. Talijan, A. Milutinović-Nikolić, J. Stajić-Trošić, Ž. Jovanović

Institute of Chemistry, Technology and Metallurgy, Njegoševa 12, Belgrade

Abstract: *During the investigation and design of a laboratory model of a sintered* $SmCo_5$ *magnet, a group of methods for characterizing sintered and heat treated magnets was defined. The direct dependence of the magnetic properties of sintered magnets on the microstructure and phase composition gives special significance to the methods of scanning electron microscopy (SEM) with appropriate software for quantification of visual information (QVI) and X-ray diffraction analysis. The chosen characterization methods are discussed in this paper with a separate presentation of the importance of the SEM and X-ray-diffraction methods in optimizing the sintering and heat treatment phases in the procedure for obtaining these magnets.*

Keywords: *Sintering;* $SmCo_5$ *Magnets.*

Резюме: *В течение исследования и проектирования лабораторной модели спеченного* $SmCo_5$ *магнита определен комплект методов для характеризации спеченных и термически обработанных магнитов. Прямая зависимость магнитных свойств спеченных магнитов от микроструктуры и фазового состава придает особое значение методам сканирующей электронной микроскопии с соответствующим программным обеспечением для количественного определения визуальной информации, а также рентгеноструктурному анализу. В данной раноте обсуждали отобранные методы характеризации, а также показана важность методов сканирующей электронной микроскопии и рентгеноструктурного анализа для оптимизации фазы спекания и термической обработки в процессе получения данных магнитов.*

Ключевые слова: *Спечекание;* $SmCo_5$ *магнит.*

Садржај: *У току истраживања и израде лабораторијског модела синтерованог* $SmCo_5$ *магнета дефинисан је скуп метода за карактеризацију синтерованих и термички обрађених магнета. Директна зависност магнетних својстава синтерованих магнета од микроструктуре и фазног састава даје посебан значај методама скенирајуће електронске микроскопије (SEM) са одговарајућим софтвером за квантификацију*

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визуелних информација (KVI) и рендгенској дифрактометријској анализи. У овом раду образложене су одабране методе карактеризације, са посебним приказом значаја методе SEM и рендгенске дифрактометрије за оптимизацију фазе синтеровања и термичке обраде у поступку добијања ових магнета.

Кључне речи: *Синтеровање; SmCo$_5$ магнети.*

1. Introduction

In the course of studying the field of permanent magnetic materials of the Sm - Co type, it was noticed that there is an exceptionally large number of parameters that directly influence the magnetic parameters of the final magnet, which are also interrelated. Although numerous, these parameters may be classified into two groups: parameters related to the character and behavior of the initial SmCo$_5$ powder and parameters related to the technological procedure of obtaining sintered SmCo$_5$ magnets.

By summing up the experimental results in the course of investigation the technological parameters of the production procedure on the properties of the final SmCo$_5$ magnet, as well as during the characterization of the sintered and heat treated magnets, the group of methods for characterizing the final magnets was defined.

The chosen characterization methods enable the realization of the following basic goals:

- characterization of the final magnets,
- clarification and definition of the dependence of the magnetic properties of the final magnet on the individual technological parameters, and
- the possibility of the broader utilization of the obtained experimental characterization results to optimize individual phases of the technological production procedure.

2. Choice of methods and experimental results

The following investigations were carried out to characterize the sintered and heat treated SmCo$_5$ magnets:

- chemical composition,
- oxygen content,
- microstructure analysis,
- phase analysis,
- study of the magnetic properties.

Micro-X-ray diffraction spectral quantitative analysis was used for quantitative chemical analysis. The samarium content in the sintered SmCo$_5$ type magnets ranged from 32 to 39 mass% [1,2].

The high reactivity of rare earths and the direct dependence of the magnetic properties of the final magnets of this type on the oxygen content requires continuous control of the oxygen content. In order to achieve maximal values of the magnetic properties of the sintered SmCo$_5$ type magnets, the allowed oxygen content in the final magnet ranges from 0.6 to 0.8 mass% [2,3]. An additional amount of 800 ppm of oxygen leads to oxide formation decreasing the content of the magnetic SmCo$_5$ phase by 0.5 mass% which directly causes a decrease in the magnetic properties of the final magnet. A LECO instrument was used in the quantitative chemical determination of oxygen after each step of obtaining a sintered magnet as well as in the final magnet.

SEM was used to analyse the microstructure of the sintered and heat treated $SmCo_5$ magnets in the surface layer and in the interior of the sample. SEM analysis enabled the study of changes in the site and the association of the particles as a function of the sintering and heat treatment conditions, as well as the determination of the degree of porosity. SEM analysis of the microstructure of the surface layer of sintered and heat treated $SmCo_5$ magnets was used to establish the existence of an oxide zone.

Sintering was investigated in the temperature range from 1100-1180°C in intervals of 20°C, with sintering times of 30, 45 and 60 min each investigated temperature. The heat treatment for all the investigated sintering times and temperatures was always at 900°C for 90 min. The maximal thickness of the oxide zone for all the investigated sintering and heat treatment conditions was 45μm [4].

Software for quantification of visual information (QVI) together with SEM allows measurement of the thickness of the oxide zone on the surface of the cross-section of the sintered and heat treated magnets for various sintering conditions and constant heat treatment conditions. By correlating the thickness of the oxide zone in the surface layer of sintered and heat treated $SmCo_5$ magnets with the temperature and time of sintering the mathematical model was obtained. [4].

A graphical presentation of the obtained mathematical model of the dependence of the thickness of the oxide zone (Δ) on sintering temperature and time with the corresponding regression equation are shown in Fig. 1. as an illustration of these investigations.

$$\Delta=5134{,}52-9{,}09321T-3{,}26353\tau+0{,}004039T^2+0{,}002537\tau^2+0{,}002786\tau T$$

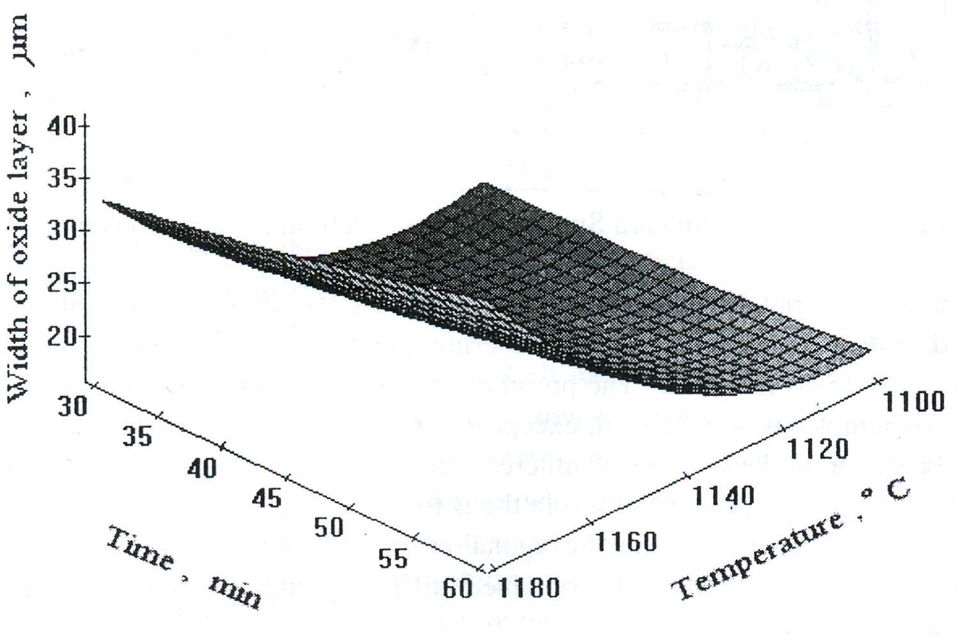


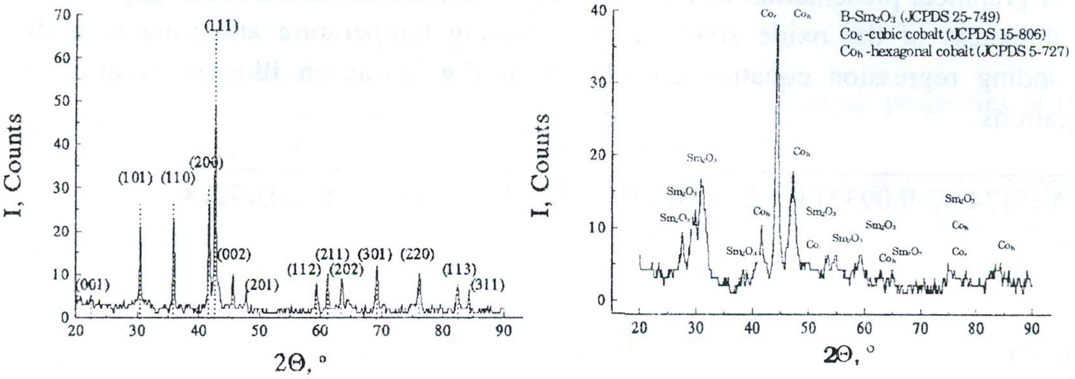
Fig. 1. Graphical presentation of the thickness of the oxide zone on sintering temperature and time for heat treatment at 900°C, time 90 min.

The obtained mathematical model enables observation of the sintering process and makes possible to define the critical temperature and time of sintering when growth of the oxide zone in the surface layer causes noticeable degradation in magnetic performance.

X-Ray diffraction analysis was used to qualitatively determine the phases present. The results of X-ray diffraction analysis were used for several purposes [5,6]:

- for identifying the phases present in the surface layer,
- the mathematical modeling of the sintering process was performed by measuring the intensity of the peaks from the obtained diffractograms and correlating the intensities of the peaks of the (111) plane for the $SmCo_5$ phase with the sintering temperature and time,
- the parameters a and c of the hexagonal crystalline lattice of the $SmCo_5$ phase were calculated on the basis of the obtained diffractograms for various sintering and heat treatment conditions.

Fig. 2. shows representative diffractograms with identified phases of a $SmCo_5$ magnet sample sintered at 1140°C for 45 min and heat treated at 900°C for 90 min. Figure 2a shows the diffractogram of the cross-section of the interior of the sintered and heat treated sample of $SmCo_5$, while Figure 2b shows the diffractogram of the surface layer of the same sample.



a) b)

Fig. 2. Diffractograms of the sintered $SmCo_5$: a) cross-section, b) surface layer

Continuous X-ray diffraction was used to analyse the phases in the sintered and head treated $SmCo_5$ magnets. For all the sintering and head treatment conditions, only $SmCo_5$ (min. 95%) was identified. The presence of oxide or other inclusions in any part of the sintered samples was not found, except in the surface layer. X-Ray diffraction of the surface layer, for all the samples of sintered $SmCo_5$ magnets, revealed hexagonal and tesseral metallic cobalt, as well as Sm_2O_3 in the B form [4,5,6].

The parameters *a* and *c* of the hexagonal crystalline lattice for the $SmCo_5$ phase were calculated on the basis of the obtained diffractograms and correlated to the sintering and heat treatment conditions.

Tab. I shows the experimentally calculated values of the parameters *a* and *c* of the $SmCo_5$ hexagonal crystalline lattice of the starting powder, milled powder and $SmCo_5$ samples sintered under various conditions at constant heat treatment conditions, together with the values of the standard [7].

The experimentally calculated values of the parameters *a* and *c* of the $SmCo_5$ hexagonal crystalline lattice of the starting, milled powder and of the sintered magnets under different sintering regimes negligibly differ from the standard values. Applied sintering conditions did not induce defects in the crystalline lattice of $SmCo_5$.

Tab. I Comparative presentation of the parameters *a* and *c* of the $SmCo_5$ hexagonal crystal lattice

SAMPLE		PARAMETER LATTICE (with standard error)	
		a, nm	*c*, nm
STANDARD VALUES	JCPDS 35 - 1400	0.4995± 0.0001	0.3987± 0.0001
	JCPDS 27 - 1122	0.4995± 0.0001	0.3987± 0.0001
STARTING POWDER $SmCo_5$		0.50052950 ± 0.00010310	0.3968199 ± 0.00014191
POWDER $SmCo_5$, MILLED 45 MIN.		0.50055676 ± 0.00008058	0.39721911 ± 0.00009788
SINTERED $SmCo_5$			
TEMPERATURE, °C	TIME, MIN.		
1100	45	0.50026259 ± 0.00014563	0.39714360 ± 0.00018978
1120	45	0.50076864 ± 0.00018181	0.39894229 ± 0.00023930
1140	45	0.50038653 ± 0.00014112	0.39850378 ± 0.00018557
1160	45	0.50093074 ± 0.00018440	0.39904882 ± 0.00023762
1180	30	0.50100157 ± 0.00022161	0.39899700 ± 0.00029142

It was established in these investigations that there is a dependence between the intensity of the dominant diffraction peak, which corresponds to the (111) plane of the $SmCo_5$ phase and the sintering temperature and time. By correlating these parameters with mathematical treatment mathematical models were established [5,8]. Two different heat treatment regimes were investigated, for all investigated sintering conditions. In the first case after each sintering regime, heat treatment was performed at 900°C for 90 minutes, and in second case the heat treatment was at 920°C, also for 90 minutes. The obtained mathematical models show that there is a complex dependence between the intensity of the diffraction peak and the sintering time and temperature for defined heat treatment conditions. For both heat treatment regimes, the smallest average square errors were obtained when the following type of the regression equation is used:

$$I = k_1 t^2 + k_1 \tau^2 + k_3 t \tau + k_4 t + k5\tau + k_6 \qquad (1)$$

Where: k_1, k_2, k_3, k_4, k_5 and k_6 are parameters; t- the sintering temperature in°C; τ- the sintering time in minutes, I - intensity of dominant diffraction peak in Cts.

A graphical representation of the regression dependencies for heat treatments at 900°C, and 920°C are given in the Figs. 3 and 4, respectively.

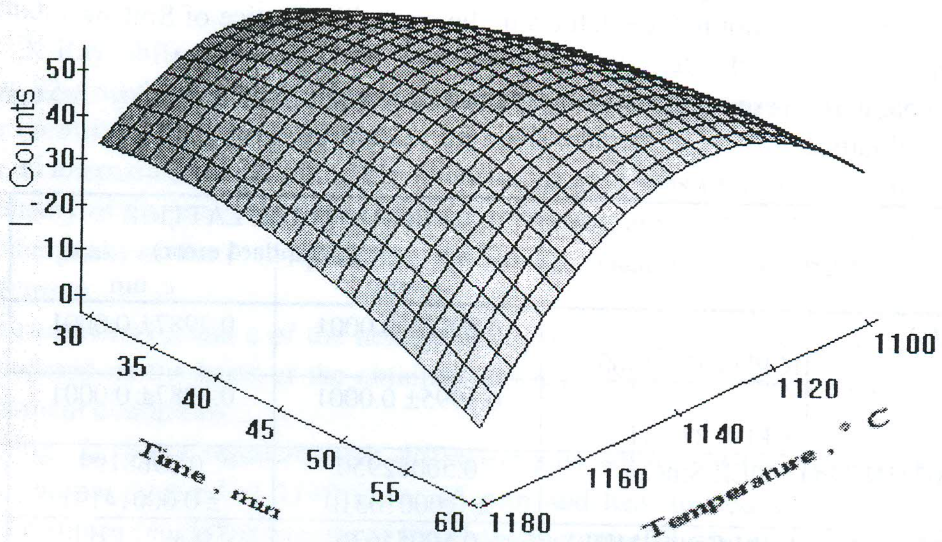


Fig. 3. Graphical presentation of the regression equation for heat treatment at 900°C

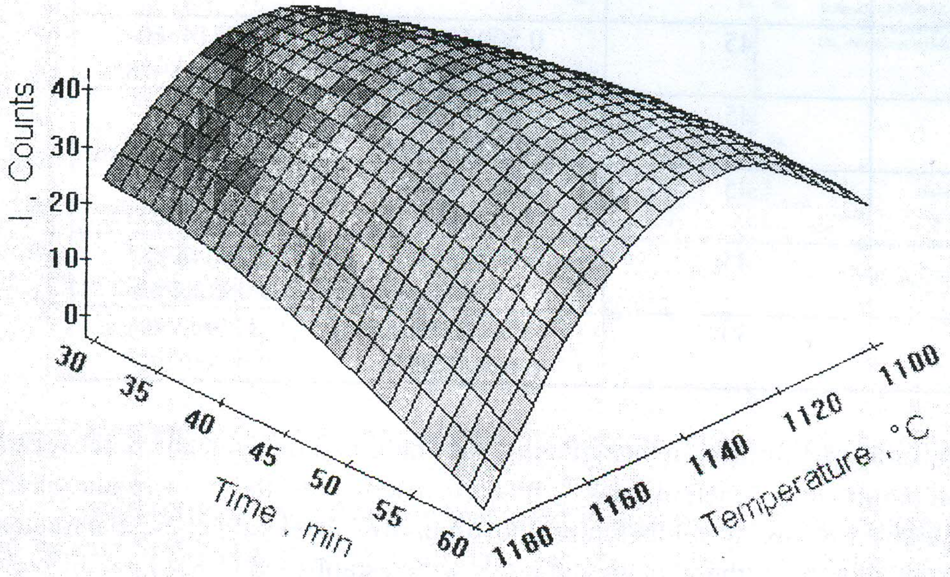


Fig. 4. Graphical presentation of the regression equation for heat treatment at 920°C

These models indicate that the intensity of the peak of the (111) plane of the $SmCo_5$ phase depends on the square of the temperature and square of the time of sintering for constant heat treatment conditions. It was experimentally confirmed that magnetic properties are obtained when sintering occurs under conditions at which the intensity of the diffraction peak of the (111) plane for the $SmCo_5$ phase is maximal [5,8].

It is possible to study magnetization and measure magnetic properties using various types of magnetizers. The basic condition is that the chosen instrument enables magnetization of the studied sample to complete magnetic saturation yielding peak values of the magnetic properties. A field strength greater than 2000 kA/m is required to achieve complete magnetic saturation of $SmCo_5$ type magnets.

A Hysterisis graph magnetizer with magnetic field strengths ranging from 2100 to 2400 kA/m was used to study the magnetization and magnetic properties of sintered $SmCo_5$ magnets.

Fig. 5 shows hysterisis curves of a $SmCo_5$ magnet sintered under different sintering conditions with heat treatment at 900°C, 90min.

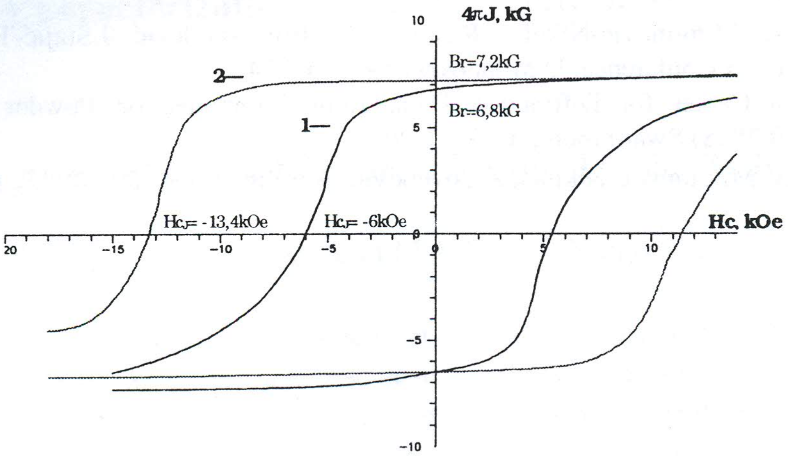


Fig. 5. Hysterisis curves of a sintered and heat treated $SmCo_5$ magnet: 1 - Sintering temp. 1100°C, time 60 min; 2 - Optimal sintering regime [5,8], 1140°C, time 45 min

3. Conclusions

In the course of the investigations and the design of a laboratory model of a sintered $SmCo_5$ magnet, a group of methods was chosen for the characterization of sintered and heat treated $SmCo_5$ magnets.

Micro-X-ray diffraction spectral quantitative analysis was proposed for quantitative chemical analysis. A LECO instrument was found to be the most reliable for the quantitative chemical determination of oxygen.

SEM with appropriate software for quantification of visual information (QVI), was proposed for analysis of the microstructure.

X-Ray diffraction was proposed for qualitative phase analysis. The results of the X-ray diffraction analysis were used to:

- determine the content of the magnetic $SmCo_5$ phase as a function of sintering and heat treatment conditions,
- identify the phases present in the surface layer,
- optimize the sintering process by applying the mathematical model obtained by correlating the intensities of the peak of the (111) plane of the $SmCo_5$ phase and the sintering temperature and time under constant heat treatment conditions,
- calculate the parameters *a* and *c* of the $SmCo_5$ hexagonal crystalline lattice to be able to observe the influence of sintering conditions on possible defects in structure.

References

1. V.V. Sergeev and T.I. Bulygina., Magnitotverdye Materialy, Energiya, Moskva, 1980.
2. M.F. De Campos and F.J.G. Landgraf, Proc. 14th Int. Symposium on Magnetic Anisotropy and Coercivity in RE-Transition Metal Aloys, Sao Paulo, Brazil, 1996, p. 321
3. J. Ormerod, J.Less-Common Met., 111, (1985), 49
4. N.M.Talijan, A.M.Nikolić, Ž.D.Jovanović, Sci. Sinter.Spec Iss. 28, (1996), 179
5. N.Talijan, A. Milutinović-Nikolić, R.Jančić, I.Petrović-Prelević, J.Stajić-Trošić, Mat.lett. 32, (1997), 85
6. N.Talijan, A. Milutinović-Nikolić, R.Jančić, I.Petrović-Prelević, J.Stajić-Trošić, Proc. XXVIII October Conference, D.Milanovac, 1996, p. 714
7. International Center for Diffraction Data, Joint Committee on Powder Diffraction Standards (JCPDS) Swarthmore, USA, 1990
8. N.Talijan, A. Milutinović-Nikolić, Ž. Jovanović, Sci. Sinter.Spec 29, (1997), 69