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Oxidative processes during heat treatment in intermetallic $SmCo_5$ powder

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Understanding of the thermal stability of intermetallic $SmCo_5$ powder is essential for designing the working atmosphere in all phases of the technological procedure in the production of sintered $SmCo_5$ magnets to obtain maximal magnetic properties. The thermal stability of the $SmCo_5$ powder with defined chemical composition and particle size was investigated in the interval from 20 to 900 °C. It was found by thermogravimetric analysis (TGA) that up to 240 °C, the oxidation of $SmCo_5$ does not occur. X-Ray diffraction of the thermogravimetric experimental residue of the $SmCo_5$ powder, heated at 240 °C, yielded only the presence of the $SmCo_5$ phase. By X-ray diffraction analysis different crystal forms were identified depending on the maximal heating temperature. The following phases were identified: Sm_2O_3, Co, CoO, Co_3O_4 and $SmCoO_3$. According to T and X-ray results, for each of the investigated temperatures, the corresponding chemical reactions were established. The experimental data from both the thermal and X-ray investigations confirm that the phases of pressing and aligning the $SmCo_5$ powder, in the process of producing sintered $SmCo_5$ magnets, may be performed without a protective atmosphere.

Key words: $SmCo_5$ magnet, $SmCo_5$-powder, oxidation, thermogravimetric analysis, X-ray analysis

The appearance of rare earth-transition metal based permanent magnetic materials enabled the improvement of existing, as well as the construction of completely new plants and systems with active magnetic components, in almost all technical and technological fields.

Sintered permanent magnetic materials of the $SmCo_5$ type have shown the best permanent magnetic properties both as a powder and a compact body formed by procedures of powder metallurgy. These magnetic materials are characterized by high stability of the permanent magnetization during the effect of a demagnetization field and they possess the best ratio of the energy product BH_{max} and the temperature interval of exploitation.

The high reactivity of rare earth metals requires special precautions in each technological stage of the production of permanent magnets based on $SmCo_5$.[1-4] Each variation of the chemical composition caused by the presence of metallic and non-metallic impurities damages the magnetic properties of these materials. A mere 800 ppm shift in oxygen content from its control level can, indeed, change the rare earth composition by 0.5%,[5,6] beyond the range within which the optimal properties can be obtained.

From the point of view of magnetic properties, it would be ideal if the magnetic material consists of a pure $SmCo_5$ phase, as the carrier of magnetic properties. This goal is impossible to reach in commercial production, and a purity of 95-97 mass% has been considered to be the most desireable.[2,5,7]

Most authors insist on a protective atmosphere in all technological procedures of production, not only in phases that are performed at elevated temperatures such as sintering and heat treatment, but they also suggest the use of a protective atmosphere during pressing and aligning of the $SmCo_5$ powder.[1,2,4,5]

Understanding of the thermal stability of the powder of intermetallic $SmCo_5$, is necessary for designing the working atmosphere in all steps of the technological procedure during the preparation of sintered $SmCo_5$ magnets[8,9] in order to obtain the maximal magnetic properties of the final product.

EXPERIMENTAL

Commercial $SmCo_5$ powder was used in these experiments and the chemical composition, given by the producer, in mass percent was: Sm = 34.7 ± 0.3% and Co = 64.8 ± 0.3%. The powder was milled in anhydrous toluene in an agate mortar to fine powder of quality used in the production of sintered magnets. All the experiments were carried out with powder of an average particle size of 7.23 μm, established by scanning electron microscopy (SEM), using a Texture Analysis System (TAS+). The thermal stability of the $SmCo_5$ powder in static air atmosphere was investigated by thermogravimetric analysis (TGA) using a DuPont Thermal Analyzer. Investigation of the behavior of $SmCo_5$ powder during heating were carried out using new samples of $SmCo_5$ powder for each of the investigated temperature cycles.

For each investigated temperature the structural changes were observed using the powder X-ray diffraction method using a Philips diffractometar and a copper anticathode with the wave length λ = 0.154178nm.

RESULTS AND DISCUSSION

Numerous samples of $SmCo_5$ powder of the same quality and particle size, were heated in different temperature intervals. The maximal heating temperatures for each investigated sample are presented by points in Fig. 1. For each investigated temperature the corresponding increase of mass is given. The increase in mass during the

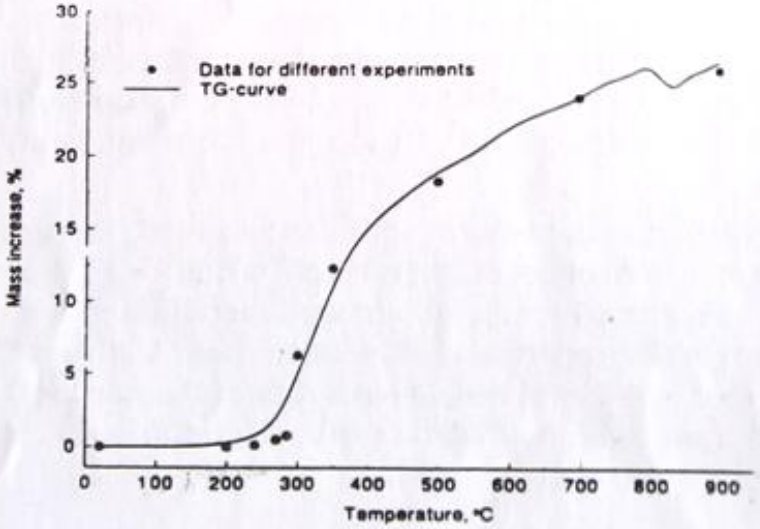

Fig. 1. TGA curve of $SmCo_5$ powder. Heating rate 20K/min.

heating of $SmCo_5$ powder in air atmosphere, is also presented in Fig. 1. by the TGA curve obtained in the temperature interval from 20 to 900 °C.

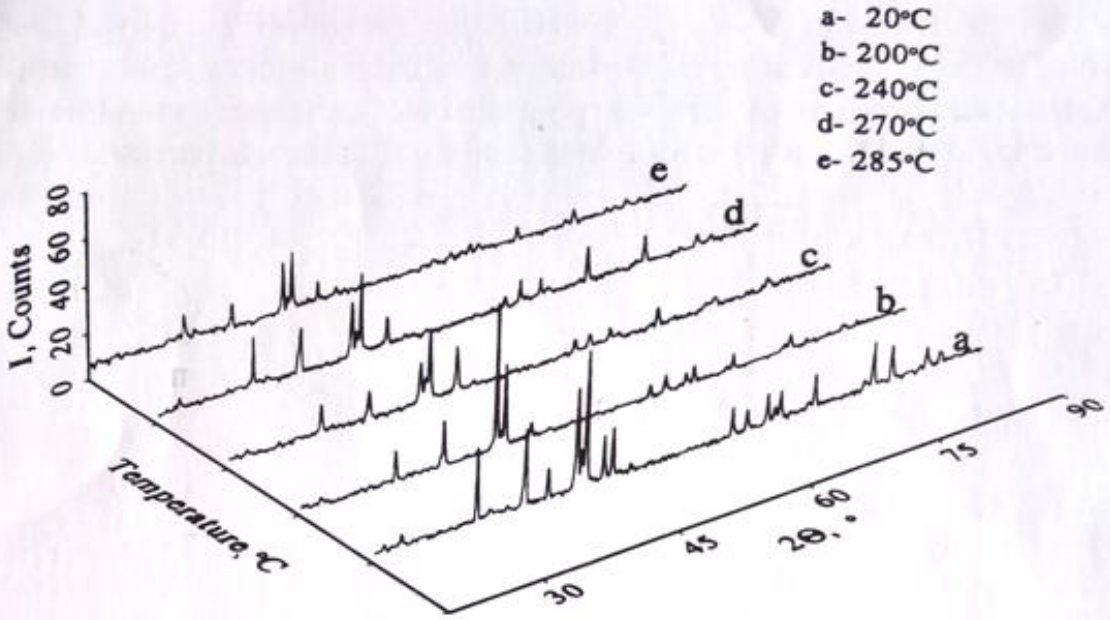

Fig. 2. X-ray diffractograms of $SmCo_5$ powders: a. starting powder; b. heated at 200 °C; c. heated at 240 °C; d. heated at 270 °C; e. heated at 285 °C.

The phases present after each heat treatment were determined by X-ray diffraction. The X-ray diffractogram of milled $SmCo_5$ powder (Fig. 2a) was presented as a reference, together with diffractograms of samples of $SmCo_5$ powders heated up to different temperatures (200-285 °C) (Figs. 2b-e).

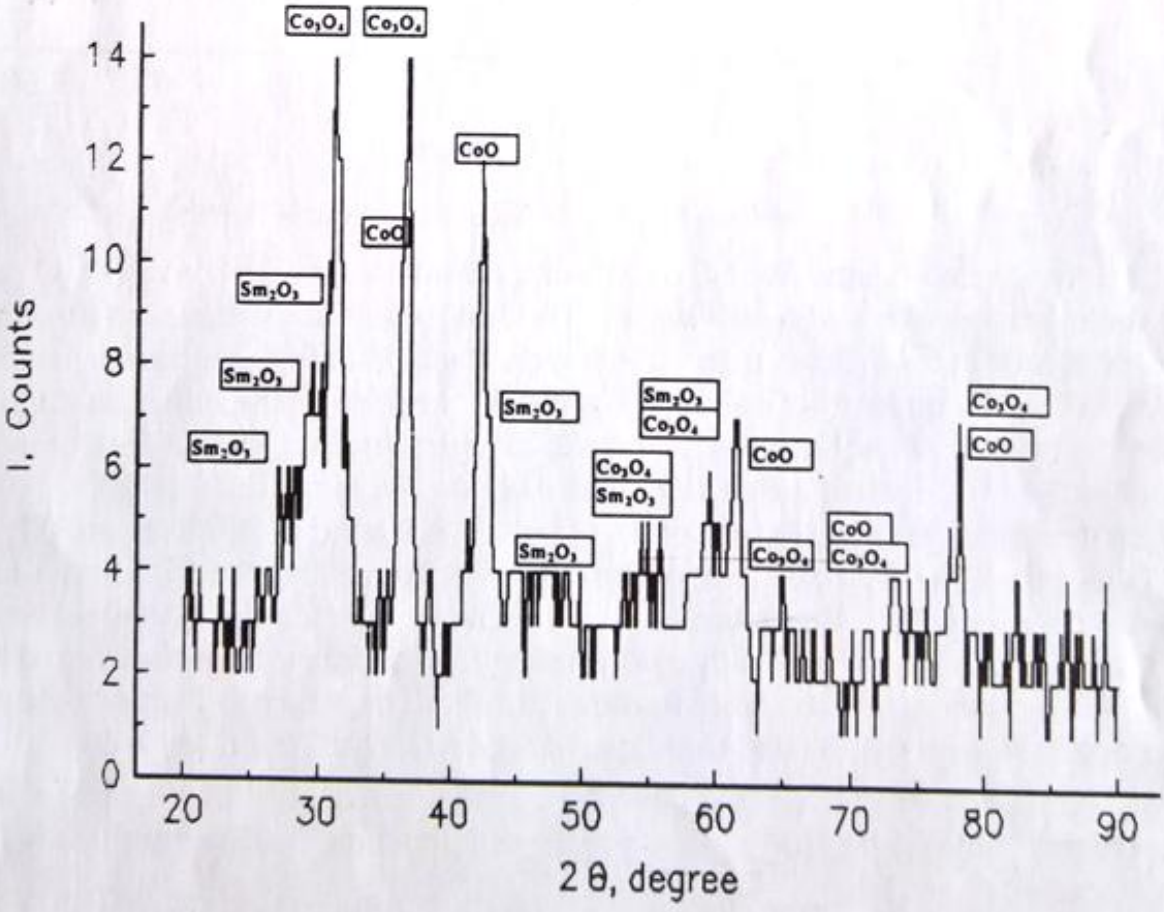

Fig. 3. X-ray diffractogram of $SmCo_5$ powder heated at 500 °C.

The result of the X-ray analysis of a $SmCo_5$ powder heated up to 500 °C, as shown in Fig. 3 and the diffractogram of $SmCo_5$ heated at 700 °C in Fig. 4.

The results of the TGA (Fig.1) and X-ray analysis (Figs. 2-4) of $SmCo_5$ are presented in Table I, indicating the dependence of the mass increase and the identified structures on heating temperature. The points in Fig. 1 correspond to the mass increase presented in Table I for every investigated sample, *i.e.*, temperature interval.

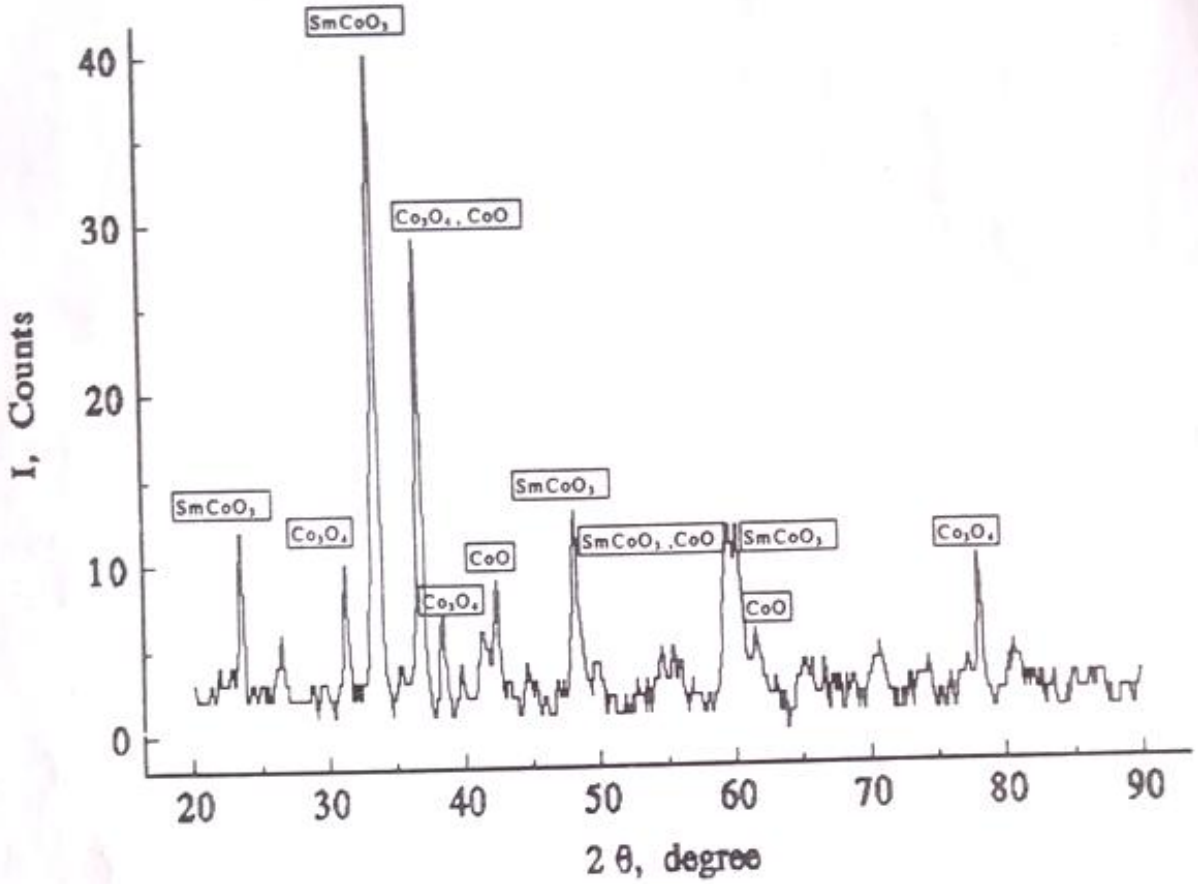

Fig. 4. X-ray diffractogram of $SmCo_5$ powder heated at 700 °C.

Between 285 °C and 300 °C the complete oxidation of $SmCo_5$ to Sm_2O_3 occurs and the oxidation of metal cobalt begins. The results of X-ray diffraction for a $SmCo_5$ powder heated at 500 °C, were very much the same as at 350 °C, the same phases were identified, only a quantity of cobalt(III) arises in the form of the mixed oxide Co_3O_4. X-ray diffraction of the thermogravimetric experimental residue of $SmCo_5$ powder, heated at 700 °C, yielded a $SmCoO_3$ phase beside the two cobalt oxides Co_3O_4 and CoO. The ratio of the Co_3O_4 phase to CoO phase is similar at 700 °C as at 500 °C. On the TGA curve (Fig. 1) in the temperature interval from 800 to 850 °C a mass decrease was observed, having a minimum at 835 °C. The reason for this is the reduction of Co_3O_4 to CoO, a reaction already confirmed in the literature.[9] For the sample heated at 900 °C the same structures were found as at 700 °C, only the CoO phase is dominant in comparison with Co_3O_4 due to the partial reduction of Co_3O_4 to CoO.

The results of the X-ray analysis are summarized in Table II presenting the temperature dependence of the first five most important[10] diffraction peaks for the $SmCo_5$ phase.

TABLE I. Results of thermogravimetric and X-ray analysis

Temperature (°C)	Mass increase (%)	The phases identified by X-ray diffraction (sorted by intensity of diffraction peaks)		
		First	Second	Third
200	0.01	$SmCo_5$	-	-
240	0.16	$SmCo_5$	-	-
270	0.51	$SmCo_5$	-	-
285	0.78	$SmCo_5$	-	-
300	6.30	Sm_2O_3	Co	CoO
350	12.30	Sm_2O_3	CoO	Co_3O_4
500	18.27	Sm_2O_3	Co_3O_4	CoO
700	23.86	$SmCoO_3$	Co_3O_4	CoO
900	25.71	$SmCoO_3$	CoO	Co_3O_4

By observing the TGA curve (Fig. 1), it is evident that the oxidation of the $SmCo_5$ powder did not occur up to 240 °C, and by X-ray diffraction, only $SmCo_5$ is identified for this sample (Fig. 2c).

In the temperature interval from 240 °C to 285 °C there is an increase in mass, caused by oxidation, but the amount of resulting oxides is small enough that they can not be identified by X-ray diffraction (Figs. 2c-e).

TABLE II. Temperature dependence of the first five most important diffraction peaks for the $SmCo_5$ phase

Temperature (°C)	d=0.212 nm plane (111) peak (cts)	d = 0.293nm plane (101) peak (cts)	d=0.250nm plane (110) peak (cts)	d=0.216nm plane (200) peak (cts)	d=0.199nm plane (002) peak (cts)
20	100	59	62	76	40
200	62	25	45	104	10
240	42	14	15	22	31
270	58	45	34	41	16
285	46	15	15	42	19

From the diffractograms in Figs. 2b-e and by comparison of the experimental data in Table II, it can be stated that the temperature increase causes a decrease of the diffraction peaks of $SmCo_5$ from 240 °C to 285 °C. This indicates that between 200 °C and 285 °C the crystallinity decreases, and that this could be the reason for the decrease of the magnetic properties in the final sintered magnet.[9,11]

According to the results of TGA and X-ray analysis the corresponding chemical reactions were established:

- until 240 °C - there is no oxidation of $SmCo_5$ powder

(Fig. 1 and Fig. 2a, 2b and 2c)

- 240 - 300 °C - complete oxidation of $SmCo_5$ to Sm_2O_3 (Fig. 1, Table I):

$$4\,SmCo_5 + 3\,O_2 \rightarrow 2Sm_2O_3 + 20\,Co \qquad (1)$$

- 285 - 900 °C - the oxidation of cobalt:

$$5\,Co + 3O_2 \rightarrow 2CoO + Co_3O_4 \quad (2)$$

- 500 -900 °C - the formation of $SmCoO_3$:

$$Sm_2O_3 + Co_3O_4 \rightarrow 2SmCoO_3 + CoO \quad (3)$$

- 800 - 900 °C - the reduction of Co_3O_4:

$$Co_3O_4 \rightarrow 3CoO + 1/2O_2 \quad (4)$$

From the results obtained by the investigation of the behavior of $SmCo_5$ powder at elevated temperatures we may draw the following conclusion:

- The results of thermogravimetric analysis proved that up to 240 °C the oxidation of $SmCo_5$ does not occur.

- By X-ray analysis of $SmCo_5$ powder, heated at 240 °C, only the $SmCo_5$ phase was identified in a minimum amount of 95 mass%, and fulfills one of the essential conditions for obtaining maximal values of the magnetic properties.

- The thermal stability of the $SmCo_5$ powder proved by TGA and X-ray investigations, that the phases of pressing and aligning $SmCo_5$ powder, in the process of producing sintered $SmCo_5$ magnets, could be performed without a protective atmosphere.

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И З В О Д

ОКСИДАЦИОНИ ПРОЦЕСИ ПРИ ЗАГРЕВАЊУ ПРАХА ИНТЕРМЕТАЛНОГ ЈЕДИЊЕЊА $SmCo_5$

НАДЕЖДА М. ТАЛИЈАН, АЛЕКСАНДРА МИЛУТИНОВИЋ-НИКОЛИЋ и ЖАРКО Д. ЈОВАНОВИЋ

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Познавање термичке стабилности праха интерметалног једињења $SmCo_5$ неопходно је за пројектовање радне атмосфере у свим фазама технолошког поступка добијања синтерованог $SmCo_5$ магнета да би се обезбедиле максималне магнетне особине. Испитана је термичка стабилност праха $SmCo_5$, дефинисаног хемијског састава и величине честица у интервалу од 20 до 900 °C. Термогравметријском анализом (TGA) је установљено да на температурама до 240 °C, не долази до оксидације праха $SmCo_5$. Такође, рендгенском анализом $SmCo_5$ праха загреваног до 240 °C идентификована је једино $SmCo_5$ фаза. Рендгенском анализом идентификоване су различите кристалне фазе, у зависности од максималне температуре загревања. Идентификоване су фазе: Sm_2O_3, Co, CoO, Co_3O_4 и $SmCoO_3$. На основу резултата TGA и рендгенске анализе, за сваку испитану температуру, наведене су одговарајуће хемијске реакције. Експериментални резултати термијских и рендгенских испитивања показују да се фаза пресовања и усмеравања праха $SmCo_5$, у поступку добијања синтерованих $SmCo_5$ магнета, може одвијати без коришћења заштитне атмосфере.

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