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X-RAY DIFFRACTION OF NANOCRYSTALLINE Sm-Y-Co ALLOYS

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Abstract: The synthesis for nanocrystalline $Sm_{0.5}Y_{0.5}Co_5$ alloys was performed by arc furnace and mechanical milling. Alloys of $Sm_{0.5}Y_{0.5}Co_5$ as-cast in an arc furnace were characterized by X-ray diffraction. Rietveld analysis for $Sm_{0.5}Y_{0.5}Co_5$ as cast was completed, and the lattice parameters were as follows: a= 4.967 Å and c= 3.973 Å, while the quantitative analysis for $Sm_{0.5}Y_{0.5}Co_5$ alloys showed the presence of two phases with a weight Fraction of 42.41 for the $Sm_{0.5}Y_{0.5}Co_5$ phase and a weight Fraction of 57.59 for the YCo_5 phase. Here, the interplanar spacing value is used to show that $Sm_{0.5}Y_{0.5}Co_5$ alloys contain one phase for $Sm_{0.5}Y_{0.5}Co_5$ and another phase for YCo_5; furthermore, structural characterization is proven important because affects the magnetic properties.
Keywords: Nanocrystalline alloys, X-ray diffraction

INTRODUCTION

A characterization of the crystal structure and microstructure of nanocrystalline $Sm_{0.5}Y_{0.5}Co_5$ alloys is actual due to that shows an enhancement of the magnetic properties associated with the change in the structural parameters, such as crystallite-size, crystallographic texture, interplanar distances, lattice parameters and unit cell volume. The $RECo_5$ compound showed large magnetic anisotropy, which is due to the spin-orbit interaction of the 4f moments of the RE atom and the spin-orbit interaction of the 3d moments of the Co atom in the anisotropic crystalline environment [9]. Recently, we showed that nanocrystalline $Sm_{0.5}Y_{0.5}Co_5$ alloys can be applied in magnetic recording, MEMS, as an ideal magnetic memory medium, such as permanent magnets [1,4]. In the $Sm_{0.5}Y_{0.5}Co_5$ unit cell, the Co atoms occupied two crystallographic sites, 2c and 3 g, while the RE occupied the center of the hexagons. It is also known that the YCo_5 compound showed an increase in the lattice spacing, and due to it, an increase in the magnetic moments showing the magneto volume effect is observed [11]. On the other hand, when $RECo_5$ is used to obtain nanocomposites of the two phases, hard magnetic and soft magnetic phases require crystals in the range of 20-50 nm. For example, when a soft magnetic phase with this crystallite-size is used in nanocomposites of $RECo_5$, an enhanced remanence develops due to the magnetic interactions present in the magnetic materials. Recently, we reported the complication in the index of X-ray diffraction pattern from nanocrystalline $Sm_{0.5}Y_{0.5}Co_5$ alloys obtained by melt spinning. Here, we showed that the presence of crystallographic texture obscures and difficult recognize if only $Sm_{0.5}Y_{0.5}Co_5$ or two phases of YCo_5 and other $SmCo_5$ exist in the alloys [7]. When yttrium is replaced by samarium in $Sm_{0.5}Y_{0.5}Co_5$ alloys obtained by melt spinning the appearance of crystallographic texture and enhancement of the magnetic properties are observed due to the high anisotropy field of the $SmCo_5$ phase and the refined microstructure. The purpose of this work is to study the importance of the interplanar distance determination through X-ray diffraction patterns for the index materials where it is difficult to identify the present phases. In addition, more details on the enhancement of the magnetic properties are informed before by the authors [4]. Nevertheless, it is vital to note that the $Sm_{0.5}Y_{0.5}Co_5$ alloys were obtained particularly to study the structural parameters through of Rietveld method due to their importance earlier remark. For this issue, nanocrystalline $Sm_{0.5}Y_{0.5}Co_5$ alloys obtained by mechanical milling are used.

SAMPLE PREPARATION AND TECHNIQUES.

Alloys with $Sm_{0.5}Y_{0.5}Co_5$ nominal compositions were attained by electric arc

melting under Ar atmosphere (99.999 % Praxair). The starting materials were pieces of Y (Alfa Aesar, 99.9%), pieces of Sm (Alfa Aesar, 99.9%) and pieces of Co (Alfa Aesar, 99.5%). The alloy milling process was performed under an Ar atmosphere in a high-energy mill (Spex 8000 mixer/mill). The milling was carried out at 15 minutes, 30 minutes, 60 minutes and 240 minutes of mechanical milling under Ar atmosphere (99.999 % Praxair) and more details of sample preparation are shown by the authors in previous studies [5]. X-ray diffraction patterns were obtained on a Siemens D5000 diffractometer with Cu-Kα radiation (λ = 1.5406 Å). For the identification of phases in the $Sm_{0.5}Y_{0.5}Co_5$ alloys, the X-ray diffraction patterns were measured with step $\Delta(2\theta) = 0.01°$ and time for step of 10 seg, in an angular interval $20° < 2\theta < 99°$. A refinement of mathematical models to fit the structure of the studied samples and to obtain more realistic structural parameters and the application of the Rietveld method [10], and the software Full Prof was used [3]. For the Rietveld analysis was used Datas of the X-ray diffraction patterns in format .dat and a file out of refined parameters for the $Sm_{0.5}Y_{0.5}Co_5$ alloys was obtained of the refinement. Fig. 1 shown the atomic positions of the hexagonal close-packed (hcp) structure $CaCu_5$ type.

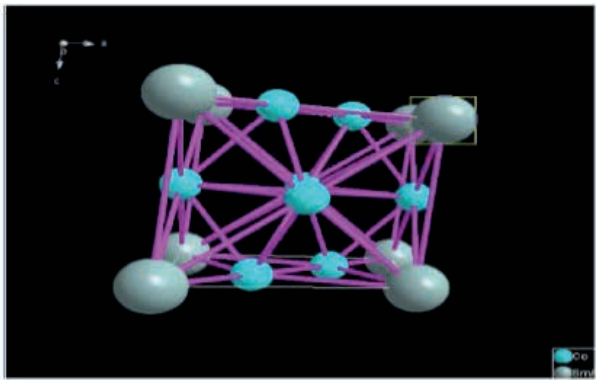

Fig. 1. Atomic positions of the hexagonal close-packed (hcp) structure $CaCu_5$ type (Crystal Structure of Wyckoff) Crystallographic information for $Sm_{0.5}Y_{0.5}Co_5$.

Space group	P 6/m m m
Crystal Structure	Hexagonal

Lattice parameters a=4.960 Å, c=3.995 Å

Atomic positions

Element	x	y	z
Co	0.500	0.000	0.500
Co	0.333	0.667	0.000
Sm	0.000	0.000	0.000
Y	0.000	0.000	0.000

RESULTS

X-RAY DIFFRACTION

Fig. 2 shows the X-ray diffraction patterns for alloys of $Sm_{0.5}Y_{0.5}Co_5$ a) as-cast, b) after 15 minutes, c) after 30 minutes, d) after 60 minutes, e) after 240 minutes of mechanical milling, and f) after 240 minutes of mechanical milling. Subsequently, the alloys of $Sm_{0.5}Y_{0.5}Co_5$ with 240 minutes of mechanical was thermally treated at 1173 K for 1 minute. In all X-ray diffraction patterns, the peaks were indexed with a hexagonal close-packed (hcp) structure $CaCu_5$ type and space Group P6/mmm. In this diffraction pattern, the $Sm_{0.5}Y_{0.5}Co_5$ phase was identified with the with the structure ICSD # 96-152-5258, where ICSD is the International Center for Diffraction Data [8]. While that another phase was indexed as the structure ICSD # 96-152-8222 for the YCo_5 phase. Fig. 2 e) shown that X-ray diffraction patterns for alloys of $Sm_{0.5}Y_{0.5}Co_5$ accomplished the amorphous state next 240 minutes of mechanical milling. Nevertheless Fig. 2 f) shown that X-ray diffraction patterns for alloys of $Sm_{0.5}Y_{0.5}Co_5$ was thermally treated at 1173 K for 1 minute shown width peaks that is characteristic of materials in nanocrystalline state.

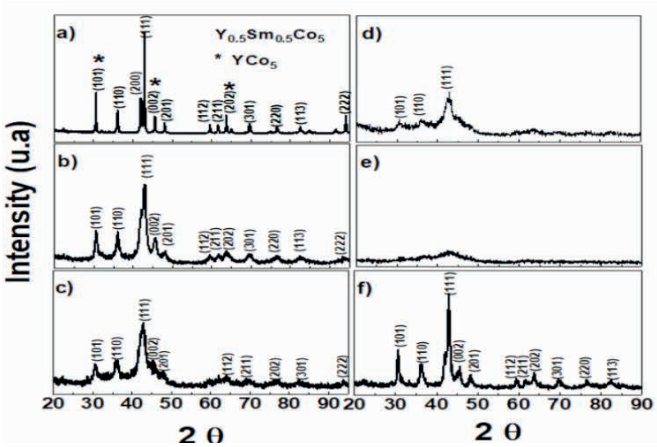

Fig. 2. X-ray diffraction patterns for the alloy of $Sm_{0.5}Y_{0.5}Co_5$: a) as cast, b) after 15 minutes, c) after 30 minutes, d) 60 minutes, e) 240 minutes of mechanical milling, and f) after 240 minutes; samples were subsequently thermally treated at 1173 K for 1 minute.

RIETVELD METHOD

Fig. 3 shows the experimental and modeled X-ray diffraction patterns for $Sm_{0.5}Y_{0.5}Co_5$ as cast obtained by arc melting via Rietveld analysis. $Sm_{0.5}Y_{0.5}Co_5$ as cast was used because this sample is more crystalline, and the red data represent Y_{obs}, dark data Y_{cal}, blue data Y_{obs}-Y_{cal} is the difference. The blue and red vertical line segments refer to the positions of Bragg from different phases, $Sm_{0.5}Y_{0.5}Co_5$ and YCo_5 phases.

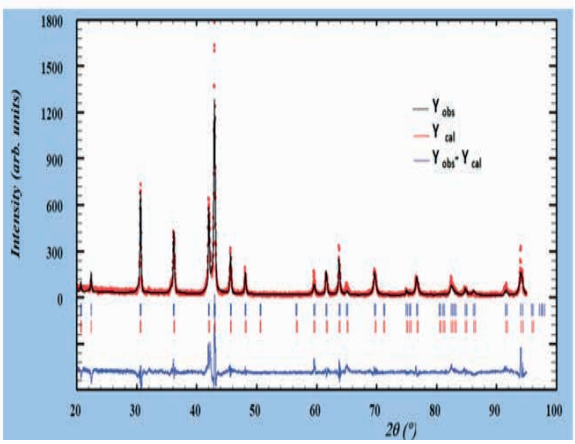

Fig. 3. Rietveld analysis for $Sm_{0.5}Y_{0.5}Co_5$ as cast.

A value of R_F-Factor of 12.0 was obtained for the $Sm_{0.5}Y_{0.5}Co_5$ phase, while a value of 11.3 was obtained for the YCo_5 phase. The value of R_F-Factor is important because this value is indicative of the quality of the model with respect to the unit cell. On the other hand, the value of the weighted profile factor R_{wp} is used to determine if the experimental X-ray patterns are a good fit by the calculated model. Here, a value of R_{wp} = 37.4 was obtained, which is a respectable value, as previously shown [2]. Table 1 shows the refined parameters and the weight Fraction for $Sm_{0.5}Y_{0.5}Co_5$ as cast found with the Rietveld analysis. The scale factor, background, lattice parameters (a, b, and c) of texture (G1) were refined in the Rietveld analysis.

Phase	Initiate parameters (Å)	Refined parameters (Å)
$Sm_{0.5}Y_{0.5}Co_5$	a= 4.960, c= 3.995 Weight Fraction	a= 4.967, c= 3.973 Weight Fraction: 42.41
YCo_5	a= 4.951, c= 3.975 Weight Fraction	a= 4.964, c= 3.973 Weight Fraction: 57.59

Table 1. Refined parameters with the Rietveld method for $Sm_{0.5}Y_{0.5}Co_5$ as cast obtained by arc melting.

For $Sm_{0.5}Y_{0.5}Co_5$ phase the statical error of refined parameters (a and c) are equal to $\mp$ 0.44 % and $\mp$ 0.17, while that for the YCo_5 phase the error in the refined parameters (a and c) are equal to $\mp$ 0.17 % and $\mp$ 0.13 % respectively, it is considered in the table 1. It is actual comments that crystallite-size and micro strain can be obtained from Rietveld refinements for $Sm_{0.5}Y_{0.5}Co_5$ alloys obtained by electric arc furnace next mechanical milling. However, is important comment that by realize the analysis of crystallite-size and micro strain in the Rietveld refinement it is need measured the peaks in an X-ray diffraction pattern

with a finer step and count > 10 000 that is a requirement of the Rietveld refinement by obtain the crystallite-size and micro strain accuracy. Here, the crystallite-size and micro strain for $Sm_{0.5}Y_{0.5}Co_5$ alloys obtained by electric arc furnace next mechanical milling was determined direct of the X-ray diffraction pattern with the equations presented. Here only the $Sm_{0.5}Y_{0.5}Co_5$ alloys obtained by electric arc furnace was analyzed with the Rietveld refinement due to that sample was measured with the accuracy quality with count > 1000 as is mentioned in the sample preparation. In the section of Rietveld analysis, a value of R_{wp} = 37.4 was obtained and considered as a respectable value because to that also others useful numerical criterion was obtained as is the "χ Factor ", a value of 1.3 was obtained where a value of 1.3 or less is frequently careful to be relatively suitable.

CHANGE IN THE LATTICE PARAMETERS AND UNIT CELL VOLUME.

Determination of the lattice parameters, unit cell volume and average crystal size in the nanocrystalline $Sm_{0.5}Y_{0.5}Co_5$ alloys is important because these parameters, such as the presence of the other phases in the alloys, change the magnetic properties. Using the Equation (1) the lattice parameters were determined:

$$sin^2\theta = \frac{\lambda^2}{4}\left[\frac{4}{3}\frac{(h^2+hk+k^2)}{a^2} + \frac{l^2}{c^2}\right] \quad (1)$$

The unit cell volume for $Sm_{0.5}Y_{0.5}Co_5$ alloys obtained by electric arc furnace and the alloys ground for 15 and 30 minutes was obtained by the Equation (2):

$$V = \frac{\sqrt{3}}{2}a^2c \quad (2)$$

The lattice parameters and unit cell volume are shown in Table 2.

$Sm_{0.5}Y_{0.5}Co_5$	a (Å)	c (Å)	Unit cell volume (Å)
Freshly melted	4.967	3.970	84.807
Milled 15 minutes	4.983	3.961	85.165
Milled 30 minutes	4.985	3.970	85.447

Table 2. Lattice parameters and unit cell volume for nanocrystalline $Sm_{0.5}Y_{0.5}Co_5$ alloys obtained by electric arc furnace followed by mechanical milling.

The changes of the lattice parameters are anisotropic, and it is observer that exit a volume dependence of the lattice parameters ratio c/a. It is observer a volume reduction $\Delta V/V = 1.3 \mp 0.5$ %, this value is calculated with the information of the X-ray diffraction patterns. An error equal ∓ 0.01 was considered for the lattice parameters presented in the table 2.

DISCUSSION

Interestingly, the peaks in this X-ray pattern with miller indices (101) and (002) are displaced, and therefore, these peaks are indexed with the phase of YCo_5. We recently showed that the presence of the secondary phase of YCo_5 in nanocrystalline $Sm_{0.5}Y_{0.5}Co_5$ alloys can be determined by measuring the magnetic properties with the methods of isothermal remanent magnetization (IRM) and direct current demagnetization (DCD) [5]. Other authors propose that when other atoms with a different atomic ratio are introduced into the unit cell of the $SmCo_5$ phase, certain peaks in the diffraction pattern are shifted, and there is a change in the unit cell volume and in the lattice [13]. On the other hand, it is also known that when a certain peak in the X-ray pattern is displaced, it is due to uniform strain introduced in the process of arc melting,

but that is necessary to obtain the image of high resolution with transmission electron microscopy for confirmation. We recently showed a form of determinate if in a material exist more of one phase through of determine the Interplanar distance for the $Sm_xGd_{1-x}Co_5$ alloy [6]. It is also important to consider that the interplanar distance can also be affected by edge grains; however, to determine whether the change in the Interplanar distance is due to edge grains in $Sm_{0.5}Y_{0.5}Co_5$ alloys, such as for other materials, it is necessary to determine the Interplanar distance through transmission electron microscopy through the obtention of selected area electron diffraction patterns [12]. Therefore, here, the obtention of the interplanar distance through X-ray diffraction patterns is analyzed by testing and validating the existence of the YCo_5 phase in the $Sm_{0.5}Y_{0.5}Co_5$ alloys. Additionally, is important to said that the compounds of YCo_5 and $SmCo_5$ are isostructural compounds and this difficult index the X-ray diffraction patterns. To probe, test and validate that in the $Sm_{0.5}Y_{0.5}Co_5$ alloys, the peaks (101) and (002) correspond to YCo_5 alloys, using the Equation (3) the Interplanar distance was calculated:

$$\frac{1}{d^2}=\left[\frac{4}{3}\frac{(h^2+hk+k^2)}{a^2}+\frac{l^2}{c^2}\right] \quad (3)$$

The Table 3 shows the theoretical and calculated interplanar distance for $Sm_{0.5}Y_{0.5}Co_5$ alloys obtained by an electric arc furnace.

Interplanar distances	$Sm_{0.5}Y_{0.5}Co_5$ as-cast (Å)	YCo_5 theoretical (Å)	$Sm_{0.5}Y_{0.5}Co_5$ theoretical (Å)	$SmCo_5$ theoretical (Å)
$d_{(002)}$	1.987	1.988	1.998	1.982
$d_{(101)}$	2.917	2.915	2.925	2.924

Table 3. Interplanar distances theoretical and calculated for alloys of $Sm_{0.5}Y_{0.5}Co_5$ obtained by electric arc furnace.

It is observed that the experimental values of the interplanar distance for peaks (101) and (002) are closer to the values of the interplanar distance of phase YCo_5. For this reason, it is concluded that the (101) and (002) peaks in the X-ray diffraction patterns are indexed to the YCo_5 phase.

CONCLUSIONS

The analysis of X-ray diffraction patterns for $Sm_{0.5}Y_{0.5}Co_5$ alloys all diffraction patterns have been indexed with a hexagonal close-packed (hcp) structure $CaCu_5$ type and space Group P6/mmm. Rietveld analysis for $Sm_{0.5}Y_{0.5}Co_5$ as cast alloys was realized. The lattice parameters, unit cell volume, average grain size and Interplanar distance for $Sm_{0.5}Y_{0.5}Co_5$ alloys were determined. The interplanar distance was used to determine the existence of the YCo_5 phase in the $Sm_{0.5}Y_{0.5}Co_5$ alloys. By confirming that the peak (002) in the $Sm_{0.5}Y_{0.5}Co_5$ alloys corresponds to YCo_5 alloys, the lattice parameter was calculated with a value of c=3.975 Å which corresponds to the lattice parameter for the YCo_5 phase with the structure ICSD # 96-152-8222.

DECLARATION OF COMPETING INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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