

# SYNTHESIS AND CHARACTERIZATION BY SCANNING ELECTRON MICROSCOPY OF THE SYSTEM $\text{Ca}_5\text{Bi}_3$ DURING THE MECHANICAL ALLOYING, SINTERING PROCESSES AND PHASE TRANSFORMATION

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## ABSTRACT

The  $\text{Ca}_5\text{Bi}_3$  intermetallic compound was synthesized by milling Ca and Bi.  $\text{Ca}_5\text{Bi}_3$  was obtained using a high-energy mill. A stoichiometric mixture of elemental powders was formed after three hours of milling. Next, the grade reagents, calcium and bismuth, were melted by heating at 1613 K for 12 h in sealed steel ampoules to prevent oxidation. The intermetallic compound was compacted using a hot isostatic press with 300 MPa and sintered at 673 K. The compound was characterized by chemical analysis, X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM). The product contains 1.68% Ca, 94.56% Bi and 5.43% O after milling, melting and press-sintering.

**Keywords:** Phase transformation, Mechanical alloying and milling, Diffraction, Hot isostatic pressing, Electron Microscopy

## SÍNTESIS Y CARACTERIZACIÓN DEL SISTEMA $\text{Ca}_5\text{Bi}_3$ OBTENIDO POR ALEADO MECÁNICO Y SINTERIZACIÓN Y SU TRANSFORMACIÓN DE FASE POR MICROSCOPIA ELECTRÓNICA DE BARRIDO

## RESUMEN

El compuesto intermetálico  $\text{Ca}_5\text{Bi}_3$  se sintetizó mediante la molienda de Ca y Bi.  $\text{Ca}_5\text{Bi}_3$  se obtuvo utilizando un molino de alta energía. Una mezcla estequiométrica de polvos elementales se formó después de tres horas de molienda. A continuación, los reactivos elementales, calcio y bismuto, se fundieron a 1613 K durante 12 h en cápsulas selladas de acero para limitar la oxidación. El compuesto intermetálico se compactó usando una prensa isostática en caliente con 300 MPa de presión y sinterizado a 673 K. El compuesto se caracterizó por análisis químico, difracción de rayos X y Microscopia Electrónica de Barrido (MEB). El producto obtenido contiene 1.68 % de Ca, 94.56% Bi y 5.43% O después de la molienda, fusión y sinterizado.

**Palabras clave:** Transformaciones de Fase, Molienda Mecánica, Difracción, Sinterizado, Microscopia Electrónica.

## INTRODUCTION

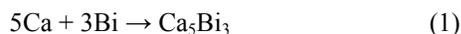
Bismuth is produced as a by-product of lead refining and is used in various materials, such as welding and fusible alloys, electronics, materials in the chemical industry and ceramics [1]. Bismuth is recovered primarily during the process of melting copper and lead ores [2, 3]. In lead refining, the Kroll-Betterton Process is used to remove bismuth from molten lead bullion. This process uses calcium and magnesium metals to react with bismuth to form the solid intermetallic compounds, i.e.  $\text{Mg}_3\text{Bi}_2$  and

$\text{Ca}_5\text{Bi}_3$ , which rises to the surface of the molten lead bullion. The solid debismuthizing dross is subsequently skimmed from the surface of the molten lead bullion and contains from 2 to 15 wt. % Bi with residual Mg and Ca [4, 5]. Kim et al. [6] determined the thermodynamic properties of Ca–Bi alloys by electromotive force (emf) measurements to assess the suitability of Ca–Bi electrodes for electrochemical energy storage applications. The excess partial molar Gibbs energy of bismuth estimated

from the Gibbs–Duhem equation and the integral change in Gibbs energy at 873 K, 973 K and 1073 K were measured; the Ca–Bi system was also characterized by differential scanning calorimetry. Poizeau and Sadoway [7] estimated the thermodynamic properties of multiple liquid alloys with strong negative deviation from ideality by the molecular interaction volume model (MIVM). The partial Gibbs free energy of calcium in Ca-Bi liquid alloys at 600°C was predicted within 1.6 kJ/mol by the MIVM from experimental data at 800°C. Kim et al. [8] investigated the feasibility of combining a liquid Ca-Bi positive electrode with a molten salt electrolyte for use in liquid metal batteries at from 500 to 700 °C. However, the formation of the  $\text{Ca}_{11}\text{Bi}_{10}$  compound at the electrode-electrolyte interface limited the calcium deposition rate capability of the electrodes. There have been no reported phase transformations in Ca-Bi systems during its production process, so the aim of this paper is to initiate a study of this phenomenon.

## MATERIALS AND METHODS

Commercial Alfa-Aesar calcium (99.5 wt.%, -6 mesh) and bismuth (99.5 wt.%, -325 mesh) powders were used as raw materials to produce the stoichiometric composition of  $\text{Ca}_5\text{Bi}_3$  (atomic percentage). Five grams of the compound were prepared as follows: the raw materials, Ca and Bi powders, were homogenized using a high-energy mill (SPEX) for three hours with a stainless steel container and balls of ¼ inch (0.635 cm). The ball-powder ratio was 1:5. The elemental mixtures were melted at 1613 K (1340 °C) in hermetically sealed steel ampoules in order to obtain the following reaction, as shown in the phase diagram of Figure 1 [9].



An alumina tube was used as a furnace tube. The samples were heated in a step-wise regime, heating at the rate of 3

K min<sup>-1</sup> followed by an isothermal arrest of 120 min. Once the temperature reached 1613 K, the sample was kept at this temperature for 12 h.

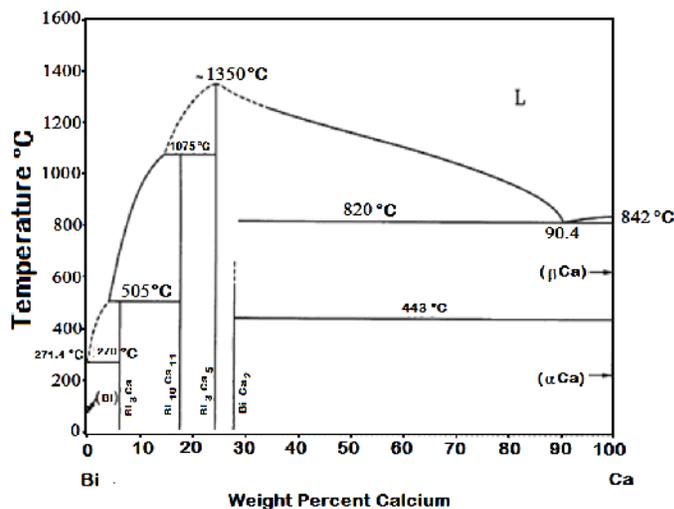


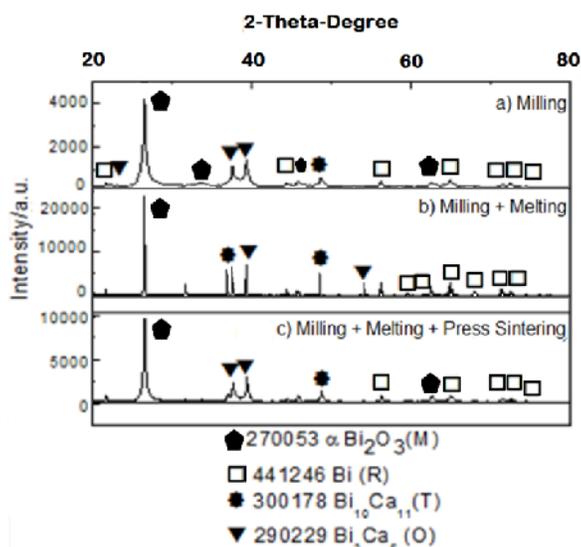
Fig. 1. Phase Diagram of Ca-Bi system [9].

Next, the material was slowly cooled at 1 K min<sup>-1</sup> to room temperature. The temperature was measured with an R-type thermocouple (Pt - Pt, 13% Rh). All manipulations of the starting reagents and materials obtained by reaction (1) were conducted in an argon-filled box. The intermetallic compound previously obtained was uniaxial pressed on a graphite die at 300 MPa using an AVS press, sintered for 50 minutes at 673 K and air cooled. The products were characterized by X-ray powder diffraction method using a Bruker D8 Focus, Cu K $\alpha$  radiation with  $\lambda = 1.5404 \text{ \AA}$ , with a speed of 2° min<sup>-1</sup> and the angle  $2\theta$  from 20° to 80°. A SEM JEOL JSM 6701F Microscope equipped with an energy dispersive spectrometer (EDS) was used. The final samples were analyzed on bismuth by Atomic Absorption Spectrophotometry, whereas the calcium was analyzed by the titration technique. XRD patterns were analyzed using the database software from the international center for diffraction data ICDD PDF-2 (2003).

## RESULTS AND DISCUSSION

### X-RAY DIFFRACTION

Figure 2 shows the X-Ray pattern of the products where it is observed that milled, sintered and heat treated samples have polycrystalline structure with several phases.



**Fig. 2.** XRD patterns of Ca-Bi samples a) Milling, b) Milling + Melting, c) Milling + Melting + Press-Sintering.

Figure 2a shows the XRD pattern of the milled powders where the main phase in this sample is bismuth oxide, as could be observed by the higher intensity peak in the angle  $27^\circ$ , this phase corresponds to that reported in the crystallographic database PCPDFWIN 2003,  $\alpha\text{-Bi}_2\text{O}_3$  (JCPD 27-0053) with monoclinic primitive structure and lattice parameters  $a = 5.848 \text{ \AA}$ ,  $b = 8.166 \text{ \AA}$  and  $c = 7.510 \text{ \AA}$ , its crystal size average according to calculations by Scherrer Equation (2) are 3.3 nm. In this pattern the following phases are also observed:  $\text{Ca}_{11}\text{Bi}_{10}$  (JCPD file 30-0178) with a tetragonal body centered structure and lattice parameters  $a = 12.22 \text{ \AA}$  and  $c = 17.79 \text{ \AA}$ , and  $\text{Ca}_5\text{Bi}_3$  (JCPD file 29-0229) with an orthorhombic primitive structure with the parameters  $a = 12.72 \text{ \AA}$ ,  $b = 9.66 \text{ \AA}$  and  $c = 8.432 \text{ \AA}$ , and finally, metallic bismuth (JCPD file 44-1246) with a rhombohedral centered structure with lattice parameters  $a = 4.547 \text{ \AA}$  and  $c =$

$11.861 \text{ \AA}$ . Crystal size was not calculated in those phases due to the low intensity and shape of the peaks.

Figure 2a and Figure 2b show samples as obtained by milling and milling + melting are similar; however, the amount of  $\text{Ca}_{11}\text{Bi}_{10}$  is slightly higher in the milling + melting processing technique.

According to the intensity of the peaks of the XRD pattern observed in Figure 2b and 2c, in the milling + melting process there is a higher amount of  $\text{Ca}_5\text{Bi}_3$  phase. The intermetallic compound  $\text{Ca}_5\text{Bi}_3$  apparently is a function of the crystal size, it is observed because in milling + melting process in the peaks between  $35\text{-}40$  degrees the width of the peak changes in the milling and milling + melting + press sintering processes. The relation between width and crystal size is according to equation (2) and it is discussed in the following sections.

In the production process of these materials, it is possible to observe a phase transformations, the milled phase  $\text{Ca}_5\text{Bi}_3$  transforms to  $\text{Ca}_{11}\text{Bi}_{10}$  when it is heated at 1613 K, and after sintering at 300 MPa, at 673 K for 50 min the phase becomes again  $\text{Ca}_5\text{Bi}_3$ .

An important phenomenon must be noted, the amount of  $\alpha\text{-Bi}_2\text{O}_3$  change during the production process. The weight percent of all phases was calculated from XRD patterns using the intensity method. The results are presented in **Table 1**. Initially after milling, the weight percentage of  $\alpha\text{-Bi}_2\text{O}_3$  is 49.6; it increases during the first heat treatment about 5 times and decreases by half after sintering. This phenomenon gives us an idea of the importance of the mobility of bismuth atoms during phase formation of Ca-Bi system.  $\text{Ca}_{11}\text{Bi}_{10}$  phase percentage is very small and much energy is required to form the intermetallic compound so that there are more free bismuth atoms in the system. The  $\text{Ca}_5\text{Bi}_3$  phase is present in a higher proportion and free bismuth in the system is much less, in both cases, the bismuth may form precipitates whose size gives a chemical activity such as easy its oxidation (Table 1). The crystal size of  $\alpha\text{-Bi}_2\text{O}_3$

calculated by the Scherrer equation (2), in milled powders is 3.3 nm, in milled + melted is 10 nm and milled + melted + press-sintered returns to 5 nm (Table 2).

$$T = \frac{K\lambda}{\beta \cos\theta} \quad (2)$$

The phases between Ca-Bi are more stables in bigger crystals (tetragonal system) on the other hand; there is major stability in smaller crystals (orthorhombic system).

**Table 1.** Mass balance for bismuth in different ways of synthesis

Phase	Milling Process (MP) (% wt.)	Milling and Melting Process ((MMP) (% wt.))	Milling, Melting and Press-Sintering Process (MMPSP) (% wt.)
Bi	21.21%	16.97%	22.84%
$\alpha\text{Bi}_2\text{O}_3$	50.55%	49.61%	48.11%
$\text{Ca}_5\text{Bi}_3$	22.43%	27.47%	23.31%
$\text{Ca}_{11}\text{Bi}_{10}$	5.81%	5.95%	5.74%

## CHEMICAL ANALYSIS

In (Table 1) the results of chemical analysis are also presented. Chemical analysis was performed by EDX and by an AAnalyst 200, Atomic Absorption Spectrometer of Perkin Elmer Co.; by this technique Calcium was determined.

Table 1 shows the mass balance for bismuth in the milling process, milling + melting process and milling + melting + press-sintering process, nevertheless, no contamination was observed by milling.

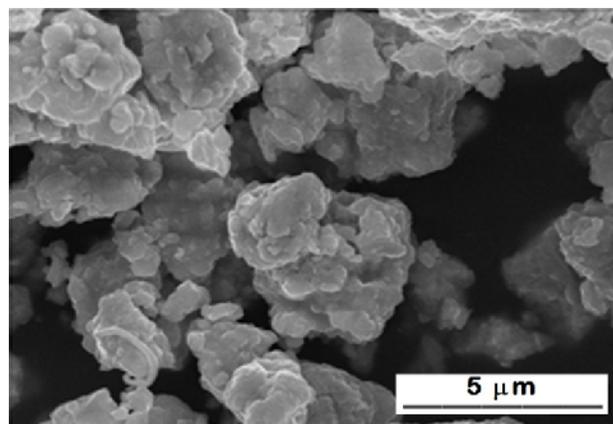
The weight amount of free bismuth in this system can be due to  $\text{Ca}_5\text{Bi}_3$  being a stoichiometric compound, as is shown in the Ca-Bi phase equilibria diagram of Figure 1 [9].

## SCANNING ELECTRON MICROSCOPY

In scanning secondary electron microscopy, powder samples were observed and measured. Phase determination was performed by EDX and considering XRD results. In (Figure 3) SEM micrograph corresponds to milling powders.

Then in (Figure 4), milling + melting powders were studied and finally (Figure 5) shows the SEM micrograph of milling + melting + press-sintering samples.

In (Figure 3), one may observe that milled powders shapes are flakes. According to the chemical analysis performed by EDX and XRD results, it can be considered that  $\text{Ca}_5\text{Bi}_3$ ,  $\text{Ca}_{11}\text{Bi}_{10}$  and  $\alpha\text{Bi}_2\text{O}_3$  phases are observed. In the case of EDX analysis, several samples were tested and because of average chemical composition of flakes, a phase was selected. All results were also compared to XRD phases and particle sizes established also by this technique. Due to its size, the larger and smaller flakes in micrograph may correspond mainly to  $\alpha\text{Bi}_2\text{O}_3$  with flakes diameter of 3.5 nm wide, 4 nm high and 0.13 nm wide, 0.16 nm high. The rest of compounds were hard to measure because there is a mixture among Ca, Mg and Bi. According to EDX results the chemical composition by weight is 23.51% O, 15.19% Ca and 61.30% Bi.



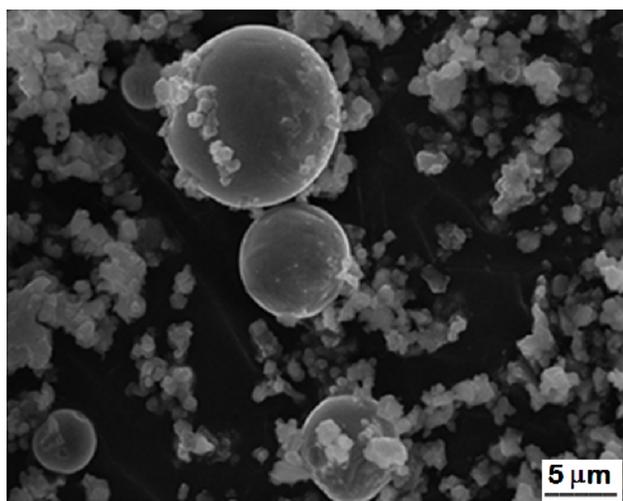
**Fig. 3.** SEM micrographs of the samples after Milling.

(Figure 4) shows the formation of spheres of  $\alpha\text{Bi}_2\text{O}_3$  with a particle size of 12.8 nm from the melting process. The composition of the sphere by weight is 10.92% O and 89.08% Bi, (Figure 5) shows a columnar particle formed by stacked layers, its chemical composition, by weight percent consists of 31.92% O, 19.41% Ca and 48.70% Bi. Calcium oxide was hard to find by X-ray diffraction; however in EDX particles with 22.1 nm high and 6.1 nm wide have a chemical composition that correspond to this kind of compound. Bismuth is an element with low symmetry, and maybe this is the reason why there are no large crystal formations of the compounds.

In Table (2), we present as a summary of results of the crystal size of  $\alpha\text{-Bi}_2\text{O}_3$  calculated by the Scherrer equation (2)

**Table 2.** Summary of results of crystal size of  $\alpha\text{-Bi}_2\text{O}_3$  calculated by the Scherrer equation.

Phase/ Crystal Size	(MP)	(MMP)	(MMPSP)
$\alpha\text{Bi}_2\text{O}_3$	3.3 nm	10 nm	5 nm



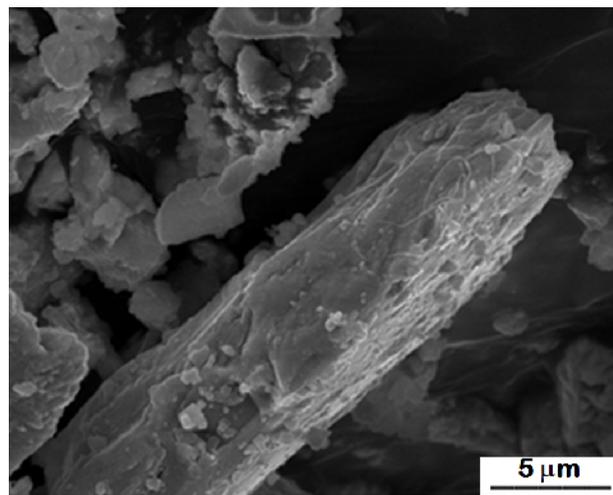
**Fig. 4.** SEM micrograph of the sample obtained by the milling and melting method.

(Table 3) shows a summary of the structure; experimental and theoretical phases ICDD PDF-2(2003) of milling, milling + melting, milling + melting + press sintering process of the Ca-Bi system.

**Table 3.** Experimental and Theoretical phases obtained in SEM.

Structure	Experimental Phases		Theoretical Phases	
	Flakes	O	Tetr	O
Sphere	M		M	
Columnar	O	Tetr	O	Tetr

The columnar structure shown in (Figure 5) is formed by the intercalation of structures of the species obtained by the milling + melting + sintering process. The EDS chemical analysis of this particle shows a high amount of oxygen, possibly there is a precipitation of bismuth oxide. The temperature applied to milled samples, promotes the increment of the crystal size and the formation of the tetragonal phase  $\text{Ca}_{11}\text{Bi}_{10}$  and press-sintering promotes the decrement of the crystal size, possibly due to the deformation and cracks suffered by the sample during compaction and heat treatment forming again the intermetallic compound  $\text{Ca}_5\text{Bi}_3$ .



**Fig. 5.** SEM micrographs of a sample after milling + melting + press-sintering

## CONCLUSIONS

Some samples of the Ca-Bi were synthesized by three processing techniques: milling, milling + melting, milling + melting + press-sintering, giving the following conclusions:

a) The intermetallic compound  $\text{Ca}_5\text{Bi}_3$  was synthesized and analyzed, indicating that it contains 1.68% wt. Ca, 94.56% wt. Bi and 5.43% wt. of O. SEM micrographs demonstrate the formation of flakes, spheres and columnar particles, with smaller sizes ranging from 4.48 nm to 22.1 nm.

b) A mixture was held in % weight of 24 Ca and 76 Bi to form the intermetallic compound  $\text{Ca}_5\text{Bi}_3$  by milling process in a high energy mill, the phases obtained were  $\alpha\text{Bi}_2\text{O}_3$  (main phase),  $\text{Bi}_3\text{Ca}_5$  (orthorhombic phase) and Bi.

c) It is required higher vacuum to avoid the formation of bismuth oxide, it inhibits the formation of compounds Ca-Bi, or, a process with more energy in less time to avoid the presence of oxygen.

d) It is observed that crystalline phases presents, are function of the crystal size, in the case of the compounds Ca-Bi was observed if the crystal is small, the phase is orthorhombic  $\text{Bi}_3\text{Ca}_5$ ; and if the crystal is bigger the phase is tetragonal  $\text{Bi}_{10}\text{Ca}_{11}$ .

e) The temperature applied to milled samples, promotes the increment of the crystal size and the formation of the tetragonal phase  $\text{Bi}_{10}\text{Ca}_{11}$  and press-sintering promotes the decrement of the crystal size, possibly due to the deformation and cracks suffered by the sample during compaction and heat treatment forming again the intermetallic compound  $\text{Bi}_3\text{Ca}_5$ .

## ACKNOWLEDGMENTS

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## REFERENCES

- [1] Jasinski S. M. (1995). “*Bismuth from Mineral Commodity Summaries*”, U.S. Bureau of Mines, p. 30.
- [2] Kirk-Othmer. (1992) “*Bismuth Encyclopedia of Chemical Technology*” ed. Wiley, fourth edition, (4):238.
- [3] Zarubitskii O.G. (2003). “Refining of lead to give bismuth-enriched drosses”. *Russ. J. Applied Chem.* (76):191-194.
- [4] Harris R., Li Rui-Qing. (2003) *Process for bismuth recovery from lead-bismuth dross* Patent N. WO2003074743.
- [5] Naumov A.V. (2007). “World market of Bismuth: A review”. *Russ J. Non-Ferrous Metals.* (48):13-19.
- [6] Kim H., Boysen D.A, Bradwell D.J., Chung B., Jiang K., Tomaszowska A.A., Wang K., Wei W., Sadoway D.R. (2012). *Electrochim. Acta*, (60):154-162.
- [7] Poizeau S and Sadoway D. R. (2013). “Application of the Molecular Interaction Volume Model (MIVM) to Calcium-Based Liquid Alloys of Systems Forming High-Melting Intermetallics” *J. Am. Chem. Soc.* (135):8260–8265
- [8] H. Kim, D. A. Boysen, T. Ouchi, D.R. Sadoway, (2013) “Calcium-Bismuth Liquid Metal Batteries for Large-Scale Energy Storage”, *Journal of Power Sources*, (241):239-248
- [9] Ca-Bi Phase Diagram ASM International (1992). *Alloy Phase Diagr*, ASM Handbook, 484.