Electron Emitting Barium-Calcium Aluminate Obtained from Chemical Solution Techniques

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***Abstract* — This paper reports a chemical technique to obtain barium-calcium aluminates used in impregnated thermionic cathodes. This procedure has been employed to improve the thermionic emission characteristics of the cathodes and to facilitate the preparation process of the emitting material. The crystallized powders were obtained using a mixed solution that contains barium, calcium, and aluminum in their chemical formula. Thermogravimetry and X-Ray diffraction were used to investigate the final product of the experiments. Results reported from solid state reaction are compared with those obtained using crystallization techniques.**

***Index Terms* — Barium-calcium aluminate, crystallization, power microwave vacuum devices, thermionic cathodes.**

I. Introduction

Impregnated cathodes find application in power microwave vacuum electronic devices, as traveling-wave tubes (TWTs) and klystrons amplifies. This kind of cathode provides a better poisoning resistance compared with oxide cathodes. The latter uses mixtures of alkaline earth carbonates, such as $BaCO_3$, $CaCO_3$ and $SrCO_3$, its activation procedure produces some gases (such as carbon dioxide) which reduces the cathode performance [1]-[3].

Barium-calcium aluminate impregnated cathodes (or dispenser) have been widely investigated since their development by Levi. This investigation has been carried out to improve the poisoning resistance [2]. There are some common impregnate compositions, including 5:3:2, 4:1:1 and 3:1:1, where the notation indicates the molar stoichiometric coefficient of BaO, CaO, and Al_2O_3 , respectively [1].

There are many different processes to obtain this emitting material. One of them is the solid state reaction. Other processes to manufacture high purity aluminates are the chemical solution techniques, such as crystallization, precipitation, Pechini's method, and sol-gel process. Using one of those routes, it is possible to obtain powders of high purity where the solid phases can be decomposed without their melting by means of calcination at relatively low temperature [2]-[3]. The properties of a material are largely dependent on its method of synthesis [4]-[5].

A typical procedure for crystallization technique is presented in Fig. 1.

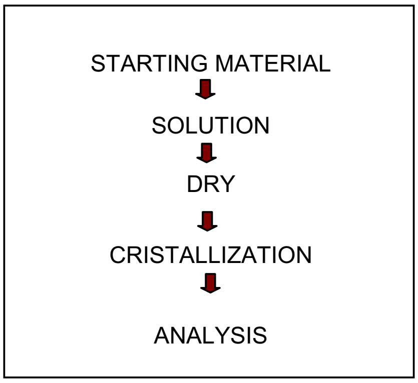

Fig. 1. Procedure of crystallization.

There are several parameters that can influence crystallization mechanisms, such as temperature, impurities and solution concentration. The process described in this work provides the homogenization of the mixture because the reaction occurs in liquid means.

This paper is organized as follows: in Section II, it is presented the electron emitter material preparation. In Section III, it is described the oven developed especially for the aluminate preparation, and Section IV and V present the characterization of the materials and the experimental setup, respectively. In the Section VI it is described the results obtained from thermal analysis and X-Ray diffraction. Finally, in Section VII it is shown the conclusions of this work.

II. Electron Emitter Material Preparation

To obtain the barium-calcium aluminate, the reaction equations involved are:

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$$5BaCO_3 + 10HNO_3 \rightarrow 5Ba(NO_3)_2 + 5H_2O + 5CO_2 \quad (1)$$

$$3CaCO_3 + 6HNO_3 \rightarrow 3Ca(NO_3)_2 + 3H_2O + 3CO_2 \quad (2)$$

$$4Al + gHNO_3 \rightarrow 4Al(NO_3)_3 \cdot yH_2O + xNO_z \quad (3)$$

The final crystallization product, after calcination, is a white powder:

$$\begin{aligned} 5Ba(NO_3)_2 + 3Ca(NO_3)_2 + 4Al(NO_3)_3 \rightarrow \\ 5BaO \cdot 3CaO \cdot 2Al_2O_3 + iNO_x \end{aligned} \quad (4)$$

This technique offers homogeneity and closed composition control. These characteristics are important for a good performance of dispenser cathodes. Dudley [6] demonstrated the emission properties of barium-calcium aluminate impregnated cathodes as function of the impregnant composition. Figure 2 shows the cathode emission current as a function the barium and calcium content.

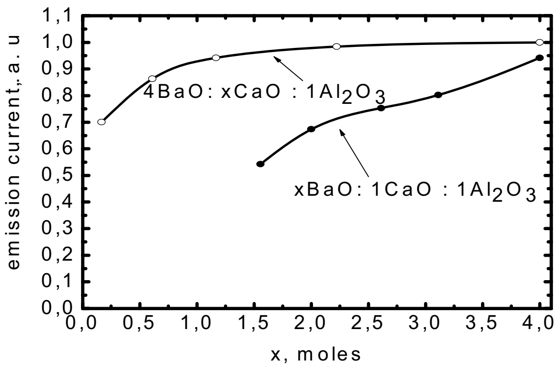

Fig. 2. Emission current as a function of impregnant composition [6].

The curves presented in Fig. 2 show that when *BaO* or *CaO* proportion is reduced, there is a change in the emission current of the dispenser cathode. This variation is due to the evaporation process of barium. Because of this, it is important to control the impregnant composition during the manufacturing process.

For a conventional method of aluminate process (solid state reaction) used to convert carbonates in the respective oxide, it is necessary high temperature and a controlled atmosphere, and, in this conditions, elementary carbon is present in the aluminates, as shown in Fig. 3 [7]. On the other hand, by means of the crystallization technique, it is possible to obtain an emitting material without elementary carbon if the fired step is carried out with barium, calcium and aluminum nitrates.

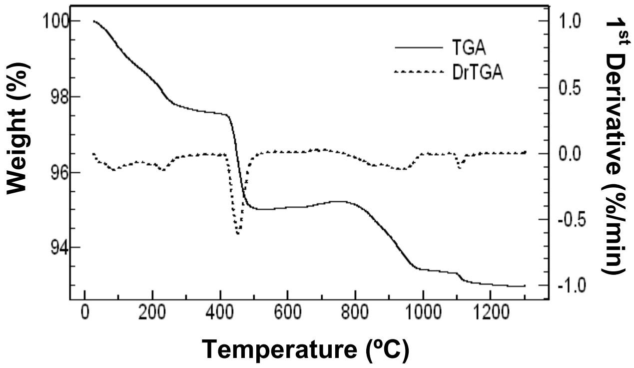

Fig. 3. TG/DTG curves of a product obtained by solid state reaction (in a reduction atmosphere) under dynamic O_2 atmosphere (100 mL min^{-1}), β = 10ºC min^{-1} and sample masses about 50 mg. These curves show the elementary carbon loss (about 7.0 %) [7].

III. Special Oven for Several Atmospheres

A special oven was developed to prepare the emitting material. All pieces used in the oven were manufactured with special materials, such as high alumina, to avoid contamination or poisoning during the process, as such presence of impurities [8].

Studies were carried out to determine the temperature profile inside the oven to avoid temperature gradients on the sample. It was also developed a vacuum system to remove any gases present inside the oven before the beginning of firing process.

IV. Characterization Techniques

Measurement techniques used in this investigation include thermogravimetry (TG) and X-Ray diffraction.

A. Thermogravimetry

Thermogravimetric experiments were carried out in order to determine the decomposition temperatures and the procedure time to obtain the aluminate. TG curves were obtained using sample masses about 5 mg with heating rate (β) of 10ºC min^{-1} under O_2 dynamic atmospheres. It was used TGA-PERKING-ELMER and TGA 50H SHIMADZU thermobalance.

B. X-Ray Diffraction

By means of X-Ray diffraction, it was analyzed the final product of the process. The X-Ray patterns were obtained with copper radiation ($CuK\alpha$) using a RIGAKU D-MAX 2100 diffractometer.

V. Experimental Setup

A. Emitting Aluminate Fabrication Process

The starting material was a mixture of barium and calcium nitrates and metalic aluminum powder in the proportional molar, 5:3:4, respectively. The aluminate fabrication by means of crystallization techniques is illustrated in Fig. 4.

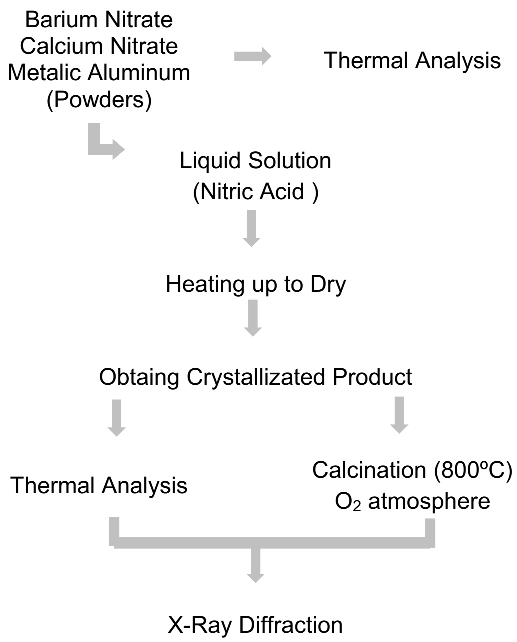

Fig. 4. Cristallization technique by nitrate route.

VI. Results and Discussion

A. Thermogravimetry

Figure 5 presents TG curves of the compounds employed to obtain the aluminate ($Ba(NO_3)_2$, $Ca(NO_3)_2$, $Al(NO_3)_3$) and the crystallization product under dynamic O_2 atmosphere.

Barium nitrate TG curve evidences that this compound presents various thermal decomposition steps (weight loss about 76,7%) and it is thermally stable about 700ºC.

Aluminum nitrate TG curve presents a high weight loss (about 82,8%) between 50 and 600ºC due to release of nine water molecules as well thermal decomposition of nitrate.

Calcium nitrate TG curve evidences loss mass (about 29,2%) between 50 and 250ºC due to dehydration. The anhydrous species are thermally stable up to 550ºC and loss mass (44,6%) quickly up to 600ºC to form calcium oxide. The thermal decomposition processes of the nitrates mixture correspond to the thermal process which individually occurs from each species of the mixture.

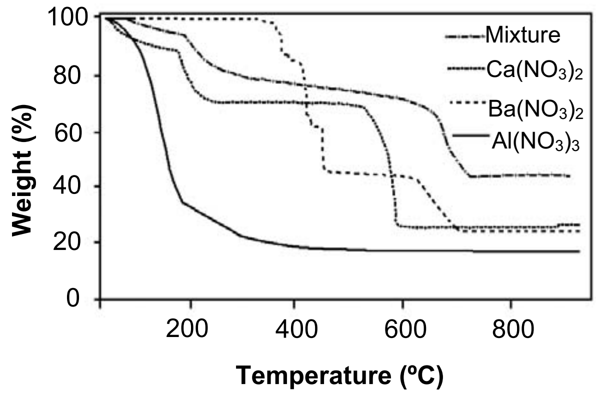

Fig. 5. TG curves of $Ba(NO_3)_2$, $Ca(NO_3)_2$, $Al(NO_3)_3$ and mixture under dynamic O_2 atmosphere (120 mL min^{-1}), β = 10ºC min^{-1} and sample masses about 5 mg.

Figure 6 compare the TG curves of two different samples. One of them was obtained from carbonates mixture and the other from the nitrate crystallization techniques.

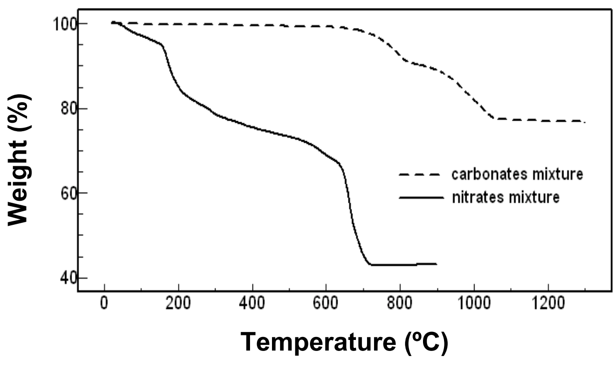

Fig. 6. TG curves of the carbonates mixture and the nitrates mixture obtained by crystallization technique under dynamic atmosphere: $H_2 + Ar$ for carbonates mixture and *Air* for nitrates mixture (100 mL min^{-1}). β = 10ºC min^{-1}, sample masses of 50 mg for carbonates mixture, and 7 mg for nitrates mixture.

Crystallization TG curves (nitrate mixture) evidences that by means of crystallization techniques is possible to obtain aluminate in a lower temperature than by conventional process (carbonates mixture). Therefore, the aluminate process in this case can be carried out at 800ºC instead of 1000ºC for conventional process.

B. X-Ray diffraction analysis

Figure 7 shows diffraction pattern of product process. The result was compared with data reported by Maklakov [9]. It is possible to observe that some peaks and the angles are very near each other. However, there are some peaks that can be related with impurities in the sample.

X-Ray fluorescence was utilized to determine these impurities. Results showed copped impurities in the sample.

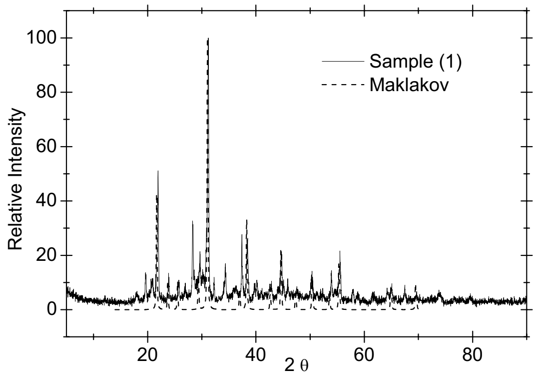

Fig. 7. Diffraction pattern of sample (1) obtained by means of crystallization technique.

V. Conclusions

In this paper it was described a route of barium-calcium aluminates production using nitrate crystallization technique. The composition of the emitting material influences the emission characteristics of thermionic cathode and, therefore, it has been investigated a better procedure to obtain the aluminates. By means of thermal analysis and X-Ray diffraction, it was possible to optimize the procedure conditions for preparing barium-calcium aluminate compounds to be used in the crystallization technique.

By means of thermogravimetry, it was verified the presence of water in all nitrates which influences the molar composition of the emission material and, because of this, it was used barium and calcium carbonates and metallic aluminum as starting material. It was also observed that the formation aluminate temperature, in this case is lower than the one for solid state reaction.

By means of X-Ray diffraction, it was possible to verify the characteristic phases of aluminate obtained in this process, which were very similar to be product obtained by solid state reaction.

Results showed that the crystallization technique decreased the calcination temperature from 1000ºC to 800ºC, a homogenous mixture was obtained during the crystallization process, there was no elementary carbon in the product, and it was not necessary to use a dynamic H_2 atmosphere. These facts represent time and energy saved in the process and improved the quality of the final product.

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