

Investigation of Electron Emitting Barium-Calcium Aluminate Fabrication Process for Impregnated Microwave Tube Cathodes

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Abstract — In this paper it is reported the fabrication process of electron emitting barium-calcium aluminates used on impregnated cathodes which constitute high power vacuum microwave devices such as klystrons and TWTs (traveling wave tubes). The compound thermal behavior and the analysis of the formed phases during processing are evaluated, respectively, by means of thermal analysis and X-Ray diffraction. Results about the influence of firing temperature and atmosphere are also presented.

Index Terms — Aluminates, cathodes, electron thermionic emission, thermal analysis, X-Ray diffraction.

I. INTRODUCTION

Electron beams used in high power vacuum microwave devices such as klystrons and TWTs (traveling wave tubes) are usually obtained from thermionic cathodes. Independently of the investigated cathode type, its lifetime depends on its operation conditions and it limits the maximum working period of vacuum microwave tube [1].

The first attempt to reduce the high work function of the first developed cathodes (made of tungsten), which have $\phi = 4.6$ eV and needed elevated temperatures to obtain a satisfactory emission, was the addition of a small amount of thoria to tungsten. Researches made possible the development of a new emitting material, a mixture of BaO , CaO and SrO , so called oxide cathode. However, its operating features limited emission density and the compound was sensitive to poisoning. Thus, many efforts have been carried out to develop another generation of emitting material: the aluminate [1].

Cathodes that use aluminate were firstly applied in the 1950's and presented satisfactory working features, as high emission density with moderate temperatures (about 1100°C) and better resistance to poisoning originated from residual gases of the tube. The compound usually used is made of $5BaO$, $3CaO$ and $2Al_2O_3$ (molar proportion) that, correctly manufactured, becomes an emitting material. This compound is called 5:3:2. Other variations, as 3:1:1 and 4:1:1 are also possible [1]-[2].

Shroff [2] indicates that the preparation process of the aluminate can be carried out by means of dry or wet mixing in alcohol or in distilled water. After homogenizing, the mixture must be fired between 1100 and 1200°C in furnace air during 100 hours or, using atmosphere of hydrogen, it is possible to obtain the aluminate at 1000°C for 5 hours. The complete conversion of carbonates into aluminates can be controlled verifying the weight loss during firing. The reaction of carbonates and alumina make possible to obtain $BaAl_2O_4$, $Ca_2BaAl_2O_6$ and $Ba_3Al_2O_6$, which probably are the phases responsible for the electron emission during the working of a TWT tube.

In this paper it is reported the thermal behavior and phases characterizations concerning the fabrication process of aluminates using 5:3:2 compounds. It is also evaluated and controled the processing parameters based on the characteristics of the final product.

This paper is organized as follows: in Section II it is presented the experimental setup that describes the fabrication process of aluminates, the methods used to analyse the starting material, and the final products. In Section III it is described the results and discussion where is shown the thermal behaviour of carbonates, oxide and the final products. It is also presented the aluminate diffraction patters. Finally, in Section IV, it is shown the conclusions of this work.

II. EXPERIMENTAL SETUP

A. Starting material

To obtain the aluminates, it was used the following chemical reagents: barium carbonate p.A. ($BaCO_3$) VETEC, calcium carbonate p.A. ($CaCO_3$) VETEC, alumina p.A. (Al_2O_3) VETEC, and anhydrous ethyl alcohol (C_2H_5OH) Merck.

B. Thermal analysis

Thermogravimetric experiments (TG) were carried out in order to determine weight losses due to the elimination of water and CO_x compounds. TG/DTG curves were obtained using sample masses from 7 to 50 milligrams with a heating rate (β) of $10^\circ\text{C min}^{-1}$ under different dynamic atmospheres: $H_2 + Ar$ (it was used TGA 51H SHIMADZU), O_2 (it was used TGA7-PERKING-ELMER) and N_2 (it was used TGA 50H SHIMADZU). It was used platinum and alumina crucibles.

C. Emitting Aluminate Fabrication Process

It is known that alkaline earth element oxides are unstable under environment atmosphere and, because of this, the aluminate was prepared using barium and calcium carbonates adding alumina [3]. Cronin [4] indicates that the barium-calcium aluminate can be constituted by three phases ($Ba_3Al_2O_6$, $Ba_2CaAl_2O_6$ and CaO) and it was tried to evaluate their presence in the manufactured material by X-Ray diffraction. The aluminate fabrication process sequence is illustrated in Fig. 1.

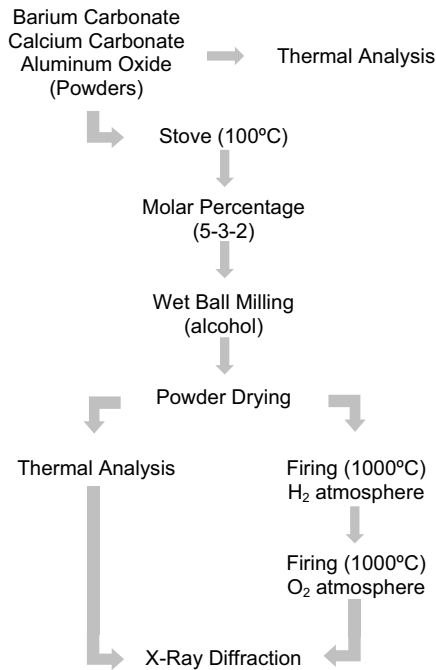
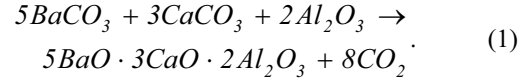


Fig. 1. Impregnant fabrication process.

D. X-Ray Diffraction

X-Ray diffraction was used to investigate the aluminate formation conditions and phases obtained by means of

firing carbonates mixture [5], according to the chemical reaction



It can be verified in (1) that it is necessary the total carbon dioxide release to occur the complete conversion from carbonates in oxides, and then the aluminate are obtained.

The phase composition of the aluminate was determined by X-Ray diffraction with copper radiation. The X-Ray patterns were obtained with RIGAKU DMAX-2100 diffractometer.

III. RESULTS AND DISCUSSION

A. Thermal Analysis

Figure 2 presents TG curves of the compounds employed to obtain the aluminate ($BaCO_3$, $CaCO_3$, and Al_2O_3) and of the resultant mixture under dynamic O_2 atmosphere.

Alumina TG curve evidences that this compound is thermally stable to 900°C and there is just one initial weight loss due to water. Other curves also present the initial weight loss originating from water and the beginning of the carbonates decomposition. Considering just the mixture TG curve, there is a change in the carbonate reaction onset temperature.

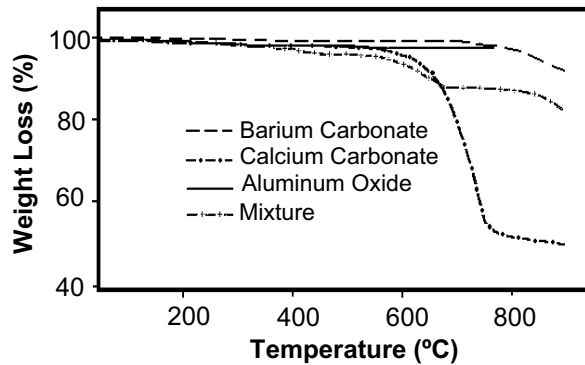


Fig. 2. TG curves of $BaCO_3$, $CaCO_3$, Al_2O_3 and mixture under dynamic O_2 atmosphere (120 mL min^{-1}), $\beta = 10^\circ\text{C min}^{-1}$ and sample masses = 10 mg.

In another set of experiments it was investigated the decomposition temperature under inert atmosphere (N_2). It was desirable to obtain the barium carbonate thermal behavior until 1300°C without atmosphere interference.

Figure 3 shows the TG/DTG curves, which indicate that $BaCO_3$ presents two main thermal decomposition steps. The first is related to the water release, with a weight loss of 0.57%. The second step occurs between 700°C and 1300°C, and the weight loss is 20.8%. Considering that CO_2 theoretically constitutes 22.3% of barium carbonate (% wt), it is possible to verify that the conversion from barium carbonate in barium oxide was not complete.

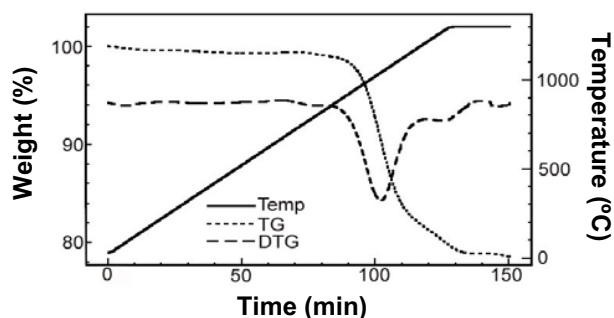


Fig. 3. TG curves of $BaCO_3$ under dynamic N_2 atmosphere (50 mL min^{-1}), $\beta = 10^\circ\text{C min}^{-1}$ and sample masses = 7 mg.

Figure 4 shows the aluminate compounds and mixture TG curves under reductive atmosphere ($H_2 + Ar$). It can be seen that aluminum oxide presents initial steps of water release without any other kind of decomposition (thermal stability up to 1300°C).

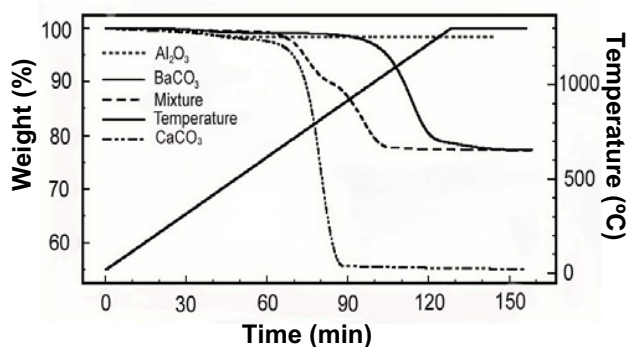


Fig. 4. TG curves of $BaCO_3$, $CaCO_3$, Al_2O_3 and mixture under dynamic $H_2 + Ar$ atmosphere (100 mL min^{-1}), $\beta = 10^\circ\text{C min}^{-1}$ and sample masses = 50 mg.

TG curves of barium carbonate presents two decomposition steps. The first corresponds to water release and the second, between 870 and 1300°C, to CO_2 elimination with a weigh loss of 22.0% (similar to the theoretical value). It denotes that up to 1300°C under H_2 atmosphere, it is possible to achieve the thermal stability of this material.

TG curves of calcium carbonate evidences that the compound presents two thermal decomposition steps. The

first is related to water release and the second is due to carbonate decomposition, corresponding to a weight loss of 42.2%. The thermal stability is obtained at 900°C.

The mixture TG curve presents three decomposition steps. The first step occurs due to water release that was present in the mixture components. The second and the third steps are directly related to calcium and barium thermal decomposition, respectively. Mixture stabilization of the aluminate compound is obtained at 1100°C under H_2 atmosphere.

B. Emitting Aluminate Fabrication Process

It was investigated the barium-calcium aluminate preparation procedure. All pieces used during the process were made with special material (ceramics and polymers) to avoid impurities in the aluminate. After the knowledge of the thermal behavior, it was possible to carry out an adequate sequence to obtain the aluminate. Several experiments were studied and it was observed that it is not necessary to have a firing time higher than five hours.

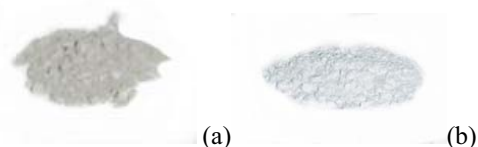


Fig. 5. Different samples of aluminate. (a) Barium-calcium aluminate obtained from conventional method. (b) Barium-calcium aluminate obtained from thermal analysis.

Figure 5 shows two different aluminate samples. One of them was obtained from the thermal analysis and the other from the conventional process. The sample in Fig.5 (a) is gray indicating the presence of elementary carbon. By other hand, Fig.5 (b) presents a white aluminate. This can be explained due to the high heating rate in the conventional process and, therefore, the presence in this case of some carbonate not converted in aluminate.

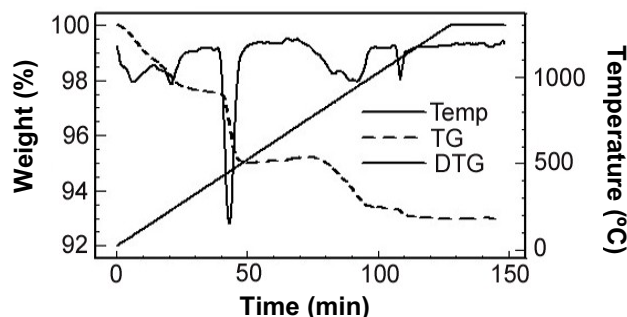


Fig. 6. TG curves of mixture under dynamic O_2 atmosphere (100 mL min^{-1}), $\beta = 10^\circ\text{C min}^{-1}$ and sample masses = 50 mg.

Aluminate samples obtained from conventional method were thermally analyzed, as shown in Fig. 6. It was observed that the aluminate presented many decomposition steps. In these steps the carbon was converted in carbon dioxide and carbon monoxide. Because of this, it was included an additional firing step in oxidant atmosphere for 2 hours.

B. X-Ray Diffraction Analysis

The control of the products obtained by thermal analysis was carried out by means of X-Ray diffraction to identify the formed phases. Fig. 7 shows diffraction pattern of the mixture before firing.

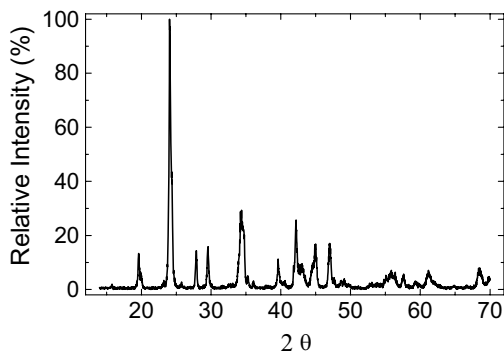


Fig. 7. Diffraction pattern of mixture before firing.

Diffraction pattern of the barium-calcium aluminate obtained during this investigation is presented in Fig. 8. There are peaks displacements that represent the carbonate decomposition and barium-calcium aluminate formation.

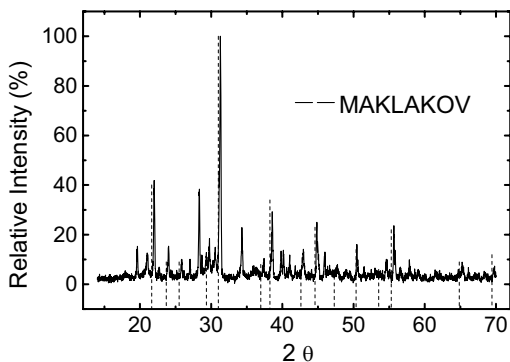


Fig. 8. Diffraction pattern of barium-calcium aluminate obtained from thermal analysis ($H_2 + Ar$ atmosphere).

Analyzing Fig. 8 which compares the results of this research with data reported by Maklakov [5], it is possible to notice that the peaks, the relative intensities and the angles are very similar. It shows that the sample obtained

from the thermal analysis presents the same phases of the product already reported.

The others aluminate obtained by conventional method were analyzed for X-ray diffraction and it was verified that the diffraction pattern presented the same phases reported by Maklakov [5].

IV. CONCLUSIONS

In this paper was carried out a research to obtain a route of production of barium-calcium aluminates with satisfactory electron emission characteristics. It was verified that during powder processing all existing parameters influence the final product. Temperature and atmosphere during aluminate production were studied. By means of thermogravimetric analysis it was verified the presence of water in all carbonates and oxides which influence the molar composition of the emission material. Thus, the proportion 5:3:2 could not be maintained. It was also observed the thermal behavior of each carbonate separately and, then, it was evaluated the thermal behavior of each compound in the mixture. During the aluminate formation, there is an influence of calcium carbonate in the barium carbonate decomposition reaction, reducing the time to the decomposition. When the atmosphere was changed during aluminate firing, it was observed that the decomposition reactions in an O_2 atmosphere and inert environment takes more time and/or the temperature must be higher compared to H_2 atmosphere. The phases that constitute the obtained material indicated the formation of the barium-calcium aluminate.

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