Synthesis and characterization of Ni-Mo sintered alloy foils for microwave tube manufacturing

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***Abstract*— The Ni-Mo composite alloy, to be used in microwave vacuum tube manufacturing, was prepared from metal powders previously homogenized, pressed and sintered at 1200°C by induction heating. The Ni-Mo sintered discs were annealed at 1150°C for 20min, and submitted to the roller process in 5 cycles to obtain a thin foil with 0.10 mm of thickness, for brazing process adopted to join the cathode components. The samples were submitted to scanning electron microscopy (SEM) coupled to energy dispersive spectroscopy analysis (EDS) to characterize the composition and microstructure. X-ray diffraction (XRD) was performed to determine the crystalline structure and energy dispersive X-ray fluorescence spectroscopy (EDX) was performed to determine the chemical composition and the homogeneity of the composite alloy.**

Keywords*— *induction heating; sintering; brazing; thermionic cathodes, composites.

I. Introduction

Impregnated thermionic cathodes made of a porous tungsten pellet impregnated with barium calcium aluminates are important components used in microwave tube devices, including TWT and klystron amplifiers [1,2], showing low work function, long lifetime, and high current density [3]. The cathode components (Fig. 1), generally are join by brazing, using a filler material that melts above the cathode working temperature, close to 1200°C [4].

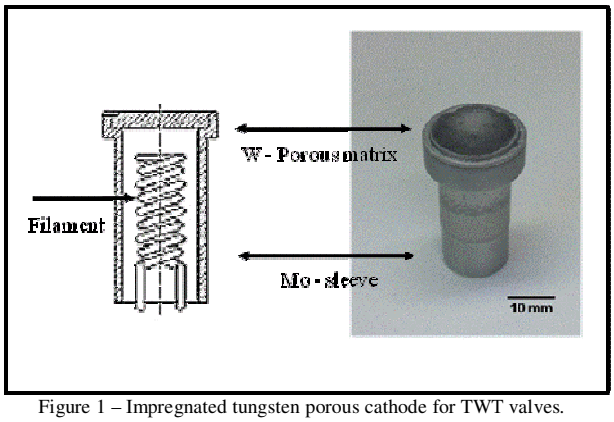

Figure 1 – Impregnated tungsten porous cathode for TWT valves.

Brazing is a thermal activated process usually used to join components, and it is done by the addition of a melted filler material or brazing alloy. When the filler is in the liquid state, it wets the surface of the parts to be joined, and after cooling, the components are bonded together [5,6].

For the impregnated porous tungsten cathodes, the brazing alloy must wet both tungsten matrix and molybdenum sleeve (parts of the cathode), and the brazing temperature must be above the cathode working temperature (1200°C), without causing any structural damage to the cathode components. Thermal shock followed by crack propagation, re-melting of the filler material, and contamination from other parts of the tube are other issues to be considered.

The Ni-Mo system and it alloys are studied and reported by different authors [7-9], and are an alternative filler material [10-12]. The phase diagram of this system can be seen in Fig. 2 and shows the eutectic composition (35.8 at% of molybdenum) at 1310°C [13].

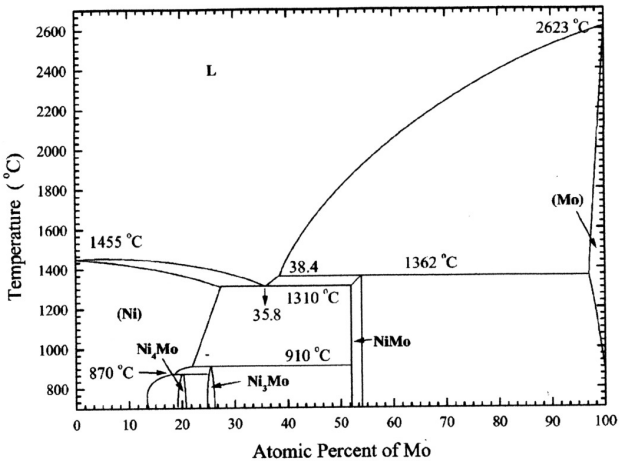

Figure 2 – Binary phase diagram for high temperatures for Ni-Mo system [13].

The aim of the present work is related to the manufactory process reliability of microwave tubes, and involves the development of a sintered Ni-Mo foil alloy as a filler material for brazing process which uses induction heating to join porous tungsten to dense molybdenum components.

This work was organized in the following: In Section II, the experimental part involving sample preparation, cold-rolled process, and characterization are described. In Section III, the

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results and discussion are presented. Conclusions are presented in Section IV.

II. Experimental Procedure

A. Sample preparation

Ni-Mo samples were prepared from nickel and molybdenum powders (99.9% purity) with average particle size of 17.80μm for Ni and 37.74μm for molybdenum determined in previews works [12]. The nominal amount of molybdenum was 35.8 at%, according to the eutectic composition shown in the binary phase diagram. Nickel and molybdenum powders were mixed and milled in a hardsteel ball mill for 24 hours, under constant rotation velocity of 63 rpm, uniaxially pressed at 110 MPa in a 12 mm diameter cylindrical matrix, and sintered in H_2 reducing atmosphere for 2h at 1200°C in a electromagnetic induction furnace. After sintering, the material was annealed in the same furnace for 15min at 1150°C.

The density, ρ, presented was determined by Archimedes method,

$$\rho = \left(1 - \frac{\rho_{Ce}}{\rho_C}\right).100 \quad (1)$$

where ρ_c is the theoretical density for the composite material (9.23 g.cm^{-3}) and ρ_{ce} is the experimental density determined for sintered matrix by Archimedes method. The theoretical density was estimated by the law of mixtures,

$$\rho = \rho_1 \, v_1 + \rho_2 \, v_2 \quad (2)$$

where ρ_1 and ρ_2 are nickel and molybdenum densities, respectively, and v_1 and v_2 are the volumes of nickel and molybdenum, respectively.

B. Cold-rolled plate process

After annealed, the sintered sample was cold-rolled to reduce the thickness and obtain a thin foil. The cold-rolled plate process was performed 5 times until the sample shows average thickness close to 0.1mm. The plate roller machine was developed for the Linear Accelerator Research Group of the Physics Institute of the University of Sao Paulo.

C. Microstructural analyses and chemical composition

The sintered composite alloy microstructure was characterized by scanning electron microscopy (SEM) (Jeol, model 6400), coupled to the energy dispersive spectroscopy (EDS) analysis (Thermoelectron).

The chemical composition and the homogeneity of the samples were determined by energy dispersive X-rays fluorescence spectroscopy (EDX), using a spectrometer Shimadzu, model EDX 720.

X-ray diffraction was performed to determine the crystalline phases present in sintered composites. These analyses, in addition to the powder size distribution determined by laser diffractionanalysis, and SEM, are important techniques to characterize the mechanisms related to homogenization and milling.

III. Results and discussion

A. Sample preparation

The density of the samples was determined for green and sintered samples by Archimedes method. The values for density are shown in the Table I. The average density after sintering is 8.623g.cm^{-3} and the average standard deviation is 0.26g.cm^{-3}.

TABLE I. SAMPLES DENSITY DETERMINED USING THE ARCHIMEDES METHOD. P AND P ARE THE GREEN AND SINTERED DENSITIES, RESPECTIVELY.

Sample	ρ_G (g.cm^{-3})	ρ_S (g.cm^{-3})
1	6.721	8.501
2	7.131	8.792
3	6.853	8.995
4	7.251	8.351
5	7.170	8.477

B. Cold-rolled plate process

Figure 3 presents the samples thickness, measured by a precision micrometer, as a function of the cold-rolled process cycle, where each cycle of strain involves a previews annealing at 1150°C during 20min. The initial average thickness (x) for the samples is 0.70mm.

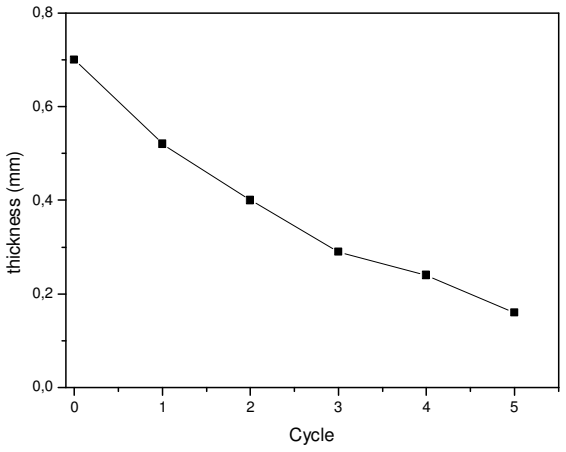

Figure 3 - The thickness of the sintered sample as a function of the cycle of strain.

C. Compositional and structural analysis

Figure 4 presents the micrographs obtained by SEM for different regions of the sintered samples, previously polished.

From the micrographs it can be noticed that the sample presents two principal different regions or phases. The dark phases are rich in Mo and the bright region is rich in Ni. These results, are an evidence of the atomic interdiffusion, for both elements.

The chemical composition for the numbered spots from 1 to 7 (see Fig. 5) was determined by EDS coupled to the SEM. Table II presents the amount of Ni and Mo for each analyzed spot cross the interface, respectively. The average standard deviation is 0.05 wt%.

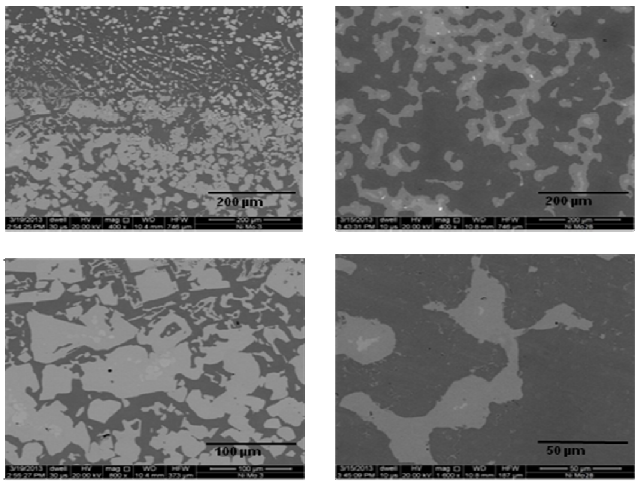

Figure 4 – Micrographs for different regions of sintered samples.

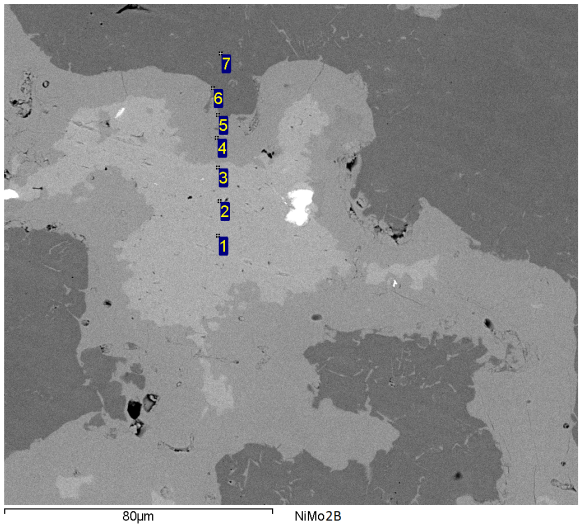

Figure 5 – Micrograph for a sintered sample shown the spots analyzed by EDS.

TABLE II. CHEMICAL COMPOSITION SURFACES DETERMINED BY EDX

Spot	Ni (at%)	Mo (at%)
1	30.50	69.50
2	33.76	66.24
3	36.52	63.48
4	43.07	56.93
5	55.84	44.16
6	69.21	30.79
7	72.11	27.89

The nominal composition of the metallic powder used for the sample preparation is 35.8 Mo - 64.2 Ni (at%), and the real composition, determined by EDX, for the sintered samples surface are shown in the Table III. These average values were determined for 5 spots per sample. The standard deviation was 0.06at% for each analyzed sample, and the analyzed spot surface area was 0.5cm^2.

TABLE III. CHEMICAL COMPOSITION SURFACES DETERMINED BY EDX.

Sample	Ni (at%)	Mo (at%)	Co (at%)	Ca (at%)	Fe (at%)
1	49.35	47.32	0.08	0.28	0.05
2	48.14	48.51	0.07	0.17	0.07
3	50.57	19.40	0.09	0.31	0.06
4	50.31	28.56	0.08	0.11	0.02
5	52.95	26.32	0.08	0.09	0.05
6	50.08	32.54	0.07	0.15	0.06
7	52.96	33.26	0.08	0.09	0.07
8	53.93	38.42	0.06	0.22	0.04
9	47.68	33.82	0.09	0.27	0.01
10	52.36	39.63	0.07	0.16	0.03

Figs. 6 and Fig. 7 present the X-ray diffraction pattern performed in the homogenized and milled Ni-Mo powders, and for the surfaces of pressed and sintered samples. In Fig. 7 it is noticed that the XRD pattern presents some peaks related to Ni-Mo alloy, Ni, and Mo crystalline phases. These results are an evidence of the presence of the Ni-Mo alloy after the sintering.

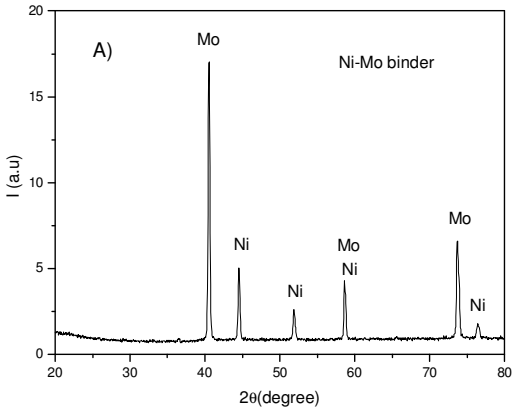

Figure 6 – XRD pattern for the homogenized metallic powders.

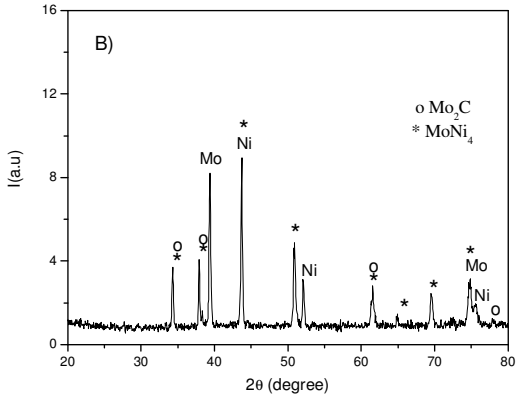

Figure 7 – XRD pattern for a Ni-Mo sample after sintering.

IV. Conclusion

The process involving powder metallurgy, induction heating in controlled atmosphere is appropriated to obtain a sintered preform sample, shown phases related to the Ni-Mo alloy and different phases rich in nickel or molybdenum, without damages to the microstructure and free of oxidation and relevant chemical contamination.

The cold-rolled plate method, followed by the annealing at 1150°C during 20 min, allowed changing the thickness from 0.70mm to 0.15mm in 5 cycles. These results allow the use of this material as filler for brazing process of the linear microwave tubes components.

The control of the sintered Ni-Mo alloy foils thickness and it composition, are relevant parameters for the manufactory process reliability of microwave tubes.

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