SPECIAL CARES FOR THE PRODUCTION OF THIN METALIC COBALT FILMS BY THE VACUUM EVAPORATION TECHNIQUE

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ABSTRACT

A method for the choice of materials used in the production of metallic elements, by the evaporation method is described. This method is based on the study of alloys and phase diagrams of the material to be evaporated and the possible crucible materials. The method was used for the production of cobalt films and the results can be extended to other elements with similar properties such as iron and nickel.

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INTRODUCTION

The aim of this paper is not just to present the method of preparation of metallic cobalt films but also to present a general procedure to be followed when one wants to evaporate other elements. This method is based on the study of alloys and phase diagrams of the material to be evaporated, by possible crucible elements and the other components of the evaporation process.

Our initial task, and the original motivation of this work was the production of metallic cobalt films, with thicknesses in the range of 300-1000 $\mu g/cm^2$, to be used in inbeam gamma ray spectroscopy. We have tried initially the centrifugation method, which did not give satisfactory results due to problems related with the cobalt suspension in the solution used. The evaporation technique was then, successfully used. This technique requires some care when one wishes to produce Co, Fe and Ni targets, due to the great facility of these elements in forming alloys when in contact with other materials such as Ta, W and Mo, usually used as crucibles, at temperatures below their respective melting points (1). This difficulty may be overcome, as proposed by Rose (2), when the cobalt is placed on a ceramic coating made of zirconium carbide (ZrC). In order to produce this coating one should use a cylindrical carbon crucible, previously submited to a Zr bath on the surface region where the Co will be, later on, deposited for evaporation. Based on this paper by Rose we tried to investigate with some detail how this coating can be obtained and also to extend the methodology of

search of the suitable materials to be used in the vacuum evaporation for the production of other element films

SELECTION OF CRUCIBLES FOR THE COBALT EVAPORATION

When one wishes to place a liquid metal inside a crucible, the main characteristics of this crucible is for it to have no interaction with the liquid metal and to be a refractory material. The cobalt melting point is 1494ºC and therefore one would be tempted to suggest, as a crucible for liquid cobalt, refractory metals with high melting points such as molibidenium (2610ºC), tantalum (2896ºC) and tungsten (3450ºC). However, if one looks at the binary phase diagrams of these elements with cobalt (see figures 1, 2 and 3) one can verify that the solubility of these elements in the liquid Co are very high for temperatures above the Co melting point. Table I shows this solubility at 1600ºC and 1800ºC, temperatures near the ones used for the Co evaporation. There is no need to determine the kinetics of dissolution until the compositions indicated on table I are reached because due to the high temperatures used one may expect a quick enrichment of Co, and consequently the decrease of the Co volatility due to the decrease of its activity with the mentioned elements (6,7). This fact makes the production of cobalt films difficult, as it shows that crucibles made of W, Mo and Ta are not suitable ones and therefore one must seek the suitable materials for such application.

In the following the possibility of utilization of zirconium carbide (melting point = 3445 + 25ºC (8)) as

the ceramic refractory material to hold the liquid cobalt, as suggested by Rose, is analysed. Due to the low stability of the cobalt carbide (8), the reaction ZrC + Co does not need to be considered, and therefore the chemical interaction analysed is ZrC (s) = $\underline{Zr}_{Co} + \underline{C}_{Co}$

where ZrC (s) is solid zirconium carbide.

$\underline{Zr}_{Co}$ is zirconium dissolved in liquid cobalt.

$\underline{C}_{Co}$ is carbon dissolved in liquid cobalt.

From this equation one could find the equilibrium concentrations, but due to the lack of data it was not possible to calculate them. However, the variation of the standard free energy of decomposition of the zirconium carbide in pure zirconium and pure carbon (9) indicates a high stability of the zirconium carbide at 1600ºC and one may also expect low concentrations of Zr and C dissolved in liquid Co at 1600ºC. Furthermore, data obtained by differential thermal analysis (8) shows that the Co - ZrC system is eutetic, with determined temperature of 1360ºC and composition of ~5 mol % of ZrC. One may suppose that the solubility of ZrC in liquid Co has this magnitude order for the evaporation temperatures of Co. This value, although not so low, is much lower than the ones found for the refractory metals W, Ta and Mo, which enables a better performance of ZrC as a crucible for the liquid cobalt.

PRODUCTION OF THE CRUCIBLES AND FILMS

In the production of the crucible and films a commercial evaporator (Edwards E12E3) of the Pelletron Laboratory of the University of São Paulo was used, which allows the use of three different systems for evaporation: current flow, electronic bombardment and sputtering. The system used was the bombardment by electrons emitted from a heated W fillament and a movable support for the crucible, which allows the focus of the electrons. To the crucible support, adjustable high voltage and current are applied, enabling the control of the temperature and the rate of evaporation.

The zirconium used for the coating of the carbon crucible consisted of small rectangular pieces of ~3 mg. The coating procedure requires the control of the temperature of the material and the time of the operation - the temperatures used were near the Zr melting point and the time was ~15 minutes. When the Zr melting point is reached it starts the process of its diffusion through the C, and the temperature must be kept constant in order to allow a uniform diffusion. Furthermore, the coating time can not be too short in order to avoid the formation of just a superficial layer of ZrC, which would allow possible crackings of the crucible, due to the ceramical properties of the layer. The temperature control at the central region of the crucible was done by the use of an optical pyrometer. After the coating, some Zr which may have not reacted with C is evaporated when one increases the temperature. Figure 4 shows the phase diagram of Zr - C,

and from this diagram it can be ensured that the coats formed are made of ZrC. The thickness of the coat depends on the parameters described above. Many different crucibles were produced by this method.

With these crucibles many cobalt films were evaporated on thick lead backings. In order to produce the required ~500 $\mu g/cm^2$ thickness, and to avoid over heating problems, the evaporations were done in several steps and using two crucibles. The films produced by this method show high uniformity and high degree of purity (11).

Table 1

Solubility of W, Ta and Mo in liquid Cobalt at 1600°C and 1800°C.

System	Solubility at 1600°C (atomic %)	Solubility at 1800°C (atomic %)
Co - W	33	38
Co - Ta	26	27
Co - Mo	52	58

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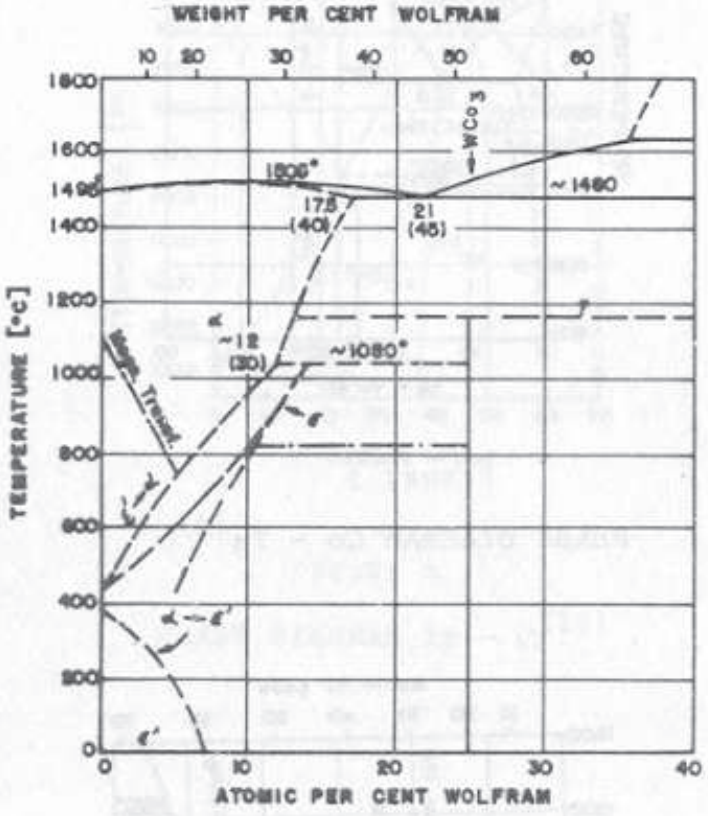

FIGURE 1

PHASE DIAGRAM Co - W[3]

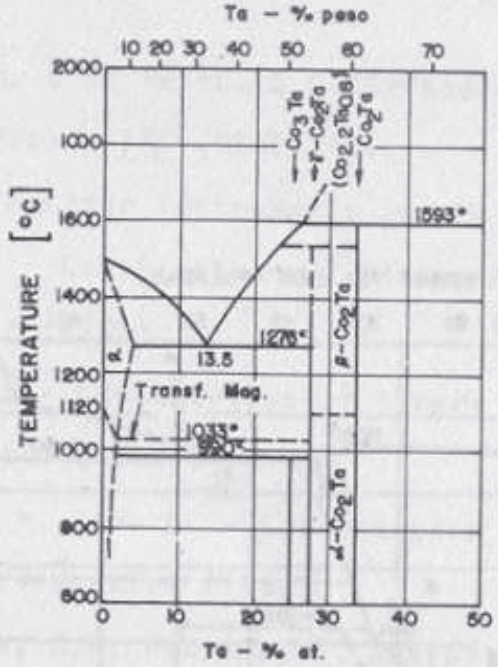

FIGURE 2

PHASE DIAGRAM Co - Ta[4]

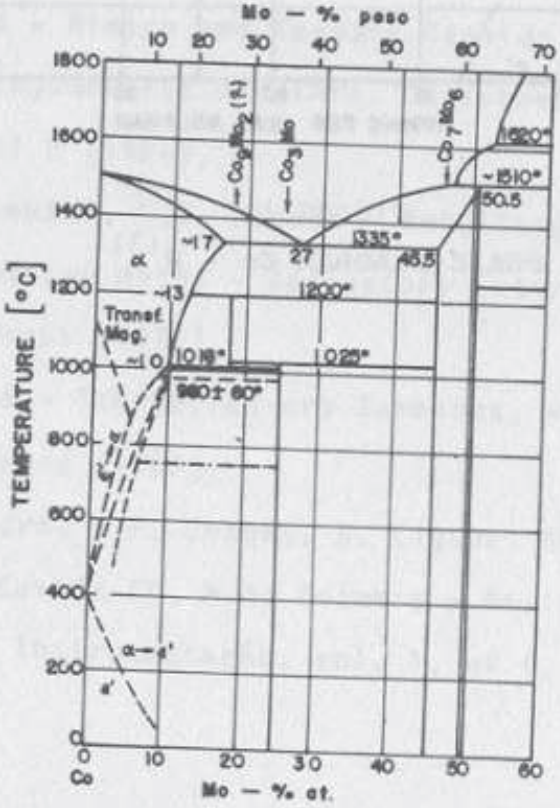

FIGURE 3

PHASE DIAGRAM Co - Mo[5]

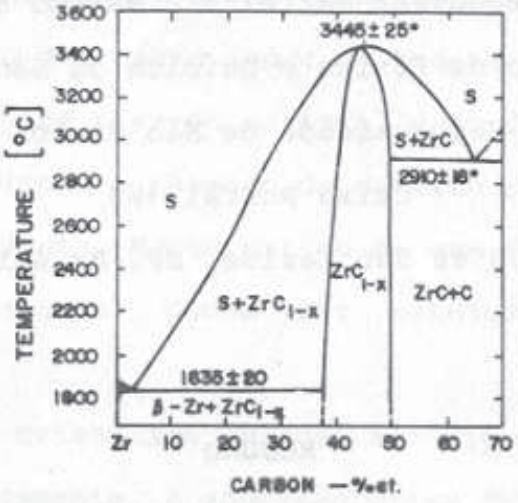

FIGURE 4

PHASE DIAGRAM Zr - C[10]