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PREPARATION OF HIGH-PURITY BERYLLIUM FOILS*

R. D. Taylor

MASTER

Oak Ridge National Laboratory
Solid State Division
Oak Ridge, Tennessee 37830

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ABSTRACT

A technique is described for the preparation of beryllium foils by vapor deposition. The high-purity, pinhole-free foils are vacuum tight and suitable for many x-ray analysis applications.

The beryllium is evaporated from an electron beam heated crucible source onto a heated substrate. Substrate temperatures of 450 to 700°C are necessary to obtain the desired mechanical properties of the foils. At these temperatures, contamination of the foils by diffusion of the substrate material into the beryllium can be a significant problem, as impurity levels of more than several hundred ppm are detrimental to the x-ray transparency of the windows. This problem is minimized by careful selection and preparation of the substrate. A clean deposition system and pure source material are necessary to preserve elemental integrity of the vapor-deposited foils.

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To solve the problem of preparing beryllium thin foils of thickness less than 0.025 mm suitable for use in x-ray energy spectroscopy applications, a physical vapor deposition approach has been applied. Production of such foils by mechanical reduction (rolling) is difficult because of the inherent brittleness of beryllium, and commercial availability of rolled foils is very limited.

Figure 1 shows the basic configuration of an x-ray spectroscopy system. When an energetic beam strikes the sample, x-rays are emitted characteristic in energy of the constituent elements of the sample. Some of these x-rays pass through a window, transparent to x-rays but opaque to light, and strike a detector. Beryllium is ideally suited for use as a window material because of its small x-ray cross-section and high strength. Because the window isolates the detector from the sample chamber, it must be sufficiently strong to withstand an indefinite number of pressure cycles between 0 and 1 atmosphere differential pressure.

Typical beryllium window specifications for use in x-ray energy spectroscopy are:

Diameter	12.7 mm $+0.25$ mm -0.00 mm
Thickness	7.6 μ m $+2.5$ μ m -0.0 μ m
High Purity	99.8% Be minimum chemical purity 100 ppm maximum of any single contaminant
Vacuum Tight Optically Opaque	

Maximum diameter and thickness may extend up to 25 mm and 0.125 mm, respectively, depending on the application.

Figure 1. Configuration of X-Ray Energy Spectroscopy Instruments Utilizing Thin Beryllium Windows

Bunshah and Juntz [1] developed a technique for the preparation of framed beryllium windows by a high-rate physical vapor deposition process. Beryllium was evaporated from an electron beam-heated vapor source at about 25 $\mu\text{m}/\text{min}$ (0.001 in.) onto a copper or monel substrate heated to a temperature between 675K and 975 K. Use of lower substrate temperatures resulted in a deposit having less than theoretical density and containing pores. Subsequent to deposition, the substrate was dissolved with concentrated nitric acid in the window area after masking off the area which formed the frame. The principal problem encountered was in eliminating the porosity of deposits having less than 50 μm thickness.

Mah and Nordin [2] performed characterization studies of physical vapor-deposited beryllium. In their experiments, 0.125 mm (0.005 in.) thick copper substrates were heated to temperatures between 475 K and 975 K, and the deposition rate was varied from 2.5 - 12.5 $\mu\text{m}/\text{min}$. The substrate was subsequently dissolved with a 50% (by volume) HNO_3 solution. Their results showed that as substrate temperature increased, grain size increased, hardness decreased, and fracture strength increased. The copper content increased from 0.05 wt. % (70 ppm) at temperatures less than 625 K to 0.5 wt. % (700 ppm) at temperatures greater than 725 K. They concluded that

"...substrate temperatures of 480°C or above would produce deposits with desirable physical properties and physical integrity."

Preparative Considerations

The objective of the research reported in this paper is to develop a technique for the vapor deposition of high purity beryllium foils suitable for use in x-ray energy spectroscopy applications. The basic evaporation parameters for deposits having the desirable physical and mechanical properties have already been established [1,2]. The problem of foil purity, i.e., contamination from the substrate at the necessary elevated temperatures, appears to be the most significant remaining problem.

A review of substrate selection criteria limits the choice of materials:

1. The beryllium deposit must be separated readily from the substrate.
2. The substrate must have a low vapor pressure--stable in high vacuum at temperatures exceeding 725 K.
3. The substrate should have a thermal expansion coefficient reasonably comparable to beryllium or should be a thin ductile material to minimize stress in the deposit.
4. The contamination of the deposit by the substrate material must be negligible, i.e., less than 100 ppm.

Thin copper sheet satisfies all criteria with the exception of the last, as determined by Mah and Nordin [2], and was used as the primary substrate for these experiments. In order to reduce copper contamination,

a diffusion barrier between the substrate and depositing layer is necessary. Halide compounds or organic parting agents are not suitable because of their high vapor pressures or their characteristic coarseness resulting from recrystallization at elevated substrate temperatures. However, very thin metallic coatings would not significantly alter the physical properties of the primary copper substrate.

Silicon and molybdenum were selected as possible diffusion-limiting films. Silicon solubility in beryllium is less than 200 ppm in the temperature range of interest. However, copper readily diffuses into silicon and a thicker layer of silicon than was thought desirable originally might be required to reduce the copper contamination to acceptable levels. Copper and molybdenum are completely immiscible, but diffusion of molybdenum into the beryllium deposit could be excessive. Since the molybdenum-silicon diffusion rate is very low, it was thought that a Cu/Mo/Si substrate should be satisfactory.

Experimental Procedure

Copper sheet, 0.13 mm (0.005 in.) thick, served as the primary substrate. The copper surface was polished with 0.05 μm alumina prior to subsequent coating. A layer of molybdenum (having a thickness varying up to 0.5 μm) was sputtered or evaporated onto the polished copper. Silicon was evaporated onto copper or molybdenum-coated copper substrates at thicknesses of up to 0.5 μm . The surface roughness of the deposited films was noted to increase as the thickness increased, particularly in the case of silicon.

Figure 2. Schematic Representation of Beryllium Coating Apparatus

The beryllium coating apparatus consisted of an Edwards Model 19E Vacuum Coating Unit; the evaporation source was a Temescal Model SF1H-270-1 electron beam gun operated in conjunction with a Temescal Model CV-10 power supply (10 kW). The stainless steel substrate mask assembly was located 25 cm above the source, was rotated at 20 rpm, and was radiant-heated from the back by a 2-kW quartz heat lamp assembly. The apparatus is shown schematically in Figure 2 and pictorially in Figures 3 and 4.

The system was evacuated to a base pressure of 1×10^{-6} torr and the substrate was heated to 825 K. Using electron beam power of 3.0 kW (10 kV, 300 mA), the beryllium was evaporated and deposited on the substrate at a rate of about 5 $\mu\text{m}/\text{min.}$ to a thickness of 7.5 μm (0.0003 in.).

After cooling to room temperature, the copper substrate was dissolved with a 50% HNO_3 solution. Effervescent action caused by the acid reacting with the copper also removed most of the barrier films, and light brushing under water served to remove residual adherent material.

The self-supported beryllium foils were examined by optical microscopy for surface morphology and pinholes. A scanning electron microscope with an x-ray energy spectroscopy attachment was used for microstructural characterization and preliminary chemical analysis. Tube-excited fluorescence was utilized for more quantitative determination of elemental constituents.

Figure 3. Beryllium Vacuum Coating System

Figure 4. View of Evaporator and Substrate Assembly
Inside the Bell Jar

Results

The macrograph in Figure 5 shows typical beryllium foils obtained by the physical vapor deposition process. The scanning electron micrograph of Figure 6 illustrates the columnar grain growth common to vapor-deposited beryllium; average grain diameter was $2.0\text{ }\mu\text{m}$. Porosity and pinholes occurring in the foils were primarily attributed to contaminants and roughness of the substrate surfaces. Careful polishing and cleaning of the primary copper substrate was found to be critical to avoid pinholes. Surface roughness of the thicker barrier film deposits was also found to be detrimental.

Chemical analysis of the foils showed a significant reduction of the copper content with increasing thickness of the barrier films. Molybdenum films greater than $0.1\text{ }\mu\text{m}$ thick effectively reduced the copper content of the beryllium foils to acceptable levels, but the resultant molybdenum contamination was not acceptable.

Use of silicon as a barrier film resulted in problems more physical than chemical in nature. Barrier films of thickness greater than $0.2\text{ }\mu\text{m}$ thick exhibited a strong physical bond to the beryllium foil and were difficult to remove. Silicon inclusions in the beryllium foil after removal of the bulk of the film were evident. Sputter etching of the foils was somewhat effective in removing residual silicon, but residual stress in the beryllium was evidenced by curling of the foil after removal of the silicon films greater than $0.2\text{ }\mu\text{m}$ in thickness.

Figure 5. Macrograph of Typical Beryllium Foils

Figure 6. Scanning Electron Micrograph of Beryllium Foil Showing Fracture Cross Section and Surface Texture

Best results were obtained by using a combination of molybdenum and silicon barrier films. Beryllium deposited on copper coated with a 0.2 μm thick layer of molybdenum and 0.2 μm layer of silicon showed residual concentrations of less than 20 ppm of either copper or molybdenum. A residual silicon content of less than 200 ppm in the foil is considered acceptable for x-ray spectroscopy applications because of its small cross section and consequently low specific absorption for the element. The silicon content may be further reduced by sputter etching the surface of the beryllium foils.

Figures 7 and 8 are representative of the x-ray fluorescence spectra of the beryllium foils. Figure 7 shows the spectrum of beryllium deposited on a bare copper substrate followed by dissolution of the copper substrate; position of the background spectrum is also shown. The residual copper in the foil was estimated to be 0.5 wt. %. Figure 8 shows the spectrum for beryllium deposited on a copper substrate with molybdenum and silicon barrier films, each barrier film being 0.2 μm thick. Copper content in the beryllium is reduced to trace levels with the multibarrier approach.

Compositions of the beryllium source material and deposited foil material are provided in Table I. The distillation inherent in the evaporation process resulted in a deposit of better than 99.9% purity when the best multi-film barrier was employed to minimize contamination from the substrate.

Figure 7. X-Ray Fluorescence Spectra of Beryllium Foil Evaporated on Bare Copper Substrate (550°C)

ID: CMS-18

EEDS-11 /BLANK

EG&G

PST: LT= 203S

CPS: 10401

DT: 45

FS: 1K

LINEAR

ORTEC

Figure 8. X-Ray Fluorescence Spectrum of Beryllium Foil Evaporated on Copper Substrate With Molybdenum-Silicon Barrier Film

Table 1. Chemical Composition of the Beryllium

<u>Element</u>	<u>Source</u>	<u>Deposit</u>
Be - %	99.56%	>99.8%
O - %	0.18	-
Al-ppm	300	-
C	537	-
Cr	90	20
Cu	20	20 ppm to 700 ppm*
Fe	596	20
Mg	175	-
Mn	80	50
Mo		20 ppm to 200 ppm*
N	278	-
Nb	20	-
Ni	175	-
Si	275	100 ppm to 200 ppm*
Ta	40	-
Ti	60	-

*Composition varies with barrier.

- Indicated quantity not determined.

Best barrier choice for minimum impurities:

Mo 1000 A to 2000 A
Si 1000 A to 2000 A

Conclusions

Physical vapor deposition of beryllium onto copper substrates previously coated with thin diffusion barrier films to mask the copper has been used to produce foils with physical and chemical properties suitable for x-ray spectroscopy applications. Critical barrier film thicknesses for chemical isolation of the deposit from the primary copper substrate are dependent on surface preparation of the copper substrate, mobility of copper through the barrier films, and surface roughness of the vapor-deposited barrier films. A multi-barrier approach using molybdenum and silicon sequentially deposited on the primary copper substrate provided the best results. The principal factors contributing to porosity and/or pinholes in the beryllium foils were particulate contaminants and surface roughness of the substrate prior to deposition.

Results of the empirical diffusion barrier film investigation are summarized in Figure 9, showing the bilayer barrier region with which satisfactory beryllium deposits could be obtained.

Figure 9. Summary of Experimental Results

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