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CHARACTERIZATION STUDIES OF PHYSICAL
VAPOR-DEPOSITED BERYLLIUM

George Mah
Carl W. Nordin

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George Mah
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Research and Ecology
COATINGS GROUP

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CHARACTERIZATION STUDIES OF PHYSICAL VAPOR-DEPOSITED BERYLLIUM

George Mah and Carl W. Nordin

Abstract. Beryllium flat foils of 0.5 to 5 mils thick and shapes of 3 to 4 mils thick have been produced by thermal evaporation, utilizing an electron-beam gun for heating. A study was made of the relationship between the substrate temperature during deposition and the microstructure of the resulting foils. An absence was noted of cone growth in the foils which were deposited at high substrate temperatures ($>400^{\circ}\text{C}$). The foils show an (0002) preferred orientation. Physical and mechanical properties (electrical resistivity, fracture strength, total elongation, and hardness) of the foils were measured as a function of the substrate temperature. The effects of thermal treatments on the foils are reported. (For metric use: 1 mil = 3×10^{-5} meters.)

INTRODUCTION

One of the problems in conventional fabrication of beryllium concerns the production of thin foils (less than 4 mils) with uniform thicknesses. The physical vapor-deposition process appeared to offer a solution and investigations were initiated to study the following:

1. Relationship between deposition variables and microstructures of films.
2. Relationship between deposition variables and properties of films.
3. Effects of thermal treatments on deposits.
4. Feasibility of fabricating simple shapes by physical-vapor deposition.

The films were made by the electron-beam evaporation technique. Deposition rates ranged from 0.0001 to 0.0005 inches per minute (or 0.00254 to 0.01270 millimeters per minute). Copper and copper with a layer of evaporated sodium chloride were used as substrates.

Other researchers (1, 2)¹ have used the electron-beam evaporation technique as a vacuum-distillation process to reduce impurity contents of beryllium. Studies (3, 4, 5, 6, 7) have been performed on the growth mechanism and texture of beryllium films. However, little has been done to establish a relationship between deposition variables and properties of films.

¹ Numerals in parentheses refer to references at end of text.

DISCUSSION

A study was made of the relationship between substrate temperature during deposition and microstructure of the resulting foils. The grain size was increased with increases in the substrate temperature; also, an absence of cone growth was observed in the films deposited at high substrate temperatures ($>400^{\circ}\text{C}$). The orientation of the films was dependent on substrate material and temperature. Compared to substrate temperature, deposition rate (from 0.0001 to 0.0005 inches per minute) had only a minor influence on the microstructure of the films.

The mechanical and physical properties of the foils were improved with increase of substrate temperature. The improvements in properties were slight when the substrate temperature was increased above 500°C .

Initial results from the thermal treatments show the properties were improved. The heat-treated tensile specimens had lower fracture strength and more elongation. Time required for the improvements at 800°C was about a half hour.

Flat sheets of 4.25 by 4.25 inches of 0.5 to 3 mils thick and free-standing beryllium shapes of 3 to 4 mils thick have been produced. (For metric use: 1 inch = 25.4 mm and 1 mil = 3×10^{-5} meters.)

EXPERIMENTAL PROCEDURES

Evaporation:

The beryllium was evaporated by the electron-beam technique. The system was pumped down to a low 10^{-6} torr range (1 torr = 133 pascals), and the substrate was heated to a given temperature. The substrate temperature was measured by a thermocouple embedded in a 0.125-inch (or 3.175 millimeters) copper plate which remained in contact with the copper substrate. On heating the beryllium, the pressure was increased to a low 10^{-4} range, as a result of out-gassing of the beryllium. Typical deposition parameters for the evaporation are listed in Table I.

For each deposition, 3 tensile specimens, 2 disks for metallography, and 2 strips for electrical-resistivity measurements were produced. To obtain the desired geometry of specimens for the characterization studies, a mask was laid over the substrate. The copper substrate

TABLE I. Typical Deposition Parameters for the Evaporation of Beryllium.

Electron-Beam Current (milliamperes)	Acceleration Voltage (kilovolts)	Temperature (°C)	Source-to-Substrate Distance (inches)	Deposition Rate (mils per minute)
450	10.6	varied	13	0.5

NOTE: One inch = 25.4 millimeters; 1 mil = 3×10^{-5} meters.

TABLE II. Chemical Composition of the Beryllium.

Element	Source	Weight Percents	
		As-Deposited	Changes in Composition (ΔC)
Beryllium Oxide (BeO)	0.05	—	—
Iron (Fe)	0.0135	0.001	-0.0125
Aluminum (Al)	0.010	0.018	+0.008
Calcium (Ca)	<0.003	<0.003	—
Cadmium (Cd)	<0.001	0.001	—
Cobalt (Co)	<0.001	0.001	—
Chromium (Cr)	0.002	0.002	—
Copper (Cu)	0.003	*	—
Magnesium (Mg)	<0.001	0.004	+0.003
Manganese (Mn)	0.008	0.016	+0.008
Molybdenum (Mo)	<0.003	0.005	+0.002
Nickel (Ni)	0.013	0.003	-0.010
Lead (Pb)	<0.001	<0.001	—
Silicon (Si)	0.010	<0.001	-0.009
Titanium (Ti)	0.029	<0.001	-0.028
Tungsten (W)	<0.020	—	—
Zinc (Zn)	<0.010	<0.010	—

*Findings showed that the weight percent of copper in the foils was dependent on the substrate temperature.

was etched away from the specimens with a 50 percent nitric acid (HNO₃) solution. Chemical composition of the source and the as-deposited beryllium are shown in Table II.

The changes in the composition, ΔC , can be explained. In general, elements with lower vapor pressure than beryllium were reduced, and elements with higher vapor pressure than beryllium were increased. The amount of copper varied from 0.5 weight percent (wt %) for foils deposited above 450 °C to 0.05 wt % for foils deposited below 350 °C. The increase in the amount of copper was caused by interaction between beryllium and copper (substrate) during the deposition. A study of the interaction is in progress. An etching process has been developed to reduce the amount of copper.

Measurements:

All measurements were made at room temperature. Electrical-resistivity values were obtained by a four-point probe DC method; and measurements were made on 3 by 0.125-inch strips of various thicknesses. Tensile tests were performed on specimens of 1.25-inch gauge length and 0.215-inch width. To test the specimens, a specimen holder and testing grips were specially designed. The devices were used to prevent handling damage and misalignment to the specimen while being positioned in the Instron. Since the tensile specimens in the as-deposited condition were in the required geometry, no other specimen preparation needed to be done. The specimens were pulled with a cross-head speed of 0.005 inches per minute (1 inch = 25.4 mm).

RESULTS

Microstructures:

The grain size increased with increases in the substrate temperature, as shown in Figures 1, 2, 3, and 4. Two other significant differences were observed between films of high and low substrate temperatures. An absence of cone growth was noted in the films deposited at high substrate temperature. Cone growth could be stopped by forming laminated films, as shown in Figure 1. The columnar grains were preferentially grown perpendicular to the surface of the substrate in the films deposited at high substrate temperatures; while in the films deposited at low substrate temperatures, the columnar grains were at an angle of about 30 degrees with the normal of substrate surface.

This change of orientation of the grains was verified by X-ray studies. The films of low substrate temperatures had an (10 $\bar{1}$ 3) orientation while those of high substrate temperatures had an (0002) orientation. The interplanar angle between the (0002) and (10 $\bar{1}$ 3) is 31.3 degrees. Other researchers (3, 6, 7) had also found that the orientation of beryllium films changes with substrate temperature and material.

In the films of high substrate temperatures, deformation twins are apparent (see Figure 4). Klokholm (8) has shown that when the substrate temperature is above one fourth of the melting temperature of the metal (evaporant), intrinsic stress in the film will be small. Thus, stress in the films deposited at high substrate temperatures is mainly thermal stress. Since copper (substrate) has a larger coefficient of thermal expansion than beryllium, on cooling from high substrate temperatures (550 °C), a compressive stress is developed in the film. The compressive stress caused deformation twins to appear in the film.

FIGURE 1. Specimen A, Substrate Temperature from 20 to 140 °C. Polarized light. Magnification 400X.

FIGURE 2. Specimen B, Substrate Temperature from 200 to 270 °C. Polarized Light. Magnification 600X.

FIGURE 3. Specimen C, Substrate Temperature from 480 to 550 °C. Polarized Light. Magnification 600X.

FIGURE 4. Specimen D, Substrate Temperature from 625 to 685 °C. Polarized Light. Magnification 600X.

Crystallographic theory of twinning shows that for a close-packed hexagonal metal with a c/a ratio less than the theoretical value (1.633), where c and a are lattice parameters, twinning is favored by compressive stress parallel to the basal plane. Beryllium has a c/a ratio of 1.567. The thermal stress in the film was compressive and parallel to the substrate surface. The basal planes of the film were oriented parallel with the substrate surface. Thus, all factors were favorable for twinning to occur in the film. For beryllium, the twinning plane is the $(10\bar{1}2)$ plane and it makes an angle of 43 degrees with the basal plane. The twins are at about 45 degrees with respect to surface (or basal planes) of the film, (see Figure 4); again, the result is in agreement with the theory.

Properties:

Properties of the films were measured as a function of the substrate temperature. Measurements were made at room temperature. The results are shown in Table III. The properties were improved with increases in the substrate temperature. For films deposited at low substrate temperature, such as Specimen 1 and 2, the films were extremely brittle and lacked physical integrity; thus, few measurements were possible. Palatnik and Fedorenko (4) also found the films deposited at low substrate temperatures to be brittle and to contain cracks. At low substrate temperatures, the mobility of atoms in the films is low; thus, structural defects are *frozen* in the film. The structural defects create high intrinsic stress which causes brittleness and cracks. As would be expected, the films of the low substrate temperature behaved in a manner similar to a cold-worked metal; this is supported by the high

values of hardness and electrical resistivity (see Table III). When the substrate temperature was increased from 500 to 650 °C, changes in properties were slight.

Effects of Thermal Treatments:

Some of the films were heat-treated in a vacuum of 10^{-7} torr and at 800 °C. This thermal treatment caused grain growth and eliminated deformation twins (see Figures 5, 6, and 7). The substrate temperature of Specimen E in Figure 5 was approximately 600 °C. The effects of thermal treatments on the properties of the specimen are shown in Table IV. The measurements were made at room temperature.

The mechanical properties show little change between specimens held for a half hour and one hour at 800 °C; also, changes in the microstructure for the specimens were insignificant as shown in Figures 6 and 7.

In all cases, the thermal treatment lowered the hardness and fracture strength; however, in some cases the percent elongation remained constant. More research is required to obtain better understanding of the effects of thermal treatments.

Beryllium Sheets and Shapes:

From the results of the study, it was decided that substrate temperature of 480 °C or above would produce deposits with desirable properties and physical integrity. Free-standing sheets of 0.5 to 3 mils (see Figure 8) and simple shapes of 3 mils have been produced. The thickness variation of the sheets was less than ± 10 percent.

TABLE III. Properties of Beryllium Films versus Substrate Temperature.

Specimen No.	Substrate Temperature during Evaporation (°C)	Electrical Resistivity (micro-ohm centimeters)	Knoop Hardness No. (100-percent gram load)	Fracture Strength (1000 pounds per square inch)	Total Elongation (percent)
1	200 to 270		488 to 490		
2	300 to 345	9.62 to 12.9	267 to 326		
3	350 to 425	8.85 to 9.22	250 to 230	19 to 21	0.1
4	480 to 550	4.2 to 4.9	204 to 233	39 to 43	0.3
5	625 to 685	4.5 to 4.8	168	40 to 52	0.45

TABLE IV. Effects of Thermal Treatment on Mechanical Properties of Specimen E.

Specimen Condition	Heat Treating Temperature (°C)	Time (hours)	Fracture Strength (1000 pounds per square inch)	Total Elongation (percent)	Knoop Hardness (100-gram load)
As-Deposited	—	—	48.3	0.48	208 to 222
Heat-Treated	800	0.5	33.7	1.3	170 to 181
Heat-Treated	800	1	33.1	1.1	178 to 181

FIGURE 5. Specimen E, Substrate Temperature from 580 to 615 °C, As-Deposited Condition. Polarized Light. Magnification 600X.

FIGURE 6. Specimen E, Heat-Treated at 800 °C for a Half Hour. Polarized Light. Magnification 600X.

FIGURE 7. Specimen E, Heat-Treated at 800 °C for One Hour. Polarized Light. Magnification 600X.

FIGURE 8. Beryllium Sheet (4.5 by 4.5 inches by 1 mil).

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