A UNIQUE BERYLLIUM CARBIDE THIN FILM: SYNTHESIS, CHEMICAL AND THERMAL CHARACTERIZATIONS

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ABSTRACT

Plasma-deposited coatings containing beryllium in excess of 50 atomic percent and oxygen content <5 atomic percent would meet the requirements for the outermost coating, the outer ablator of the multilayered microsphere for inertial confinement fusion (ICF). Films containing a Be_2C composite with Be contents as high as 75 atomic percent (O < 2 atomic percent) have been deposited on a variety of substrates via magnetron sputtering of Be into a methane/argon plasma. The elemental composition was controlled by adjusting the methane/Ar flow rate ratio during the deposition process. The films were characterized by Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), neutron diffraction (ND), differential thermal analysis (DTA), and thermogrravimetric analysis (TGA).

I. INTRODUCTION

Fusion energy is an environmentally attractive and possibly essential alternative energy source for the world in the middle of the next century and beyond [1]. Fusion reactions, in which the d-t(deuterium-tritium) reaction has the lowest ignition temperature ($\approx 4 \times 10^7$ K), provide the source from which the energy of the sun is derived [2]. At the fusion temperature, gases are totally ionized and known to form a hot plasma of high density gases. To produce useful amounts of fusion energy, the requisite plasma temperature has to be achieved and the hot plasma has to be confined long enough. In inertial confinement fusion (ICF), the reaction conditions are created by simultaneously firing intense laser beams from different directions onto a tiny capsule called the target which contains the fuel, deuterium and tritium. The hollow spherical capsules have a multilayer plastic wall made of hydrocarbon-based plasma polymers of a desired thickness as an outer ablator [3]. Other ablator materials have been used such as pure Be and Al [4, 5] and metal-doped hydrocarbon plasma polymers [3, 6-8]. The minimum condition for the production of practical fusion power is that the energy released from the fusion reactions after conversion to electricity must exceed the energy required to run the ignition lasers [2]. To meet this condition, the chosen candidates of the fuel capsule shell materials must be composed of low atomic number elements, like beryllium, boron, carbon which have low potentials for radioactive plasma power losses [9] and high X-ray transparency [10, 11] to ensure efficient energy transportation for the ignition. The materials must also be hydrogen permeable so as to easily fill the capsules with fuels. The current plastic capsules meet the requirements, but they can only withstand several million Pascals (several tens of atmospheres of internal pressure), because of the poor tensile strength of the materials [3]. The capsule should further withstand a pressure of 35 million Pascals (350 atmospheres) at environmental temperatures to allow room temperature handling of the capsule until it is cooled to form the cryogenic layer [12]. Beryllium has an excellent X-ray transparency, and mechanical strength. Beryllium has also proven to be a good ablator, based on the experience of its use as a plasma facing component [13-24]. Beryllium also has good thermal conductivity which gives it high thermal shock resistance during the fusion process and provides a low barrier to the permeation of hydrogen. From a fuel kinetic energy point of view, pure beryllium may not be the best choice for the capsule material as compared to carbon-containing beryllium composites or compounds [6]. The low melting point and appreciable sublimation are also disadvantages of pure beryllium [18]. Carbon-containing beryllium composites with a beryllium content in excess of 50 atomic percent and up to 75 atomic percent have been recommended as candidates for coating the hollow microspheres [15].

Several techniques have been conducted to make coating materials containing beryllium. To produce coatings with smooth enough surfaces (grain size < 10 nm) [4, 6, 7, 12] assuring implosion performance [5], the options are restricted to thermal spray, plasma-enhanced thermal evaporation [6, 25, 26] drill-plug techniques [27], PECVD (plasma-enhanced chemical vapor deposition) [25, 27], and magnetron sputtering [12, 25] techniques.

In this work, the primary investigation has focused on the development of a deposition process whereby Be has been introduced (via magnetron sputtering) into an argon/methane plasma to deposit thin films of Be_2C onto a variety of substrates. The resulting films were thoroughly characterized to determine elemental and molecular composition, the crystal structure and chemical stability.

II. EXPERIMENTAL

The sputtering system is composed of a vacuum chamber, a pumping unit, a power supply unit, a gas feed-control unit, and a substrate holding-magnetron assembly, as shown in Figure 1. The vacuum chamber, NRC, model 3115, manufactured by Varian-Norton Co. is a domed glass jar with a stainless bottom plate. A motor driven, spiral pole hoist is used to lift and lower the jar. The system leaking rate under vacuum is about 7.6×10^{-3} cm^3/min (standard cubic centimeter per minute). A 40 kHz audio frequency generator made by Advanced Energy (model PE 1000) is equipped to provide power to the electrodes. Gases can be fed via feed lines which are constructed of stainless steel tubes through Nupro valves, KMS flow rate monitors and can be controlled by KMS 260 controllers connected with the monitors. The substrate holding-magnetron assembly is composed of two electrodes and a plate. Each electrode has a square beryllium sheet with four inch sides and quarter inch thickness and a magnet assembly, which consists of eight magnets of 1.27 × 1.27 × 0.64 cm (0.5 × 0.5 × 0.25 inch) arranged like petals and sandwiched between a glass and a steel thin plate, both with the same area size of the beryllium sheet. Two Be electrodes with a purity of 99.7% were used as the beryllium source. The gas used as the sputtering medium was high purity argon and that used as the reactant was high purity methane. Substrates consisted of 18 × 18 mm premium cover glass distributed by Fisher Scientific, regular window glass cut into 3.8 × 3.8 (1.5 × 1.5 inch) pieces, and silicon wafers with a (100) plane surface obtained from MEMC Electronic Materials, Inc, high purity aluminum foil from Johnson Matthey, and ceramic membranes of Whatman® International coated with polydimethylsiloxane rubber from General Electric were used as substrates for different analyses. Under the general deposition conditions in Table I, experiments were carried out to prepare films by changing the methane to argon flow rate ratio.

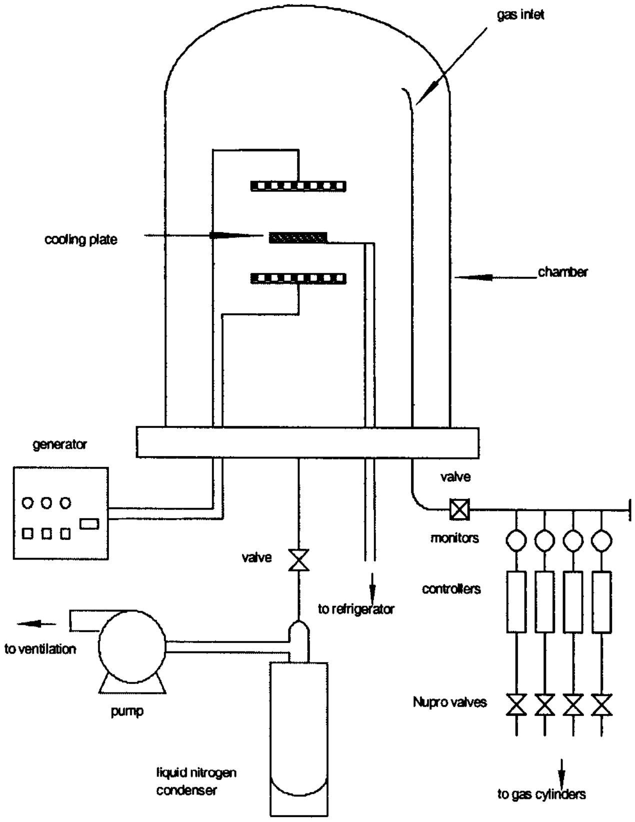

Figure 1. Magnetron Sputter Deposition System

Table I. General Deposition Conditions

Power Supply, Watt	200
Pressure, mTorr	200 - 250
Substrate Temperature, °C	200 ± 50
Deposition Period, Hour	48 - 240
Argon Flow Rate, sccm	0.80

A PHI 545 Auger spectrometer manufactured by

Physical Electronics was used for film element composition analysis at a sputtering rate of 5 nm/min for depth profiling. The films were analyzed with a model 548 X-ray photoelectron spectrometer made by Physical Electronics. X-ray diffraction patterns were taken on a Scintag XRD 2000 diffractometer at λ = 1.5406 Å (the wavelength of Cu K_a). A stepped scan using a step size of 0.03° was employed. Powder neutron diffraction data were collected using the high resolution diffractometer at the University of Missouri-Columbia Research Reactor. The powder samples were analyzed by a Perkin-Elmer DTA Series 7 and a Mettler Instrument Corporation TGA, model T-OH.

III. RESULTS AND DISCUSSION

A. Elemental Composition of Be-C Films

Low oxygen-containing Be-C films have been made by magnetron sputtering of beryllium into a methane plasma. Elemental compositions can be controlled by varying the flow rate ratio of the reactive gas methane to the sputtering media. The results of AES for the films under the operating conditions in Table I are shown in Table II.

According to the data in Table II, increasing the methane flow rate reduces the beryllium concentration in the deposited films. The reason could be twofold. Increasing the methane flow rate increases the carbon concentration in the reactive plasma, and also decreases the beryllium sputtering rate. The average elemental concentration changes in the films with changing flow rate ratios are almost linear.

A typical elemental composition depth profile is shown in Figure 2. These films have very good uniformity except at the top surfaces due to adsorption of CO_2, H_2O, air, etc.

B. Chemical States of the Elements in the Films

All AES spectra of the samples show the carbon satellite peaks which constitute the "fingerprint" of the carbide state, strong evidence for the presence of beryllium carbide in all the film compositions. All this suggested that XPS analysis should be carried out as it would provide further information as to the compounds in the films. Table III gives the electron binding energy level in the element's inner shell for different chemical states. In most cases, XPS data are collected only from the top surfaces of samples. However, for beryllium-containing materials (beryllium is a strong oxygen getter), we chose to carry out the XPS analyses at an approximate depth of 300 nm.

Table II. AES Results of Film Compositions

Group No.	Flow Rate Ratio of Methane/Ar	Be at. %	C at. %	O at. %
1	0.1	74-76	23-25	0.1-2
2	0.15	64-65	31-33	2-3
3	0.2	61-63	33-36	2-3
4	0.25	56-58	35-39	2-4
5	0.3	45-52	46-53	1.3-2.5

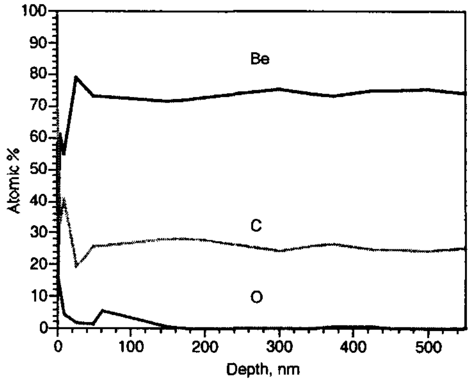

Figure 2. Depth Profile of Film Composition for a Group 1 Sample

Table III. Binding Energy, eV

Be_{1s} [28]	111.5
Be_{1s} (BeO) [29]	114.1
Be_{1s} (Be_2C) [29]	112.4
C_{1s} (Be_2C) [29]	282.1
C_{1s} (Miscellaneous)	284, Diamond; 284.2 Graphite [30-32]; 284.6 Hydrocarbon [8]
O_{1s} [28]	543.1
O_{1s} (BeO) [8]	531.6

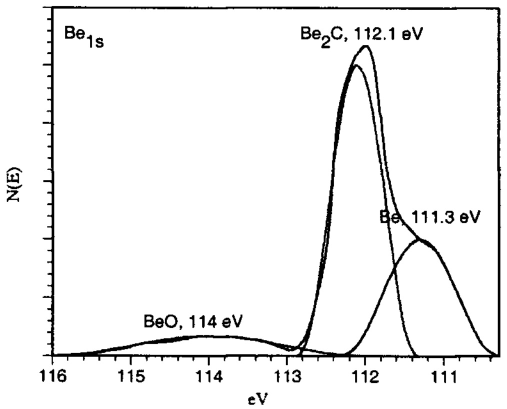

Figure 3. Typical Deconvolution of XPS Spectrum (Group 1)

The deconvolution of the peaks in the XPS results in resolution of the elemental peaks to provide the chemical states. Figure 3 demonstrates a typical peak separation for a sample deposited at a flow rate ratio of methane to argon of 0.1.XPS analysis of the films made under this condition gives the following results. The Be_{1s} peak is separated into three symmetric peaks corresponding to Be, at 111.3 eV, Be_2C at 112.1 eV, and BeO 114 eV. Due to charging, all the peaks are shifted 0.1-0.3 eV lower than the values given in the literature. The C_{1s} peak at 281.8 is assigned to Be_2C, and the O_{1s} peak is assigned to BeO. For the same reason they are shifted in the same direction from those in the literature as are the Be_{1s} peaks.

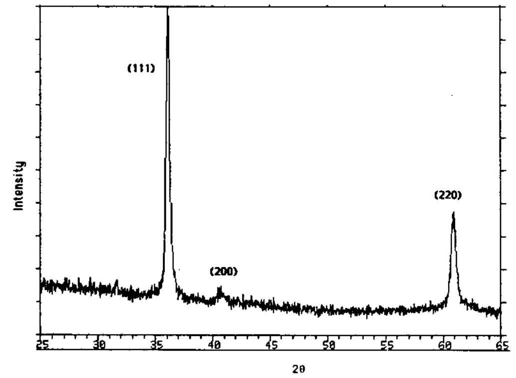

Figure 4. X-ray Diffraction
Pattern of Thicker film (Group 1)

C. X-Ray and Neutron Diffraction Study

AES and XPS analyses showed that the films deposited by reactive magnetron sputtering contained carbon, beryllium, and oxygen, and the major compound present in all films was beryllium carbide, Be_2C. The AES data indicated oxygen to be less than 3 atomic percent. Accordingly, X-ray diffraction spectra were taken for the films to confirm the conclusions drawn from the AES, XPS studies. All patterns show two peaks at 2q = 36.2° and 61.0° and some of them have a peak at 40.8° corresponding to the (111), (200), and (220) planes of fcc beryllium carbide. Figure 4 is a typical film X-ray diffraction pattern. There is no evidence for the presence of free Be as well as for its oxide. It is interesting to note further that the ratio of the peak heights of (111) to (220) is the reverse of that given in the powder diffraction files for Be_2C. This indicates that these films possess preferred orientation that places the most densely populated (111) planes parallel to the substrate surface.

Since XPS showed free Be to be present and not oxidized while films were exposed to air, it was suggested that Be might occupy a part of the four octahedral interstitial sites in the fcc Be_2C structure. Modeling studies of the Be_2C structure using DIDO 95 software [33] indicated that the volume of an octahedral site would not accommodate a Be atom. However, a neutron diffraction pattern was obtained of several powdered high Be-containing films. Figure 5 is the resulting neutron diffraction pattern from the high Be-containing films. Peaks corresponding to the (111), (200), (220), (311), (222), (400), (331) and (420) planes of Be_2C are evidenced. Matches of refined powder neutron diffraction patterns from Figure 5 were obtained by subtracting the blank glass holder pattern and the calculated results based on a stoichiometric Be_2C crystal, and on one with 20% of the octahedral holes occupied by Be, using a modified version of the Rietveld method [24]. There is a considerable mismatch between calculated and experimental intensities in the case of octahedral occupation which confirms the conclusion reached from the modeling study. Furthermore no peak corresponding to that of hcp Be is evidenced and one can only conclude that, the excess Be is present in an amorphous form and protected in some fashion by the Be_2C from reaction with air.

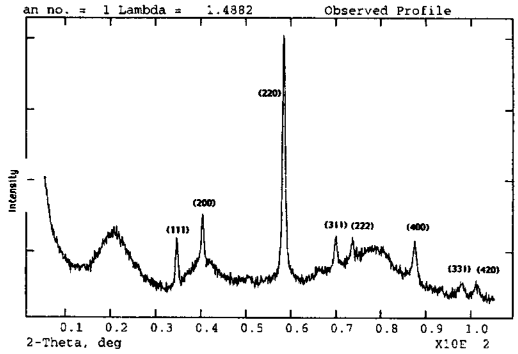

Figure 5. Neutron Diffraction Pattern
of the Powder Composite (Group 1)

D. DTA and TGA Measurements

Figure 6 is the experiment result of DTA on a 40 mg powder sample from high Be-containing films under a purge of high purity argon protection. At temperatures lower than 750 °C, the curve maintains a positive slope. A maximum occurs at about 750 °C which is unexpected since Be_2C is very stable up to greater than 2000 °C. However this film sample is the Be-rich composite which contains amorphous free Be. As mentioned previously, Be has a strong tendency to sublime [18]. Thus a possible explanation would be that the change to a negative slope results from sublimation of the beryllium dispersed in the Be_2C matrix.

Powder TGA results as seen in Figure 7 under argon protection show no evidence of sample weight change below about 790 °C. When the temperature reaches about 790 °C, the sample begins to lose weight slightly, which is consistent with the explanation of Be sublimation occurring above 750 °C on the DTA plot (Figure 6). Under dry air conditions, when the temperature reaches about 80 °C, the sample begins to show a positive weight change up to ~410 °C, thereafter the slope decreases somewhat, i.e., the rate of weight increase slows down. The positive weight change of the sample is attributed to the oxidation of the material to BeO. Surface oxidation produces an oxide barrier which is known to slow down the diffusion of Be through the formed BeO layer to the surface in the rate determining step [29] which probably explains the decrease in the rate of weight change. Under wet air conditions, the weight increase of the sample is faster than that for dry air, and at about 930 °C, the rate of weight change begins to decrease slightly.

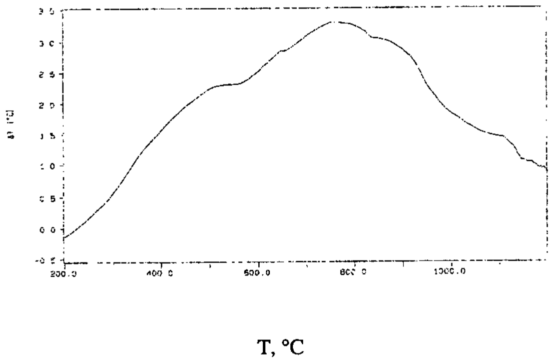

Figure 6. Powder DTA measurement of the sample (Group 1)

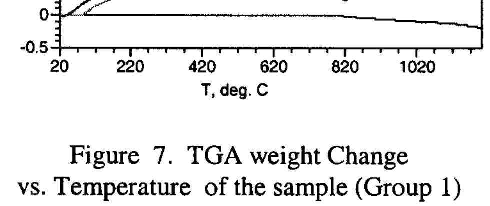

Figure 7. TGA weight Change vs. Temperature of the sample (Group 1)

The beryllium carbide films and/or samples are apparently very resistant to oxidation in dry air at ambient temperature. The films' exposed to laboratory environments for 30 days show no weight change and little or no change in appearance. This has been observed previously [25, 34]. The films are even fairly resistant to a wet environment at low temperatures, but begin to oxidize appreciably as the temperature exceeds 50 °C, which is consistent with the fact that bulk Be_2C undergoes hydrolysis to form $Be(OH)_2$ and CH_4 [34].

IV. CONCLUSIONS

Magnetron sputtering of Be into a methane/argon plasma at an audio frequency was used to make beryllium carbide films for ICF (inertial confinement fusion) target capsule applications. Based on the AES analysis, films containing 50 to 75 atomic percent of Be and the balance elemental carbon and oxygen (< 2 at % oxygen) were obtained by adjusting the methane to argon flow rate ratio in the deposition process. The beryllium atomic percentage increases linearly and the carbon atomic percentage decreases linearly as the methane to argon flow rate ratio decreases. AES, XPS, and XRD analyses provide strong evidence that beryllium carbide, Be_2C is the major phase in the films, and that "free" beryllium exists in the Be-rich films, and graphite-like carbon in the C-rich films. XRD patterns of these films and a ND pattern of the powder sample prepared from the films confirm the AES findings of less than 3.00 atomic % oxygen and that a beryllium carbide composite with amorphous Be distributed in the Be_2C matrix is the resultant phase. Additionally the absence of certain peaks corresponding to planes of fcc Be_2C and the fact that the intensity of the (111) plane is greater than for bulk powdered Be_2C suggest a preference for orientation that places the most densely populated planes parallel to the substrate surfaces. This is commonly seen in low temperature sputter deposition of metals [35]. Neutron diffraction data taken on a Be-rich powder sample were subjected to Rietveld refinement and the model results confirm that there is no interstitial Be. Furthermore, there is no evidence of free Be in the ND spectra. It is concluded that the Be in the Be-rich films which is not evidenced in the X-ray and neutron diffraction patterns must be amorphous (extremely small crystallites) and that in some manner the Be_2C substantially decreases the oxidation of Be when the samples are exposed to air.

DTA and TGA analyses of the Be-rich samples under argon suggest the possibility of Be sublimation at a temperature higher than 750 °C, which further supports the presence of free Be in the Be-rich samples. TGA experiments in dry air and wet air establish the greater resistance of Be_2C to oxidation in dry air as opposed to its behavior in moist air. The films' exposure experiment confirms that the films are air stable at ambient temperature.

The microstructure, surface morphology, and performance of the resulting films will be described in a subsequent paper.

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