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DOWNWARD VACUUM VAPOR DEPOSITION
OF RARE EARTHS
ONTO HOLLOW MICROSPHERES

W. J. Coleman

February 1970

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ERRATA

On page 1, add the following as footnote references.

L. Holland. Vacuum Deposition of Thin Films, Chapman & Hall, 1963.

G. Hass and R. E. Thun. Physics of Thin Film, Volumes 1, 2, and 3, Academic Press.

On page 8, the last sentence should read:

...on the order 5×10^{-9} Torr to 4×10^{-9} Torr.

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ABSTRACT

In the development of a method to contain polonium for isotopic heat source application, the hollow microsphere concept was originated. In order to make this concept work, many new fabrication processes were required. One of these processes was the deposition of a 6 μ uniform rare earth coating onto 0.006 in. diameter spheres.

This paper deals with the procedures developed to deposit uniform rare earth coatings using vacuum vapor deposition techniques. This involves developing techniques to evaporate and monitor thick rare earth coatings, obtain proper sphere movement for uniform coatings, prevent oxidation of the rare earth film and determine routine coating procedures. This paper will discuss these problems and their solutions.

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INTRODUCTION

In the development of a method to contain polonium for isotopic heat source application, the hollow microsphere concept was originated. Many new fabrication processes were required in developing this concept into a working model. One of these processes required the deposition of a 6- μ uniform spherical rare earth coating onto 0.006-in. diameter spheres. The ^{210}Po reacts with rare earth under specific conditions to form a stable compound. The fueled microspheres are then coated with a strength cladding to form micro heat sources. These micro heat sources can be loaded into a capsule and densified to give power densities of up to 30 W/cm³.

This paper deals with the procedures developed to deposit uniform rare earth coatings using vacuum vapor deposition techniques. This process involves developing techniques to evaporate and monitor thick rare earth coating, obtain proper sphere movement for uniform coatings, prevent oxidation of the rare earth film, and determine routine coating procedures. This report will discuss these problems and their solutions.

EVAPORATION METHODS

The polonium encapsulation program requires large numbers of small, 0.006-in. diameter microspheres to be coated with rare earth coatings to a spherical thickness ranging from 4 to 1 μ . Evaluation of several approaches resulted in vacuum vapor deposition as the recommended technique.* The size of

* *François P. Gaydou. "A High Current Vacuum Discharge for Triode-Sputtering in the 10^{-4} Torr Range," Vacuum, vol. 27, no. 6, p. 325.*

the substrates dictated that the microspheres be laid on a flat surface and that downward deposition methods be used. It was also desirable but not mandatory that uniform coatings be achieved. It was important that the amount of material deposited onto each microsphere be monitored and controlled because too much material could cause the micro heat source to fail from over-temperature and too little material could result in reduced power density.

Normal thin film thickness for vacuum vapor deposition is below $2\ \mu$. Thicker deposits normally experience peeling problems. Film thicknesses of this magnitude, requiring evaporation of considerable amounts of material, presents evaporation source problems.

The initial process used resistance heated refractive metal boats, as seen in Figure 1, to evaporate gadolinium. Several problems involving excessive heat, poor rates, insufficient material capacity, and short boat life were experienced.

DOWNWARD
EVAPORATION SOURCE

FIGURE 1. Downward Resistant Heated Evaporation Boat

The boat required between 2 to 3 kW of power to obtain deposition rates of 1000 Å/min. This amount of power caused overheating of the vacuum chamber. Due to this heat problem, duty cycle was limited to approximately 20%. Use of resistance evaporation methods while conceivable, were not deemed desirable.

The most attractive method, electron beam evaporation, was clouded with the downward evaporation requirements. A downward electron beam evaporation source, which just became commercially available, was purchased and evaluated for this application. This unit used a 1/4-in. diameter rod which was evaporated by the electron beam. The rod is fed through a water-cooled copper block and the electron beam melts the exposed end. The molten material forms a drop held by surface tension. When the weight of the drop overcomes the surface tension force, the molten drop falls. The evaporation rate thus is limited because high evaporation rates require high power levels, most of which is removed as heat through the water-cooled copper block. The higher power level, coupled with the heat transfer properties of the evaporating material, results in the forming of a large molten drop which falls from the rod into the substrate area. This problem required the development of operating techniques to prevent dropping molten material but to allow near maximum evaporation rates. With the exception of rate limitation, the downward electron beam evaporation source met the requirements of a continuous duty cycle and of sufficient material capacity for thick coating without recharging the evaporation source.

THICKNESS MONITORING

The deposited material was monitored by means of a quartz crystal thickness monitor." Figure 2 shows the basic

* R. P. Riegert. "Getting the Most from a Quartz Crystal Monitor," Research-Development, vol. 19, no. 6, p. 46, 1968.

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FIGURE 2 Quartz Crystal Monitoring System

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block diagram for a quartz crystal monitor. The sensor head located in the vacuum vapor stream contains a quartz crystal driven by an oscillator at its fundamental frequency. Normally this frequency is 5 MHz on commercial monitoring units. Now, let's take a close look at the quartz crystal. Normally the crystal, when properly excited, oscillates in a thickness shear mode with a 5 MHz fundamental frequency. The fundamental frequency of the crystal is controlled by crystal thickness corresponding to a half wavelength of the fundamental frequency. By changing the crystal thickness, the fundamental oscillator frequency will change proportionally to a change in the mass, Δm , of the crystal. By depositing a thin film, provided the additional Δm is sufficiently small, the same effect is observed. Specifically then,

$$\Delta f \propto \Delta m. \quad (1)$$

For 1% linearity, Δm should not exceed 0.5% of the fundamental frequency or for a 5 MHz crystal, 25,000 Hz. Now this limit is not to be confused with the accuracy available from the quartz crystal monitor, but is a 1% deviation from linearity of frequencies expected in the crystals for a 0.05% Δf change in the basic crystal frequency. The item of most interest is the relationship between Δf and thickness. The mass change, Δm , can be represented by $\rho t A$, where ρ is the density, t the thickness, and A the area of the deposited thin film. Then, Δf becomes proportional to the product ρ and t . Thus, we have a relationship for the frequency shift directly proportional to the thickness. From the relationship $\Delta f \propto \rho t A$, one expects and observes twice the shift in frequency for the same thickness of a new material which has twice the density of the original material used to calibrate the monitor.

The signal received from the quartz crystal oscillator is sent into a mixing circuit, which also receives a signal from a variable frequency oscillator. The variable frequency oscillator is adjusted to match the frequency of the quartz crystal mounted on the sensor head. The monitor then records the beat frequency between the sensor head and the variable frequency oscillator through the accompanying electronic circuitry. This beat frequency is then put into some type of an output meter. By differentiating this signal, a rate can be established. The rate signal can then be used to control the evaporation source using an SCR controlled power supply. This unit was used to automatically control the electron beam power supply.

Each crystal has a frequency range of 30 kHz to 50 kHz, depending on the crystal and optical dense mask in use. A 40% optical dense mask was normally used to increase from 1.5 to 2.0 μ the monitoring range per crystal before the variable frequency oscillator range was exceeded, or before crystal failure was experienced. This thickness relates to the flat surface thickness and must be divided by a factor of 4 to obtain the spherical thickness. Thus, to obtain a spherical thickness of 5 μ requires a minimum of 10 crystals. This thickness was achieved without opening the system by installing an automatic crystal changer. This unit has the capacity to hold 25 crystals, which can be remotely changed by the operator. Figure 3 shows the internal structure, including the monitor head.

The accuracy of the quartz crystal monitor is normally 2%. This accuracy degenerates when maximum range is approached. The crystals were used in this unit until they failed, then a new crystal was injected. Operating in this manner, the accuracy was degenerated to $\pm 10\%$. The initial reaction results in an attempt to terminate operation before degeneration of the monitor accuracy begins. This area is very gray in that

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FIGURE 3. Vacuum Chamber Interior

crystals fail with deposit thickness of from 0.5 to 2.0 μ (30 to 50 kHz shift of the crystal's fundamental frequency). The present recommendation is to try a newer, ion sensing rate monitoring system which operates independently of thickness. Use of an integrator to monitor the total thickness. presently appears better adapted for this application and should improve the overall accuracy. This unit, recently placed on the commercial market, senses a vapor stream by ionizing part of the vapor stream and detecting the ionized portion. The unit can monitor very thick deposits for hours before any service is necessary.

OXIDATION PREVENTION OF RARE EARTH DURING VVD

The oxide form of the rare earths, by failing to react with polonium, presents handling problems due to the reactivity of rare earths to form an oxide. This reaction readily takes place at room temperature in air. To prevent the formation of an oxide, special techniques were developed to protect the rare earth from oxidation during the evaporation process and removal from the vacuum chamber.

In the evaporation process, certain materials act as getters. That rare earth is a very good oxygen getter was verified by monitoring the partial pressure of oxygen in the vacuum chamber and observing a decrease in this partial pressure on the order of 10^{-7} Torr to 5×10^{-8} Torr during the evaporation. To reduce and minimize this effect, a hot zirconium gettering apparatus, consisting of zirconium ion pump filaments, was installed. This apparatus reduced the oxygen partial pressure by a factor of 10 to 15. More specifically, the oxygen pressure dropped from 10^{-7} Torr to 10^{-9} Torr range. After this apparatus was installed and in operation a recheck of the rare earth gettering disclosed the change to be on the order of 5×10^{-5} Torr to 4×10^{-9} Torr.

In removing the rare earth coated microspheres from the vacuum chamber, a plastic glove bag was fabricated and installed to minimize the oxidation problem. The plastic glove bag was filled with argon and flushed several times to obtain an inert atmosphere. A small positive pressure was maintained to prevent in-leakage of air. The vacuum chamber was backfilled with argon and the zirconium gettering unit left on while the microspheres were loaded into a container for removal. The microsphere container was sealed and the microspheres were then ready to be transferred to the fueling system. Figure 4 shows the system with the plastic glove bag in place.

MICROSPHERE MOVEMENT

Deposition of a uniform rare earth coating 4 to 8 microns in spherical thickness was required. Either a prescribed rotating motion or a random motion capable of producing a uniform deposit must be used. The initial work used a vibrating tool scribe. The unit, used outside the system and coupled to a mechanical feedthrough, produced fair results indicating feasibility of the method. The next unit used an electro-mechanical vibrator in conjunction with a modified inductor coil and a spring loaded rod. The frequency of the electrical drive unit could be varied from 2 to 20 cycles, and the unit also allowed limited amplitude variation. This unit, capable of running on only a 50% duty cycle, was very inefficient. The second unit was built using a 60-cycle, 100 W solenoid. This unit was modified by spring loading to provide the desired action. A new power supply producing frequency variations from 3 to 30 Hz was built. Addition of an automatic frequency ramp changing the frequency by ± 5 Hz from a set frequency proved to be a very useful feature.

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FIGURE 4. Modified sphere Container

From a monitoring standpoint, it is important to move the microspheres on a monolayer basis. The initial container consisted of an aluminum dish 7 in. in diameter connected to an electro-magnet vibrating unit. Using this arrangement, uniform coatings were achieved but monolayer conditions were not maintained. The variation was so bad that monitored thickness, compared to thickness measured from metallograph photos, varied from 25 to 50%. The correlation between monitored and measured thicknesses results from bunching, and variations in these thicknesses are the result of variations in bunching from run to run. The new vibration power supply with the automated frequency ramp helped to reduce this error, but it still varied from 35 to 50% of the monitored thickness. Our interpretation is that the spheres were covered up at least 35 to 50% of the time and, with half of the container dish void of spheres, the time necessary to deposit the film and the amount of material required thus was doubled. These reasons made it important to devise a method to obtain closer correlation between the monitored and measured thickness.

By observing the motion of the microspheres, it appeared that the desired action could be achieved by reducing the container size. With $3/8$ in. diameter containers, the bunching problem virtually disappeared and 100% correlation was achieved between monitored and measured thickness. The final container configuration is shown in Figure 5.

ROUTINE COATING PROCEDURES

The microspheres were coated with several rare earths and some refractive materials. The basic deposition procedures, the same for all materials except lanthanum, will be discussed later. The thickness monitoring unit was used to control rate. This unit would increase the input power level to maintain the set rate. The power input level and rate varied

FIGURE 5. Vacuum System with Plastic Glove Enclosure

depending on the rod position in the copper cooling block. The rod feed unit was not automated but was a manual mechanical feed as seen in Figure 6. Figure 7 shows two views of this unit in more detail. Table 1 gives the various rare earth deposition parameters. As can be seen from this table, the deposition rate varies from 350 to 100 $\text{\AA}/\text{sec}$. It is also interesting to note that the low rate is associated with the highest input power level.

It thus appears that several factors affect the deposition rate. Some, such as the rod location in the copper cooled block and input power level, are controllable. Others are dependent upon such parameters as melting temperature, boiling temperature, and vapor pressure. Table 2 shows these parameters. All except lanthanum, of the rare earths listed in Table 2, were successfully deposited. It was very difficult to prevent the molten lanthanum from dropping from the rod. The formation of

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FIGURE 6

Electron Beam Gun and Rod Feed Mechanism in
Vacuum Chamber

FIGURE 7 Electron Beam Gun and Rod Feed Assembly

TABLE 1. Rare Earth Deposition Parameters

Element	Deposition Power, kW	Average Deposition Rate, A/sec	Precautions
A. Gadolinium	1.25	100	1
B. Dysprosium	0.5	200	1, spheres "Stick" together
C. Erbium	0.5	150	1
D. Lutetium	0.5	350	1

General Precautions all materials:

1. Material drops from rod - operator technique develops with experience to minimize this problem.

TABLE 2. Rare Earth Melting and Boiling Points

	Melt Point, °K	Boiling Point, °K
Dysprosium	1680	2710
Erbium	1770	2850
Gadolinium	1585	3000
.Lutetium	1925	3300
Lanthanum	1193	3610

droplets was not difficult, but the much higher evaporation temperatures required caused larger droplets to form. The droplets would fall with the start of evaporation. Very slow evaporation rates were possible, but even then droplets would occasionally fall. Evaporation of lanthanum in this manner may be possible, but additional development will be necessary.

While it is simple to list the deposition parameters, the complete listing and description of operator techniques necessary to deposit materials near their maximum rate is very difficult if not impossible. The rate, semicontrolled by the monitor, is also dependent upon the position of the rod with respect to the cooling block. The dropping of molten material is dependent on several parameters, most of which are operator controlled.

CONCLUSIONS

In conclusion, the problem of evaporating uniform coatings of rare earth onto 0.006-in. diameter spheres was successfully accomplished. Parts of the procedure were automated. The automation included certain functions performed by the operator. The problems of monitoring and uniformity were solved. The thickness monitoring accuracy, however, was not satisfactory. Evaluation of an ion type rate monitor to improve the accuracy is recommended. Oxidation problems were encountered and solved by means of a gettering apparatus and an inert gas cover maintained by a plastic glove tent. With these precautions, the required coatings were deposited.

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