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DEVELOPMENT AND FABRICATION
OF REFRACTORY METAL MICROBALLOONS

June 1969

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DEVELOPMENT AND FABRICATION
OF REFRACTORY METAL MICROBALLOONS

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DEVELOPMENT AND FABRICATION OF REFRACTORY
METALS MICROBALLOONS

K. R. Sump

ABSTRACT

The deposition of refractory metals upon expendable microspherical substrate to form thin-walled refractory metal microballoons was successfully demonstrated. Both tungsten and rhenium were deposited upon these spherical cores by the process of chemical vapor deposition. The substrate was removed by heating in a vacuum environment to leave the refractory metal microballoons.

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DEVELOPMENT AND FABRICATION OF REFRACTORY METAL MICROBALLOONS

K. R. Sump

SUMMARY

A technique was developed for fabricating thin-walled hollow tungsten and rhenium microballoons. The microballoons were developed for use as micro-sized gas plenums for individual microspheres containing helium-generating alpha isotopes.

A refractory metal was deposited on an expendable spherical core. This clad microsphere was then heated in vacuum. A crack formed in the cladding and the expendable core was removed by vaporization (Figure 1). A few hundred grams of refractory metal microballoons were fabricated by this process.

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FIGURE 1. Microballoon Fabrication

INTRODUCTION

A void volume was required for helium generated in an alpha isotope-fueled heat source. It was desired that the generated helium be retained on a particle basis and that a minimum of excess material and a maximum amount of void volume be used.

A thin-walled hollow microballoon of refractory metal on which the isotope fuel and containment claddings could be deposited was designed as the basic building block.

EXPERIMENTAL PROCEDURE

MICROBALLOON DESIGN

Two sizes of refractory metal microballoons, a 1X design and a 5X design (terminology based on relative internal void volume), were fabricated. The 1X design used -100 + 120 mesh (125 to 149 μ) magnesium microspheres. The spheres were clad with a 5 μ thickness of tungsten. The 5X design used -60 + 70 mesh (210 to 250 μ) magnesium and 7 μ tungsten cladding.

The wall thickness could be less than 2 μ . However, microballoons of this wall thickness were quite fragile and some loss was experienced during subsequent processing. Microballoons fabricated with wall thicknesses >15 μ were found to render core removal more difficult.

Walls of greater thickness, where desirable, can be built up by chemical vapor deposition (CVD) after removal of the core from the thin-walled microballoons.

EXPENDABLE CORE

The refractory metal is deposited by CVD onto an expendable spherical core possessing the following requisite properties: (1) coefficient of expansion much greater than that of the refractory metal, (2) melting point greater than the refractory metal deposition temperature, (3) a relatively low boiling point, and (4) acceptable compatibility with the refractory metal. Magnesium has a coefficient of expansion of $27.1 \times 10^{-6}/^{\circ}\text{C}$, a melting point of 651 $^{\circ}\text{C}$, and a boiling point of 1107 $^{\circ}\text{C}$. Tungsten has a coefficient of expansion of $4.6 \times 10^{-6}/^{\circ}\text{C}$ and is deposited by CVD at 500 to 550 $^{\circ}\text{C}$. Therefore, magnesium microspheres were used as the spherical substrate for tungsten and also for rhenium in the fabrication of the microballoons.

The magnesium microspheres should be dense, have a good spherical shape, and be free of surface defects and agglomerations. The microspheres were obtained commercially. Those fabricated by a wheel run atomization process were found to be of a higher quality than the jet atomized material. The best material obtained was wheel run atomized magnesium containing 0.15% zinc, 0.1% calcium, and 0.5% zirconium as additives. A cross section of random sized magnesium microspheres is shown in Figure 2.

Sizing of the microspheres was done by screening. The sized microspheres are shown in Figure 3.

Neg 4B632A

32X

Neg 4B632B

80X

FIGURE 2. Microstructure of Random Sized Magnesium Microspheres

Neg 4C138

32X

FIGURE 3. *Sized Magnesium Microspheres*

CHEMICAL VAPOR DEPOSITION

The magnesium microspheres were clad with tungsten or rhenium by CVD. The CVD, fluidized bed-coating process consisted of suspending the magnesium microspheres in a heated vertical reactor tube by an upward flow of a mixture of hydrogen and coating gas (Figure 4). Considerable agitation of the particles occurred which prevented agglomeration and permitted a uniform coating of the particles. The basic coating reaction for tungsten was $\text{WF}_6 + \text{H}_2 \rightarrow \text{W} + \text{HF} + \text{excess H}_2$. The coating gas was introduced through an orifice in a conical-shaped injector at the bottom of the tube. An expansion chamber at the top of the reactor served to reduce the chance of particle

FIGURE 4. Chemical Vapor Deposition Process
(Fluidized Bed - Halide Reduction)

Neg 0672173-9

carryover (Figure 5). Argon was passed through the preheated reactor while the spheres were loaded. The system was then closed and the argon was gradually replaced by the hydrogen while maintaining the fluidized bed.

Neg 0672303-2

FIGURE 5. CVD Reaction Chamber, Nozzle, and Preheat Coil

A large $H_2:WF_6$ gas ratio was used to minimize the fluorine content (as low as 100 ppm) in the coating. The WF_6 flow rate was measured with a mass flowmeter and the hydrogen was controlled with a standard gas flowmeter. A pressure gage was placed close to the reactor tube inlet nozzle to detect plugging in the system. After flowing through the reactor, the coating gas was passed through a scrubber to chemically remove the HF and any free fluorine. The excess hydrogen was burned.

The CVD parameters used for depositing a 5 μ coating on 1X design magnesium microspheres were as follows:

Substrate weight (reference only)	5 g
Coating weight	13 g
Deposition time	30 min
Substrate temperature	550 °C
WF_6 temperature	50 °C
WF_6 flowrate	50 scc/min
H_2 flowrate	4 liter/min

The wall thickness can be controlled to + 1/2 μ by varying the run time and holding the other parameters constant. The parameters for the 7 μ wall, 5X design were quite similar. Metallography of 1X and 5X design tungsten microballoons is shown in Figures 6, 7, and 8.

Rhenium CVD parameters were:

Substrate temperature	230 °C
ReF_6 temperature	70 °C
ReF_6 flowrate	25 scc/min
H_2 flowrate	4 liter/min
Re deposition rate	4-8 μ /hr

Metallography of rhenium microballoons is shown in Figures 9 and 10. Because of the relatively thick wall ($\sim 20 \mu$), the crack in the shell was wide and extended over 180° around the microballoon, as evidenced in the referenced figures. The widest

Neg 4C139 1X Design 32X Neg 4C140 5X Design 32X

FIGURE 6. *Hollow Tungsten Microballoons*

Neg 4C183A Etched 250X

Etched 400X

FIGURE 7. *Microstructure of 1X Design Tungsten Microballoons*

Neg 4C182B Etched 80X Neg 4C182A Etched 250X

FIGURE 8. *Microstructure of 5X Design Tungsten Microballoons*

Neg 4C137 32X

FIGURE 9. *Hollow Rhenium Microballoons*

Neg 4C184B

80X

Neg 4C184A

Etched

250X

FIGURE 10. *Microstructures of Rhenium Microballoons*

portion of the crack was approximately equal to the shell thickness of the microballoons. The 20 μ rhenium cladding was deposited in 5 hr.

EXPENDABLE CORE REMOVAL

The expendable core was removed by heating the microsphere in vacuum. The tungsten shell was cracked by excessive swelling of the magnesium core due to the relative thermal expansion properties. The magnesium was then vaporized through this crack.

The clad microspheres were loaded into a molybdenum container (Figure 11) approximately 1 1/2 in. in diameter and

Neg 0691784-1

FIGURE 11. *Molybdenum Core Removal Container*

4 in. long. The spheres filled only a small volume at the bottom of the container. A lid and a -120 mesh stainless steel screen were placed on top of the container. The screen prevented the spheres from jumping out of the container during heating.

This container was placed inside an induction heater coil. Only the bottom half of the container was heated. The vaporized magnesium was drawn toward, and deposited upon, a water-cooled plate located about 1/4 in. above the container lid and screen. This entire assembly was enclosed in an alumina and vycor tube provided with vacuum tight fittings on each end (Figure 12). Vacuum was maintained by a diffusion pump. A good vacuum (2×10^{-4} torr) and the condensation plate prevented the induction coils from arcing due to released magnesium vapor.

The core removal parameters for 1X design microballoon were as follows:

Weight of magnesium to be removed (reference only)	10 g
Tungsten weight	26 g
Heating rate	0-1200 °C in 1 hr
Time at 1200 °C	3 hr
Cooling rate	Furnace cool (2 hr)
Vacuum	2×10^{-4} torr

The removal parameters were similar for 5X design tungsten microballoons and also for rhenium microballoons. At the present stage of development, a small percentage of microspheres retain some magnesium.

Further development of the core removal process, including perhaps a chemical dissolutions step, would be required to assure complete core removal. Another alternative is the separation of hollow microballoons from those containing magnesium by some density dependent process.

FIGURE 12. *Induction Heating and Vacuum System Used for
Core Removal*

CONCLUSIONS

The development of a process for fabricating refractory microballoons was quite successful. The tendency of some spheres to retain magnesium is presently the most difficult problem. Wall thickness and diameter were controlled and uniform.

This technology could be used in fabricating microballoons from other refractory metals such as molybdenum and tantalum. Due to the deposition temperatures, copper spheres would probably be required and the removal process would incorporate chemical dissolution.

The tungsten microballoons can be fabricated for ~\$14/gram based on a yearly production of ~4 kg. However, this estimate does not include any additional scale-up of the process (13 g coating run, 26 g core removal) which could reduce unit cost.

The microballoons provide a lightweight basic building block of refractory metal adapted to several individual applications, as well as for use in a bonded form (refractory metal sponge).

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