AN ELECTROLYTIC PROCESS FOR ULTRA-FINE BERYLLIUM

by

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ABSTRACT

Studies were made on the electrolysis of a molten $BeCl_2$-NaCl bath using a mercury cathode and beryllium anode. A quasi amalgam was obtained. The beryllium was consolidated by direct hot pressing of the amalgam at temperatures in the range of 800°C and using pressures of 5,000, 10,000 and 20,000 psi. The work performed in this program confirms the ability to produce ultra-fine beryllium particles by electrolysis.

1. INTRODUCTION

The work described herein is a continuation of the work performed on NASA contracts - NASW 1099 and 1542 (reference 1 and 2). The overall objectives of the program was (1) to study the production of ultra-fine beryllium powder by electrolyzing beryllium into a mercury cathode and (2) to consolidate the quasi amalgam by hot pressing.

The fine powder studied in this program was produced by electrolysis. A beryllium anode was used for this work, the electrolysis bath consisted of a fused beryllium chloride-sodium chloride mixture and the cathode was mercury. In the earlier work, a graphite anode was used and this resulted in extreme carbon contamination in the product. With a beryllium anode, it was expected that the cell would function an an electrorefining cell and consequently an improvement in the purity of the beryllium could be expected.

The hot pressing experiments carried out in the earlier work (reference 2) was performed with low pressure and it was found that temperatures above 950°C were required or extended pressing time at 950°C were required for full densification. Hot pressing for this contract (NASW 1844) was performed using dies which could withstand high pressure so that lower hot pressing temperatures could be used.

2. ELECTROLYSIS

The electrolysis was carried out in a stainless steel cell with an internal diameter of 15.75 inches and a height of 22 inches. The mercury cathode was about four inches deep and the fused salt mixture was approximately 12 inches deep and floated on the mercury.

To minimize contact of the salt with the metal cell, a pyrex glass liner was used. This cylinder fit inside the cell with its lower edge immersed into the mercury cathode. The salt bath mixture was maintained at the operating temperature of 300°C with external heater strips fastened to the outside of the cell. Figure 1 is a schematic layout of the cell and auxiliary equipment.

The electrolysis was carried out in a dry nitrogen atmosphere in order to minimize oxidation. The flow of gas also served to aid in the removal of chlorine which evolved during electrolysis. The deposition of the fine beryllium in the mercury cathode resulted in the formation of a quasi amalgam. This quasi amalgam was removed periodically, cooled, and filtered. The filtered mercury collected in the reservoir was pumped from the reservoir to the holding tank and then fed to the cell as required to replenish the cathode.

The beryllium content of the quasi amalgam was about 0.25% and after filtering it was about 2.0%. The concentrated amalgam was transferred to plastic bottles and sealed in a nitrogen atmosphere until required for the hot pressing studies.

3. HOT PRESSING

The plastic bottles of quasi amalgam were stored in a glove box with a nitrogen atmosphere. This material was further concentrated using a cold pressing operation. Within the glove box, about 260 cc of quasi amalgam was loaded into a steel die which was one inch in diameter and 12 inches long. A load of three tons was applied to the liquid and a compact was obtained which was one inch diameter and

about 3 inches long. The mercury was squeezed out of the die through a porous punch and was collected in a container within the glove box.

The slug that was obtained was ejected from the die and transferred to the hot pressing die. After this transfer, the plugs were placed into the hot press die and this assembly was then removed from the glove box and placed within the vacuum hot press vessel. During the evacuation and heat-up cycle, the remaining mercury was removed from the compact. Because of the mercury vapor that was evolved during hot pressing, the pressure in the vacuum chamber was about 70×10^{-3} millimeters.

The die material for the initial hot pressing was HT-6, a sintered titanium carbide (45 volume %) in a matrix of nickel-base age hardening alloy. The die blank and punches were received in the soft condition, finish machined and then heat treated to obtain the hardness desired. A small longitudinal slot was ground into both punches to facilitate evacuation of the mercury evolved from the quasi-amalgam. The aim in each hot pressing was to produce a 1" diameter x 1" high compact. Upon completion of the hot pressing cycle, the die assembly was cooled to about 200°C and then removed from the vacuum hot press vessel. Pressure was then applied to the punches to remove the punches and eject to compact. During the removal of the compact from the sixth hot press cycle, the die body failed. Examination of the failed die revealed pitting and wear around the specimen location which suggested that there had been a reaction between the beryllium and the HT-6 die material. The reaction was apparently progressive with each cycle and with the sixth cycle reaction resulted in extreme bonding of the

compact to the die wall. The high pressure required to break the bond in order to eject the compact caused the fracture.

An Inconel die used in an earlier study (reference 3) was modified for the additional hot pressing studies. The inner diameter was rebored to a tapered configuration varying from 1.25 inch inner diameter to 2.0 inch diameter. Split and tapered graphite liners were machined to fit the tapered inner diameter of the Inconel die body. A one-inch inner bore was retained with the graphite inserts. With hot pressing pressures greater than 10,000 psi, the graphite fractured and had to be replaced for each pressing.

Below 10,000 psi, the die liner survived 3 or 4 cycles.

4. EVALUATION

Visual examination of the amalgam indicated appreciable quantities of black powder floating on the surface. This black powder had been observed in earlier work and was attributed to oxidation of the amalgam. On exposure of the amalgam to air in the earlier work, it was noted that the contained beryllium would float to the surface of the mercury, oxidize and appear as a fine black powder (reference 3). Prior to use of the amalgam for the hot pressing studies, this black, oxidized beryllium was removed. Analysis of the beryllium pellets made by hot pressing showed high oxide content and in addition serious iron and carbon contamination. These analytical results suggest that the atmosphere in the cell was not adequate to prevent oxidation of the extremely fine powder. Examination of the powder confirmed the results reported in reference 3 that the particle size was in the

range of 0.2 μ.

The hot pressing studies were carried out at 750, 800 and 900°C. Pressures used were 5,000, 10,000 and 20,000 pounds per square inch. Sintering times of 30, 60 and 120 minutes were used.

Density of hot pressed compacts were measured in two ways. All samples were checked in the as-pressed condition by a technique involving immersion in water. The samples were then machined all over to remove surface contamination to expose sound metal. Pieces in this condition were then checked for density by determining the sample weight in air and the volume using measurements of the piece, and from this data the density was calculated. The densities obtained for each sample are listed in Tables I, II, and III.

In reviewing the density measurements it is apparent that in some cases they are higher than theoretical for beryllium. This can be accounted for by the higher than normal oxide content in the material. After machining, the samples were sectioned to obtain material for chemical analysis. Analyses were carried out for the major impurities only, these being oxide resulting from inadequate protective atmosphere during electrolysis and iron and carbon resulting from contamination by erosion or corrosion of the materials of construction of the cell and auxiliary components. The results of these analyses are shown in Tables I, II, and III.

Taking into account the apparent increase in density resulting from the presence of the impurities shown by chemical analysis, it is still

possible to observe trends in densification as a result of the hot pressing conditions used. At 750°C, the highest density was achieved in 60 minutes only when the pressure was increased to 20,000 psi (Table I). For samples pressed at 800°C densities equivalent to the highest at 750°C was obtained with a lower pressure (10,000 psi) and for pressing times as short as 30 minutes (Table II). Highest density at 800°C was measured on samples pressed for 60 minutes at 20,000 psi (Table II).

Several samples were polished for metallographic examination and results on these confirm the general findings of our previous investigation (reference 3) as to microstructure and grain size. It was evident that, as indicated by chemical analysis, the samples contained a great deal of BeO as visible black inclusions. It was found that it was much more difficult to reveal the grain size of the latest specimens compared to the previous work.

Some attempts were made to replicate the polished metallographic samples for electron microscopy but only preliminary results were obtained. The grains can be seen optically with polarized light, but electron microscope replicas of the same specimen did not reveal recognizable grains.

Unfortunately, the quasi amalgam produced for evaluation as hot pressed material was impure and had a high beryllium oxide content. Any additional work on this process should be concentrated on electrolytic cell design and material selection and protective atmosphere provisions in order to minimize contamination from all sources. Powder particle size in the range of 0.1 to 0.2 microns reported in the earlier work (reference 2) can only be properly studied and evaluated as high purity

material.

The work performed in this program confirms: (1) the ability to produce fine beryllium particles by electrolysis, and (2) that the material can be consolidated by hot pressing in the range of 800°C and 10,000 psi. The normal hot pressing conditions for beryllium are 1100°C and 1,000 to 2,000 psi. The lower than normal hot pressing temperatures were investigated as a means of minimizing grain growth. Because of the lower temperatures, higher than normal pressures in the range of 10,000 to 20,000 psi were required for densification.

5. SUMMARY

Quasi Amalgam of beryllium and mercury was produced electrolytically using a beryllium anode and a mercury cathode. This material was hot pressed directly at 750, 800, and 900°C. Inconel was the die material found to be most satisfactory for use at these lower than normal hot pressing temperatures and higher than normal pressures. These conditions were used in order to minimize grain growth. A die liner or sleeve of graphite was found to be desirable and aided in the removal of the sample from the metallic die body.

The conditions investigated for hot pressing indicated that 800°C and 10,000 psi produced dense samples. These conditions appear to be a satisfactory compromise, taking into account the conflicting requirements of achieving full density, and minimizing grain growth.

REFERENCES

1. Gale, C. O. et al, "The Preparation of Ultra-Fine Beryllium Powder by the Amalgam Process." Technical Report NASA Contract, NASW 1099, 1965.

2. Hanson, G. T., Griffiths, Vand Habashi, F., "Ultra-Fine Beryllium Powder by the Amalgam Process," Progress Report NASA Contract NASW 1542, 1967.

3. Hanson, G. T. and Griffiths, V., "Ultrafine Beryllium by the Amalgam Process." Progress Report NASA Contract NASW 1542, June 1968.

TABLE I

Effect of Time and Pressure on Density for Parts Hot Pressed at 750°C

Sample No.	Time Min.	Pressure Psi	Density, g/cc		Chemical Analysis		
			Immersion	Geometric	BeO %	Fe ppm	C ppm
43	120	10,000	1.853	1.855	3.26	1670	1840
44	120	10,000	1.837	1.841	3.87	1700	1940
45	120	10,000	1.845	1.847	4.35	2110	1700
14	60	10,000	1.805	1.815	11.60	3740	3340
15	60	10,000	1.710	N.A.*	11.10	3630	3380
17	60	10,000	1.778	N.A.*	8.20	3720	3000
37	60	10,000	1.835	1.823	2.40	1790	3220
22	60	10,000	1.832	1.884	4.28	1390	2210
42	60	10,000	1.858	1.858	2.26	1690	1860
24	60	20,000	1.884	1.885	3.28	1670	2310
25	60	20,000	1.890	1.882	3.13	2330	2570
26	60	20,000	1.882	1.877	3.75	2050	2230

* N.A. = Not Available

TABLE II

Effect of Time and Pressure on Density for Parts Hot Pressed at 800°C

Sample No.	Time Min.	Pressure Psi	Density, g/cc		Chemical Analysis		
			Immersion	Geometric	BeO %	Fe ppm	C ppm
4	60	20,000	1.905	1.889	5.78	5340	2290
5	60	20,000	1.975	1.887	5.20	3480	2140
7	60	20,000	1.994	1.969	5.45	4790	
46	60	20,000	1.862	1.864	2.66	1820	1870
8	60	10,000	2.132	2.130	4.60	5390	12900
9	60	10,000	2.045	1.873	6.28	3770	7830
10	60	10,000	1.947	1.938	7.38	4440	4300
11	60	10,000	1.928	1.924	4.58	3420	6130
39	60	10,000	1.863	1.865	2.61	1860	1960
40	60	10,000	1.874	1.869	2.86	2060	2100
41	60	10,000	1.874	1.867	3.62	1930	1980
31	30	10,000	1.879	1.871	4.00	1800	2150
32	30	10,000	1.874	1.870	3.35	1570	2300
33	30	10,000	1.867	1.863	5.25	1710	2730
34	30	10,000	1.873	1.867	2.74	1860	2510
36	30	10,000	1.854	1.863	3.92	1810	2220
27	60	5,000	1.843	1.852	3.80	1790	2280
28	60	5,000	1.836	1.847	3.46	1820	2130
29	60	5,000	1.845	1.849	4.40	1730	2500
30	60	5,000	1.838	1.837	4.50	1810	2560
35	60	5,000	1.839	1.839	4.05	1870	2470

TABLE III

Effect of Time and Pressure on Density
for Parts Hot Pressed at 900°C and 10,000 psi

Sample No.	Time Min.	Density, g/cc		Chemical Analysis		
		Immersion	Geometric	BeO %	Fe ppm	C ppm
20	30	1.907	1.899	5.85	1650	2290
18	60	1.945	1.937	7.70	4750	3710
19	60	1.912	1.900	4.68	1950	2710
21	60	1.898	1.892	5.05	1470	430

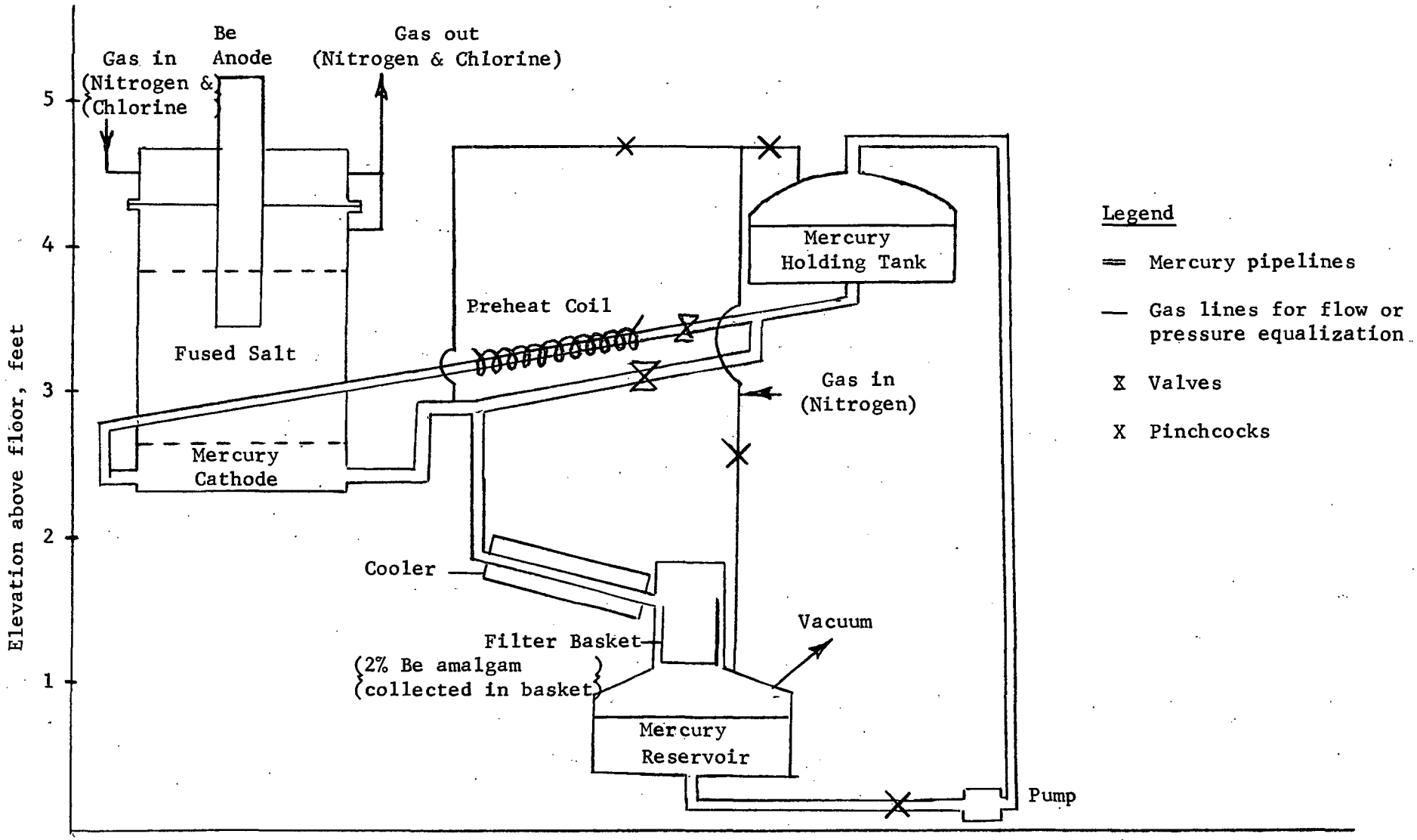

Figure 1: - Approximate Layout of Amalgam and Mercury System