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CENTRAL FILES NUMBER

CF-55-8-170

DATE: August 31, 1955

SUBJECT: OBSERVATIONS ON THE BEHAVIOR OF A PRESSED
THORIUM AMALGAM COMPACT DURING THE RETORTING CYCLE

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FROM: E. S. Bomar

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SUBJECT OBSERVATIONS ON THE BEHAVIOR
OF A PRESSED THORIUM AMALGAM COMPACT
DURING THE RETORTING CYCLE

PURPOSE

The retorting of cold pressed compacts prepared from amalgam supplied by Chemical Technology has resulted in a variety of textures for the retorted samples. Efforts to date have been unsuccessful in relating this variation with chemical or metallurgical variables. It was decided that direct observation of a sample during the entire re-torting cycle might reveal a clue to the origin of the various defects and in turn suggest a solution. There are at least four ways in which defects might be generated:

1. Failure in shear of the cold pressed compact on ejection from the die due to expansion of that portion extending beyond the die while the remainder of the compact is constrained in the die cavity.
2. Internal pressure generated by the too rapid evaporation of "free" mercury, exceeding the tensile strength of the pressed compact.
3. Internal pressure generated by the rapid decomposition of a thorium-mercury intermetallic at some specific temperature.
4. Failure of the compact due to differential sintering rates between internal and external portions of the compact.

The following described experiment may yield information on the last three items.

EQUIPMENT

Arrangements were made to obtain a permanent record of the events in the retorting cycle by use of a Cine Kodak Special No. 2 16 mm camera equipped with a $f/2$ lens and a timing mechanism to control the rate at which film was exposed. With this equipment it was possible to record the major events of the 5-hr cycle on a film strip which could be run through a projector in a few minutes. The exposure rate selected for the first film was one frame each 6 sec. with the aperture wide open. Thus, 100 ft of film took about 5-1/2 hr to pass through the camera. Kodak Super-XX film was used in the first run. The photographic equipment was supplied by the Graphic Arts Department and was set up and operated by W. N. Tillery.

Visual access to the tube furnace used for the retorting cycle was through a Pyrex window at one end of the mullite tube. The flat window was oriented at an angle of 60° to the axis of the tube making it possible to reflect light into the tube from an external light source. The light source was a 500 w spot equipped with condenser and projection lenses. The camera-to-sample distance was 30 in.

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Temperatures were determined throughout the cycle by means of a chromel-alumel thermocouple in a thermocouple well located immediately above the sample. EMF values were read on a direct-reading potentiometer.

Vacuum was supplied by a Cenco-Megavac, 1/2 HP motor, forepump and a DPI model VMF-200-R oil diffusion pump. This equipment maintained the noncondensable gas pressure in the system at or below 0.15 μ throughout the cycle.

SAMPLE PREPARATION

The amalgam was pressed as-received at 10 tsi in a 0.8-in diameter die. Stearic acid was used to lubricate the die wall. Following pressing, the sample was successively rinsed with 1 M HCl, water, acetone, and immediately loaded into the furnace for the run.

Metallurgy Code No. 142-1

Chemical Technology Code No. A-30

OBSERVATIONS

Observation of the behavior of the cold compressed amalgam during the retorting cycle was accomplished by running the film at a speed of 16 frames/sec and stopping it at intervals to measure the dimensions of the compact. The former permitted the observation of surface film formation, mercury evolution, and crack formation; the latter made possible the plotting of volume of compact as a function of time. A log of events is given below in chronological sequence.

Log of Events Observed on Film

<u>Lapsed Time,</u> <u>Min.</u>	<u>Temp.</u> <u>°C</u>	<u>Events</u>
0	41	Power on -- film started -- single horizontal crack present, probably formed at time of ejection following pressing. See Fig. 1 (Y-16309)
8	100	Dark film forming around crack. See Fig. 2 (Y-16310)
12	185	Dark film at crack disappearing. See Fig. 3 (Y-16308)
32	500	Entire sample beginning to darken. See Fig. 4 (Y-16312)
36	520	Entire sample dark -- almost black.
52	590	Increase in the rate of evolution of mercury as indicated by the collection and run-off of mercury in the cold zone of tube.
60-70	650	Thermocouple failed -- replaced during this period.
65	650	Start of small crack at left side of sample--directed from lower right to upper left.
80	681	Vertical movement of thermocouple tube noted -- peculiar since the thermocouple well is a rigid part of the tube assembly and there is no phase change for this material.
90	715	Cracks becoming less visible--radiation from sample becoming main source of light, therefore crack more difficult to see.
100	741	Sample beginning to tip -- indicative of the formation of a blister on the bottom of the compact. See Fig. 5 (Y-16311)

Measurements of diameter and height of the compact were taken at one-minute intervals from a projection of that portion of the film covering the first hour of the cycle, and at 5-min intervals for the balance of the exposure. From these measurements, the volumes of the sample at the appropriate times were calculated, assuming the sample to have retained a right-cylindrical shape. A plot of volume of sample as a function of time appears in Fig. 7 (Y-16394) along with a plot of the temperature of the environment of the sample as a function of time. There are two breaks in the time-temperature plot: the lower one represents the point at which the thermocouple failed and was replaced, and the upper break is the point at which the tap setting on the power transformer was shifted from the initial setting of 45 to 60 v.

The plot of volume as a function of time results in a more interesting curve, the correct interpretation of which may help in selecting a retorting cycle which will yield sintered thorium having better texture. The following interpretation of the significance of the form of the volume-time and time-temperature curves assumes the temperature of the environment of the sample was close to that of the sample proper. This is, of course, only approximately true since the thermocouple is not an integral part of the sample; therefore, it may either lead or lag the true temperature of the sample. Also, the volume at any instant is not independent of the time-temperature history of the sample. This makes the form of the resulting curves peculiar to the single sample and may mean that the conclusions to be drawn are not applicable to cold pressed thorium amalgam in general.

The following points seem significant:

- a. The sample attained a temperature of 500°C in 33 min before any change in volume was detected. This is indicative of two things: (1) fairly rapid removal of "free" or uncombined mercury does not result in an increase in volume of the sample, and (2) the sample at this time must be a skeleton of intermetallic particles with a network of voids left behind by the removal of free mercury.
- b. The free mercury has been observed to offer a degree of protection to the thorium-mercury intermetallic at room temperature. The darkening of the surface at about 32 min could be interpreted as the result of the formation of a heavier oxide film due to the loss of a protective film of mercury.
- c. The slight break in the volume-time curve at 52 min (590°C) indicates an accelerated rate of sintering and may mean that (1) a temperature has been reached at which the atoms of the intermetallic compound have the mobility to permit more rapid sintering, or (2) a change in the species of material present is occurring with an accompanying change in sintering characteristics. This possibility exists if decomposition of the intermetallic present has occurred. The latter possibility is, perhaps, supported by the observation that, in running the film through at regular speed, an increase in the rate of evolution of mercury occurred concurrent with the subject increase in rate of volume change.
- d. The third break in the volume-time curve at 90 min (700°C) may have the same significance as is indicated for the second break discussed in item c. A marked increase in the rate of evolution of mercury was not detected at this time, however.
- e. The fourth break in the volume-time curve at 120 min (775°C) is probably due to the increase in rate of heating resulting from a step-up in the input power.
- f. Sintering has been completed at 160 min (1010°C) indicating that the controlling quantity in the cycle is mercury elimination, which requires about 1 hr at 1100°C , rather than a cycle to yield maximum sintered density.

ADDITIONAL WORK

Plans are being made to make a duplicate run to that reported except that a thermocouple will be located in the body of the sample. It is hoped that the temperature at which the intermetallic decomposes may be detected by an arrest in the rate of heating curve. Since there is some evidence (see item a above) to the effect that mercury has been removed from the compact at a fairly high rate without damaging the structure of the sample, it may prove of interest to pass through the early stages of the cycle rapidly, then decrease the heating rate in the latter stages to minimize the difference in rate of sintering between the internal and external portions of the compact.

E. S. Bomar
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Fig. 1 (Y-16309)--Time lapse 7 min.
Horizontal crack visible

Fig. 2 (Y-16310)--Time lapse 11 min.
Formation of dark film at crack

Fig. 3 (Y-16308)--Time lapse 12 min.
Dark film at crack disappears

Fig. 4 (Y-16312)--Time lapse 35 min.
General darkening of surface beginning

Fig. 5 (Y-16311)--Time lapse 130 min.
Distortion of sample due to sintering
in progress

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Fig. 6 (Y-16364)--Sintered compact after retorting 1 hr at 1100°C.
Magnification about 11X

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Fig. 7 (Y-16394)--Retorting Cycle of Metallex Sample
1. Temperature-Time
2. Volume-Time

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Log of Run 142-1

<u>Time Lapse</u> <u>Min</u>	<u>Millivolts Cold-</u> <u>Junction at 25°C</u>	<u>Temp</u> <u>°C</u>	<u>Pressure</u> <u>Philips Gage</u>	<u>Furnace Pow-</u> <u>er Setting, v</u>	<u>Remarks</u>
0	0.65	41	0.06	45	Camera timer started.
5	1.25	55	0.06		
10	5.20	151	0.06		
15	9.35	255	0.06		
20	14.12	370	0.06		
25	17.24	443	0.06		
30	18.97	478	0.06		
35	20.17	513	0.08		
40	21.40	541	0.06		
45	22.25	562	0.05		
50	23.13	582	0.045		
55	24.02	603	0.045		
60	24.85	623	0.045		
					Thermocouple failed-- replaced.
70	26.93	673	0.05		
75	27.29	662	0.10		
80	27.32	681	0.10		
85	28.13	700	0.10		
90	28.79	715	0.10		
95	29.36	729	0.10		
100	29.87	741	0.10		
105	30.36	752	0.10		
110	30.85	765	0.10		
115	31.24	775	0.10		
120	31.49	780	0.10	45 to 65	
125	34.24	846	0.10		
130	36.34	896	0.15		
135	37.52	929	0.15		
140	38.55	955	0.15		
145	39.30	974	0.12		
150	39.98	991	0.12		
155	40.50	1005	0.11		
160	41.03	1019	0.11		
165	41.44	1027	0.10		
170	41.57	1033	0.10		
175	41.80	1039	0.10		
180	42.10	1047	0.095		
185	42.46	1056	0.09		
190	42.81	1065	0.09		
195	43.08	1071	0.08		
200	43.40	1080	0.085		
205	43.51	1084	0.085		
210	43.87	1092	0.06		
215	43.96	1095	----		
↓					
305		1100	----	65	Power off
320	-----	-----	----		Camera stopped