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REPORT NO. 3

AUTHOR: James H. Moore

DEPT: Metals

DATE: April 2, 1947

SUBJECT: Experimental Heats of Alloy Metals

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NATIONAL RESEARCH CORPORATION
BOSTON 15 MASSACHUSETTS

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PROGRESS REPORT

January 1 through March 1

Contract W-19-065 Ord 1046

"Experimental Heats of Alloy Metals"

J. E. Moore
National Research Corp.
Boston 15, Massachusetts
April 2, 1947

SUMMARY

Work on this project has progressed along the following lines since the last report: experimental purification of electrolytic chromium, construction of equipment for large scale purification and reduction of chromium oxide, development of furnaces and techniques suitable for the melting and casting of chromium, and completion of initial requirements in mechanical testing facilities.

While waiting for the completion of the equipment necessary for producing very high-purity chromium for the fundamental investigations, purification of electrolytic chromium by high vacuum techniques is being studied. The results have indicated the possibility of producing chromium of sufficient purity to permit machining of castings into forms for experimental work in such ordnance application as gun liners or nozzles. The machining and testing of specimens of this metal to be used for a comparison with very high-purity metal will probably give us a more exact idea of its potentialities. The casting and testing of ingots are to be done as soon as possible.

The design of equipment for relatively large-scale distillation of chromium trioxide, conversion to chromic oxide, and then reduction with calcium hydride has been completed, and the construction is well under way.

All of the beryllia refractory forms necessary for initial melting and casting of chromium are on hand, and the casting of ingots and precision-cast test specimens is due to begin shortly. To date, the general characteristics of the furnaces have been checked, and some changes in design have been found necessary. Chromium has been successfully treated in the molten condition.

Excepting for some trouble with high temperature grips, the long and short time tensile testing equipment is ready for operation. An attachment for the recording of an additional curve on the stress-strain recorder, a plot of elongation vs. time, has been installed and checked.

PURIFICATION OF ELECTROLYTIC CHROMIUM

Since we have been forced to wait for the necessary equipment to be built before proceeding with the production of very high-purity chromium from the oxide, an interim program of purification of electrolytic chromium has been under way. This program has two major purposes. It enables us to work out the techniques for melting and casting, and it provides data for comparison with the forthcoming high-purity metal.

In the last report the possibility of using vacuum-refining treatments in the production of high-purity chromium was discussed and rejected as a primary process. However, it was indicated that some combination treatment using a hydrogen atmosphere might have merit as a final step, but no data were available for equilibrium calculations.

We have since made several experimental treatments of an electrolytic starting material—including vacuum treatment at temperatures below melting, sublimation under high vacuum, melting under argon, melting under argon plus hydrogen, and distillation in a hydrogen atmosphere. Not all the data are available as yet, but some discussion is possible. Before discussing the results, a short summary of the work of previous investigators with vacuum treatments seems advisable for a background.

Kroll[1,2] discussed briefly the technique of degassing chromium by heating in a high vacuum at temperatures below that at which appreciable sublimation occurs. He mentioned only hydrogen as being definitely evolved but said that nitrogen may have been coming off at higher temperatures as evidenced by a red glow. By applying an inert atmosphere, the chromium could be melted and a distillation carried out if desired. Distillation was preferred to sublimation because of the increasing difficulty of induction heating of the charge in the latter process as the sublimation cut down the contact between pieces. As was to be expected, the distillation caused an increase in the very volatile impurities in the product. Kroll mentioned the problem of a large oxide content in electrolytic chromium and noted that it was carried over into a sublimate but did not mention it in connection with distillation.

Adcock[3] gave figures of from 1.3 to 1.7 per cent for chromic oxide content in his special electrolytic chromium. Vacuum melting in a lime crucible did not prove effective in cutting down this oxide. An attempt was made to deoxidize molten chromium by passing a stream of hydrogen over it, and in so doing, some distillation occurred. No analytical results were given for either the melt or the distillate, excepting for X-ray evidence of body-centered cubic crystal structure in the distillate. It was stated that the melting of chromium under either vacuum or hydrogen atmosphere always resulted in oxide increase, and the cause was suggested to be interaction with the crucibles.

Our first experimental work consisted in a simple vacuum treatment in which the temperature was increased slowly while maintaining a high vacuum. In accordance with French data[4] the first evolution of gas, which is apparently hydrogen, occurs rapidly at about 300° C. and is substantially complete by 700° C. A second evolution occurs noticeably between 1300° and 1450° C. It is thought to be nitrogen, since the decomposition of the nitride should occur under equilibrium conditions at temperatures well under 1000° C. at 1 micron pressure. The high temperature at which this evolution is actually observed is attributed to the fact that the pumping capacity must be exceeded before a noticeable pressure increase occurs. This means that the reaction must become very rapid to be picked up. The heating of solid chromium in high vacuum

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[1]Kroll, W., METAL INDUSTRY, vol. 47, 1935, pg. 5.
[2]Kroll, W., "Das Ductile Chrom.," ZEIT. FUR ANORG. UND ALLGE. CHEM., vol. 226, 1945, pg. 23.
[3]Adcock, F., "Alloys of Iron Research, Part V--Preparation of Pure Chromium, J. IRON AND STEEL INST., vol. 115, 1927, pg. 269.
[4]Guichard, Blausmann, Billan, and Lanthony, "Sur La Teneur En Hydrogene et La Dureté du Chrom Electrolytique," COMPTES RENDUS, vol. 196, 1933, pg. 1660.

should be effective in removing hydrogen, but indications are that nitrogen has an appreciable solubility throughout the solid state. Analysis has shown a residual nitrogen content of about 0.01 per cent.

Previous investigators have been primarily concerned with oxide impurity content. On the basis of a few analytical results, it appears that the oxide content may be cut down appreciably by sublimation in the high vacuum or by sublimation in a low pressure of hydrogen. By the former method the oxygen content (here on includes all wanderal) was cut to 0.1[illegible] per cent from [illegible] per cent in the sublimate. Subsequent sublimation runs failed to get such a [illegible] and the average product contained about 1.0 per cent oxygen. The sublimate obtained in hydrogen contained 0.0[illegible] per cent oxygen as compared with 2.[illegible] per cent in the melt. This treatment also cut down the carbon and nitrogen content by about half (.003 C and .00[illegible] N_2).

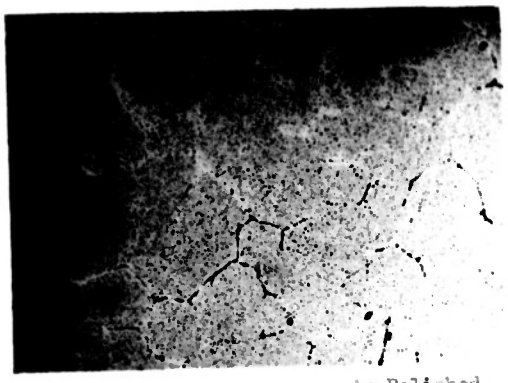
A series of photomicrographs show the appearance of the oxide constituent in the electrolytic chromium as received (Figure 1), sublimed in vacuum (Figure 2), melted under 100 mm. [illegible] mm. H_2 (Figure 3), and distilled under 20 mm. H_2 (Figure 4). The electrolytic flake exhibits a large amount of insulating material [illegible] as seen in the picture. It is thought that the oxide content may vary greatly from flake to flake, making an [illegible] interpretation. The sublimed metal exhibits a large number of finely divided particles plus some grain boundary material. The [illegible] nature is good evidence that the oxide is sublimed at about the same rate and deposited simultaneously, i.e. that the vapor pressures of the metal and oxide must be very similar. The chromium melted under argon and hydrogen exhibits a large amount of globular oxide. Apparently the oxide and metal have approximately the same melting point. The hydrogen melt should be expected very little visible oxide. Most of the black spots in the sections are polishing pits.

It is hard to draw any conclusions as to oxide pick-up during melting on the basis of photomicrographs, and we still have but few analytical data. However, on the basis of per cent of insoluble matter, there is apparently an appreciable increase upon melting under any of the conditions. We have used zirconia crucibles which do not exhibit visual evidence of reduction of the metal either by the appearance of more oxides in the metal adjacent to the crucible or by an attack of the surface. However, this does not rule out the possibility, and when we use the hydrogen [illegible] atmosphere we may get some position evidence. The use of [illegible] has been satisfactory from another standpoint, however. The chromium penetrates the crucible either as liquid or vapor for some distance (See Figure [illegible]) and causes a bonding between the metal and crucible during solidification in the crucible. Accordingly, a crucible has had to be sacrificed with each melt. This penetration is thought to be responsible for the failure of some crucibles during melting. Another factor in the failure of the zirconia was probably the fact that the temperature must have been well over 2000° C., since the surface some exhibited a condition of either a high degree of sintering or partial melting.

One ingot which had been solidified in the crucible after having been melted under hydrogen and argon appeared to have some ductility. Accordingly, it was set up in a lathe, and the face was partially machined off as shown in Figure 5. It machined quite freely and, in addition, exhibited some degree of malleability under hammer blows at room temperature. Previous ingots had been so brittle that a hammer blow fractured them easily. The ingot had a Rockwell B hardness of from 50 to 65. Further data on this material will be reported as soon as ingots and test specimens can be cast.

100X As Polished

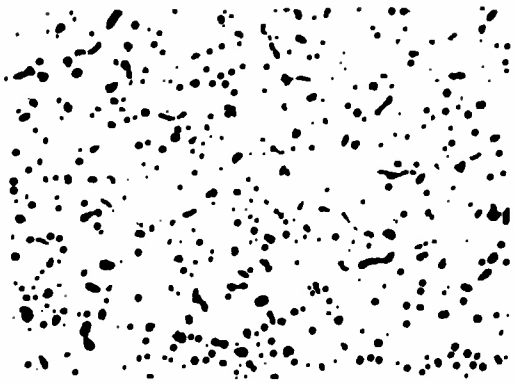
Figure 1



100X As Polished

Figure 2

Figure 1 Electrolytic Chromium as received.
Figure 2 Product of Vacuum Sublimation.



100X As Polished

Figure 3

100X As Polished

Figure 4

Figure 3 Chromium Melted under Argon and Hydrogen.
Figure 4 Product of Distillation in Hydrogen.

Figure 5

Photograph of the Partially Machined Face of a Chromium Ingot which had been Melted under Argon and Hydrogen.

100X As Polished

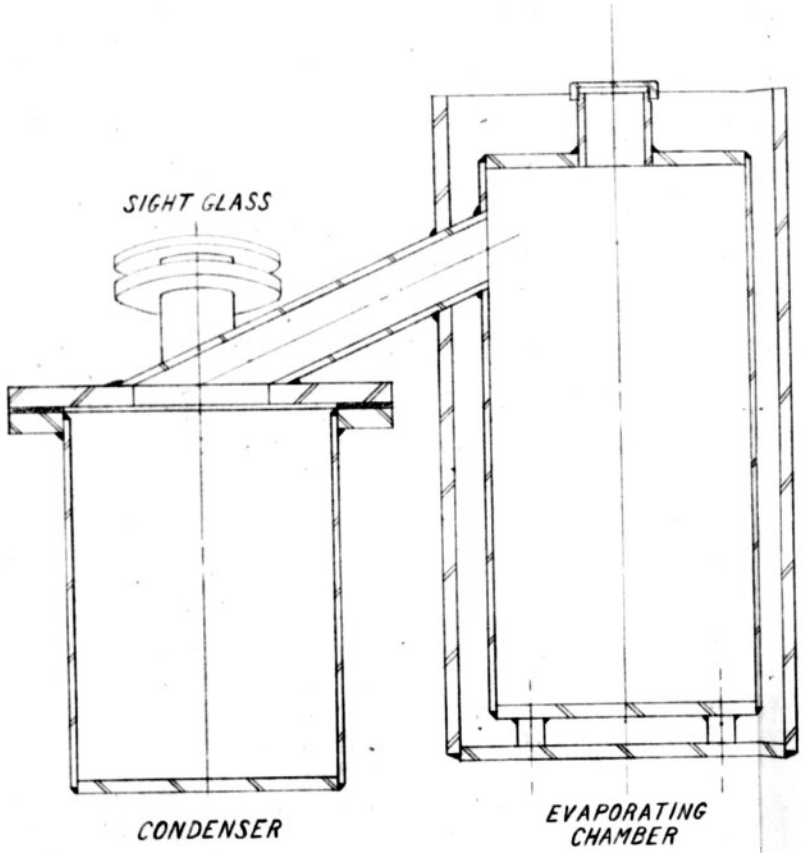
Figure 6

Photomicrograph of the Interface between a Zirconia Crucible and Chromium Solidified in it. Penetration of the Crucible by the Metal is Evident.

EQUIPMENT FOR PURIFICATION AND REDUCTION OF CHROMIC OXIDE

The previous report mentioned that apparatus for the purification of chromium trioxide, conversion to chromic oxide, and then reduction with calcium hydride was being designed. The diagram in Figure 7 shows the final design of the stainless steel apparatus for the first two steps in the process. This is nearly ready for operation. A print of the retort for the final step is not available, but a picture will probably be included in the next report.

The first step in the process will be the charging of chromium trioxide of 98 + per cent purity into the evaporating chamber. A bath of molten Fisher bath wax in the space between inner and outer containers will maintain a temperature of 210° C. while a vacuum pump acting through a port in the condenser maintains a pressure of 1 mm. of Hg. The oxide vapor will be collected in the condenser which is to be immersed in a water bath. The sight glass enables observation of the progress of distillation. The distillate will be removed and transferred to the retort for conversion to chromic oxide by heating to 850° C. It may be necessary to remove the oxide to mix it with calcium hydride. A copper oxide burner and an ice trap connected between a vacuum pump and the retort will absorb hydrogen and water vapor produced in the reduction. The temperature for this final reaction has not been definitely established, but Alexander has indicated that it can be done as low as 470° C. when a vacuum is used to start the reaction.



PUMPING PORT IN CONDENSER COVER NOT SHOWN

FIGURE 7

ALT.	CHANGE	DATE	APP'D BY

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OUTLINE

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CHECKED BY			
PRODUCTION			DWG. NO. BO-5160
ENGINEERING	R.H.K.	3-19-47	ALT.

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FURNACE DEVELOPMENT

In the past month we have received enough beryllia materials to set up a furnace for melting and casting chromium. A schematic diagram (Figure 12) shows the arrangement in the furnace and casting chamber, which are pictured in Figures 10 and 11.

The apparatus is designed so that we may treat the chromium charge under either main vacuum or an atmosphere before pouring. After pouring into the investment mold, the vacuum slide valve may be closed and the pressure increased in the casting chamber to produce a more accurate, denser casting. We have not been able to pour chromium to date because of the lack of some of the necessary refractory parts. However, we have done enough treating of the electrolytic chromium in a crucible of the same size as that in the casting set-up to get some initial problems solved. Some changes have been made in the general vacuum system and induction heating coil.

The technique for making precision casting investments for the .250" diameter tensile specimens has been developed to the point of testing them for vacuum characteristics. In addition, molds for 2" diameter ingots are to be tried.

MECHANICAL TESTING EQUIPMENT

The Baldwin Southwark tensile machine is still lacking grips suitable for the more elevated temperatures, but testing will be possible up to at least 1000° F. This range should be sufficient for the initial work with chromium. In the meantime we are trying to get high temperature grips made of a low carbon N-155 alloy.

The attachment for adapting a stress-strain recorder to obtain an additional curve for elongation vs. time has been set up and found to operate satisfactorily. It will take some degree of practice for an operator to become proficient with it, however. A photograph of it may be seen in Figure 8.

The stress-rupture or long-time tensile tester is ready for partial operation in the same range of temperatures as the tensile machine. High temperature grips are also being obtained for it. A photograph of the control panel and one of the four test frames are shown in Figure 9. For controlling the temperature and timing the tests, the wiring circuit shown in Figure 13 has been designed and found to work satisfactorily. By means of the double-pole, double-throw switch, we are able to bring the furnaces up to temperature, using only the Powerstat (auto transformer) and then with the correct power input set throw the controller into the circuit. During the heating cycle and power adjustment, the controller functions only as an indicator. The microswitch

leads go to microswitches on the testing frame. These are normally closed until failure occurs when they open and cut off both controller and timer circuits for the particular furnace. To eliminate the necessity for a cold junction ice bath, the whole panel is enclosed and maintained at a constant temperature by the thermoswitch-resistance heating circuit.

J. H. Moore

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Figure 8

Stress-strain Recorder with an Attachment for Elongation vs. Time Recording.

Figure 9

Long Time Tensile Testing Equipment.

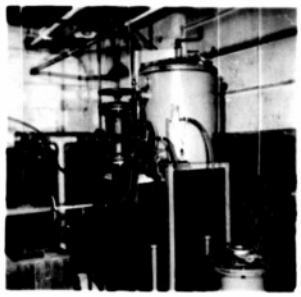
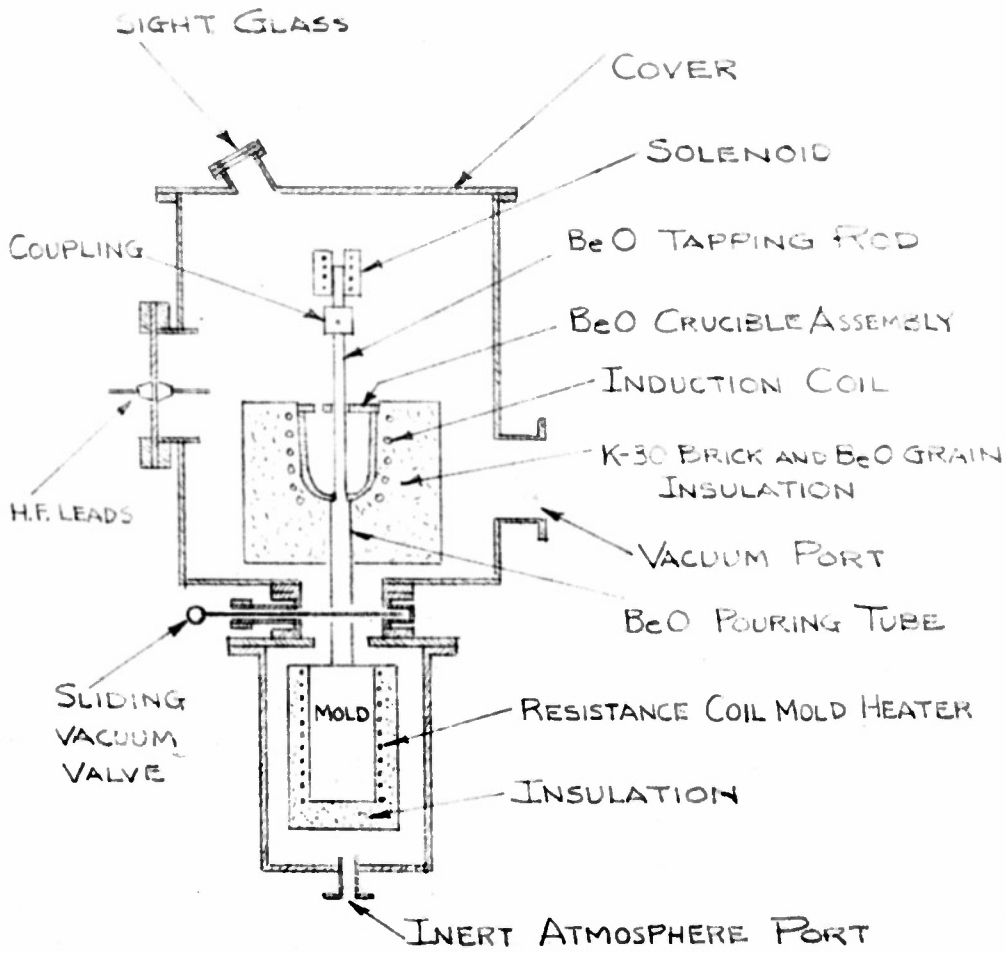


Figure 10

One of Twin Vacuum Furnaces for Experimental Melting and Casting.

Figure 11

Casting Chamber for the Furnace in Figure 10.



SCHEMATIC DIAGRAM
OF
MELTING AND CASTING APPARATUS
FIGURE 12

ASR-1187

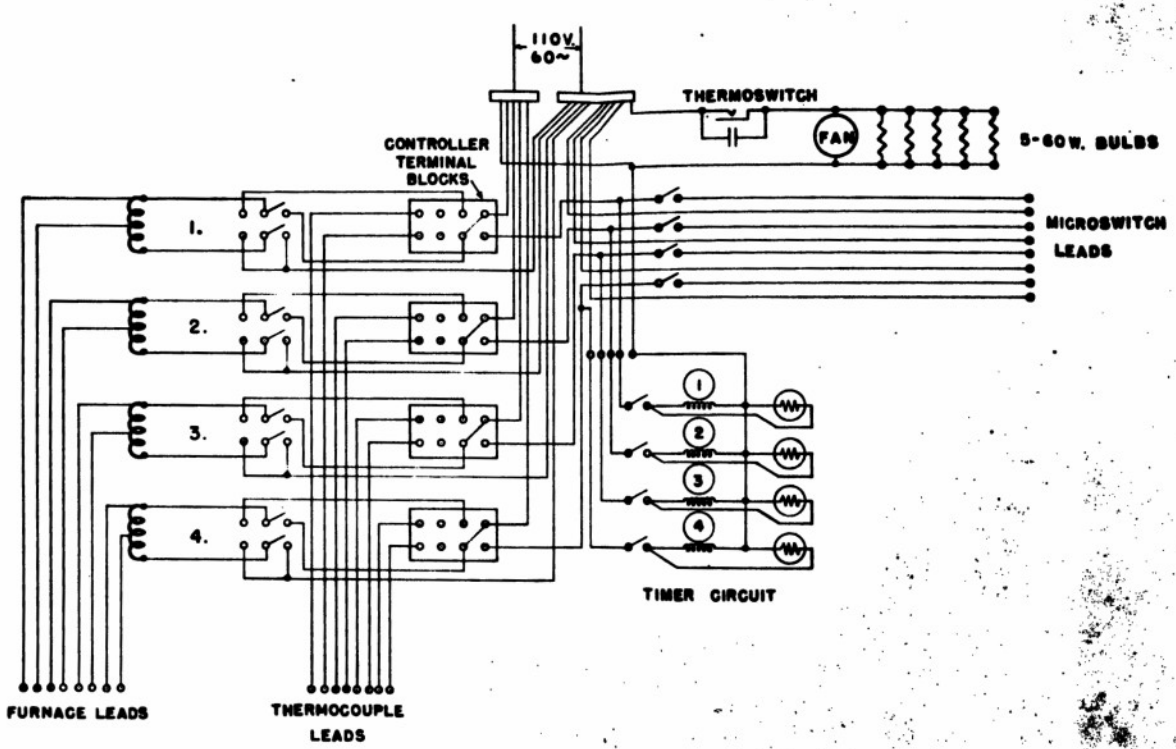


FIGURE 13
CIRCUIT DIAGRAM
STRESS RUPTURE CONTROL PANEL

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TITLE: Experimental Heats of Alloy Metals

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SUBJECT HEADINGS: Metallurgy (61000); Metals - Casting (61019); Nozzles (66901); Metals, Hard - Production (61176)

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Casting Alloys, Gun liners

Chromium Pile

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