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NATIONAL DEFENSE RESEARCH COMMITTEE

ARMOR AND ORDNANCE MEMORANDUM NO. A-78M (OSRD NO. 2082)

DIVISION 1

THE PREPARATION OF CHROMIUM BY THE THERMAL DECOMPOSITION OF CHROMIUM IODIDE

by

Don R. Mosher

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Don R. Mosher

Don R. Mosher, Author
Westinghouse Electric and
Manufacturing Company

Approved on November 26, 1943
for submission to the Committee

L. H. Adams

L. H. Adams, Chief
Division 1
Ballistic Research

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Preface

The work described in this memorandum is pertinent to the project designated by the War Department Liaison Officer as OD-52 and to the project designated by the Navy Department Liaison Officer as NO-23. The investigation of the properties of high-purity chromium was carried out at the Research Laboratories of the Westinghouse Electric and Manufacturing Company, East Pittsburgh, Pennsylvania, under Contract OEMsr-915. It was performed as a part of the major project, a study aiming to prepare metallic chromium having properties that would make it suitable for use in erosion-resistant liners for gun barrels.

The electrolytic chromium made available to the Westinghouse Research Laboratories was prepared at the National Bureau of Standards with NDRC funds provided under Symbol No. 2329. Additional treatment of the chromium was done by the Geophysical Laboratory of the Carnegie Institution of Washington under Contract OEMsr-51.

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The NDRC technical reports section
for armor and ordnance edited
this report and prepared it for duplication.

THE PREPARATION OF CHROMIUM BY THE THERMAL DECOMPOSITION OF CHROMIUM IODIDE

Abstract

This memorandum describes a method for the preparation of crystalline metallic chromium of a considerable degree of purity by the interaction of powdered electrolytic chromium with iodine vapor, the sublimation of the chromium iodide, and its subsequent decomposition on a hot tungsten filament, all in an evacuated quartz apparatus. This represents a new application of a process previously used for the preparation of zirconium by de Boer and Fast.[1] The chromium thus prepared contains oxygen equivalent to 0.117 percent Cr_2O_3.

In our investigation of the properties of high-purity chromium the fundamental idea has been that the mechanical properties are strongly affected by the presence of small amounts of impurity, and that oxygen is particularly detrimental. With this in mind, we have directed our efforts toward the refinement of chromium to an extremely high order of purity.

As one approach to the problem, it was suggested[2] that the preparation of chromium by the thermal decomposition of chromium iodide be attempted. It was believed that the decomposition temperatures of the impurities would be sufficiently remote from that of the iodide to eliminate them from the final product. Our plan, similar to that for the preparation of ductile zirconium,[1] was to form the chromium iodide, vaporize it and decompose it on a hot tungsten filament. In this way it was hoped to obtain a deposit of metallic chromium of sufficient continuity to permit investigation of its mechanical properties.

1/ J. H. de Boer and J. D. Fast, "Preparation of zirconium from zirconium tetraiodide by thermal decomposition on a hot tungsten filament," Z. anorg. Allgem. Chemie 153, 1-8 (1926).

2/ This suggestion was made by P. H. Brace, of Westinghouse Electric and Manufacturing Co.

In our work on this problem[3] we have used as starting material a high grade of electrolytic chromium,[4] which was powdered and vacuum annealed.[5] Conditions of annealing varied with different lots of chromium, temperatures of 600° to 900°C for varying lengths of time being used.

Before effective apparatus involving a tungsten filament could be designed, it was necessary to perform certain exploratory experiments to determine the nature of the materials involved. For the first of these, an apparatus was used whose design is shown in Fig. 1. The

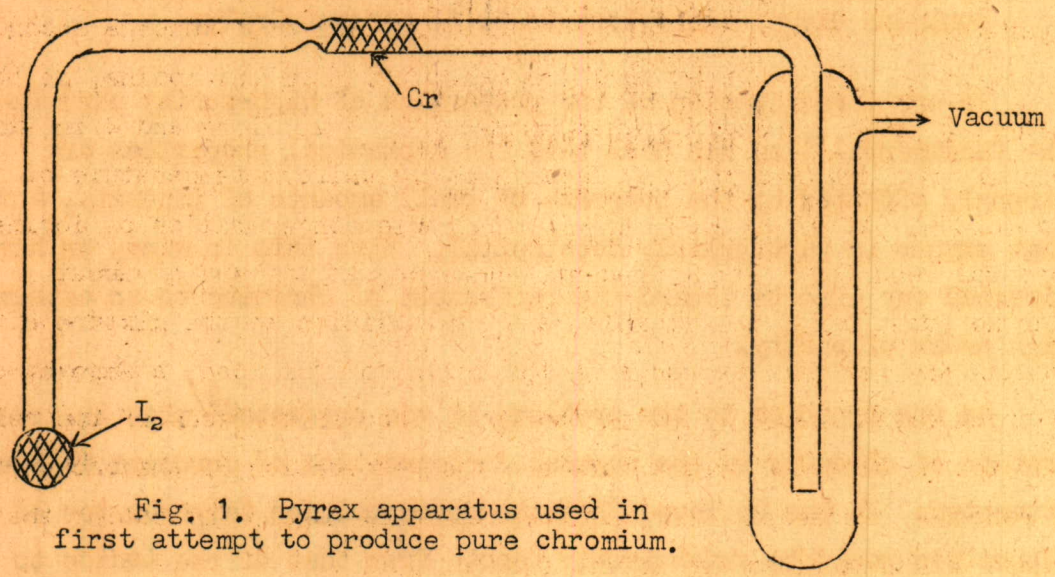

Fig. 1. Pyrex apparatus used in first attempt to produce pure chromium.

apparatus was first evacuated, after which the chromium was heated with a gas burner while iodine from the bulb was vaporized and passed over it. As the iodine vapor passed over the hot metal, a condensate was

3/ Carried out with the assistance of C. M. Laffoon, Jr.

4/ Prepared by Dr. William Blum, National Bureau of Standards.

5/ Done at the Geophysical Laboratory, C.I.W.

seen to form on the cooler portions of the tube beyond the chromium, indicating that some reaction was taking place. This substance was dirty yellowish or dark brown in color depending on the temperature. After the supply of iodine was exhausted, the apparatus was broken open and the contents examined. The reaction product was very hygroscopic, forming a green solution indicating chromic ions (Cr^{+++}). It was concluded that although some reaction between chromium and iodine had taken place, the use of Pyrex apparatus would probably be impossible since the reaction had been carried out at a temperature that softened the glass. However, since the apparatus had been subjected only to localized heating, it was suggested that perhaps a uniform temperature of a lower magnitude would be sufficient. Hence a second experiment in Pyrex was performed in which chromium and iodine, in the ratio of 2 gm to 2.5 gm, in an evacuated bulb 8 in. long and 2 in. in diameter, was maintained at an approximately uniform temperature of about 600°C. After about 1½ hr, considerable concentration of iodine vapor was seen to be still present. However, at the end of about 20 hr no free iodine was visible, and, in addition to the mixture of chromium and reaction products on the bottom of the tube, a deposit of red-brown crystals was found on the upper, cooler surfaces of the bulb. Owing to the elevated temperature and the restoration of the vacuum as the reaction proceeded, the bulb had collapsed, again indicating that the use of Pyrex glass was impracticable.

The next step was an attempt to carry out the reaction in a quartz tube. Chromium and iodine in the ratio of 5 gm-mole of chromium to 1 gm-mole of iodine were placed in a chamber of design shown in Fig. 2. The total weight of the charge was 20 gm. The material was heated by means of a blast burner to a dull red heat, at which time a reaction took place that caused it to glow a much brighter red. Heating was continued until the reaction ceased, whereupon the tube was broken open and the contents transferred to and sealed in an evacuated glass tube. The product was a dark brown, crystalline material which in solution gave a pale blue color, indicative of chromous ions (Cr^{++}). Oxidation by means of hydrogen peroxide caused the solution to change

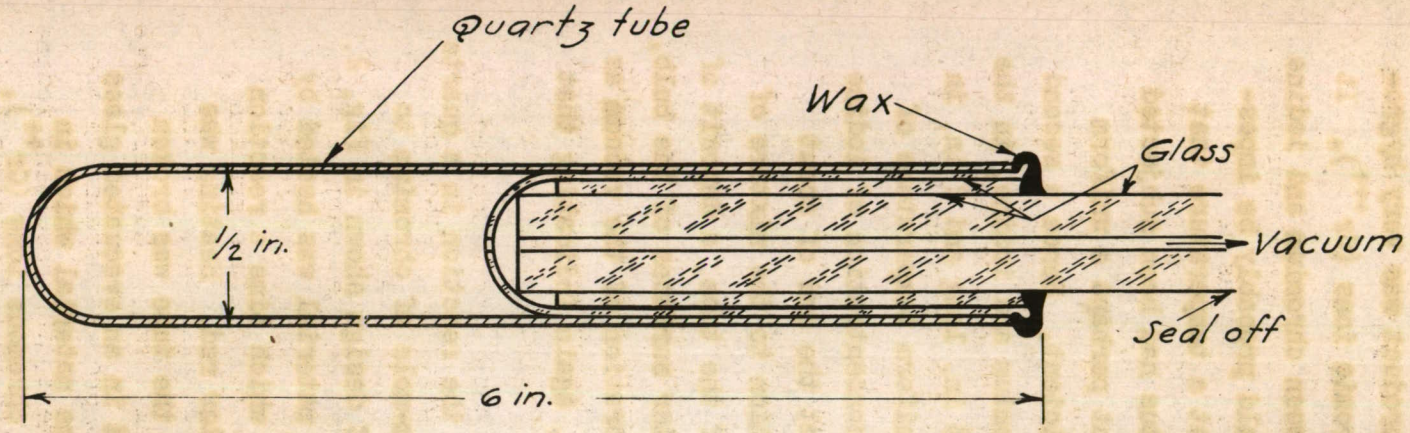

Fig. 2. Diagram of simple quartz reaction tube.

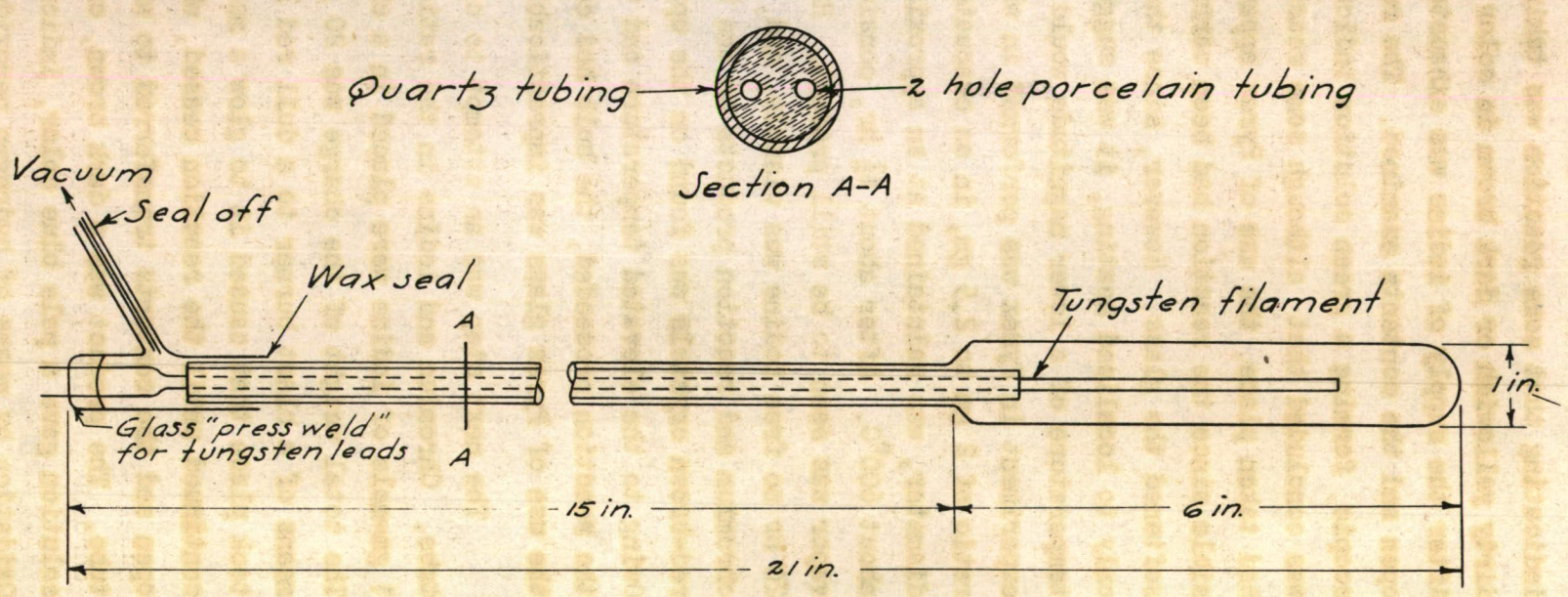

Fig. 3. Diagram of quartz apparatus that utilized tungsten filament for decomposing chromous iodide.

first to the green color of chromic ions (Cr^{+++}) and then to the green-brown color of chromic acid (H_2CrO_4). A few crystals of the material were then heated in an evacuated glass tube. On the hottest portion of the glass a mirror was formed, which upon analysis proved to be very pure chromium. It was thus shown that the decomposition of chromium iodide takes place at a relatively low temperature.

A small evacuated quartz tube (3/8 × 6 in.) containing chromium and iodine was then placed in a furnace in such a way as to have a temperature gradient of about 100°C from end to end. The end containing the reactants was maintained at about 800°C while the other was at about 900°C. After about 2 hr the tube was opened for examination. In the hot end was found a very thin layer of chromium, and in the other end the iodide, while the central portion seemed to be free of both. Examination under the microscope showed the chromium deposit to be bright, but much too thin to handle.

The apparatus shown in Fig. 3, incorporating a tungsten filament, was then designed and was used throughout the subsequent experimental work. To use this apparatus the bulb containing the reactants was carefully evacuated and inspected for leaks, after which it was sealed off. The reaction between the chromium and iodine was then carried out. This reaction proceeds readily at 800°C, which was the temperature used in most of our experiments. Since the iodine was in the vapor phase at the reaction temperature, care had to be exercised to avoid dangerous pressure within the bulb. An effective method of controlling this situation lies in the fact that the vapor pressure within the entire apparatus is determined by the coldest part of the tube. Hence, by keeping the chromium in a high temperature region at one end of the tube and maintaining the proper temperature gradient, the vapor pressure could be kept at any desired magnitude. In this way, larger quantities of iodine could be safely used. (However, large quantities of iodine are not essential in this process because as the chromous iodide is decomposed on the hot filament, the resulting iodine vapor migrates back to the chromium, reacts with it and proceeds again to the filament as chromous iodide; thus, a large quantity of chromium

may be transported by a relatively small amount of iodine.) After reaction between the chromium and iodine was complete, the bulb was placed in a region of uniform temperature and the filament heated. For convenience, a-c voltage controlled by a Variac was used. As chromium was deposited on the filament the current increased and the voltage tended to decrease. In most of our experiments the filament was kept at a constant voltage. With this arrangement it appeared that the temperature of the filament and deposit did not change very much during the course of a run, although no direct measurements could be made.

In all cases, the deposit consisted of more or less loosely adherent crystals that individually showed considerable ductility, although as a unit the deposit was fragile. It was possible to flatten most of the crystals very easily, and even after flattening many would withstand, without cracking, further cold-work such as that produced by pressing the point of a pin on the central portion of a flattened crystal and thus causing rather severe "dishing." Figure 4 shows a typical deposit.

Dr. H. E. Merwin, of the Geophysical Laboratory, reports these crystals to be cubic and to show octahedral faces. He found that if compressed perpendicular to an octahedral face, the crystal showed ductility, while if compressed perpendicular to a cubic face, cracking occurred.

In view of the small amounts of material prepared by this method, a chemical analysis was very difficult to obtain. The technique that has been used heretofore is Doctor Yensen's vacuum fusion method, which requires at least a 0.5-gm sample for determining O_2 in the amounts with which we are concerned. Thus to obtain any figure at all, it was necessary to use deposits from several different runs. Since no attempt could be made to separate the more plastic crystals from the rest, the resulting analysis is not too significant. However, we felt that some attempt should be made to determine the order of purity. The sample submitted was reported to have 0.037 percent O_2, although

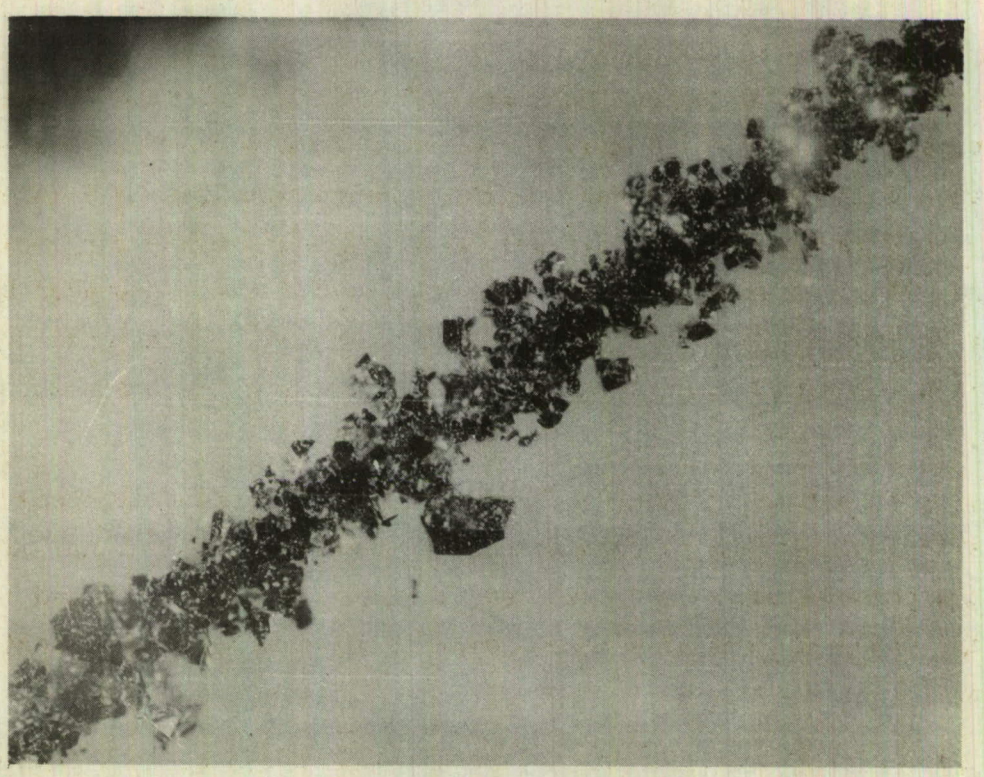

Fig. 4. A typical deposit of chromium crystals.

Table I. Summary of experimental conditions and results with quartz apparatus incorporating a tungsten filament.

Run No.	Wt. of Cr (gm)	Wt. of I_2 (gm)	Furnace Temp. (°C)	Filament Dimensions (in.)	Filament Voltage (volt)	Filament Current Starting (amp)	Filament Current Final (amp)	Operation Time (hr)	Remarks
1	50	1	800	0.010 × 3	4.7	6.50	7.50	5½	Small crystals oriented in a radial direction; wire as a whole not ductile but crystals are.
2	40	2	800	0.0045 × 3	6.5 to 5.3	1.50	8.70	15	Run over night with no voltage control; crystals larger than No. 1 but otherwise results similar.
3	50	10	800	0.0045 × 2-3/4	10	2.8	4.2	1/6	Very rapid deposition but burned out. Several long crystals that seemed fused; these were especially ductile. Beneath outer layer of crystals is a layer of soft, adherent metal about 0.001 in. in thickness that is ductile. Wire may be bent quite severely.
4	50	10	800	0.0045 × 3	10	2	2.3	49	No deposit on filament; considerable growth on lead-in wire.
5	50	10	800	0.0045 × 3	11	3.6	3.6	45	Not opened but run at lower voltage (No. 6).
6	50	10	800	0.0045 × 3	4	1.9	7.6	24	Large growth of large crystals.
7	50	10	800	0.0045 × 3	3	0.5	14.3	26	Filament did not appear unusual in any respect so without opening it was run at 9 volt, 25 amp, d.c. in an attempt to polarize the filament with respect to any oxygen present. Lead got hot and melted the wax seal. Filament oxidized.
8	50	10	900	0.0045 × 3	3	0.4	7.1	22½	The increase of furnace temperature produced no apparent change in the character of the deposit.

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it is believed that the oxygen content of the plastic crystals may be lower than this.[6/]

A tabular summary of the operating conditions for the various runs is shown in Table I.

Conclusions

1. While work has not been completed on this process, results to date have shown no way to get a deposit of sufficient continuity to test mechanical properties en masse.

2. Considerable cold ductility is exhibited by the individual crystals prepared by this method.

6/ This oxygen content is equivalent to 0.117 percent Cr_2O_3 in the untreated metal. When chromium prepared by the usual electrolytic method has been carefully annealed, it may contain oxygen equivalent to 0.08 percent Cr_2O_3; and by subsequent purification in hydrogen the Cr_2O_3 content may be reduced to 0.01 percent. -- L. H. Adams, Chief Division 1, NDRC.

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A method for the preparation of crystalline metallic chromium of a considerable degree of purity by the interaction of powdered electrolytic chromium with iodine vapor, the sublimation of the chromium iodide, and its subsequent decomposition on a hot tungsten filament is all brought about in an evacuated quartz apparatus. This presents a new application of a process previously used for the preparation of zirconium by de Boer and Fast. The chromium thus prepared contains oxygen equivalent to 0.117% Cr_2O_3.

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