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**PREPARATION OF HIGH-PURITY
ELECTROLYTIC CHROMIUM**

BY P. M. GRUZENSKY AND F. E. BLOCK

United States Department of the Interior — January 1957

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UNITED STATES DEPARTMENT OF THE INTERIOR
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SUMMARY

In view of some of the outstanding properties of chromium, considerable effort has been made in recent years to prepare the high-purity metal in ductile form. The object of this investigation was to obtain such metal by electrolysis of chromic acid solutions and to determine the conditions that yield optimum results. The apparatus is described, as well as the parameters that received consideration. Ion-exchange resins were employed to remove cation impurities from the electrolyte. Tensile specimens prepared from the electrodeposits by arc melting, press forging, swaging, and drawing were ductile at room temperature.

INTRODUCTION

Metallic chromium displays an exceptionally high resistance to corrosion, oxidation, and wear at elevated temperatures. Although these properties are utilized to some extent when chromium is alloyed with other metals, such as in stainless steels, high-chromium alloys and pure chromium are not employed as engineering materials because of a serious lack of ductility and impact resistance at room temperature. Because high-chromium alloys appear promising as refractory metals for applications such as in gas turbines, much interest has been shown recently in the preparation of uniformly ductile chromium and in determining which factors contribute to its brittleness.

This investigation was made as part of a larger study in the search for room temperature ductile chromium and high chromium alloys. Of the various methods for preparing metallic chromium, electrolysis of chromic acid solutions was chosen for this investigation because of the relative ease with which metallic impurities could be eliminated. It was known that as-deposited electrolytic chromium showed little tendency toward ductility, but it offered an excellent source of high-purity material for further purification by hydrogen treatment to eliminate residual amounts of oxygen, nitrogen, sulfur, and carbon. It was also used to a large extent in a study of the physical properties of iron-chromium alloys. Details of these secondary studies have been reported separately and are not included in this report (1,2,3,4).^{3/}

The deposition of chromium from aqueous chromic-acid solutions dates from 1926, when Fink (5) correlated the factors that govern successful deposition. His bath was used primarily for decorative chromium plating; however, in 1927 Adcock (6) used this bath for preparing massive electrodeposits. In 1948 Brenner, Burkhead, and Jennings (7) studied the properties of chromium plates deposited under a wide variety of plating conditions. They determined that the oxygen content of the deposits was governed chiefly by the bath temperature and could be lowered significantly by operating near the boiling point. Later, Greenaway (8) employed a chromic-acid electrolyte at high temperature and high current density in preparation of thick deposits of low-oxygen chromium for use in physical tests.

^{3/} Underlined numbers in parentheses refer to references in the bibliography at the end of this report.

Recently (1,9,10) it has been shown that chromium, if pure enough, will exhibit some degree of ductility at room temperature. These investigations have shown that, after chromium has been rendered ductile, subsequent heating in oxygen had little effect on ductility, while heating in nitrogen at temperatures as low as 650° C. makes the specimens completely brittle. Although this evidence might be construed as obviating the need for producing low-oxygen metal, the only room-temperature ductile chromium prepared thus far has been of low oxygen content.

One of the purposes of this investigation was to prepare quantities of chromium for use in further hydrogen treatment studies, but it was also aimed at correlating the variables that affect the purity of the electrodeposit primarily with respect to oxygen and nitrogen. The mechanism of the electrode reactions in the chromic-acid bath as used in this study has been the subject of many investigations, and their arguments have been summarized by Sully (11). No effort was made in this investigation to study this aspect of chromium electrodeposition. Instead, those factors were investigated which contribute to the efficient preparation of large quantities of massive deposits.

EXPERIMENTAL PROCEDURE AND DISCUSSION OF RESULTS

As this project developed over a period exceeding 2 years, many improvements were made in the operating procedure, and the equipment underwent several expansions. The first experimental run produced 5.5 grams of chromium, whereas some of the later runs yielded deposits weighing as high as 2,500 grams. A complete description will be given of the more recent equipment and procedure, since details of each modifications would have little additional value.

The most recent cell, which was used for many runs, is shown in figure 1. A steel shell 18 inches in diameter, 16 inches in height and 1/8 inch in wall thickness was lined with an unplasticized polyvinyl chloride liner that had a wall thickness of 1/8 inch. Preliminary work was carried out in pyrex containers, and a few runs were made in a steel cell lined with a heat-fusible rack coating designated by the manufacturer only as "PC-11", but the most satisfactory results were obtained with an unplasticized polyvinyl liner. The capacity of the cell was 42 liters. A 1-inch-thick micarta cover over the cell supported a condenser for cell fumes and also supported the cathode. The condenser consisted of 3 pyrex tubes 1 inch in diameter, all held inside of a 4-inch-diameter pyrex tube through which cooling water was circulated. The 1-inch tubes were loosely packed with scrap tantalum sheet to aid in condensing the chromic-acid vapors that were carried by escaping hydrogen and oxygen produced at the electrodes. Volatilization losses of chromic acid thus were eliminated almost entirely.

Direct current for the cell was supplied by a 4,000-ampere Henson-Van Winkle-Munning selenium rectifier.

The cathode was an aluminum pipe 6 inches in diameter, extending to within 1 inch from the bottom of the cell. An aluminum bus bar (6 inches by 6 inches by 1/2 inch) was welded to the pipe for connection to the power source. To insure adherence of the chromium deposit to the aluminum, the cathode was roughened by sand-blasting before each run, and, to facilitate removal of the deposit, the cathode was scored into 1-inch squares. Since the throwing power of chromic-acid electrolytes is low, a thinner deposit was obtained along the score marks, and the deposit could be removed from the cathode by a sharp blow with a hammer.

Lead tubing 3/4 inch in diameter and 1/4 inch in wall thickness was formed into a 16-inch-diameter coil and used as an anode. The flow of cooling water through the

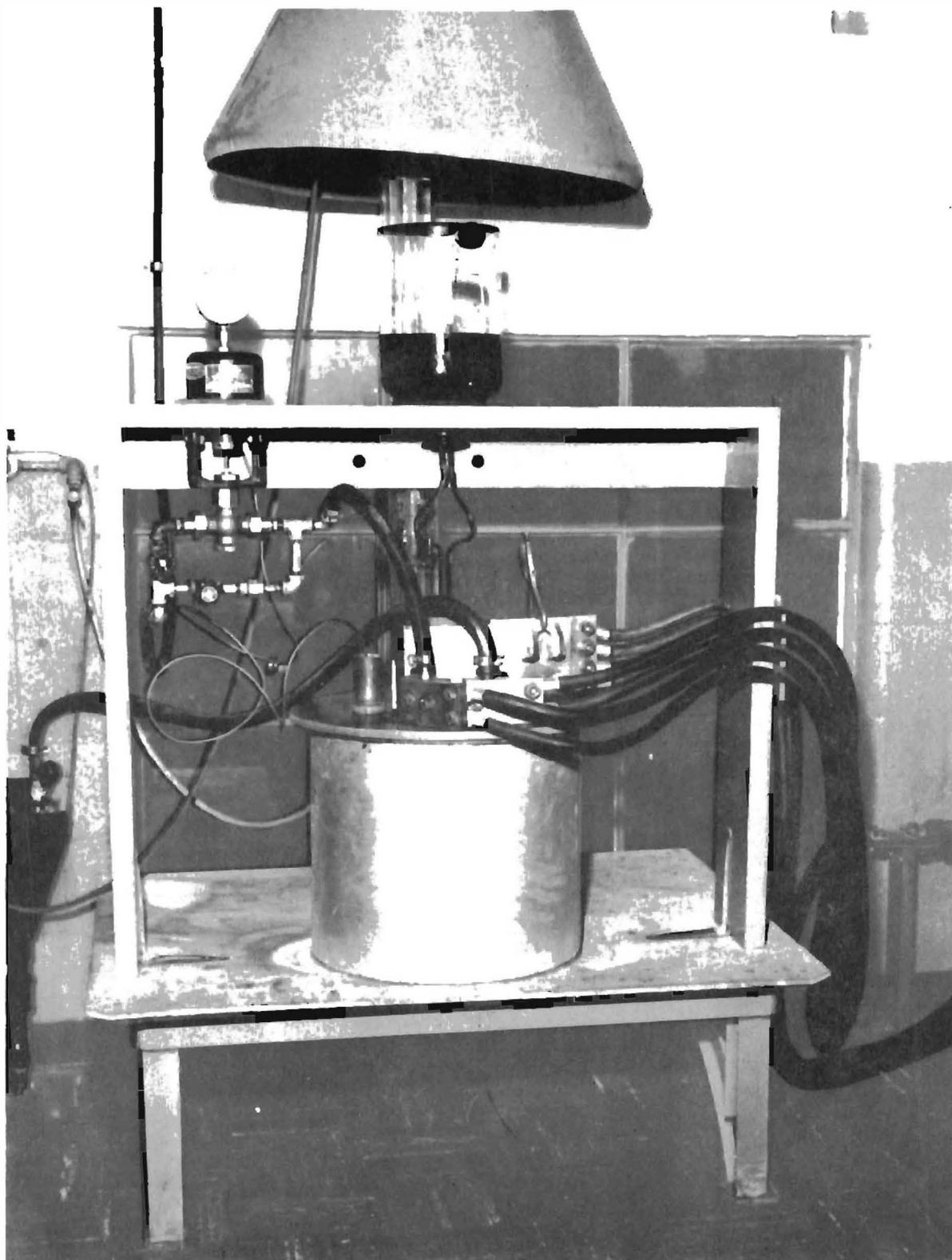


Figure 1. - Electrolytic cell.

anode for heat dissipation was regulated by a Powers regulator, the thermostatic bulb of which dipped into the electrolyte. A lead sheath around the bulb protected it from attack by the chromic acid. The regulator was adjusted to maintain the temperature of the electrolyte at $85^{\circ} \pm 4^{\circ}$ C. during operation. Maximum anode life was 360 hours as a result of the formation of lead chromate at the anode surface which subsequently flaked off.

The electrolyte contained 250 grams of chromic acid anhydride and 2.5 grams of sulfate ion (as sulfuric acid) per liter. This composition was maintained within 10 percent by checking the specific gravity of the electrolyte at least twice a day and adjusting the concentration of the feed solution accordingly. Sulfate analyses were made once a week.

An 8-liter bottle above the cell was used to supply chromic acid feed solution and to maintain the electrolyte in the cell at a constant level. Two pyrex tubes connecting the cell with the feed solution were arranged in such a manner that, as the level of the electrolyte dropped, air was admitted to the feed bottle, permitting the solution to flow into the cell.

Each run was continued 72 hours, after which the cathode was withdrawn and the deposit removed. The solid deposit was built up to a thickness of 1/16 to 3/32 inch in 72 hours. In addition, a large portion of the deposit was in the form of "tree-like" growths or dendrites. Since electrolysis for longer periods produced a higher ratio of dendrites to solid deposit (which was a disadvantage because of the higher oxygen content), it was of interest to examine the conditions that would produce a minimum amount of dendrites. During the first part of the project, the cathode current density was maintained at 1,100 amperes per square foot; later it was reduced to 800 and finally for the last 7 runs to 750 amperes per square foot. The effect of current density on the average ratio of solid deposit to dendrites is shown in table 1.

TABLE 1. - Average ratio of solid deposit to dendrites as a function of cathode current density

Current density, amp./ft. ²	Operating time, hours	Ratio, solid deposit to dendrites
1,100	1,224	0.71
800	984	1.11
750	504	2.06

To determine the ratio of solid deposit to dendrites as a function of time, one 96-hour run was made at a cathode current density of 800 amperes per square foot, in which the cathode was withdrawn after 48 hours and replaced with a second cathode for the last half of the experiment. The ratio of total solid deposit to total dendrites was increased to 2.44; however, since the thinner deposits obtained in 48 hours were extremely difficult to remove from the cathodes, additional runs under these conditions were not advisable.

Cathode current efficiencies were usually 8 - 9 percent, but on a few runs showed variations from 2 to 12 percent.

Most of the dendrites broke off from the cathode during operation and dropped to the bottom of the cell, where they became mixed with lead chromate that flaked off from the anode. Some lead chromate was also found on the surface of the solid deposit. This contamination was removed best by washing the deposit with nitric

acid, followed by washing with distilled water until the washings were neutral. Table 2 shows a typical analysis of an arc-melted sample of chromium that could be deposited consistently. In many runs a much purer deposit was obtained containing as low as 40 p.p.m. of oxygen in some instances and only traces of copper and magnesium.

TABLE 2. - Typical analysis of chromium cathode deposit

	Percent
Aluminum	0.001 - 0.01
Copper001
Iron001 - .01
Silicon001 - .01
Nitrogen	Less than 0.002
Oxygen:	
Solid deposit	0.015 - 0.02
Dendrites08 - .09
Hydrogen0005 - 0.001

In the above table nitrogen, oxygen, and hydrogen values were obtained by vacuum fusion analysis. The metallic constituents were determined spectrographically; however, it should be pointed out that the method was qualitative and the numerical values are listed only to show an approximate range. The as-deposited metal before arc melting was found to contain as high as 0.09 percent hydrogen. The low nitrogen content was of special interest in view of the deleterious effect of nitrogen on ductility (1,9,11).

Photomicrographs of solid deposits and dendrites shown in figure 2 further indicate the higher oxygen content of the dendrites.

To determine whether the dendrites were inherently higher in oxygen or if oxygen was picked up in treatment after deposition, three samples from one run were given different treatments as follows:

(1) Dendrites were taken from the cathode and washed with boiling water.

(2) Dendrites were hand picked from the bottom of the cell, given one short washing with nitric acid, then washed with boiling water.

(3) A regular sample from the bottom of the cell was leached thoroughly with two portions of nitric acid, then washed with boiling water.

Vacuum fusion analyses of the three samples indicated the following oxygen content:

<u>Sample</u>	<u>Oxygen, p.p.m.</u>
1	355
2	510
3	1,250

It appears from these results that treatment with nitric acid to remove lead chromate increases the oxygen content of dendrites, however, in spite of similar nitric acid treatment of the solid deposit, its oxygen content rarely was above 200 p.p.m.

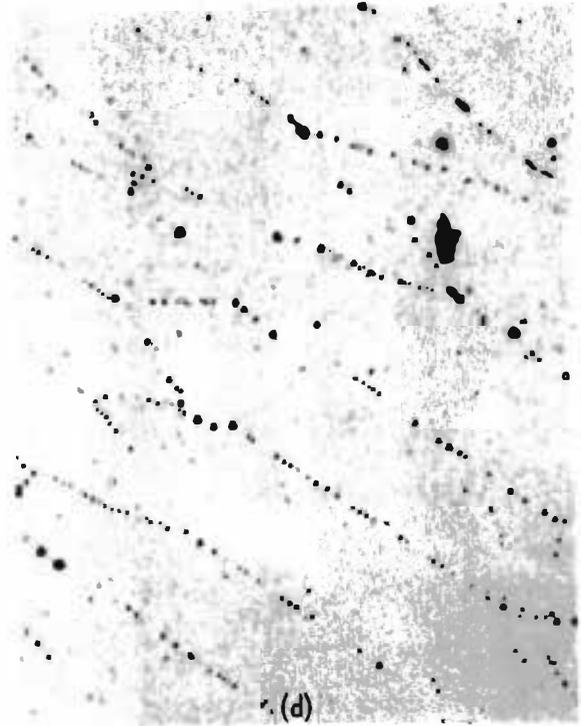
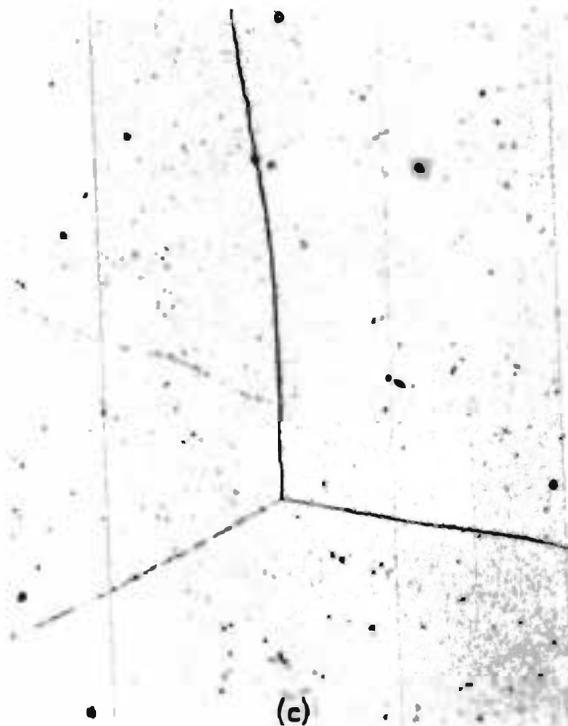
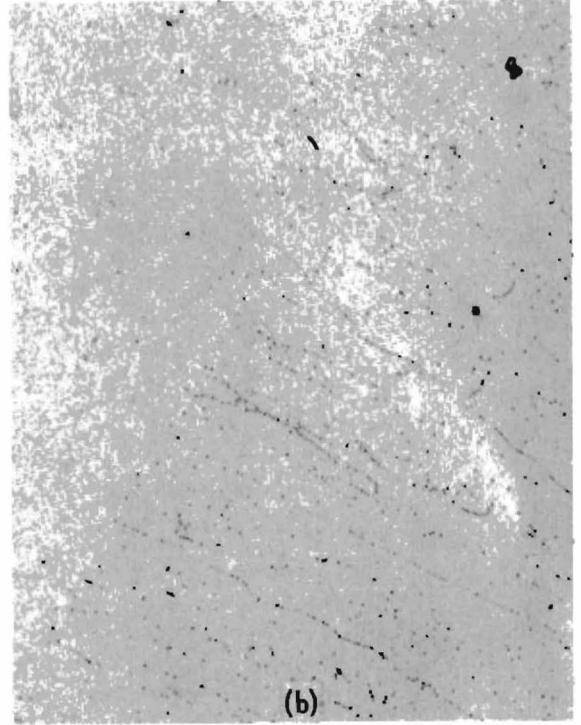
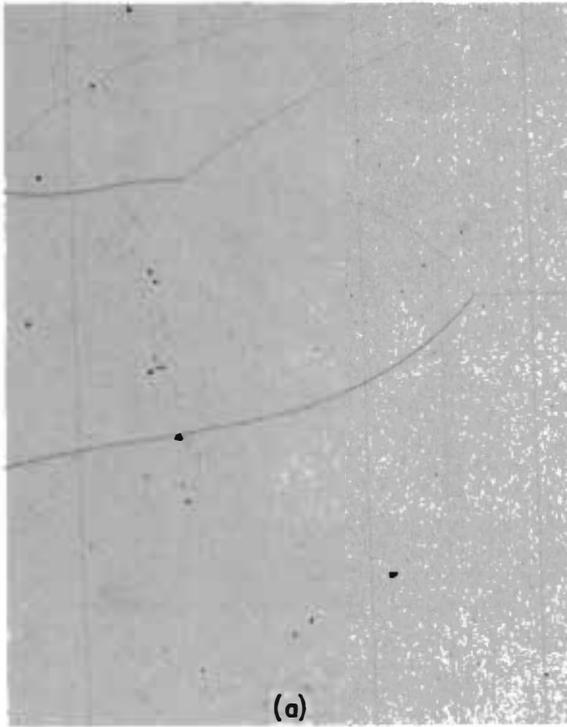


Figure 2. - Photomicrographs of arc-melted, as-cast chromium electro-deposits, chromic-acid electrolytic etch. (a) Solid deposit, 100X, 40 p.p.m. oxygen. (b) Dendrites, 100X, 600 p.p.m. oxygen. (c) Solid deposit, 500X, 135 p.p.m. oxygen. (d) Dendrites, 500X, 730 p.p.m. oxygen.

Purification of chromic acid solutions by ion-exchange resins was first reported by Costa (12) in 1950. Since then considerable work has been done on the removal of cation impurities as well as recovery of valuable chromates from rinse waters with ion-exchange resins (13,14), and such treatment has become accepted practice in many plating plants. A sulfonated polystyrene resin is generally used for removal of foreign cations.

Two cation exchange resins were tested to determine the extent to which they would be oxidized by chromic acid. Twenty-gram samples of resin were placed in test tubes and treated with 25 ml. of chromic acid solution in varying concentrations. After 24 hours the chromic acid solutions were decanted and analyzed for trivalent chromium. Table 3 shows the results of these tests. Both resins were of the sulfonated polystyrene type available commercially.

TABLE 3. - Oxidation of resin samples with chromic acid

CrO ₃ concentration, grams per liter	Cr ⁺⁺⁺ concentration after 24 hours, grams per liter	
	Resin A	Resin B
175	0.36	5.13
200	.71	6.77
225	.91	5.21
250	.78	9.53
275	1.24	11.67
300	1.75	14.79

To prevent a buildup of impurities in the electrolyte it was passed through a bed of cation-exchange resin after each 72-hour run. This resin was designated as resin A in table 3. The column is shown in figure 3. The resin was contained in a pyrex pipe 4 inches in diameter with a resin-bed depth of 30 inches. After the 42 liters of electrolyte was passed through the column, the resin was regenerated with 12 liters of 10-percent sulfuric acid. A sample of the regenerating acid from one of the runs, after passing through the resin, was evaporated to dryness and ignited. A qualitative spectrographic analysis of this material follows:

	Percent
Aluminum	1 - 5
Copper	0.1 - 1
Chromium	Over 10
Iron	1 - 5
Nickel	1 - 5
Silicon	0.1 - 1
Tin1 - 1

Near the end of the project a third resin was obtained and evaluated by the same technique as described above for resins A and B. No trivalent chromium was found in any of the chromic-acid solutions after standing in contact with the resin for 24 hours, indicating it to be highly resistant to oxidation. One resin has been reported to be stable in solutions containing 400 grams per liter of CrO₃ (15); however, attempts to obtain this material on the market were not successful during the course of the project.

Since chromium of exceptional purity was obtained in this work, it was of interest to compare some of its properties with chromium that was purified by hydrogen reduction.

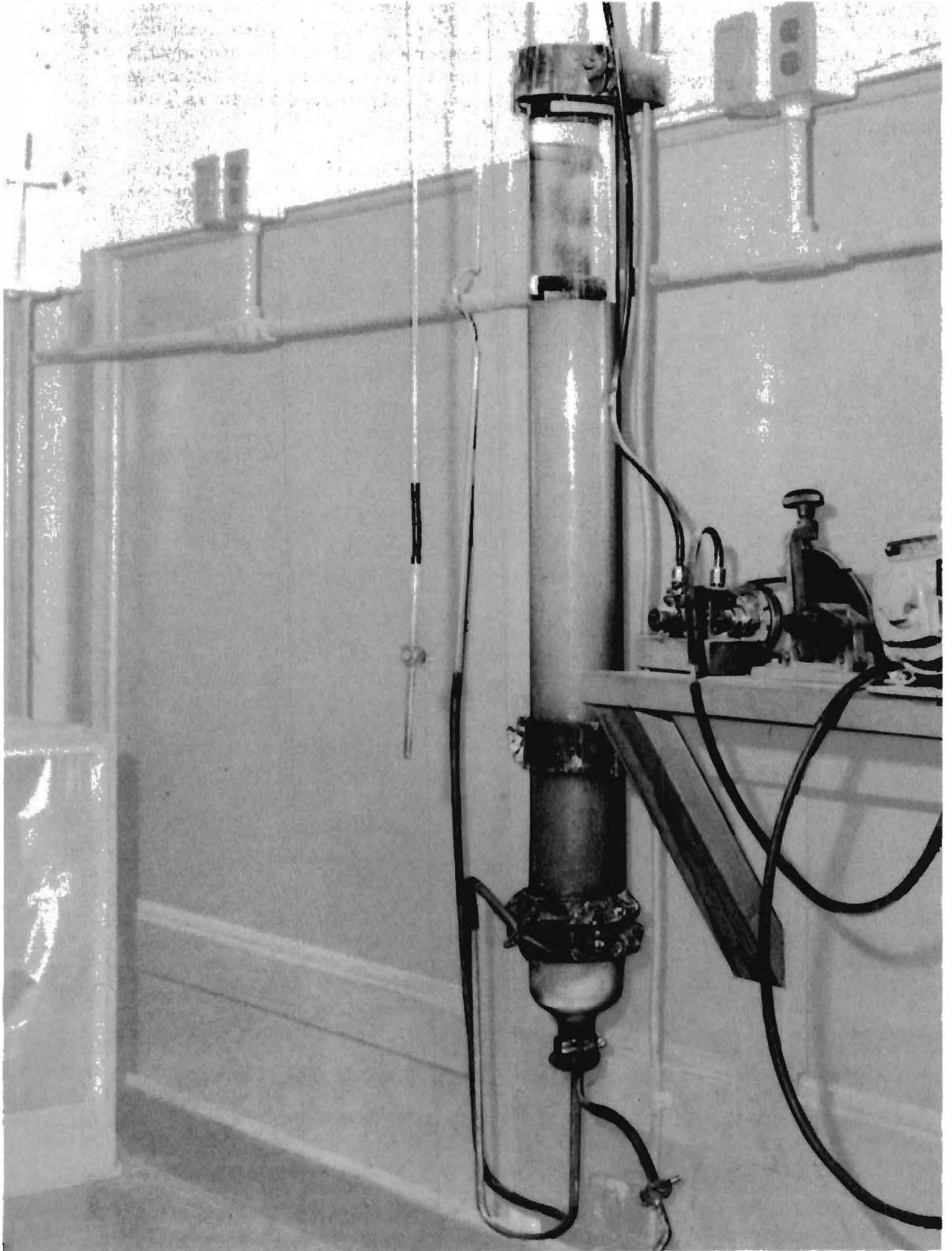


Figure 3. - Ion-exchange column.

Solid deposit from 2 of the runs totaling 1,900 grams, was crushed to minus-8-mesh, pressed into two 1 by 1 by 10-inch bars, and sintered in stagnant hydrogen at 1,200° C. for 8 hours. The bars were consumable-arc-melted into 2-inch-diameter ingots, press-forged in air to approximately 1-inch diameter, scalped, and then sheath swaged to 1/4-inch diameter rods. The rods were reduced 47 percent further by drawing through tungsten carbide dies at 400° C. Two tensile specimens were prepared from each ingot. Table 4 shows the results of tensile tests and analyses of the tensile specimens.

TABLE 4. - Results of tensile tests, 25° C.

Ingot No.	Specimen No.	Analysis, p.p.m.				Ult. tensile stress, 1,000 p.s.i.	Elongation, percent in 1 in.
		Vacuum fusion		Wet			
		O	R	N	N		
SA8826	1	245	6.7	50	40	68.6	10
	2					68.6	16
SA9050	1	80	10	50	60	71.0	5
	2					69.8	0

These results indicate that, at least in the case of the first ingot, ductility was achieved after the deposits has been consolidated and worked to wire. Further evidence of room-temperature ductility is shown by the fact that wire specimens from both ingots could be reverse-bent by hand repeatedly without fracture. Poorer ductility in the specimens from the second ingot might be explained by the increase of nitrogen content over the original electrodeposit. This increase may possibly have come about in the sintering and/or arc-melting steps. Figure 4 shows, from right to left, electrodeposit, pressed bar, arc-melted ingot, and cold ductile wire.

CONCLUSIONS

This investigation has demonstrated that chromium prepared by electrodeposition from chromic-acid solutions is pure enough for fabrication into cold ductile shapes without further purification. Nitrogen, which is currently considered to be the greatest single impurity affecting ductility, was held consistently below 20 p.p.m., the lowest detectable amount. By proper control of operating conditions the deposits contained in the range of 100 p.p.m. oxygen. The use of ion-exchange resins for purifying the chromic-acid electrolyte was found to be effective in removing all but trace amounts of some of the metallic contaminants.

Electrodeposition is a direct, effective method of preparing high-purity chromium. Although the current efficiency of this process is low compared with that obtained in present-day electrometallurgical practice, it appears much simpler than the more common technique for preparing high-purity chromium, which involves reducing the residual impurities in commercial grades of chromium with extremely pure hydrogen.

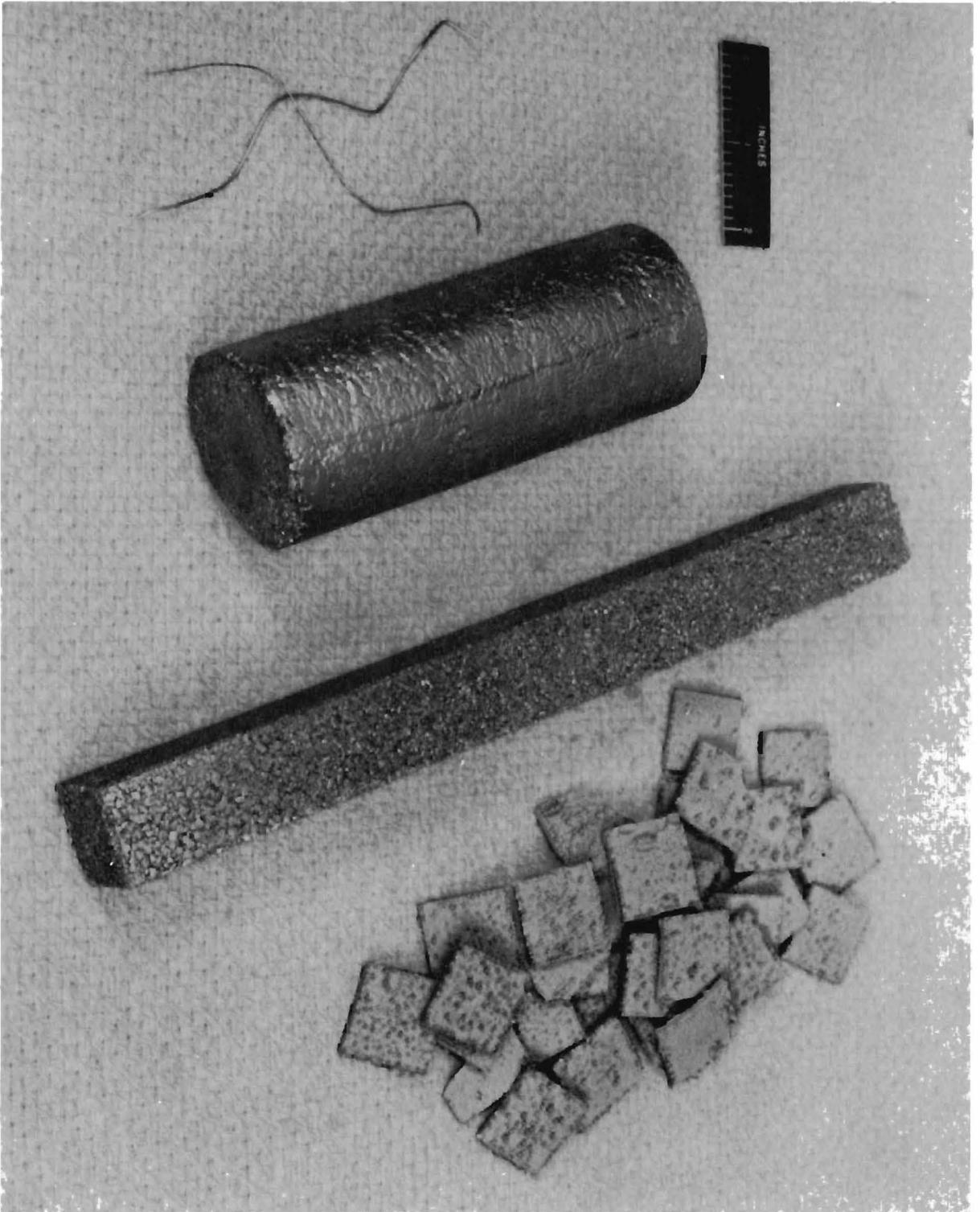


Figure 4. - Samples of electrodeposit, pressed bar, arc-melted ingot, and cold ductile wire.

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