

71-2920

4042-Fm/5

AD-A076049

WADC TECHNICAL REPORT 52-54

CATALOGED BY ASTIA
AS AT NO 159416

APPROVED FOR PUBLIC RELEASE-
DISTRIBUTION UNLIMITED

MALLEABLE CHROMIUM AND ITS ALLOYS

EARL T. HAYES
UNITED STATES BUREAU OF MINES

MARCH 1952 ✓

Reproduced From
Best Available Copy

WRIGHT AIR DEVELOPMENT CENTER

20020104147

79 10 25 092

NOTICES

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

The information furnished herewith is made available for study upon the understanding that the Government's proprietary interests in and relating thereto shall not be impaired. It is desired that the Office of the Judge Advocate (WCJ), Wright Air Development Center, Wright-Patterson AFB, Dayton, Ohio, be promptly notified of any apparent conflict between the Government's proprietary interests and those of others.

The U.S. Government is absolved from any litigation which may ensue from the contractor's infringing on the foreign patent rights which may be involved.

MALLEABLE CHROMIUM AND ITS ALLOYS

Earl T. Hayes
United States Bureau of Mines

March 1952

Materials Laboratory
Contract No. (33-038) 50-1084-E
RDO No. R605-227

Wright Air Development Center
Air Research Development Command
United States Air Force
Wright-Patterson Air Force Base, Ohio

FOREWORD

This report was prepared by the United States Bureau of Mines, Northwest Electrodevelopment Laboratory, Region II Albany, Oregon, under USAF Contract No. (33-038) 50-1084-E, during the period 15 September 1950 to 15 September 1951. The contract was initiated under Research and Development Order No. R605-227, High Temperature Materials and Application, and was administered under the direction of the Materials Laboratory, Research Division, Wright Air Development Center. The project engineer was Mr. I. Perlmutter.

Conduct of the research embodied in this report involved the special assistance of individuals too numerous to mention by name. Suffice it to say, the work would have suffered immeasurably without the exemplary cooperation of the staff of Albany station in general, and the Rare Metals and Physical Metallurgy Branches in particular.

Very special acknowledgment is made to Dr. W. J. Kroll, formerly consultant to this laboratory, whose enthusiasm and guiding genius permeated this work.

ABSTRACT

Improvements in production of high purity chromium metal by magnesium reduction of anhydrous chlorides and by hydrogen treatment of electrolytic chromium is reported.

The arc melting of hydrogen treated chromium has been accomplished and the forging, rolling, and swaging of this arc melted material has been successful.

Arc melted chromium has been forged at liquid air temperatures.

X-ray and metallographic studies indicated the recrystallization temperature of rolled chromium sheet to be about 750°C.

Experiments in drip melting, deoxidizing element additions, and treatment with molten calcium and calcium hydride are recorded. Brinell hot hardness values on arc melted chromium have been obtained at various temperatures up to 800°C.

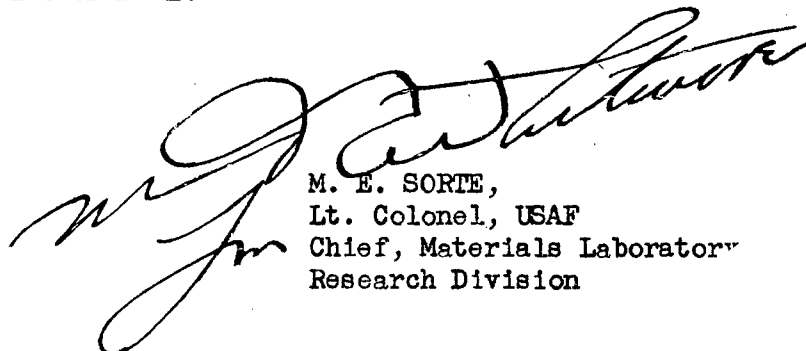
Preliminary investigation of hot bending characteristics of rolled chromium sheet shows the minimum bending temperature to be 325°C.

The heat resistance of chromium has been investigated.

PUBLICATION REVIEW

Manuscript copy of this report has been reviewed and found satisfactory.

FOR THE COMMANDING GENERAL:



M. E. SORTE,
Lt. Colonel, USAF
Chief, Materials Laboratory
Research Division

CONTENTS

	<u>Page</u>
Introduction	1
Chloride Process	2
Hydrogen Treatment Process	11
Forgeable Arc-Melted Chromium	17
Working of Chromium at Sub-Zero Temperatures	27
Miscellaneous Research	28
Ductile Chromium Metal	40
Summary	51
Bibliography	55

ILLUSTRATIONS

Figure

1.	Suction Device	6
2.	Chloride Sponge Chromium	8
3.	Hydrogen Treatment Furnace	13
4.	Arc-Melted Chromium Ingots	19
5.	As Forged Chromium Ingots	20
6.	As Cast Chromium Ingot	21
7.	As Cast, Worked, and Annealed Structures	22
8.	Arc-Melted Chromium Rolled at 800°C	24
9.	Arc-Melted Chromium Rolled at 500°C	25
10.	Hydrogen Treated Electrolytic Chromium	26
11.	Untreated Electrolytic Chromium	26
12.	Chromium Prepared by Magnesium Reduction of CrCl_3	26
13.	Goldschmidt Process Chromium	26
14.	Chromium Hot Bender	29
15.	Effect of Calcium Treatment	39
16.	Hot Hardness Worked Chromium Metal	44
17.	Hot Hardness As Cast Chromium Metal	45
18.	Chromium Cold Bender	46
19.	Drip Melter	47

INTRODUCTION:

The work reported herein is the result of research conducted over the period August 15, 1950 - August 15, 1951 by the Chromium Section of the Rare Metals Branch and the Physical Metallurgy Branch, U.S. Bureau of Mines, Northwest Electrodevelopment Laboratory, Albany, Oregon.

This is the log of the continuing effort to produce pure chromium metal on a scale such that research on high temperature chromium alloys and the concurrent investigations in the field of cold ductility of pure chromium metal may proceed without interruption.

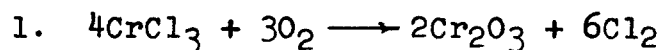
Beginning at the point described by Kroll and co-workers (1) (2), the processes and equipment employed in converting electrolytic chromium metal into a purified useable product have been refined. The previous hypothesis that much of the problem involved in producing a ductile metal lies in the removal of oxygen has been accepted. Investigations have continued on magnesium reduction of purified chromium chlorides and hydrogen reduction of powdered

electrolytic chromium plate.

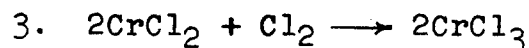
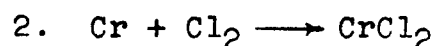
CHLORIDE PROCESS:

The well-known Kroll process for producing ductile titanium and zirconium is not applicable to chromium as no stable salt is found which will sublime or distill free from oxychlorides in a useable temperature range. Kroll has shown, however, the possibility of employing a reaction of the type described by Troost (3) and Von Zepplin (4) in the magnesium reduction of chromium chloride in a carrier bath of KCl-NaCl. Since the reduction techniques have been well established, the main effort here was directed to the problem of producing very pure chromium chlorides and transferring them into the reduction vessel in a pure, dry condition.

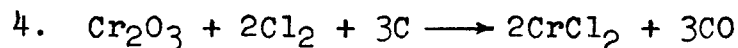
Anhydrous chromium dichloride CrCl_2 is a white, extremely hygroscopic salt, and cannot be exposed to atmospheric moisture if an oxide-free condition is to be maintained. Anhydrous chromium trichloride is a deep purple salt which is insoluble in water. However, it exposes so much surface by its flaky structure that adsorption and mechanical entrapment of contaminating gases such as oxygen and water vapor is unavoidable; hence any process for production of very pure CrCl_3 is defeated in its purpose by even momentary exposure to air. Further, upon heating, CrCl_3 vapor is known to oxidize in air according to the reaction:



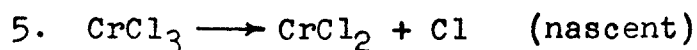
For the purposes of this work, the chromium chlorides were protected, hot or cold, by means of a fused chloride carrier salt. The chlorides were prepared by fusing 600 grams KCl with 400 grams NaCl in a 6-inch diameter graphite crucible and adding 600 grams of chromium metal and 1.5 pounds of chlorine gas over a period of 6 to 8 hours. Heating was accomplished by means of a bed of resistor carbon energized by a 500 ampere welding machine. The chromium was readily attacked by chlorine under these conditions as follows:



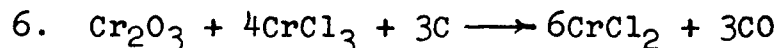
The 1 to 2 percent of contained green oxide, Cr_2O_3 , became suspended in the bath, however, and was possibly chlorinated as follows:



but:

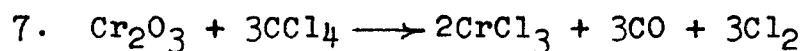


As shown by Maier (5) reaction 5 above may be expected under the conditions of operation and the nascent chlorine formed at the interface of the graphite container would give the following reaction:



In practice reaction 6 was better than reaction 4 since the chlorine was very active and "in solution" at the

carbon wall. To capitalize on this a small amount of CrCl_3 was added to the bath initially to initiate and speed the chlorination. Still more effective chlorination was possible with carbon tetrachloride in accordance with the reaction:



It was found, however, that the carbon tetrachloride also decomposed, giving by-products which further on in the process caused serious explosions.

The low melting 60-40 KCl-NaCl mixture was miscible in all proportions with CrCl_2 but could not dissolve more than 50 percent CrCl_3 . If more than 50 percent CrCl_3 was added the bath became viscous, and if the temperature was raised the CrCl_3 sublimed out rapidly.

The condition of the bath near the end of the run was determined by pipetting out a small sample of the salt mixture with a quartz tube and dissolving the salt in water. If any turbidity due to dispersed oxide was noted chlorination was continued. This was repeated until a perfectly clear solution was obtained. The chlorination was then terminated and the batch prepared for loading in the reduction retort. This was done in either of two ways. Originally, the batch was allowed to cool under helium in place in the chlorination furnace, and when cold, the graphite crucible was placed directly in the reduction retort with the required amount of magnesium. This procedure suffered from the drawback of having present in the reduction crucible

the non-chlorinated residues and stray foreign matter, such as carbon, inevitably picked up during chlorination. Separation of the clean salt mix from the extraneous material was later achieved in two ways. The first involved drilling a hole in the bottom of the chlorination crucible and placing it directly over another graphite crucible containing the magnesium. The assembly was then placed in the reduction retort and heated in helium. Upon reaching a temperature of approximately 650° C., the salt poured through the hole into the crucible containing the magnesium, leaving the contaminating materials behind. This method had the drawback of requiring twice the space required for reduction of a given quantity of chromium chlorides, hence a method was devised in which the separation of the pure salts from the flotsam and dregs was accomplished immediately following the chlorination. This had the added advantage of obtaining the salts for use immediately without a lengthy cooling time in the chlorination furnace. This procedure was carried out by means of a suction device as shown in Figure 1.

All portions in contact with salt were of graphite while the outer shell was of iron for strength. In operation the device was used with a small vacuum pump and vacuum tank connected to the exhaust line at top "A". The vacuum tank was evacuated and sealed off with cocks. The device was then inserted to the proper depth in the salt bath and the

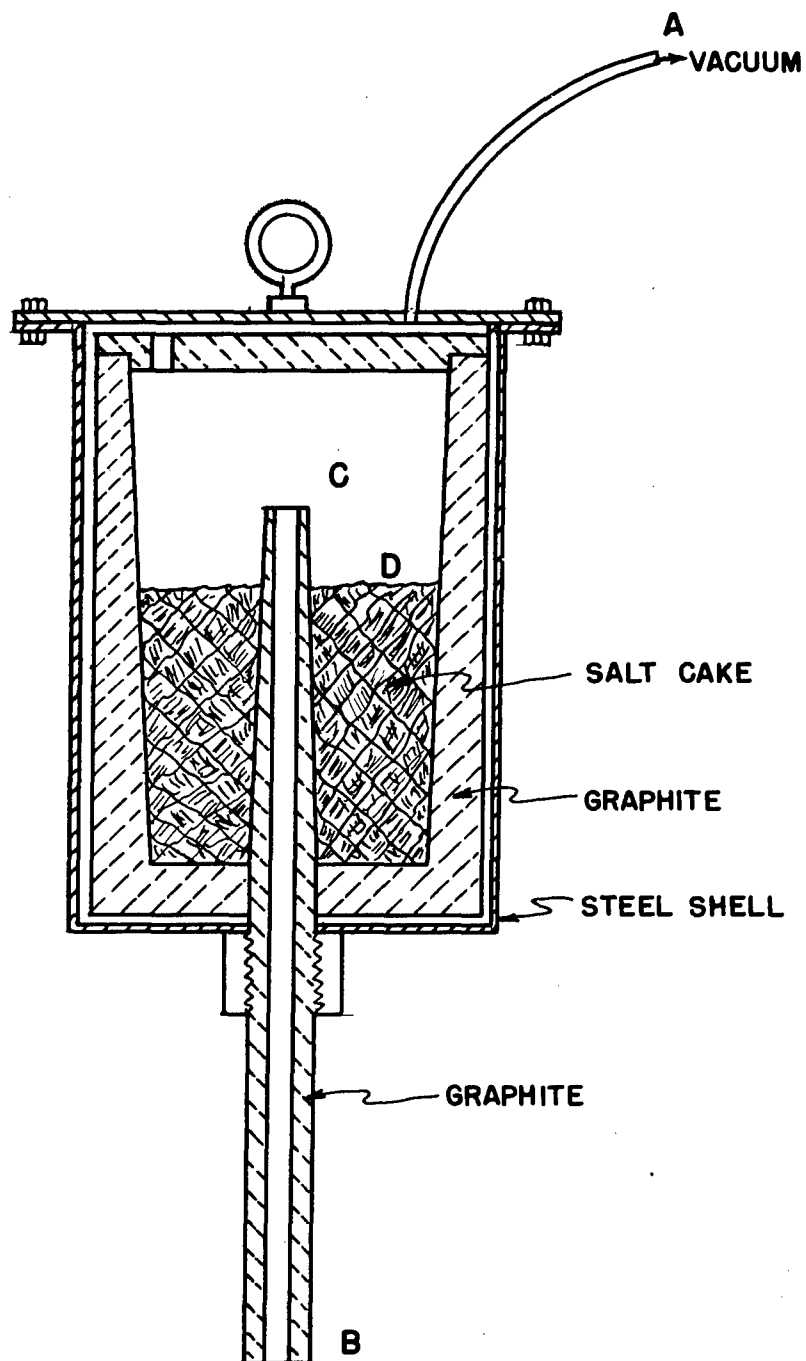


Figure 1 SUCTION DEVICE

line opened to the vacuum tank. The salt rose through the tube, "B-C", spilled over and filled to "D". Any air which was drawn through after the salt was thus harmlessly led off without being bubbled through the melt. When cool, the cake was easily removed for reduction.

Prior to the reduction a sample of the cake was analyzed for chromium content and this figure used for computing magnesium requirements. A 10 percent excess of magnesium was used; any larger excess of magnesium was avoided because of the serious flash fires which occurred when the reduction retort was opened upon completion of the run. The occurrence of these flash fires plus violent explosions which were possibly coincidental with the use of CCl_4 in the chlorination process made the removal of the chromium batch from the reduction retort quite hazardous. The reason for the explosions has not been found, although from the nature of the blasts there is evidence of formation of some unstable compounds such as sodium, potassium, or magnesium carbides.

The chromium as obtained from the reduction process was light grey in color and had a spongy appearance. Frequently the entire mass was laced with long hairlike crystals and occasionally clumps of these long crystals agglomerated into a ball of "wool". A typical example is shown in Figure 2.

The sponge metal was analyzed by wet methods and the spectrograph. In general, the spectrographic method



Figure 2 -- Chloride Sponge Chromium $1\frac{1}{2}X$

showed much lower impurities than wet methods, which is to be expected when dealing with virtual trace impurities. In a typical batch (Cr 19) the spectrograph showed Al, Ca, Fe, Ni, Si, Ti, and Zr each to be less than 0.01 percent. Magnesium was found to be about 1 percent.

Chemical analysis was as follows:

Fe	--	0.01 %
Mg	--	1.1
Cr ₂ O ₃ (insol)	--	0.81
Chloride	--	0.039

Considering the low chloride value, the magnesium

was judged to be present as the oxide. This postulate was born out by microscopic examination which showed small inclusions of white material.

In order to remove this magnesium oxide and to lower the chloride content the sponge was crushed and agitated for three hours in 30 percent nitric acid. The powder was then rinsed and decanted until the washings were neutral and then vacuum dried. The final product contained less than 0.05 percent magnesium.

The analyses for oxygen in chromium were made by the method of Adcock (6) in which chromium metal is dissolved in dilute hydrochloric acid and the residue fired and weighed as Cr_2O_3 . Later this method was found to be inaccurate as an analytical method for oxygen in chloride chromium, since the entire operation of the chlorination and reduction process was carried out in graphite and the formation of some chromium carbide and/or mechanical inclusion of carbon in the sponge was to be expected. The effect of chromium carbide on the Cr_2O_3 value was discovered when a sample from a routine preparation of chromium carbide Cr_4C by reaction of pure Cr_2O_3 briquetted with the exact stoichiometric quantity of carbon and heated to the melting point (1530°C.) was analyzed for Cr_2O_3 . The material was found to be insoluble in dilute hydrochloric acid and the resulting report indicated the material to be more than 100 percent Cr_2O_3 . The chromium carbide would of

course present a sizable gain on ignition and give completely erroneous results. Other impurities also contributed their share to the rejection of this method of analysis. Silica for example, would be read as insoluble Cr_2O_3 , as would iron oxide, chromium chloride and any chromium metal difficultly soluble in hydrochloric acid. It was significant that the leach process for removal of magnesium from the sponge metal usually decreased the Cr_2O_3 values. This may be attributed to the decantation step in the leaching in which the colloidal fines of the sponge were discarded. These fines were presumed to be carbon and chromium carbide.

For these reasons and others the oxygen analysis was abandoned and the determination of the quality of chromium produced by the chloride process was made by processing of a single 50 gram briquet from each batch through to finished sheet which was examined physically as a criterion of quality. Sixty-two runs were made and sheet of varying quality obtained. Description of the chromium made by this process will be found under section of this report on "Ductile Chromium Metal".

The termination of production of chloride chromium was attendant upon three factors: little further improvement in quality noted at 500 gram batch level, exhaustion of supplies of very pure nodular electrolytic chromium used as starting material, and the increasing hazard of unexplained explosions mentioned above. Another reason available in

retrospect was the inordinate labor required in production of one pound of metal by this process as compared with hydrogen treatment of electrolytic chromium metal.

HYDROGEN TREATMENT PROCESS:

As reported by Kroll (1) (2) zirconium hydride was used simultaneously as a circulating pump and "getter" for hydrogen treatment of electrolytic chromium powder. The simple apparatus described in (1) was elaborated to the ingenious device in (2), where two furnaces containing ZrH_2 were heated and cooled alternately to maintain a flow of dry pure hydrogen through the treatment furnace. The improved hydrogen treatment apparatus still suffered from several serious drawbacks: (1) large quantities of rubber tubing through which oxygen and other gases could diffuse served to conduct the purified gases, (2) rubber stoppers were used to close hot tube ends, and (3) the alternate heating and cooling cycles were very injurious to the refractory tubes containing the zirconium hydride and frequent replacement of these tubes was required. Despite excellent properties of zirconium as a getter, the efficiency was severely impaired by films of nitride and oxide and frequent replacement of getters due to poisoning was necessary. This latter difficulty was aggravated by the presence of more than usual amounts of water and nitrogen in the cylinder hydrogen available to the laboratory.

Flow rate of hydrogen over the chromium was insufficient for reduction of more than test sample amounts and as a consequence reduction times were unduly long.

These and other difficulties were solved by the following improvements: all hydrogen conducting tubing was replaced with Tygon and copper tube and all joints were hard or soft soldered depending on frequency of disassembly required. Use of rubber stoppers as closures for the refractory tubes was discontinued and water-cooled heads of brass installed. The alternate cycle hydride pumping system was replaced by a standard type diaphragm displacement pump. Pump and motor were totally enclosed in a steel box with rubber explosion lid. A positive pressure of hydrogen from the gasometer was fed into the pump box to provide a hydrogen atmosphere to the pump in case of minor leaks. A palladium catalyst type purifier was used in the supply line from the hydrogen cylinder in conjunction with a phosphorus pentoxide tower to remove contained oxygen as water. A single 2-inch tube furnace holding zirconium-titanium alloy getter did the main gas cleanup job, and a small amount of the same material was used as a final getter for the gas entering the reduction furnace. Zirconium-titanium (50-50 mol percent) alloy was found to exhibit somewhat lower temperature gettering properties, particularly in regard to nitrogen, than the straight zirconium previously employed.

Figure 3 gives a general view of the installation.

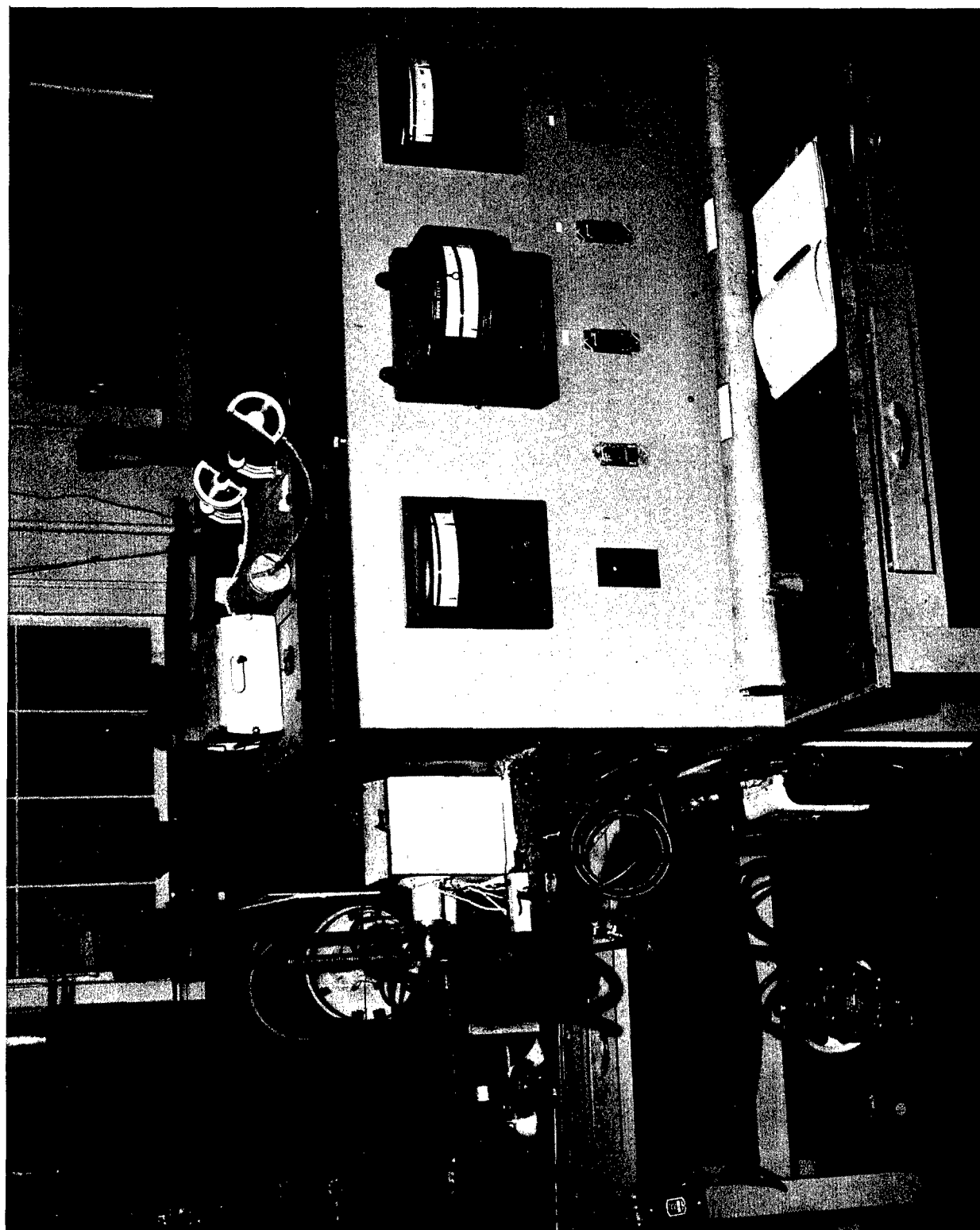
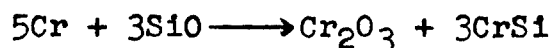


Figure 3 -- Hydrogen Treatment Furnace

The operation of the new hydrogen treatment furnace was found to be exceptionally free of difficulties. Initial runs indicated the flow rate of hydrogen to be high, so heat exchangers were placed on the exit ends of the hydride and treatment furnaces to protect the connections.

With this equipment 1500 grams of powdered chromium may be processed in a 48-hour cycle. At present two runs are made each week.

Redrying the hydrogen in circulation is an essential part of the deoxidation process. At 1000° C. Cr_2O_3 will not be reduced by hydrogen containing more than 0.05 volume percent water according to the figures of Koebel (7). More rapid reduction could be accomplished by increasing either the temperature or the rate of flow of the hydrogen but a practical limit exists for both. In the case of temperature the refractory enclosing the chromium must be considered. Pure quartz tubing is readily attacked by hydrogen at temperatures above 1200° C., and the silicon monoxide formed reacts with the chromium probably to form Cr_2O_3 again and chromium silicides. Kroll (2) suggests the reaction:



Unfortunately, X-ray examinations of chromium with known 0.1 percent silicon showed no lines other than chromium and Cr_2O_3 . The present experiments were carried out in the vicinity of 1200° C. and silicon contamination was raised by a factor of three to about 0.15 percent in some cases.

Attempts to deoxidize above 1200° C. showed severe contamination of the chromium by silicon.

Rapid circulation of hydrogen tends to remove water as fast as formed but here too a maximum has been reached. Earlier experiments showed that the use of flowgages in the hydrogen lines impeded the flow due to the characteristics of the flowgages and the relatively low pressure present in the system. Pressure measurements in early equipment showed the hydrogen pressure in the system to be very low and the reduction tube actually was under slight vacuum which gave rise to frequent losses due to leaks.

With positive pumping a pressure of 11 to 18 mm is maintained throughout the system which assures no contamination due to leaks.

By furnishing the pump with a large volume of helium from a meteorological balloon and trapping the gas pumped through the system by displacement of water, the rate of flow was determined to be approximately 25 liters per minute S.T.P. This indicates that 12 liters of dry hydrogen pass over the chromium in each tube every minute which should satisfy any equilibrium reaction requiring a minimum concentration of moisture over the chromium.

Although the drying efficiency of the zirconium-titanium getter is excellent in the 900° C. range, a calculation shows that a 1000 gram batch of chromium of about

1 percent Cr_2O_3 content would produce upon reduction about 3.75 grams of water. Close to this amount of water was collected by inserting a "U" tube cold trap in the return line with dry-ice-acetone coolant and weighing the trapped water. This water produced by the reduction ordinarily was removed by the phosphorus pentoxide tower, zirconium-titanium main getter furnace, and zirconium-titanium muff furnace, in that order. With the treatment of larger batches the replacement of the getter became so frequent and expensive that in the new equipment a dry ice-acetone trapping arrangement was made part of the permanent installation. The getter is now replaced only infrequently and then at the first sign of slight discoloration, thus insuring optimum gettering efficiency. Swelling of the hydride due to reaction with water and consequent cracking of the porcelain tubes which plagued the earlier hydrogen treatment equipment has been avoided with these cold traps.

As a consequence of the improved design an apparatus is now available in which sufficient quantities of high grade chromium for metallurgical studies may be produced. It is felt that for the present any important improvement in purity of the treated chromium will come as a result of purer electrolytic chromium employed as starting material rather than in furnace improvement. Good quality electrolytic chromium produced at the Boulder City, Nevada station of the Bureau of Mines is being used at present. A descrip-

tion of the manufacture of this product has been published recently (8).

FORGEABLE ARC-MELTED CHROMIUM:

The use of the electric arc in preparation of samples of various refractory metals is well known. Possibly the earliest successful application of this method was to the difficultly fusible metal tantalum by von Bolton (9). In 1941 Kroll (10) published results on the first successful arc melting of titanium and in 1946 the melting of zirconium (11). With the work of Parke and Ham (12), Simmons, Greenidge and Eastwood (13) and Herres and Davis (14) the arc melting of refractory metals came of age. More recently work has been reported by Kinzel on vanadium (15), and by Goodwin and Greenidge on tungsten (16).

Chromium, molybdenum and tungsten are members of the 6th group in the periodic table. The story of the winning of tungsten suitably ductile for lamp filaments is now well known. More recently the success in obtaining arc melted molybdenum sufficiently ductile to be worked hot or semi-hot to useful forms has been reported (17). Despite the growing body of information on arc melting techniques, the application of this method to chromium produced uniformly poor results or failed completely. Attempts to arc melt chromium in a button type arc furnace failed to give a material which could be forged or formed hot.

Chromium has an unusually high vapor pressure at its melting point. According to Espe and Knoll (18) chromium exhibits a saturation pressure of about 80 mm near its melting point of about 1900° C. Aluminum at 1900° C. has about the same saturation pressure. Kroll (19) used this high vapor pressure of chromium to produce pure metal by distillation in vacuum.

Since the vapor pressure at the melting point was known to be high, early failures in arc melting chromium were attributed to the high vapor pressure and some belief existed that it would be impossible to arc melt chromium for this reason. Attempts on a 20 gram scale in the above-mentioned button furnace with a variety of types of chromium metal over a period of more than a year seemed to bear out this conclusion. It has since been found, however, that more complete reduction of the metal results in a corresponding improvement in melting characteristics.

Trapping the exhaust vapors from the reduction gave a method for consistent check on the extent of reduction of the metal. The treatment time of 8 hours at 1200° C. which had been standard was lengthened to 16 hours at 1200° C. to find the extent of further reduction. Whereas a normal reduction run on 1000 grams of chromium for 8 hours produced about 2.50 grams of water in the "U" tube trap, the additional 8 hour treatment at 1200° C. produced about 0.95 grams of additional water. The best value for Cr_2O_3 obtained on

the starting material was 1.07 percent insoluble Cr_2O_3 , which would represent 3.75 grams of water. Summing the weights obtained in 16 hours reduction gives 3.45 grams or 92 percent of theoretical. Whereas 8 hour treated chromium had uniformly resisted arc melting or hot forging, 16 hour chromium was found to arc melt easily and by careful hot forging it was possible to effect a 60 percent reduction in thickness on a one-inch high ingot without cracking. Some typical arc melted ingots (about 450 grams each) are shown in Figure 4.

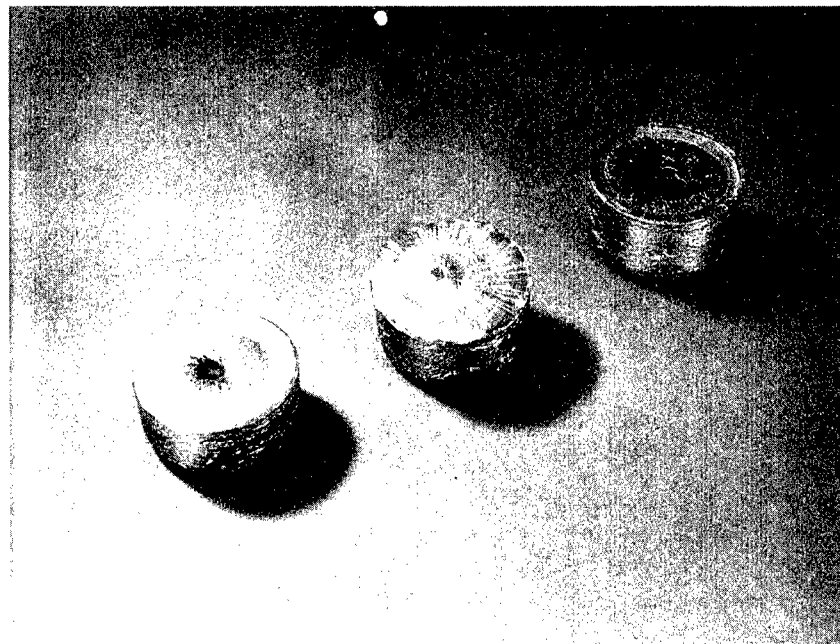


Figure 4 -- Arc Melted Chromium Ingots
As cast 2 inches in diameter, about 450 grams

Typical forged ingots are shown in Figure 5.

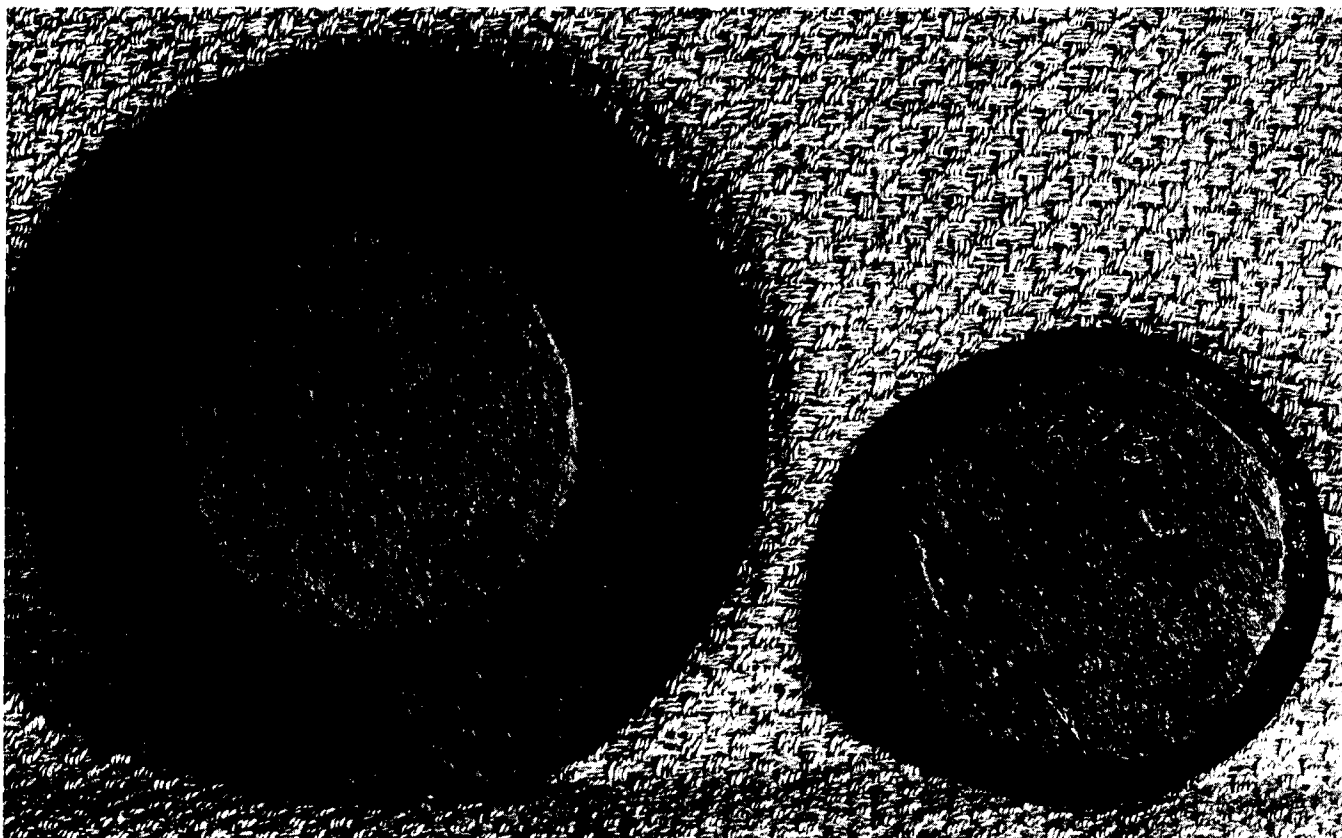


Figure 5 -- As Forged Chromium Ingots

, Forged at 900° C. to 50% reduction

At left -- iron collared ingot

At right -- uncollared ingot

Rough appearance due to slag from
collar hammered into surface

1X

The typical arc cast structure illustrated by vanadium (15) is also exhibited by chromium as shown in Figure 6.



Figure 6 -- As Cast Chromium Ingot

Section through center polished
and etched with aqua regia. 1X

It is found that a 25 percent forging followed by recrystallization gives good grain refinement as shown in Figure 7:



Figure 7 -- As Cast, Worked, and Annealed Structures
Left to right - As cast, as forged 25% reduction,
and as recrystallized from forging 25% reduction.
Annealed one hour at 1200° C. in hydrogen.
Etchant aqua regia. 2X

One peculiarity noted to date is that forging has been successful only in the direction of the casting of the metal. All attempts to forge across the grain have been unsuccessful.

Rolling sheathed, forged chromium at 800° C. presented difficulties due to the large grain size. The apparent effect of rolling was to lay the large crystals down producing a curious scaly appearance. A typical sample is shown in Figure 8.

The difficulty was overcome by annealing the rolled sheet at 1200° C. in helium for one hour, then re-rolling at 500° C. This rolling produced good sheet. The microstructure of this sheet is shown in Figure 9.

Metallographic examination of approximately 40 specimens prepared by arc melting compacted chromium powder showed the presence of oxides in the grain boundaries and often in the grains themselves.

Electrolytic powder which had been hydrogen treated was consistently cleaner than the metal produced by magnesium reduction of the chloride. Arc melted, hydrogen treated, electrolytic powder often showed no grain boundary inclusions and from this standpoint gave promise of being more ductile than the metal prepared by magnesium reduction of the chloride.

Figure 10 shows the appearance of the arc melted electrolytic powder which had been hydrogen treated. The

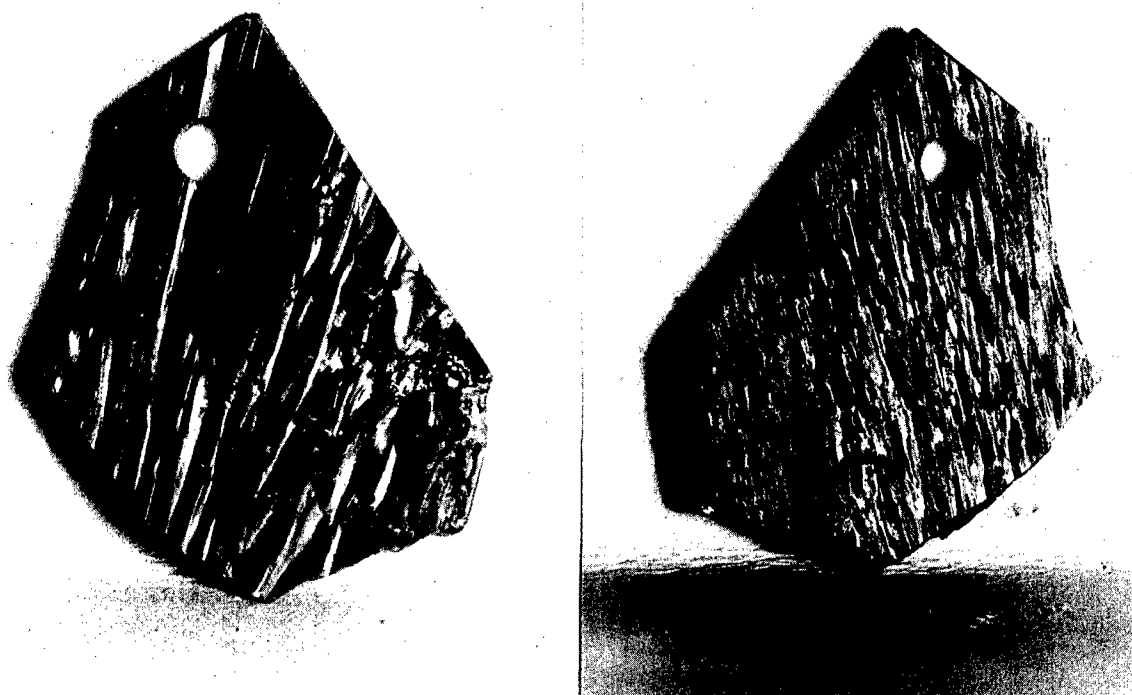


Figure 8 -- Arc Melted Chromium Rolled at 800° C.

Left -- as rolled surface showing columnar grain structure still retained.

Right -- reverse side ground and etched with aqua regia. $1\frac{1}{2}X$

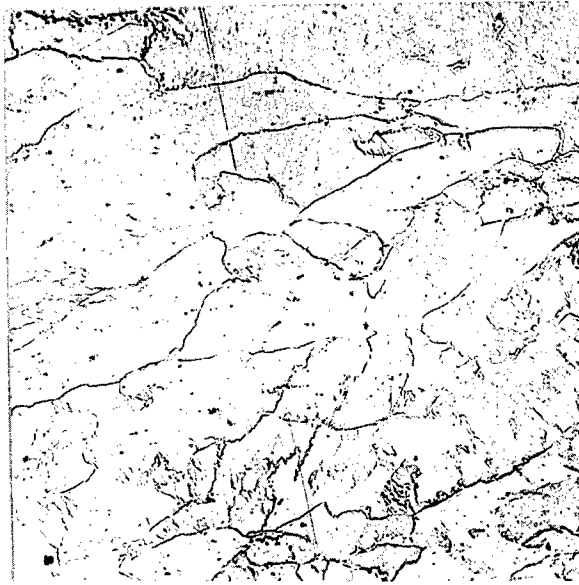


Figure 9 -- Arc Melted Chromium Rolled at 500° C.

Microstructure of material show in Figure 8 annealed at 1200° C. in hydrogen, sheathed, and rolled at 500° C. Annealed at 1200° C in helium. 150X

small amount of grain boundary material present is in marked contrast to the same base material, Figure 11, before the hydrogen treatment.

Figure 12 shows a section of an arc melted button of magnesium reduced metal. This specimen contained appreciably more oxide inclusions than the Goldschmidt reduced metal shown in Figure 13.

The hardness of the four types of metal varied widely, and no definite pattern was established.

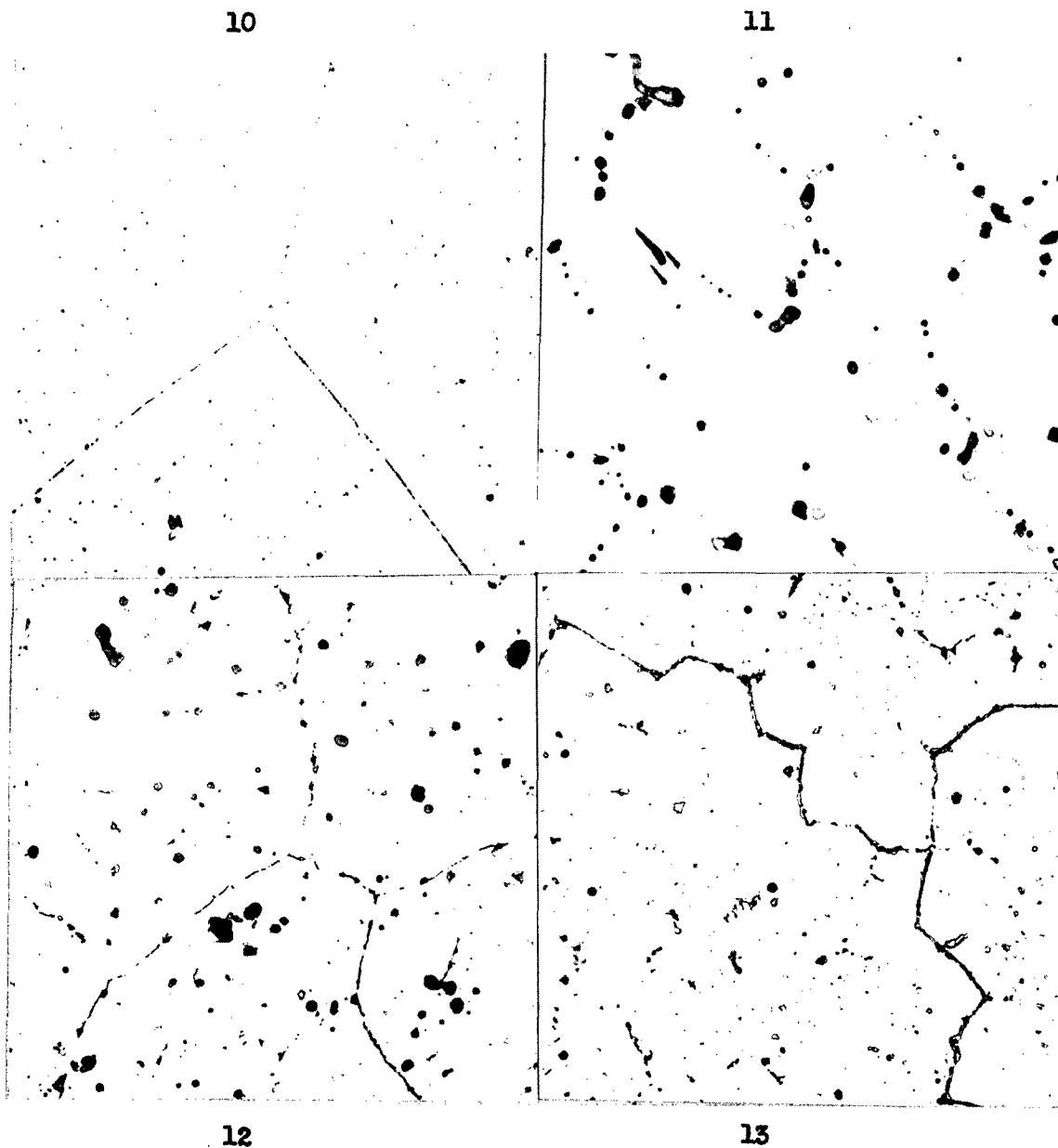


Figure 10 -- Hydrogen Treated Electrolytic Chromium

Figure 11 -- Untreated Electrolytic Chromium

Figure 12 -- Chromium Prepared by Magnesium Reduction
of CrCl_3

Figure 13 -- Goldschmidt Process Chromium

Electrolytic etch -- all magnifications 500X

WORKING OF ARC-MELTED CHROMIUM AT SUB-ZERO TEMPERATURE:

Two experiments were conducted on working arc-melted chromium at liquid air temperatures (about -190° C). Fifty gram arc-melted buttons of hydrogen reduced chromium were machined to cylinders about $3/4$ inch diameter by $3/8$ inch thick and placed in restraining rings of mild steel about two inches external diameter. The assembly was then cooled in liquid air and forged with about five percent total reduction before returning to the liquid air. One button was reduced approximately 60 percent before failure occurred. Another button was reduced 39 percent to a finished thickness of 0.21 inch and macroscopically appeared to be in excellent condition. This piece was rolled with reductions of one percent per pass with cooling between each roll pass. After a reduction of four percent, surface cracks were apparent and both the restraining ring and chromium cracked badly during the next reduction step.

This ductility at sub-zero temperatures cannot be reconciled with the room temperature brittleness and the fact that it was necessary to work chromium above 500° C. to obtain the necessary plasticity for deformation. Several investigators have reported that some physical properties such as susceptibility and electrical resistivity undergo a change in the neighborhood of 37° C. but no evidence has been forthcoming to show an accompanying change in crystal structure. A possible explanation of this behavior is that

a low temperature transformation occurs in chromium and that the low temperature form is ductile.

MISCELLANEOUS RESEARCH:

The efforts recorded concerning production of ductile chromium from chromium chlorides and the hydrogen treatment of high purity electrolytic chromium have constituted the main work of this project. However, three other techniques were investigated:

- I. Drip melting of chromium in helium and hydrogen.
- II. Deoxidation of chromium by trace additions of certain metals.
- III. Treatment with calcium metal and calcium hydride.

I. DRIP MELTING

Since the reduction of Cr_2O_3 by hydrogen is favored by high temperatures the optimum condition would be the actual fusion of the metal in an atmosphere of pure hydrogen. A plan of the apparatus used for accomplishing this is shown in Figure 19.

A bar of chromium $1/2$ inch square and 8 inches long formed by compressing chromium metal powder in a die and sintering in hydrogen, was suspended by a tungsten wire from a windlass which imparted rotary movement through a vacuum seal. With the bar suspended on this wire inside the hydrogen filled quartz tube the operator was able to lower the metal into the field of the high frequency coil at will,

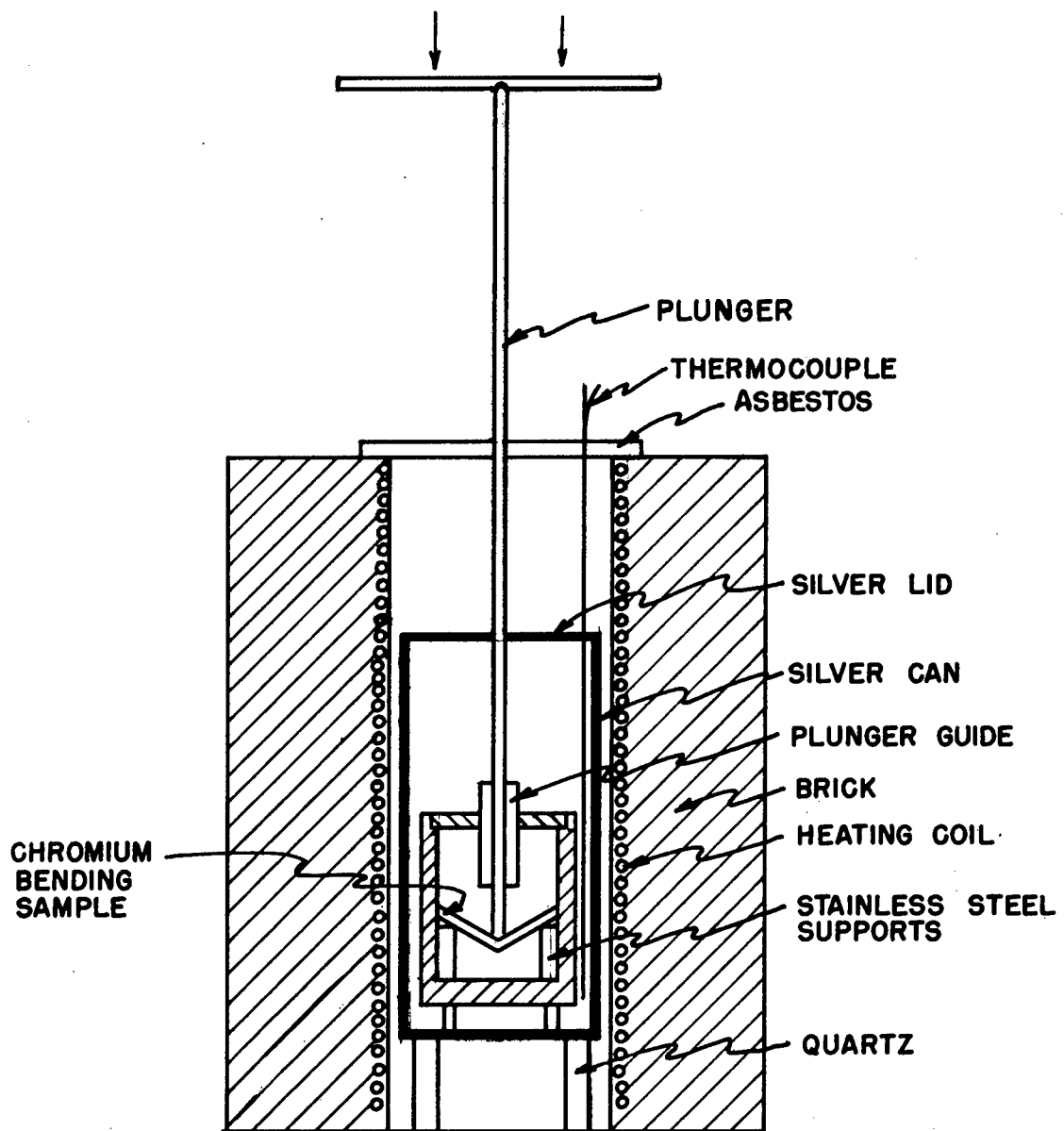


Figure 14 CHROMIUM HOT BENDER

causing incipient melting or dripping. After preliminary evacuation the system was backfilled with hydrogen and the circulating pump started. The circulation of the hydrogen was from the melting tube-to-pump-to phosphorus pentoxide-tower-to zirconium-titanium hydride getter furnace-to melting tube.

The melting of the chromium proceeded smoothly with drops of chromium forming at the end of the bar and hanging molten for several seconds before dropping through the hydrogen to the water-cooled copper cup. Distance of fall was about 5 feet.

The metal deposited in this manner had a tendency to splash, so no good ingot was produced. Metallographic examination of the dripped chromium showed no improvement in intergranular contamination and as production of suitable metal for rolling and forging tests was not obtained, the investigation was abandoned.

II. DEOXIDATION BY TRACE ADDITIONS

As shown by Kroll (20) various elements besides hydrogen may be used as deoxidizing agents for chromium. The elements which have a greater affinity for oxygen than chromium are arranged in the following table which shows the heat of formation per gram atom of the lowest oxide formed:

WADC TR 52-54

TABLE NO. 1

Heats of Formation of Some Elements with
Greater Affinity for Oxygen than Chromium

		<u>ΔH</u>	
1/2	ThO ₂	165.5	(k) cal
1/3	La ₂ O ₃	152.3	
	CaO	151.7	
	MgO	145.7	
	BeO	135.0	
1/3	Al ₂ O ₃	133.0	
1/2	TiO ₂	108.7	
1/2	SiO ₂	99.1	
	MnO	90.8	
1/2	ZrO ₂	89.3	

For comparison 1/3 Cr₂O₃ 89.1

The elements Th, La, Al, Ti, Si, Mn and Zr form intermetallic compounds and excess had to be avoided.

Additions of these elements were made stoichiometrically, basing the amount added on the analysis of the starting material for Cr₂O₃. Magnesium and calcium additions were omitted because of no suitable metal in the case of calcium and previously observed characteristics of the magnesium reduced chromium from the chloride process described earlier.

The melting tests were carried out using 50 grams of powdered chromium metal per run. The powdered metal addition was carefully mixed with the chromium and placed in a beryllia crucible. The crucible was then inserted in a vacuum tight furnace, thoroughly degassed, and the metal finally melted in helium by means of high frequency power. Each ingot was tested for hardness and a portion was sheath

rolled in iron at 800° C. for metallographic examination.

Results are recorded in Table 2:

TABLE NO. 2

Effects of Stoichiometric Additions
to Chromium (Crucible Melted)

<u>Addition</u>	<u>Amount</u>	<u>% Cr₂O₃ Start</u>	<u>% Cr₂O₃ After</u>	<u>Hardness Rp</u>	<u>Remark</u>
None	None	0.04	0.25	62	
Th	0.0564	0.05	0.025	52	
La	0.0366	0.04	0.23	62	
Be	0.0044	0.05	0.17	58	
Al	0.0071	0.04	0.22	67	
Ti	0.0095	0.04	0.80	65	
Zr	0.018	0.04	0.31	68	
Si	0.0097	0.07	0.31		Poor ingot
Mn	0.038	0.07	0.21	60	
C	0.0036	0.06	0.68		Poor ingot

Since the insoluble content increased markedly as a result of the treatment no hope was held for improvement in the physical characteristics. Despite the increase, however, the beryllium and thorium additions produced softer ingots and metallographic samples from the rolled sheet showed fairly clean grain boundaries.

As the Cr₂O₃ content increase appeared unfavorable and no improvement in ductility was noted, work in this direction was abandoned.

The Effect of Alloying Additions on Ductility;

One suggested method for the production of ductile chromium was the addition of small amounts of oxygen-avid metals such as titanium, zirconium, beryllium, silicon,

tantalum, etc. These addition agents would reduce the small amounts of oxides present in the chromium powder and render it more ductile.

The first step in the program was the addition of 1, 3 and 5 percent titanium or zirconium to two lots of chromium powder prepared by reducing chromium chloride with magnesium. The two lots were chosen because of the variation in Cr_2O_3 content, Cr 7 having an analysis of "nil" while Cr 15 contained 0.16 percent. The compacts were pressed in a 3/4 inch die, the mixed powders being moistened with benzene to prevent segregation. All compacts were heated in vacuum at 600° C. for 4 hours, sintered at 1200° C. for one hour, and then melted in a tungsten arc furnace. Hardness values and microstructures are listed in Table 3.

TABLE NO. 3

Hardness and Microstructure of Chromium-Titanium
and Chromium-Zirconium Alloys

Alloy	Composition	Hardness	Microstructure
Cr 15	0.15% Cr_2O_3	B 76	Scattered oxide inclusions
Cr 7	"Nil" Cr_2O_3	B 48	Clean - few oxides in grain boundaries
Cr 7	1% Ti	B 94	2nd phase in grain boundaries
	1% Zr	--	Dirty, eutectic in 2nd phase
	3% Ti	B 100	Dirty, 2nd phase broken up
	3% Zr	B 80	Eutectic in 2nd phase
	5% Ti	B 93	Much 2nd phase, containing acicular grains
Cr 15	5% Zr	B 77	---
	1% Ti	B 86	2nd phase, badly broken
	1% Zr	B 79	Eutectic in 2nd phase
	3% Ti	B 105	2nd phase, badly broken
	3% Zr	B 92	Eutectic in 2nd phase
	5% Ti	porous	---
	5% Zr	porous	---

Although the hardness level of the chromium was raised by the alloying agents, and the hardness values were sometimes erratic, it appears that zirconium additions had less effect on hardness than equivalent titanium additions.

The ingots were machined flat on top and bottom, sheathed in iron restraining rings and rolled in air at 700° C. with 0.003 inch reductions per pass until edge cracking became severe.

Reductions in thickness before failure are shown in Table 4:

TABLE NO. 4

Reduction in Thickness of Chromium-Zirconium and Chromium-Titanium Alloys Rolled at 700° C

<u>Alloy</u>	<u>Composition</u>	<u>Percent Reduction</u>
Cr 7	unalloyed	20.2
Cr 15	unalloyed	45.0
Cr 7	1% Ti	14.8
	1% Zr	17.2
	3% Ti	8.5
	3% Zr	Not rolled
	5% Ti	23.1
	5% Zr	12.2
Cr 15	1% Ti	Not rolled
	1% Zr	17.7
	3% Ti	Not rolled
	3% Zr	Not rolled
	5% Ti	18.6
	5% Zr	13.6

The addition of either titanium or zirconium had an adverse effect on the ductility of the starting metal, which, surprisingly, showed greater ductility in the specimen

with the greatest Cr_2O_3 content.

The addition of stoichiometric amounts of various metallic deoxidizers which would remove the oxides without the attendant effects of alloy formation also was investigated by arc melting methods.

Based on the analysis of batch Cr 34 (Cr_2O_3 - 0.19, Mg - 0.24, Cl - 0.03 percent) the following amounts in percent, of the various metals were required to completely reduce the Cr_2O_3 :

Beryllium	0.165
Alumium	0.208
Lanthanum	1.07
Manganese	0.635
Thorium	1.34
Titanium	0.278
Silicon	0.161
Zirconium	0.525
Tantalum	0.442

Twenty-gram briquettes, made by mixing chromium powder and finely divided master alloys and pressing in a 3/4-inch die at 20 tons per square inch were melted in a tungsten tipped arc furnace in a helium atmosphere. Buttons representing each deoxidizer addition were machined flat on top and bottom, placed in iron restraining rings and rolled at 700° C. with 0.010-inch reductions until edge cracking became severe. The results are given in Table 5.

TABLE NO. 5

Rolling Data on Alloys Containing Various Deoxidizers

Composition	Thickness, inches		Reduction Percent	Rockwell Hardness	
	Before	After		Before	After
0.442 Ta	0.221	0.045	79.6	B 69	B 95
0.525 Zr	0.210	0.069	67.1	B 71	B 92
0.208 Ti	0.190	0.048	74.7	B 71	B 98
0.161 Si	0.243	0.049	79.8	B 67	B 100
0.278 Al	0.205	0.056	72.7	B 68	B 100
1.34 Th	0.196	0.060	68.9	B 72	B 98
0.635 Mn	0.186	0.067	64.0	B 70	B 98

Metallographic examination of cross sections of the buttons indicated that beryllium additions produced the cleanest melts with very little oxide at the grain boundaries. Many of the buttons showed increased amounts of oxides after the deoxidizer additions. This increase was not entirely unexpected, however, since the original chromium was low in oxide and the purity of some of the added elements was not known.

Coupled with the possibility of oxide contamination from the metal additions was the problem of melting in an adequately purified helium atmosphere. In every case a getter button of zirconium was melted immediately before the chromium alloy in order to remove the small amounts of oxygen and nitrogen present in the high purity helium used as the furnace atmosphere.

High Chromium Alloys:

Several high chromium alloy systems were investigated in an attempt to produce a ductile alloy. Twenty-gram

compacts were melted in an arc furnace under a helium atmosphere.

Rockwell hardness measurements showed that the buttons were extremely hard. All alloys shattered badly when they were sheathrolled at 800° C. Hardness values are listed in Table 6.

TABLE NO. 6
Hardness of Cast High Chromium Alloys

<u>Composition</u>	<u>Hardness</u>	<u>Composition</u>	<u>Hardness</u>
5% Mo	C 35	5% Ni	B 92
10% Mo	C 29	10% Ni	C 28
20% Mo	B 98	20% Ni	C 34
5% Fe	C 20	5% Si	C 28
10% Fe	C 26	10% Si	C 40
20% Fe	C 26	5% Cu	C 23
5% Al	C 20	10% Cu	C 99
10% Al	C 25	5% Mn	B 88
20% Al	C 30	10% Mn	B 83

Hot pressing the cast buttons instead of rolling was attempted for 15 and 35 percent molybdenum alloys. The trial was unsuccessful since the alloys shattered when they were pressed at 1000° C. Similar results were obtained when 10, 20, 30, 40, 50 and 60 percent iron alloys, 10 and 15 percent tantalum, and 10 and 15 percent titanium alloys were pressed at 950° C. Rockwell hardness values for the above alloys varied from C 28 to C 40.

III. TREATMENT WITH CALCIUM AND CALCIUM HYDRIDE:

The use of calcium metal as a reducing agent for metallic oxides is well known. In the case of chromium,

calcium of special purity was required since the technique contemplated was to soak very thin sheets of chromium in high purity molten calcium metal for extended periods of time. Accordingly high purity calcium metal was produced by distillation of primary metal. Distillation was carried out in a vacuum retort and the condensed metal was stripped (with difficulty) from an iron shield. The chips were then consolidated into an ingot by melting in an iron crucible under helium. Turnings made from this ingot were used in treating chromium powder directly and in preparation of calcium hydride as described in the ACS monograph on calcium (21).

A variety of chromium samples were treated in molten calcium for periods of up to seven days at 800° C. in a helium atmosphere. Improvement in sheet was noted by metallographic examination but the same improvement was noted by heating a control to 800° C. in helium for 30 hours. As both treatments might be expected to reduce nitrogen values the conclusion was drawn that the slight improvement noted was due to nitrogen removal. A micrograph of a typical specimen is shown in Figure 15.

Analyzed nitrogen values varied but by using calcium metal with about 0.13 percent nitrogen (Kjeldahl method) for starting material, distilled metal was produced with nitrogen equal to 0.004 percent. This was used to treat hydrogen treated chromium containing about 0.03 percent

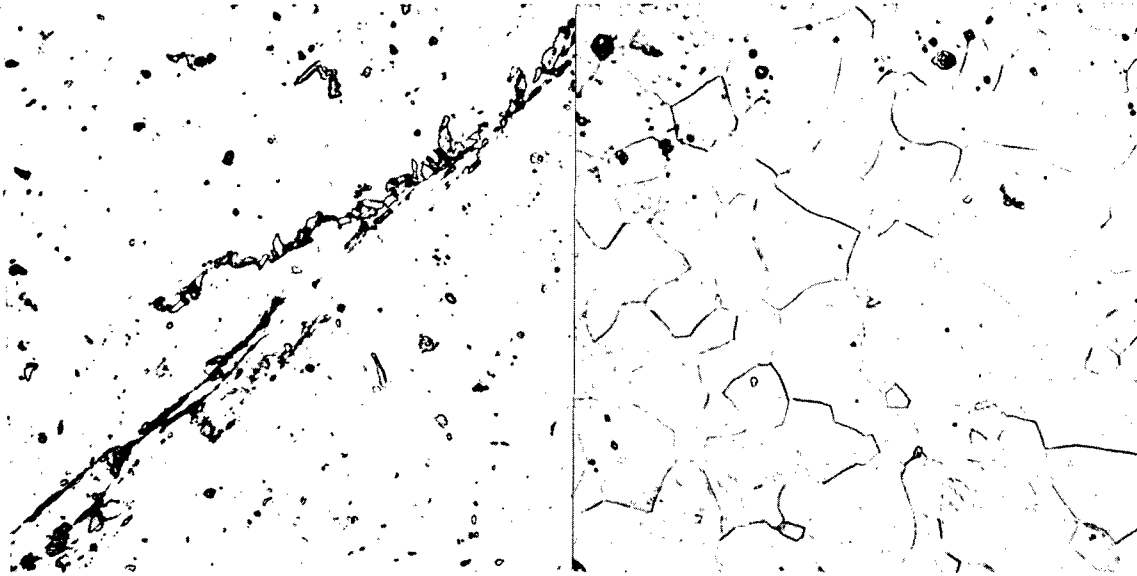


Figure 15 -- Effect of Calcium Treatment

Left -- chloride chromium as rolled at 500° C.

Right -- after calcium treatment

Both electrolytic etch 500X

nitrogen and produced chromium metal analyzing as low as 0.004 percent nitrogen. These results were not reproducible, however.

The treatment with calcium hydride paralleled the treatment with metallic calcium. The results from this treatment were generally less satisfactory than with calcium metal alone. The main difficulty was the nitrogen contamination from cylinder hydrogen used in the hydriding operation.

Distilled calcium with nitrogen equal to 0.004 percent came from the hydriding operation with nitrogen values as high as 0.024 percent. Scrupulous care in this regard, however, did produce one batch of calcium hydride analyzing only 0.008 percent nitrogen. This material was used to treat chromium sheet. Grain growth and some cleanup of the grain boundaries was noted. Ductility of the treated sheet was not noticeably improved.

DUCTILE CHROMIUM METAL:

Knowledge of the fact that chromium metal could be deformed under any conditions at all is of comparatively recent origin. The first report of its workability was published in 1935 by Kroll (19). The metals used in this case were aluminothermic chromium (99%) and electrolytic chromium. Both could be worked hot into small plates. Brinell hardness was reported to be between 120 and 180 on the worked material.

Since then, Kroll et al (1) (2) have shown that hydrogen treated electrolytic chromium and chromium produced by the magnesium reduction of anhydrous chromium chlorides could be hot rolled to coherent sheet by powder metallurgy methods.

With the exception of the forging of distilled electrolytic chromium reported by Kroll (19) none of the chromium produced by powder compact methods seemed susceptible

to swaging or forging. Since the powder technique equipment available was limited, sheet of sufficient size was not available for study.

As reported above chromium has been successfully arc-melted and the resulting arc ingots hot forged. In addition, cylinders machined from the arc ingots have withstood a 93 percent reduction in area by rotary swaging with production of sound 3 mm diameter rod. Other evidences of workability are shown by the ability to drill, saw, grind, tap, turn, and file in the cold state, and spot weld the chromium metal sheet to chromium or iron. It cannot be bent cold.

The workability of chromium has been found to be a direct function within limits of the extent of time of hydrogen treatment. The effect of time of treatment on arc melting ability has already been discussed.

RECRYSTALLIZATION TEMPERATURES OF CHROMIUM SHEET SPECIMENS:

Since the early experiments in hot rolling chromium sheet, all hot work had been done at 800° C. in iron sheaths. Examination of the sheet indicated that the grain was not being refined during the rolling and an X-ray study showed the finished sheet to be completely recrystallized. To determine the proper temperature range for best grain refinement a series of tests were made.

Recrystallization temperatures were determined on

specimens cut from sheet which had been rolled to 90 percent reduction in thickness at 600° C. in air. Longitudinal specimens were heated at 700, 750, 800 and 850° C. and examined metallographically. Knoop hardness values were determined on the same specimens. Results are shown in Table 7.

TABLE NO. 7
Annealing Studies on Rolled Chromium Sheet

<u>Lot No.</u>	<u>Condition</u>	<u>Knoop Hard- ness Number</u>	<u>Microstructure</u>
LHT 36	as rolled	441	Worked structure
	700° C	333	Partial recrystallization
	750° C	229	Partial recrystallization
	800° C	197	Recrystallized
LHT 33-1	as rolled	300	Worked structure
	750° C	232	Partial recrystallization
	800° C	240	Recrystallized
	850° C	180	Recrystallized-grain growth
LHT 33-2	as rolled	296	Worked structure
	700° C	278	Partial recrystallization
	750° C	238	Recrystallized
	800° C	217	Grain growth
	850° C	165	Grain growth
Cr 29	as rolled	348	Worked structure
	750° C	255	Partial recrystallization
	800° C	189	Recrystallized
	850° C	---	Grain growth

Hardness measurements indicated that strain relief was attained by annealing the worked chromium sheet at 750° C., the higher temperatures giving more complete softening. Microscopic examination closely paralleled the hardness data since most specimens showed partial recrystallization at 750° C. and complete recrystallization at 800° C. No significant difference was observed between the hydrogen treated electro-

lytic chromium and the material produced by magnesium reduction of the chloride.

On the basis of the above data and for other reasons it was felt that 800° C. was too high a working temperature and the rolling temperatures were successively lowered to 500° C. at which temperature failure of the iron sheath becomes a problem. Hot hardness tests on forged and annealed chromium arc ingots confirmed this. A typical Brinell (10 mm ball) 500 kilogram load versus temperature plot is shown in Figure 16. Steel is added for comparison showing that it is harder at 500° C. than the chromium.

The ball impressions show directional properties of deformation in the forged material. Cracking around the impression is noted at 700° C.

A very anomalous condition was found in hot hardness readings taken on as cast arc melted chromium. A typical curve is shown in Figure 17.

The hardness readings show a distinct break at about 250° C. Further investigation of the physical properties of arc melted chromium is under way.

In an effort to assess quantitatively the extent of improvement in the ductility of chromium two bending devices were constructed. Figure 18 shows the cold bender designed to test the cold deformability of chromium sheet. Construction of this apparatus was occasioned by the production of one batch of chloride chromium sheet that exhibited

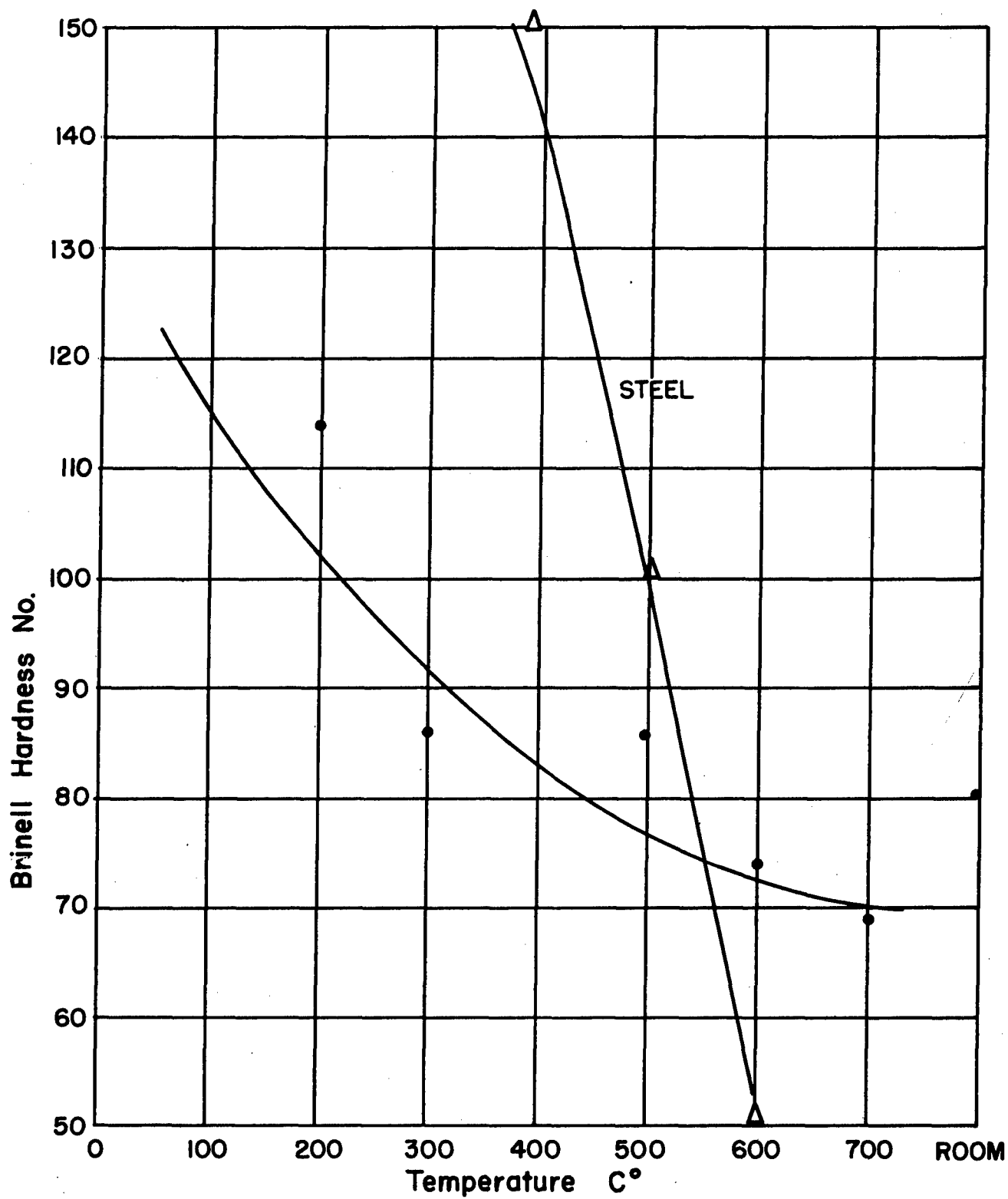


Figure 16 HOT HARDNESS- CHROMIUM METAL (Ingot)

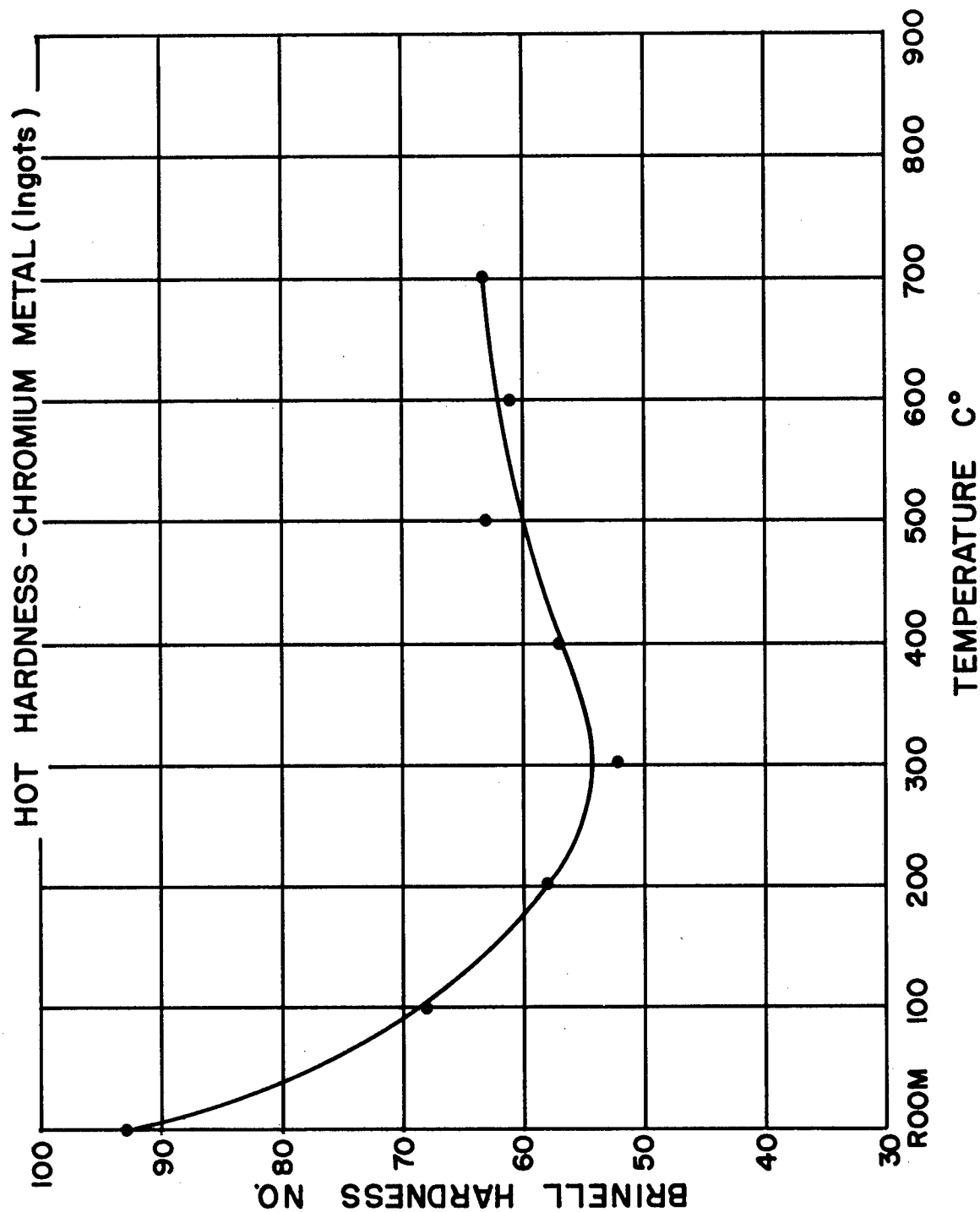


Figure 17

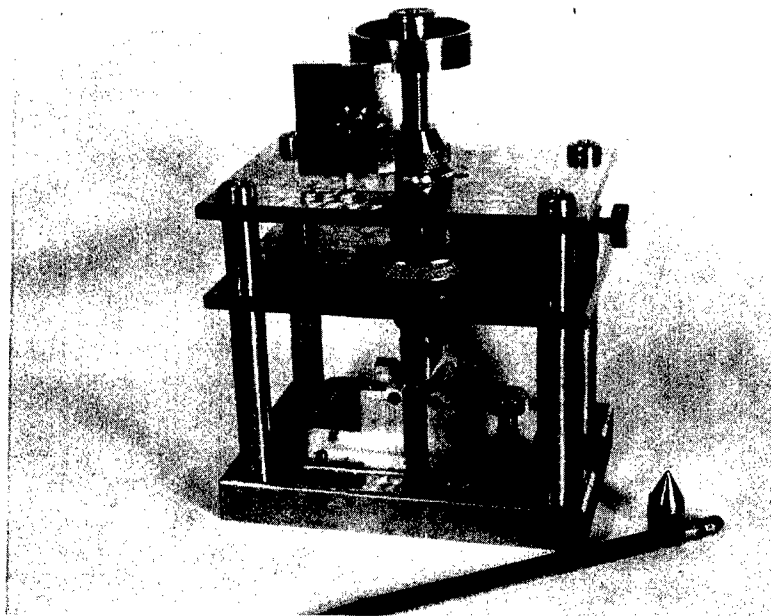


Figure 18 -- Chromium Cold Bender

slight bending characteristics at room temperature. Attempts to produce more of this material failed.

Figure 14 shows a sketch of a hot bender designed to find the minimum hot bending temperature of chromium sheet.

In use the sample is allowed to reach the desired temperature and the plunger depressed manually. Many samples were needed in this procedure until the minimum bending temperature was found. Initial tests on sheet produced from hydrogen treated electrolytic chromium showed the best value

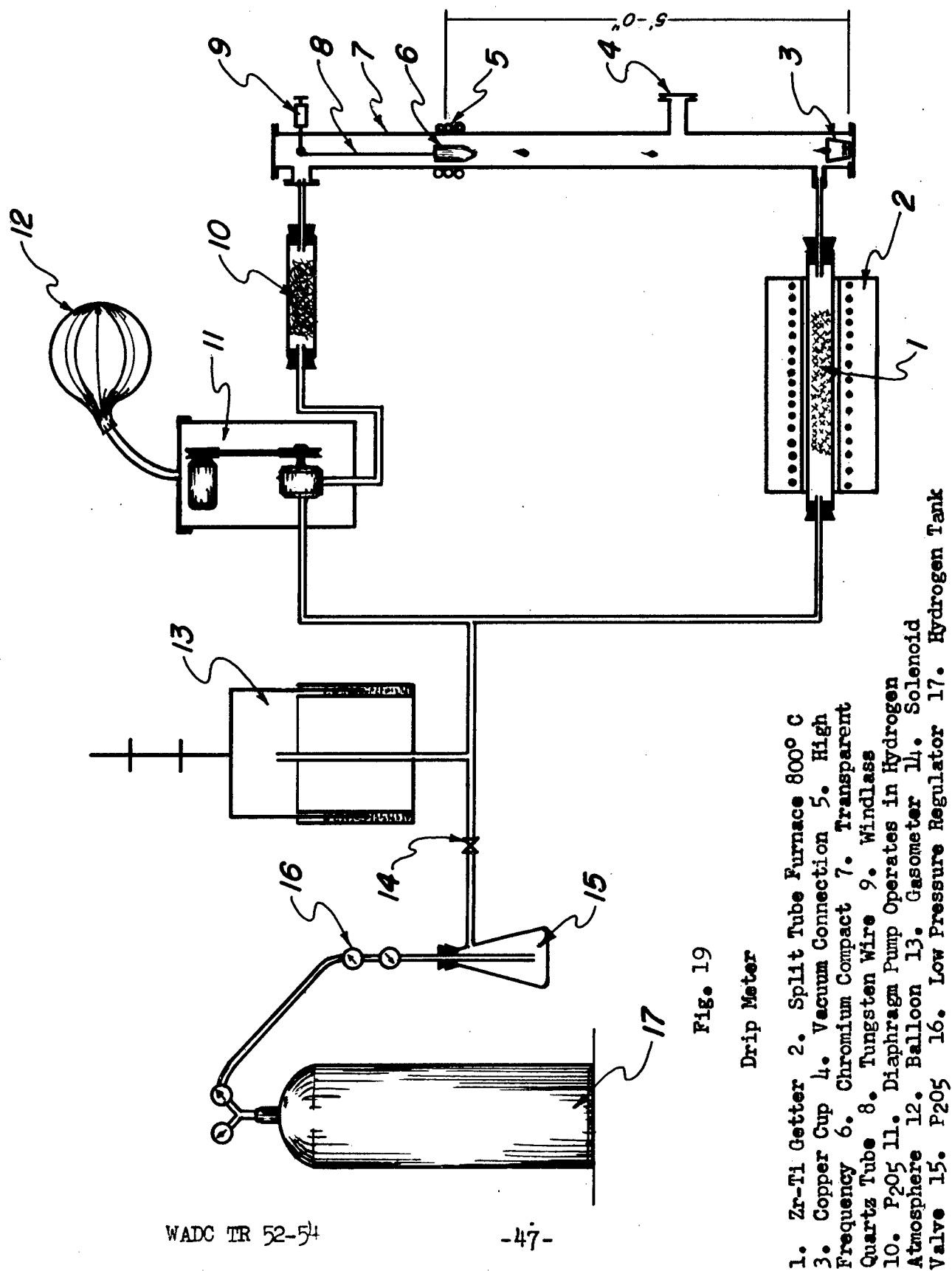


Fig. 19

Drip Meter

1. Zr-Ti Getter
2. Split Tube Furnace 800° C
3. Copper Cup
4. Vacuum Connection
5. High Frequency
6. Chromium Compact
7. Transparent Quartz Tube
8. Tungsten Wire
9. Windlass
10. P2O5
11. Diaphragm Pump Operates in Hydrogen Atmosphere
12. Balloon
13. Gasometer
14. Solenoid Valve
15. P2O5
16. Low Pressure Regulator
17. Hydrogen Tank

obtained to be about 380° C. This was on so-called 8-hour chromium. The best value obtained on 16-hour chromium has been 325° C. showing that the hot bending temperature has been decreased 55° C. by additional time in hydrogen treatment of the chromium.

A recent article by Parke (17) giving an excellent survey of the status of development of molybdenum to its present usefulness may be of assistance in the future in developing chromium to a similar useful form. As noted by Parke (17) molybdenum with its very high melting point (2627° C.) offers splendid possibilities for application to high temperature work. However, two distinctly unfavorable properties are noted: the vapor pressure of molybdenum at elevated temperatures (above 1650° C) is sufficient to prevent its use, for example, in lamp filaments, and worse, the high temperature resistance to oxidation is poor. The situation is aggravated by the fact that the oxide MoO_3 forms and volatilizes appreciably above 760° C. even with low concentrations of oxygen, hence the metal must be protected by cladding or other method even in substantially inert atmospheres. This behavior is similar to that of tungsten which also has a very volatile oxide.

Chromium on the other hand shows precisely the opposite characteristics. While molybdenum shows some tendency to vaporize at high temperatures, chromium has such an extremely high volatility that even vacuum annealing at

1000° C. for a few minutes may obtain a 1 percent weight loss. Attempted arc-melting in vacuum failed utterly and it is reported that vacuum melting is impossible, in any manner, since the metal sublims before melting. In addition, the melting point is so low, comparatively, the latest value reported being 1845° C. (22), that the high temperature application value is somewhat reduced.

On the other hand, while molybdenum shows poor oxidation resistance, chromium shows splendid oxidation resistance.

The heat resistance of hydrogen reduced chromium metal was determined by heating test specimens in air. Coupons about 1/4 x 1 x 1/16 inch were sawed from hot rolled sheet, cleaned with No. 1 emery paper and degreased. After weighing, the specimens were placed in an alumina boat and heated in a muffle furnace for periods of one and 24 hours at temperature. Relative humidity averaged about 35 percent throughout the tests.

The weight gain of chromium metal after exposure to air is shown in Table 8:

TABLE NO. 8
Weight Gain of Chromium Heated in Air

<u>Temperature Degrees C.</u>	<u>Weight Gain mg/dm²</u>		<u>Penetration, ipy</u>	
	<u>1 hour</u>	<u>24 hours</u>	<u>1 hour</u>	<u>24 hours</u>
700	5.6	4.2	0.001	0.0008
800	25.3	19.7	0.005	0.004
900	26.5	26.5	0.005	0.005
1000	18.6	13.1	0.004	0.003

All specimens showed discoloration of varying shades of green due to the formation of Cr_2O_3 . The oxide film was tight at all temperatures investigated and showed little tendency toward cracking or spalling. Microscopic examination of the specimens showed that there was little or no diffusion of oxygen into the body of the chromium even at 1000°C . and for evaluation purposes the calculated penetration (inches per year) based on weight gain is substantially correct.

It is realized that extrapolating one day data to one year is not sound practice and the penetration figures should be accepted as indicative rather than absolute.

It is felt that the present status of development of pure chromium metal is encouraging, but in view of the lack of cold ductility despite the efforts made to improve this condition, the possibility remains that low ductility may be an inherent property of the metal (20). In spite of all out efforts by Kauffmann et al (23) to produce ductile beryllium the final product was an extruded beryllium with fine grain size and preferred orientation having an elongation of only 5 to 10 percent cold, and this in the direction of extrusion. Possibility of a similar condition with chromium must be admitted. Chromium's sister element tungsten never displays an elongation better than 6 percent and if chromium behaves similarly the hopes for good elongation at room temperature are dim. However, a recent announcement

(16) shows that arc-melted tungsten can be hot forged. Since this has already been done with chromium, some hope may be entertained that eventually chromium will at least display the final ductility of tungsten, and perhaps even reach the, at present, very useful position of molybdenum.

SUMMARY:

The chloride process for production of chromium described in earlier publications was elaborated and expanded. Production on the 500 gram batch level was maintained until the supply of starting material was exhausted. Sixty-two runs were made and sheet of varying quality obtained by processing 50 gram briquets through to finished sheet.

The hydrogen treatment process described in earlier publications was modified and expanded to the 1500 gram batch. Increase in treatment time from eight to 16 hours at 1200° C. was found to produce a product suitable for arc-melting.

Chromium produced by hydrogen treatment of electrolytic chromium and arc-melted to 450 gram ingots can be hot forged to as much as 60 percent reduction without cracking. Forging has been successful only in the direction of casting. Rolling of arc-melted chromium presented difficulties due to the large grain size. Careful annealing of worked material removed this difficulty.

Metallographic examination showed that hydrogen treated electrolytic chromium consistently contained fewer intergranular oxides than the untreated material. Chromium produced by reducing CrCl_3 with molten magnesium contained more oxide inclusions than Goldschmidt chromium which in turn contained more oxide than the original electrolytic chromium used as starting material.

Hardness values could not be correlated with oxide content as determined microscopically.

Arc-melted chromium was shown to be forgeable at liquid air temperatures. The suggestion is made that a low temperature transformation may occur in chromium and that the low temperature form is ductile.

Chromium powder compact bars were drip melted in pure hydrogen by means of induction heating. No improvement in quality of the metal was noted.

Deoxidation of chromium metal powder by melting in BeO crucibles with stoichiometric additions of various metals was carried out with no significant improvements in most cases. Very soft metal was found as a result of the beryllium and thorium additions.

The addition of 1, 3, and 5 percent zirconium or titanium did not reduce the amount of oxides and resulted in a definite increase in hardness. Likewise, the ductility, as determined by rolling at 700°C. , was not improved.

The addition of stoichiometric quantities of

oxygen-avid elements to reduce the oxides in chromium powder showed that beryllium additions were most effective in reducing the oxide content in arc-melted alloys.

Chromium powder and chromium metal sheet were treated with molten calcium metal and molten calcium hydride in attempts to deoxidize the material. Metallographic examination showed some improvement in grain boundary clean up.

It was found that arc-melted chromium can be swaged, forged, and rolled. In addition, evidence of workability is shown by drilling, sawing, and grinding, tapping, turning, and filing in the cold state. Chromium sheet spot welds excellently to chromium or iron.

Recrystallization studies made on sheet rolled at 600° C. indicated that the metal recrystallized at about 750° C. No difference was noted between electrolytic or magnesium reduced chromium.

Plots of Brinell (10 mm carbide ball, 500 kilogram load) hot hardness versus temperature on annealed forged arc-melted chromium showed very little drop in hardness in the range 300° C. to 800° C. Brinell hardness values range from 120 at 100° C. to 63 at 700° C. Indeed, the as cast, arc-melted material showed a slight rise in hardness for the temperature range 400°-800° C.

Hot and cold bending test machines were constructed. One batch of chloride chromium rolled sheet was found to

display some room temperature ductility. Attempts to reproduce this material failed.

Hot bending tests on chromium sheet produced from eight-hour electrolytic chromium showed a minimum bending temperature of 380° C. Tests on 16-hour chromium showed the minimum value of 325° C -- a 55° C. improvement.

The present status of chromium in relation to the metallurgy of molybdenum and tungsten is discussed.

The heat resistance of chromium sheet from hydrogen reduced metal was found by treating specimens at various temperatures up to 1000° C. in air. Oxidation resistance was found to be excellent at all temperatures and penetration was low.

The enigma of the lack of room temperature ductility remains unsolved; however, the favorable characteristics of arc-melted chromium appear to offer hope in the achieving of some measure of cold ductility.

BIBLIOGRAPHY

- (1) W. J. Kroll, W. F. Hergert, and W. R. Carmody, U.S. Bureau of Mines Report of Investigations, No. 4752 (1950)
- (2) W. J. Kroll, W. F. Hergert, and L. A. Yerkes, J. ELECTRO-CHEM. SOC., 97, 258(1950)
- (3) M. L. Troost, COMPT. REND., 61, 109(1865)
- (4) H. von Zepplin, METALL U. ERZ, 40, 252(1943)
- (5) C. G. Maier, U.S. Bureau of Mines Bulletin No. 436, (1942)
- (6) F. Adcock, J. IRON STEEL INST. LONDON, 115, 369(1927)
- (7) N. K. Koebel, METAL IND. (LONDON), 72, No. 21, 426(1948)
- (8) R. R. Lloyd, J. B. Rosenbaum, V. E. Homme, L. P. Davis, and C. C. Merrill, J. ELECTROCHEM. SOC. 97, 227(1950)
- (9) W. Von Bolton, Z. ELEKTROCHEM. 11, 45(1905)
- (10) W. J. Kroll, TRANS. ELECTROCHEM. SOC., 78, 35(1941)
- (11) W. J. Kroll, A. W. Schlechten, and L. A. Yerkes, TRANS. ELECTROCHEM. SOC., 89, 263(1946)
- (12) R. M. Parke and J. L. Ham, TRANS. AIME INST. METALS DIV., 171, 416(1947)
- (13) O. W. Simmons, C. T. Greenidge, and L. W. Eastwood, "Titanium Symposium", Report of Symposium, ONR, Dept. of the Navy, P. 77, 16 December 1948.
- (14) S. A. Herres and J. A. Davis, STEEL, 18, 82(1949)
- (15) A. B. Kinzel, MET. PROGRESS, 58, 315(1950)
- (16) H. B. Goodwin and C. T. Greenidge, MET. PROGRESS, 59, 812(1951)
- (17) R. M. Parke, MET. PROGRESS, 60, 81(1951)
- (18) W. Espe and M. Knoll, "Werkstoffkunde der Hochvakuum-technik", P. 359, J. Springer, Berlin (1936)
- (19) W. J. Kroll, Z. ANORG. CHEM., 226, 23(1935)

- (20) W. J. Kroll, unpublished memorandum, (1950)
- (21) C. L. Mantell and C. Hardy, "Calcium Metallurgy and Technology", ACS Monograph P. 57, Reinhold Publishing Co., New York. (1945)
- (22) H. T. Greenaway, Report SM. 163, Aeronautical Research Laboratories, Commonwealth of Australia, "Pure Chromium, Its Production and Freezing Point". Fishermen's Bend, Melbourne, Australia, January, (1951)
- (23) A. R. Kauffmann, Paul Gordon, and D. W. Lillie, TRANS. A.S.M., 42, 785(1950)