Fig. 4

CHROMIUM VAPOR PRESSURE AND CORRESPONDINGLY, MINIMUM CO VAPOR PRESSURE

OPERATING RANGE

CHROMIUM VOLATILIZATION RANGE

VAPOR PRESSURE — MICRONS OF MERCURY

TEMPERATURE °C.

INVENTOR

Hugh S. Cooper

BY Evans & Pearne

ATTORNEYS

13

TO MERCURY
MANOMETER

TO McLEOD
GAUGE

18

15

26

14

11   *10*

12

25

24

22

21

20

16   *30*   *27*

32   *29*

28   *31*   *17*

+

COOLING
WATER

−

COOLING
WATER

Fig. 2

TO VACUUM
PUMP

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2,850,378

PRODUCTION OF CHROMIUM BY LOW-PRESSURE REDUCTION OF OXIDES

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17 Claims. (Cl. 75—84)

This invention relates to the production of chromium metal from chromium oxide, and particularly to the reduction of chromium oxide at subatmospheric pressures, using carbon as a reducing agent, to produce substantially pure, low carbon, chromium metal having substantial ductility and malleability at normal temperatures.

The principal objects of the invention are to provide a process for reducing chromium oxide to substantially pure chromium metal by direct reduction with carbon and at subatmospheric pressures enabling the recovery of a high percentage of the chromium in the charge material in such pure form. A further object of the invention is to produce chromium metal having cold malleability such that it may be forged into thin sheets at room temperature. A still further object of the invention is to accomplish the foregoing by a process that is economical and suited for commercial mass production of chromium metal.

For many years, chromium metal has been made by two principal, high temperature, reduction processes. One of these processes involves the reaction of silicon with chromium oxide in an arc furnace. The second and older of the two processes involves a self-propagating reaction of aluminum with chromium oxide. Because of lower cost, the silicon reduction process has almost completely replaced the earlier aluminum reduction process.

In recent years, electrolytic chromium has also been manufactured commercially. This process involves the electrolysis of an aqueous solution of chromium ammonium alum (chromic sulfate and ammonium sulfate) and yields chromium metal reported to be about 99.80% chromium content, whereas the high temperature reductions have generally yielded metal of considerably lower purity.

Regardless of the process used, metallic chromium has been an expensive metal to produce, has commanded a high market price, and has never been available in a sufficiently malleable form to be cold forged or rolled into useful shapes. There has, therefore, been a long existing need for a more economical process for producing this metal, for a process capable of use on a large scale to produce the metal in quantity with a high purity, and for a process for producing the metal in a sufficiently malleable form to be cold forged.

While vacuum reduction of a number of metals, using carbon or a carbide as a reducing agent, has been practiced with more or less success, the production of chromium metal by this process has met with such serious difficulties that it has not been considered practical for commercial use. The principal problems have been the tendency to form chromium carbide and the tendency of chromium metal to be rapidly lost by vaporization at the high temperatures and low pressures heretofore employed in attempting to effect the reduction reaction.

In April 1949, W. J. Kroll and A. W. Schlechton reported a series of experiments in reducing metal oxides in a vacuum including the reduction of chromium oxide.

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Transactions, Electrochemical Society, vol. 93, page 247. Kroll et al. apparently held the belief that increasing the temperature and using the highest possible vacuum would assist in the reduction of metal oxides with carbon according to the formula—

$$MeO + C \rightarrow Me + CO$$
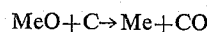
Accordingly, Kroll et al. performed their experiments by heating an intimate mixture of finely powdered metal oxide and carbon slowly, both at atmospheric pressure and under a "high vacuum," in order to determine the temperature in each instance at which the reduction reaction showed signs of initial activity and the temperature at which the reaction could be carried to completion. Because the temperature was apparently increased slowly in all of that work, the evolution of CO was presumably never so copious as to interfere with maintaining a high vacuum at all times where a vacuum was desired. At least nothing was said about any problem in this regard. In the case of the chromium oxide reduction tests by Kroll et al., the tabulated results indicate that the vacuum was probably maintained at or near 8 microns of mercury absolute pressure (0.008 mm. of mercury). When the maximum temperature reached was 1300° C., the product contained 6.3% carbon. When the maximum temperature reached was 1460° C., the product contained only 0.38% carbon and, after remelting, only 0.09% carbon. In the latter case, where the reaction was apparently carried substantially to completion, however, Kroll et al. noted the unfortunate fact that there was considerable loss of metal by volatilization. The weight loss of the charge was reported as being 68%. This corresponds to a loss of roughly half of the weight of chromium metal in the oxide and would obviously rule the process out of consideration for any commercial use.

Summarizing the results of their above described experiments, and under a "high vacuum," in order to determine the periments, Kroll et al. concluded that the high vacuum reduction procedure evaluated "would be practical only for the more expensive and rare metals." What metals were contemplated as "more expensive and rare" is not clear, but the difficulty from loss of chromium by volatilization was repeatedly emphasized in the article, and no solution to the difficulty was suggested. That the results of Kroll et al. offered no promise of commercial value was the conclusion later expressed by A. W. Sully on pages 52–53 of his book on "Chromium" (Butterworth's Scientific Publications, 1954).

In accordance with the present invention, substantially complete reduction of chromium oxide with carbon is accomplished at subatmospheric pressures with no significant loss of metal by volatilization. The product may be produced with a low carbon content and with greater purity than the present electrolytic chromium of commerce, which has heretofore been the purest form available in quantity. Presumably because of the greater purity of the product of the present invention, it has sufficient malleability at room temperatures to be cold forged or rolled into thin sheets. The impurities believed to be largely responsible for brittleness heretofore are dissolved gases, which are virtually completely eliminated by the process of the present invention.

Solution of the problem of loss of metal by volatilization resides in the present discovery that both the temperature and the pressure under which the reaction is carried out must be carefully controlled. Specifically, there is a definite relationship between the pressure and the temperature at which substantially complete reduction may be accomplished without significant metal losses by volatilization. Although high temperatures do accelerate the reaction, the higher the temperature employed, the higher must be the pressure to avoid losses by volatilization, and

the minimum permissible pressure may thus exceed the pressure range in which efficient reduction is practical regardless of temperature.

While I do not wish to be bound by any particular theory, it appears that the critical minimum pressure is determined by the relative vapor pressures of the condensable chromium vapor and the non-condensable gases (i. e., air, carbon monoxide, and the like). The pressure of non-condensable gases may be measured by a McLeod vacuum gage, for example, whereas the total pressure of both condensable and non-condensable gases and vapors may be measured by a thermocouple-type vacuum gage, or by a manometer where the pressures are not too low for accurate readings. By the use of both types of gages, it has been determined that vaporization of chromium metal is effectively suppressed only when the partial pressure of non-condensable gas is equal to or slightly in excess of the chromium vapor pressure. Since the latter pressure increases as the temperature increases, this necessarily means that the minimum permissible pressure of non-condensable gas, as measured by a McLeod gage, rises as the reaction temperature is raised. (It will be understood, of course, that the term "non-condensable" has reference to condensability at normal temperatures.) References to pressure hereinafter are to be understood as referring to the non-condensable gas pressure in the reaction zone unless otherwise indicated.

A distinguishing characteristic of the present invention, therefore, is the intentional maintenance of a partial, sub-atmospheric pressure of non-condensable gas in the reaction chamber that is higher than the partial vapor pressure of chromium metal at the prevailing temperature of the reaction mixture as the reaction proceeds. Though it has apparently been assumed heretofore, from equilibrium considerations, that any partial pressure of carbon monoxide would adversely affect the degree to which the reduction reaction will approach completion, this does not appear to be the case, and the rate at which evolved carbon monoxide is removed from the reaction chamber is preferably limited so that evolved carbon monoxide may supply the non-condensable gas pressure necessary to prevent objectionable volatilization of chromium metal.

Although the reaction pressure should not be permitted to drop, for any appreciable period of time, to as low as the partial vapor pressure of chromium at the prevailing temperature of the reaction mixture, the speed and completeness of the reduction reaction after reaching a reaction temperature appear to be impaired during such period or periods of time as the pressure may remain or be permitted to rise too high above the minimum permissible pressure. However, within limits, only the speed of the reaction appears to be impaired by delays in producing a sufficiently low pressure after reaching a reaction initiating temperature, or by allowing the pressure to rise unduly during the course of the reaction, so that the reaction need not be (and, in fact, generally cannot be) entirely carried on within what may be termed a preferred range of operating pressures. So long as the pressure is brought down into the preferred operating range within about an hour or so after reaching an efficient reaction temperature, and does not rise above that range for any substantial period of time thereafter, the completeness of the reaction does not appear to be adversely affected, although the speed of the reaction may be significantly retarded.

On the other hand, the speed of the reaction is increased as the minimum permissible pressure at the prevailing temperature is more closely approached and maintained during the course of the reaction; the completeness of the reaction is increased by keeping the pressure down as close as practical to the minimum permissible pressure at the prevailing temperature during the final stages of the reaction; and only the yield appears to be adversely affected by the extent to which the pressure may, at times during the reaction, be lowered below the minimum permissible pressure at the prevailing temperature, and by the length of time during which such undesirably low pressure may prevail.

From the foregoing, therefore, it will be appreciated that the minimum permissible pressure represents a critical lower limit for any given reaction temperature, below which the pressure cannot be dropped for a significant period of time without an appreciable loss of chromium metal by volatilization. The upper limit of a preferred operating pressure range, on the other hand, does not appear to be a sharply critical one. It represents only an approximate maximum pressure below which the operating pressure is desirably maintained as quickly and as continuously as is practical, particularly during the final stages of the reaction. This maximum effective pressure can only be determined by experience in carrying out a considerable number of runs and may well depend upon other reaction conditions which are themselves subject to no definitely determinable limits. Unlike the minimum permissible pressure (namely the vapor pressure of chromium), which is sharply definable and represents a critical limit below which appreciable loss of chromium by vaporization begins, the upper limit of the preferred operating range is primarily dependent, inter alia, upon the permissible carbon and oxide contents of the product for different industrial and scientific uses and the reaction time considered practical in production, and may be subject to considerable variation. The upper limit, therefore, cannot be fixed for all purposes or definitely defined in terms of temperature or other parameters, and can only be arbitrarily set by experience. For the purpose of defining the scope of the invention claimed herein, the preferred reaction pressure may be arbitrarily given as below about 400 microns of mercury, though still higher pressures up to 600 or even 750 microns would undoubtedly be effective at relatively high temperatures and under carefully controlled conditions, using more elaborate apparatus and techniques to prevent coalescence of the reaction mixture, which would retard the escape of carbon monoxide. The upper limit of an operative pressure range within which a useful chromium metal product may be produced in accordance with this invention, for purposes of definition, may be taken as about 1 millimeter of mercury.
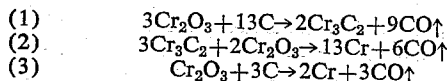
Kroll et al. indicated that the reduction reaction appears to commence at about 700° C. However, this figure may have been in error because of improper location of the temperature indicator or because of mistaking the evolution of entrained air for evolution of carbon monoxide, or both. The temperature at which the reduction reaction actually starts appears to be above 900° C. and probably very close to 925° C. In any event, below about 1200° C. the reaction is too slow for most partial uses, and an operating temperature of about 1200° C. appears to be the practical minimum for obtaining effective results in any reasonable period of time.

The use of higher temperatures increases the rate of reaction, but also increases the vapor pressure of the chromium metal and, hence, increases the minimum pressure that should exist if excessive loss of chromium by volatilization is to be avoided. For example, at 1450° C., the minimum pressure is close to 400 microns of mercury and the chromium vapor pressure curve is rising so rapidly with temperature that a minimum safe operating pressure considerably above 400 microns is essential to avoid excessive loss of chromium by vaporization. Despite the high temperature, such pressures appear to be too high to effect efficient and complete reduction in reaction masses of substantial volume, probably due to inability of CO to escape from the interior of the reaction mass, as explained more fully hereinafter. Thus, a practical operating temperature range for most purposes may be taken as running from about 1200° C. up to about 1425° C. or so. Higher temperatures in the range of, say,

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1450° to 1500° C., would appear to require suitable provision for maintaining the charge of chromium oxide and carbon in a multiplicity of small discrete masses (to facilitate the escape of CO), as by continuously tumbling a granular or finely pelletized charge, and by the use of pressures of about 500 to 750 microns or so.

Since coalescence of the mass should be avoided, the practical upper temperature limit for the types of operations contemplated by the present invention may be taken as the melting point of chromium metal, long considered to be about 1615° C., but more recently reported from about 1850° to 1940° C. (according to purity of metal tested).

Kroll et al. also indicated that the process could not be carried to completion at a temperature as low as 1300° C., as evidenced by a carbon content of 6.3% in the product remaining when cessation of the evolution of gas indicated that the reaction had ceased. However, I have obtained much better results and a virtually complete reaction using temperatures of 1200°–1205° C. and a reaction time of about seven hours, the resulting product analyzing only about 1% carbon and about 99% chromium as metal. The explanation of the incomplete reaction and high carbon content obtained by Kroll et al. at 1300° C. could be, of course, that the reaction was actually terminated before reaching its limit under the reaction conditions employed. The more likely explanation seems to be, however, that the rate of heating was responsible, since it was stated that the temperature of the reaction mixture was increased slowly. This, and also a feature of the present invention which avoids the unsatisfactory results of Kroll et al., will be more clearly understood from a consideration of the following three reactions that may occur:

(1) $3Cr_2O_3 + 13C \rightarrow 2Cr_3C_2 + 9CO\uparrow$
(2) $3Cr_3C_2 + 2Cr_2O_3 \rightarrow 13Cr + 6CO\uparrow$
(3) $Cr_2O_3 + 3C \rightarrow 2Cr + 3CO\uparrow$

Lower temperatures may favor Reaction 1, and higher temperatures may favor Reaction 3 over Reaction 1, provided oxide and free carbon remain for reaction with each other by the time the higher temperatures are reached. On the other hand, still higher temperatures or longer reaction times may be required for Reaction 2 to proceed effectively. Thus, depending upon the rate of heating of the reaction mixture and the maximum temperature reached, Reaction 1 may proceed preferentially until a temperature is reached at which Reaction 3 can begin. If the temperature is then raised to and held constant at, say, 1300° C. and the run continued until there is no further gas evolution, the remaining free carbon may be utilized to produce chromium metal by Reaction 3 with no opportunity for Reaction 2 to take place to any appreciable extent. This would leave some Cr_2O_3 and some Cr_3C_2 in the reaction mass along with the chromium metal residue from Reaction 3.

On the other hand, if the above suppositions are correct and the heating to 1300° C. is relatively rapid, it can be seen that there would be little chance for the formation of Cr_3C_2 by Reaction 1 before the temperature favoring Reaction 3 is reached. Thus, the reaction might proceed practically entirely according to Reaction 3, with little carbide formation, so as to leave a relatively low carbon content in the product. Also, according to hypotheses advanced by Kroll et al., coalescence of the reaction mass may be so pronounced under certain conditions that evolved gases cannot escape therefrom, whereby pressure builds up within the coalesced mass until an equilibrium condition is reached. It is possible that more rapid heating than that employed by Kroll et al. evolves gas at a rate sufficient to open up the reaction mass and impede coalescence, and thereby facilitate carrying the reduction reaction to completion.

The above explanation is theoretical, and is given only as a possible explanation of the practically useless results

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obtained by Kroll et al. Since other chromium carbides than Cr_3C_2 may be formed under certain conditions, and many variants of the above three equations may be required to represent the entire reaction, the above explanation is not advanced as being necessarily the correct one. The fact remains, however, that by heating the reaction mixture relatively rapidly from below the temperature at which any appreciable amount of carbon monoxide is evolved, until a temperature above about 1200° is reached, substantially complete reduction of the chromium oxide to chromium metal is readily accomplished with a total carbon content in the metal product of 0.1% or less, depending upon the duration of heating at the reaction temperature and the degree of vacuum maintained, particularly during the latter part of the reaction. Thus, a relatively rapid rate of heating of the reaction mixture up to reaction temperature appears to facilitate the desired reaction and is preferably employed in carrying out the present invention.

By maintaining a fairly low subatmospheric pressure during the major part of the reaction, while the evolution of CO is so rapid as to make low vacuums difficult to attain, and by gradually reducing the pressure into the preferred operating range, close to but short of the point at which appreciable chromium will be volatilized at the final reaction temperature, yields of the order of 99% in the form of chromium of 99+% purity are readily obtainable.

Reaction times vary according to the reaction temperature employed and according to how quickly and how closely the minimum permissible pressure is approached as the reaction proceeds. So long as the initial heating from around 900° C. to about 1200° C. is rapid enough to prevent any substantial carbide formation during such heating, the retarding effect of delays in pressure reduction may be compensated by prolonging the reaction time.

In the ensuing further description of the invention and the specific examples of its operation, reference will be made to the accompanying drawings in which Figure 1 is a graph showing a preferred range of operating temperatures and pressures, and Figure 2 is a diagrammatic representation of the apparatus used in carrying out the examples, parts being shown wholly or partly in vertical section for clarity.

To illustrate the minimum pressures at and below which appreciable chromium may be lost by volatilization at different reaction temperatures, reference is made to Fig. 1 of the drawings in which the approximate minimum operating pressures are plotted against reaction temperatures. The area below and to the right of the resulting curve represents the reaction conditions under which volatilization of chromium will occur. The area above and to the left of the curve represents the reaction conditions under which no appreciable chromium loss by vaporization will occur. The sectioned portion of the latter area represents the reaction conditions which are preferred for commercial operation without using unduly elaborate apparatus and operating techniques. However, it is to be understood that, in any event, still higher pressures than those shown to the left of the curve may exist during the early stages of the reaction or even until the reaction is close to completion, because the high rate of evolution of carbon monoxide may, for a considerable time, exceed the capacity of available vacuum pumping equipment to maintain a vacuum as low as the range of preferred operating pressures shown in the drawing. Thus, the maximum pressure during the period of most rapid reaction may be as high as several centimeters of mercury until the capacity of the vacuum pump employed can cope with the rapid evolution of gas.

As indicated above, relatively brief periods of a half hour to an hour or so during which low pressures are not easily maintainable do not seriously affect the overall reaction time of several hours and have no apparent effect upon the character of the reaction, though they

may materially prolong the required reaction time. Thus references to specific pressure ranges within which the process should be performed should be understood to refer primarily to pressures during the latter portion of the reaction period.

While the reaction becomes markedly effective at about 1200° C., as explained above, temperatures of about 1250° to 1400° or even 1425° C. are preferred in the interest of reducing the reaction time and driving the reaction as near to completion as possible with a minimum loss of chromium by volatilization.

The slope of the minimum pressure curve is so steep above 1400° C. that the use of pressures close to the theoretical minimum above that temperature require an accuracy of temperature control that may be difficult to attain. Thus at lower temperatures of 1250° to 1350° C., the minimum permissible pressure may be more closely approached in practice without requiring such fine temperature control to avoid accidentally creating a temperature-pressure relationship on the wrong side of the curve of Fig. 1.

The preferred procedure for carrying out the present invention is to first thoroughly mix finely divided chromium oxide, for example, −200+325 mesh, with an amount of finely divided carbon, in the form of graphite of about −200 mesh, calculated to react stoichiometrically to reduce the chromium to metal and oxidize the carbon to CO. A ball mill or the like may be advantageously used to insure thorough mixing of the oxide and carbon. The mixture of oxide and carbon is then preferably cold pressed into briquettes of any convenient size, primarily so as to reduce the volume of the powdered mixture and thereby facilitate handling it, and to put it into such form that a large quantity of the briquettes will still constitute a mass with substantial voids to facilitate the escape of evolved gas.

A mass of briquettes prepared as described may be placed in a crucible of suitable refractory material, such as Alundum, and the loaded crucible may be placed in a suitable electric furnace for heating the contents of the crucible while subjecting them to a high vacuum. Large furnaces adapted for use in accordance with the invention and capable of maintaining temperatures and vacuums of the desired high order are in commercial use for melting various metals as well as for the production of low carbon ferrochromium and other metals and alloys, and such furnaces need not be further described herein.

When the furnace has been charged with briquettes, it is first evacuated to a relatively low absolute pressure, preferably as low as possible, down to a small fraction of a millimeter of mercury. Since the time required for effective degasification of the charge and the degree of degasification attained are not critical conditions, a suitable pressure for this purpose may be arbitrarily taken as being about 400 microns or lower, and is preferably less than 100 microns.

Heat is then supplied to bring the charge to a substantially non-reacting temperature of about 800° to 900° C. or so for a period of about an hour to thoroughly remove entrained air and volatile material from the charge and to insure that the charge has been uniformly heated to a temperature in this range. During the early part of this degassing period, the pressure in the furnace will normally rise somewhat due to the increased rate of evolution of occluded air from the charge and due to thermal expansion of the gases as the temperature rises. As noted above, no appreciable reduction of the oxide and, therefore, no appreciable formation of carbon monoxide appear to occur at temperatures up to or slightly above 900° C.

When a reasonably stable vacuum of say, 100 microns or so is produced in the furnace, degasification may be considered sufficiently complete, and the temperature of the charge is then raised as rapidly as possible to a

selected operating temperature of at least 1200° C., and preferably 1275° to 1400° C. or higher. This causes the reduction reaction to proceed at a rate producing a relatively rapid evolution of carbon monoxide with a consequent rise in the pressure in the furnace which, depending upon the capacity of the vacuum pumping system and the size of the furnace charge, may reach 1 or 2 cm. of mercury, or even higher, for about a half hour to an hour or so. The rate of evolution of carbon monoxide gradually subsides, and over a period of time, the degree of vacuum is preferably brought as close as practical to the lower limit shown by the curve in the drawing for the prevailing temperature of the charge. Care should be taken, however, that the pressure remain a few microns above the lower limit to insure against unnecessary loss of chromium by volatilization. For example, to obtain optimum results with charge temperatures of 1200° to 1425° C., the absolute pressures in the furnace may be brought down to and maintained at about the values in microns of mercury shown in the following table:

Charge temperature, ° C.	Minimum pressure, microns
1,200	20 to 25
1,250	35 to 40
1,275	55 to 65
1,300	75 to 100
1,325	110 to 135
1,350	150 to 180
1,375	215 to 250
1,400	280 to 315
1,425	375 to 400

Normally, somewhat higher pressures than those shown in the table will still produce excellent results, with a greater margin of safety to accommodate accidental pressure drops as the reaction approaches completion.

It will be appreciated from the foregoing discussion that inability to reach the above tabulated optimum pressure ranges due to limitations of the vacuum pumping equipment, or for other reasons, is merely reflected in a prolongation of the time required for carrying out the reduction reaction. Depending upon the extent of the upward departure from the optimum pressure ranges, a slightly higher content of unreduced oxide and residual carbon in the product when the reaction has proceeded to its limit may also result.

Whether the non-condensable gas in the furnace at any time during the reaction is essentially carbon monoxide or is made up in substantial part of argon, helium or other non-condensable gas or gases inert to chromium metal at the prevailing temperatures, is not important. Thus, where desired as a means for avoiding accidental pressure reductions below the critical minimum limits, such as inert gas may be bled into the furnace in small amounts whenever the capacity at which the vacuum pumping system is operating becomes excessive. This may be done automatically and, in some apparatus setups, more quickly and reliably than cutting back on the rate of operation of the vacuum pumping apparatus.

The invention will be more fully understood from the ensuing specific examples of the process as performed in the laboratory in the apparatus of Fig. 2 of the drawings. In these examples, the process was carried out on a relatively small scale but, in other respects, the reaction condition of the examples throughout the process should closely approximate those in commercial scale operations. In all of the examples, the briquettes of chromic oxide and carbon, prepared as described above, were placed in an Alundum crucible 10 which was in turn placed in a vertically disposed, open, thin-wall, molybdenum tube 11. The tube was electrically heated by its own resistance and was placed in a water cooled, metal, bell jar 12 having sight windows 13 and 14 for observing temperatures by means of an optical pyrometer. For simplicity, no provision for the water cooling of the bell jar is shown in the

drawing. A McLeod gauge was connected into the bell jar at **15** for measuring the pressure of non-condensable gases therein, and a vacuum pumping system was connected into the bell jar at **16** through the base **17** on which the bell jar was mounted. A mercury manometer was also connected into the bell jar at **18** to measure relatively large total pressures.

The arrangement of the apparatus illustrated in Fig. 2, for convenient laboratory operation, included a water-cooled receptacle **20** resting upon the base **17** and containing a pool of mercury **21**, in which was placed a cylindrical steel block **22**. The block **22** fitted snugly into the lower end of the molybdenum tube **11** and was clamped thereto by a steel clamp **24** to obtain good electrical contact with the tube. A refractory block **25**, resting on top of the steel block **22**, served to support and position the crucible **10** substantially centrally within the tube **11**. The open upper end of the tube **11** was surrounded by a water-cooling jacket **26**. Water inlet and outlet tubes **27** and **28** were run through electrically insulating vacuum seals (not shown) in the base **17** into communication with the mercury receptacle **20**, the inlet tube **27** serving as a conductor to which an electrical lead **29** from a source of electrical power was connected. Additional water inlet and outlet tubes **30** and **31** were run through electrically insulating vacuum seals (not shown) in the base **17** into communication with the water cooling jacket **26** at the upper end of the tube **11**, the inlet tube **30** serving as a conductor to which a second electrical power lead **32** was connected. A charge to be reacted, contained in the crucible **10**, was thus heated by applying an electrical potential across the leads **29** and **32** so as to pass current longitudinally through the tube **11** and heat it by its own resistance.

In a typical run, with the charge placed in the apparatus, the system is evacuated down to about 4 to 6 microns before applying energy to heat the charge. The charge is then heated to a degassing temperature of 800° to 900° C. The succeeding time, temperature, and pressure relationships may then be about as follows:

Within a period of about 10 minutes at the degassing temperature, the pressure will rise to around 130 microns and will gradually drop. When the pressure has dropped to around 80 microns, degassing may be considered to be sufficiently complete. The temperature should then be raised as rapidly as possible (preferably within about 10–15 minutes) to above 1200° C. and on to a desired reaction temperature of, say 1350° C. over a period of about 20 minutes. Due to rapid evolution of CO, the total pressure may rise to as high as 1 or 2 cm. by the time the temperature reaches 1350° C. After about 15 minutes at 1350° C., the pressure may drop below 1 cm. and after another 15 minutes or so, to about .4 mm. (400 microns). There should then be a gradual decrease in pressure over a period of about 2½ hours down to as low as 150 microns or so, where the pressure may be maintained substantially constant until the run is terminated, after a total time at or near the 1350° reaction temperature of about 5 hours, by cutting off the energy and allowing the tube and its contents to cool for removal and analysis of the product.

The following Examples 1 to 5 were carried out in the above described apparatus in accordance with the operating procedure of the described typical run, with no significant departures in the degassing procedure or the procedure for bringing the temperature of the charge up to the selected reaction temperature. In all cases, the briquetted charges of chromium oxide and carbon were selected to contain an amount of carbon calculated to form CO with all of the oxygen of the chromium oxide. The approximate time consumed in raising the temperature of the charge from the degassing temperature of 800° to 900° C. to an active reaction temperature of about 1200° C. is given in the examples and is designated "Heating period." To illustrate temperature and pressure variations during the reaction, the ensuing time, tem-

perature, and pressure readings are given. For more convenient comparison, the results of all five of these examples are tabulated at the end thereof, together with the approximate mean temperature (T) and actual pressure range (P. R.) existing during the final stage of the reaction in each example, the corresponding minimum permissible pressure (Min. P.), and the approximate reaction time (R. t.) during which the charge was maintained at or above 1200° C.

EXAMPLE 1

Heating period _____minutes__ 5
Mean temperature (T.) _____° C__ 1200
Pressure range (P. R.) _____microns__ 372–32
Minimum permissible pressure (Min. P.)_do____ 8
Reaction time (R. t.) _____hours__ 7

Readings

Time	Pressure	Temperature, ° C.
8:20	260.0 microns	1,200
8:22	0.1 centimeter	1,200
8:30	0.4 centimeter	1,215
8:37	0.3 micron	1,195
8:49	do	1,200
9:24	0.2 centimeter	1,200
10:01	0.1 centimeter	1,210
10:40	372 microns	1,205
11:20	116 microns	1,205
12:07	70 microns	1,200
1:08	52 microns	1,200
2:09	41 microns	1,200
3:18	32 microns	[1] 1,205

[1] Heat off.

EXAMPLE 2

Heating period _____minutes__ 40
Mean temperature (T.) _____° C__ 1250
Pressure range (P. R.) _____microns__ 190–52
Minimum permissible pressure (Min. P.)_do____ 20
Reaction time (R. t.) _____hours__ 4

Readings

Time	Pressure	Temperature, ° C.
10:26	410+ microns	1,240
10:50	do	1,245
11:31	190 microns	1,250
12:30	78 microns	1,250
1:30	60 microns	1,250
2:00	52 microns	[1] 1,250

[1] Heat off.

EXAMPLE 3

Heating period _____minutes__ 15
Mean temperature (T.) _____° C__ 1275
Pressure range (P. R.) _____microns__ 270–100
Minimum permissible pressure (Min. P.)
_____microns__ 32
Reaction time (R. t.) _____hours__ 4½

Readings

Time	Pressure	Temperature, ° C.
10:15	410+ microns	1,260
10:50	do	1,275
11:20	do	1,275
12:00	270 microns	1,275
12:35	180 microns	1,275
1:30	120 microns	1,275
2:30	100 microns	[1] 1,275

[1] Heat off.

EXAMPLE 4

Heating period _____minutes 6
Mean temperature (T.) _____° C__ 1312
Pressure range (P. R.) _____microns__ 330–115
Minimum permissible pressure (Min. P.)
_____microns__ 60
Reaction time (R. t.) _____hours__ 7

Readings

Time	Pressure	Tempera- ture, ° C.
8:23	410+ microns	1,200
8:28	1.6 centimeters	1,310
8:31	do	1,320
8:36	1.1 centimeters	1,310
9:50	0.1 centimeters	1,315
10:22	330.0 microns	1,315
11:22	215.0 microns	1,315
12:36	145.0 microns	1,315
1:26 [1]	115.0 microns	1,312
2:15	120.0 microns	1,320
3:15	145.0 microns	[2] 1,310

[1] Partially closed vacuum line to maintain pressure.
[2] Heat off.

EXAMPLE 5

Heating	minutes	10
Mean temperature (T.)	° C	1400
Pressure range (P. R.)	microns	410–325
Minimum permissible pressure (Min. P.) microns		225
Reaction time	hours	4

Readings

Time	Pressure	Tempera- ture, ° C.
9:05	2.0 centimeters	
9:07	2.5 centimeters	1,400
9:09	2.2 centimeters	1,400
9:50	0.2 centimeters	1,400
10:18 [1]	380.0 microns	1,400
11:08	410+ microns	1,390
12:12	330.0 microns	1,390
12:50	325.0 microns	1,400
1:07	do	[2] 1,390

[1] Partially closed vacuum line.
[2] Heat off.

TABLE OF RESULTS
EXAMPLES 1 TO 5

Data	Example				
	1	2	3	4	5
T. (° C.)	1,200	1,250	1,275	1,312	1,400
P. R. (microns)	372–32	190–52	270–100	330–115	410–325
Min. P. (microns)	8	20	32	60	225
R. t. (hours)	7	4	4½	7	4
Cr yield (percent)	99.4	100	99	97	97.5
Prod. anal.:					
Percent Cr (as metal)	98.9	99.31	99.03	99.84	99.74
Percent C	1.16	0.67	0.73	0.11	0.06

While reduction of the operating pressure for a brief period below the minimum permissible pressure may cause only a small loss of chromium, and is not such a departure from the invention as to render the results of no value, the advantages in product purity would not normally justify intentionally departing from the preferred operating conditions in this manner. This is well illustrated by the following additional examples in which the pressure dropped below the specified minimum for varying periods of time, either in the course of or during the last part of the reaction period.

EXAMPLE 6

This example was selected from runs made before discovering that there is a critical minimum pressure.

Following the same procedure as in Examples 1 to 5 and using a mean reaction temperature of about 1350° C., the charge was degassed for a period of about 35 minutes at a temperature between 850 and 900° C., during which time the pressure quickly rose from an initial 4 microns (before applying heat) to 128 microns, and then gradually dropped back down to about 80 microns. The temperature was then raised to 1215° C. in about 5 minutes, causing the pressure to rise to 0.7 cm. During the next 9 minutes the temperature was further raised to 1360° C., and the pressure climbed to 1.2 cm. and then dropped

down to 0.8 cm. During the next hour and 20 minutes, the temperature was dropped back slightly to 1345° C. and the pressure gradually dropped to 410 microns. From this point to the end of the run, the time, pressure and temperature readings were as follows:

Time	Pressure, microns	Temper- ature, ° C.
11:52	299	1,360
12:00	230	1,350
12:11	200	1,350
12:21	175	1,350
12:52	155	1,350
1:30	115	1,345
1:52	100	1,350
2:22	135	1,350
2:40	150	1,350
2:52	150	[1] 1,350

[1] Heat off.

Whereas the minimum permissible pressure (to avoid loss of chromium) was about 105 microns, it will be noted that the pressure had dropped to 100 microns at 1:52 and might have been at or even slightly lower than that value for something under 45 or 50 minutes. Though the product analysis was reasonably good with 98.7% total chromium content and 0.43% carbon (note the abnormally long delay of nearly 1½ hours in reaching a pressure below 400 microns), the yield was only 90.0%, apparently due to chromium vaporization while the pressure was slightly below the critical minimum.

EXAMPLE 7

In a run similar to Example 6, made after discovering the criticality of the minimum pressure limitations, the effect of too low a pressure was intentionally accentuated. The mean reaction temperature in this case was about 1340 degrees over a total period of about 3½ hours during which the temperature was above 1200° C. The times, pressures, and temperatures during this period were as follows:

Time	Pressure, microns	Temper- ature, ° C.
12:15	410+	1,250
12:38	410+	1,340
1:37	410+	1,335
2:00	230.0	1,335
2:15	140.0	1,345
2:35	80.0	1,345
3:25	8.5	1,350
3:45	2.0	[1] 1,350

[1] Heat off.

This greater drop below the minimum permissible pressure, for something over an hour and 10 minutes during the latter third of the reaction period, resulted in a yield of only 80.0%, a chromium content of 98.49% (as metal), and a carbon content 0.43%.

EXAMPLE 8

In another run similar to Example 6, made after discovering the criticality of the minimum pressure limitation, the effect of too low a pressure was intentionally accentuated still further. The mean reaction temperature in this case was slightly below 1350° C. over a total period of close to 4½ hours during which the temperature was above 1200° C. The times, pressures, and temperatures during this period were as follows:

Time	Pressure, microns	Temper- ature, ° C.
9:02	45.0	1,050
9:21	410+	1,310
9:33	245	1,350
9:55	112	1,350
10:24	20	1,350
11:42	7.5	1,350
12:27	5.6	1,340
1:33	5.1	[1] 1,350

[1] Heat off.

In this case, the pressure was well below the minimum permissible pressure of about 100–105 microns for around 3½ hours, and the yield dropped to about 14.4%. The yield being so small as to be of no practical interest, the composition of the product was not analyzed.

EXAMPLE 9

In still another run, made for the same purposes as Examples 7 and 8, but using a mean reaction temperature of about 1300° C. (minimum permissible pressure, about 45 microns), the times, pressures, and temperatures, after heating from 900° C. to 1300° C. in eight minutes were as follows:

Time	Pressure, microns	Temperature, ° C.
8:57	410+	1,300
9:03	410+	1,300
9:16	173.0	1,310
9:56	62.0	1,300
10:10	53.0	1,300
10:21	43.0	1,300
10:45	25.2	1,300
12:57	4.6	[1] 1,300

[1] Heat off.

In this case the pressure was well below the minimum permissible pressure for somewhat over 2½ hours and the yield was 67.2%. The product analyzed 96.0% chromium (as metal) and 0.14% carbon, indicating that there may have been a slight deficiency of carbon in the charge mixture and, therefore, a small amount of unreduced oxide in the product.

EXAMPLE 10

In still another run, made for the same purposes as Examples 6–9, but using a mean reaction temperature of about 1400° C. (minimum permissible pressure, about 220 microns), the times, pressures, and temperatures after heating from 900° C. to 1400° C. in about fifteen minutes, were as follows:

Time	Pressure, microns	Temperature, ° C.
10:30	410+	1,400
11:20	410+	1,420
11:21	380.0	1,400
12:00	105.0	1,400
12:30	68.0	1,400
1:00	38.0	[1] 1,400

[1] Heat off.

In this case the pressure was well below the minimum permissible pressure for somewhat over one hour, and the yield was 46.0%. The product analyzed 98.8% chromium (as metal) and 0.12% carbon.

The following example illustrates the operativeness of temperatures of 1450° C. or higher and the considerations on which is based the present preference for working at somewhat lower temperatures.

EXAMPLE 11

Efforts to carry out the invention at a temperature of 1450° C. and in a pressure range somewhat above the theoretical permissible minimum at that temperature (i. e., above about 415 microns) caused only the outer surfaces of the briquettes to be reduced, forming a brilliantly metallic shell or case of chromium metal about a core of unreacted charge material. From this it was apparent that the reduction reaction can be performed at 1450° C. and higher if smaller size pieces in the nature of briquettes, granules, pellets, or the like were employed along with suitable apparatus and techniques for preventing agglomeration of the individual pieces and coalescence of a confining shell of chromium metal before the interiors of the pieces have fully reacted and the evolved carbon monoxide has escaped.

The following additional example is of interest for comparing the purity of the product of the present invention with the purest metallic chromium available on the market, i. e. chromium produced by electrolysis of an aqueous chromium salt electrolyte.

EXAMPLE 12

To demonstrate the purity of the product of the present invention compared to the purest commercial electrolytic (aqueous) chromium available on the market, the following distillation tests were performed. A sample of commercial electrolytic chromium, reported as being 99.3% chromium, was weighed and then heated to a temperature between 1460° and 1475° C. for about 3¾ hours in a closed chamber while reducing the pressure therein from an initial 195 microns existing when the temperature reached 1400° C. to a final pressure of 6.2 microns at the end of the heating period. The pressure throughout the heating period was well below the curve in Fig. 1 so that the chromium readily vaporized and was removed as a vapor from the chamber. At the end of the heating period, the residue of non-volatile material was 2.5% of the original charge, and this residue represented the percentage of the commercial chromium product which was made up of chromium oxide or other non-volatile impurities. This amount of oxide corresponds closely to what would be expected on the assumption that the 0.7% impurities in the product consisted initially of combined oxygen in the form of Cr_2O_3. In other words, the commercial electrolytic product reported as 99.3% chromium actually contained only about 97.5% chromium as metal and about 2.5% chromium oxide.

The same procedure was repeated using the product of the present invention produced at 1350° C. with a total heating period of about 5 hours above 1200° C., the pressure being lowered during the heating period to a final pressure of 100 microns. Chemical analysis of this product showed 98.74% chromium as metal and 0.43% carbon. When this product was heated at low pressure above its vaporization temperature under the same conditions described above, the final residue representing the amount of chromium oxide in the product was 0.8% of the original charge compared to the 2.5% for the commercial electrolytic product.

From the foregoing description and specific examples of the process of the present invention it will be apparent that a commercially practical and efficient process for producing relatively malleable chromium metal of high purity by carbon reduction of its oxide has been provided. It will also be appreciated that the practicality of the invention is not limited to the particular operating conditions by which optimum results are obtainable in a simple vacuum furnace, as herein disclosed. As pointed out, results vastly superior to those heretofore obtainable by carbon reduction of chromium oxide are still obtainable while departing materially from the theoretical or preferred, optimum, reaction conditions. Thus, the theoretically critical limits (such as the minimum reaction pressure) and certain preferred operating conditions (such as the maximum pressure and maximum or minimum temperature existing during the reaction), to which reference is necessarily made in explaining the invention herein or for the purpose of defining the scope of the invention in the appended claims, should be construed in the light of such facts. The invention, as claimed, is intended to embrace such variations of the present disclosure as will naturally occur to those skilled in the art, and also such departures from the various preferred or theoretical limits as may obviously be tolerated while gaining the benefits of the invention to something less than the optimum degree.

Having described my invention, I claim:

1. A method of producing chromium metal from chromium oxide by reduction of the oxide with carbon,

comprising intimately mixing finely divided chromium oxide and finely divided carbon in substantially stoichiometric proportions for combination of all of the oxygen of the oxide with all of the carbon to produce carbon monoxide, heating said mixture in a reaction chamber to an elevated temperature above about 1200° C., but below the melting point of chromium, holding the mixture at such an elevated temperature while removing evolved carbon monoxide at a rate to create and maintain a partial subatmospheric pressure of non-condensable gas consisting essentially of said carbon monoxide in said chamber, said partial pressure being substantially below atmospheric pressure but exceeding the partial vapor pressure of chromium at the prevailing temperature, and maintaining substantially said conditions of pressure and temperature until reduction of the oxide is substantially complete.

2. A method of producing chromium metal from chromium oxide by reduction of the oxide with carbon, comprising intimately mixing finely divided chromium oxide and finely divided carbon in substantially stoichiometric proportions for combination of all of the oxygen of the oxide with all of the carbon to produce carbon monoxide, heating said mixture in vacuo in a closed reaction chamber to an elevated temperature above about 1200° C., but below the melting point of chromium, holding the mixture at such an elevated temperature in vacuo while removing evolved carbon monoxide and maintaining a partial subatmospheric pressure of non-condensable gas inert to chromium in said chamber, said partial pressure exceeding the partial vapor pressure of chromium at the prevailing temperature and being brought below about 1 millimeter of mercury during the course of the reduction reaction, and maintaining substantially the last defined conditions of pressure and temperature until reduction of the oxide is substantially complete.

3. A method of producing chromium according to claim 2 in which said partial pressure of non-condensable gas is brought below about 400 microns of mercury during the course of the reduction reaction while said elevated temperature of the mixture is maintained between about 1200° and about 1425° C., and substantially the last defined conditions of temperature and pressure are maintained until reduction of the oxide is substantially complete.

4. A method of producing chromium metal from chromium oxide by reduction of the oxide with carbon, comprising intimately mixing finely divided chromium oxide and finely divided carbon in substantially stoichiometric proportions for combination of all of the oxygen of the oxide with all of the carbon to produce carbon monoxide, subjecting the mixture, in vacuo in a closed reaction chamber, to an elevated temperature below about 925° C. for removing occluded gas from the mixture, raising and maintaining the temperature of the mixture above about 1200° C., but below the melting point of chromium, to initiate the reduction reaction while removing evolved carbon monoxide, and maintaining, during continuance of the reaction, a partial sub-atmospheric pressure of non-condensable gas inert to chromium in said chamber, said partial pressure being in a range between the partial vapor pressure of chromium at the prevailing temperature and a pressure of about 1 millimeter of mercury above said partial vapor pressure, and maintaining substantially the last defined conditions of temperature and pressure in said reaction chamber until reduction of the oxide is substantially complete.

5. A method of producing chromium metal according to claim 4 in which the temperature of the mixture is raised from the degassing temperature below about 925° C. to the reaction initiating temperature above about 1200° C. at a rate sufficient to avoid the formation of any appreciable amount of chromium carbide during such temperature rise.

6. A method of producing chromium metal according to claim 4 in which the degassing temperature is below that at which any appreciable amount of carbon monoxide is generated by reaction of the chromium oxide and carbon of the mixture.

7. A method of producing chromium metal according to claim 4 in which the degassing temperature is below that at which any appreciable amount of carbon monoxide is generated by reaction of the chromium oxide and carbon of the mixture, and the temperature of the mixture is raised from said degassing temperature to the reaction initiating temperature above about 1200° C. at a rate sufficient to avoid formation of any appreciable amount of chromium carbide during such temperature rise.

8. A method of producing chromium metal from chromium oxide by reduction of the oxide with carbon, comprising intimately mixing finely divided chromium oxide and finely divided carbon in substantially stoichiometric proportions for combination of all of the oxygen of the oxide with all of the carbon to produce carbon monoxide, subjecting the mixture, in a closed reaction chamber, to a pressure substantially below atmospheric pressure and to an elevated temperature below about 925° C. to remove occluded gas from the mixture, raising and maintaining the temperature of the mixture above about 1200° C., but below the melting point of chromium, to initiate the reduction reaction while removing carbon monoxide generated by the reaction and maintaining, during continuance of the reaction, a partial subatmospheric pressure of non-condensable gas inert to chromium in said chamber below about 1 millimeter of mercury but exceeding the partial vapor pressure of chromium at the prevailing temperature, and maintaining substantially the last defined conditions of temperature and pressure in said reaction chamber until reduction of the oxide is substantially complete.

9. A method of producing chromium metal according to claim 8 in which the degassing temperature is between about 800° C. and 925° C.

10. A method of producing chromium metal according to claim 8 in which the degassing temperature is between about 800° C. and 925° C., and the degassing pressure is at least as low as 400 microns of mercury at the end of the degassing operation.

11. A method of producing chromium metal according to claim 8 in which the temperature of the mixture during the reaction is maintained between about 1200° C. and about 1425° C.

12. A method of producing chromium metal according to claim 8 in which the temperature of the mixture is raised from the degassing temperature to a reaction initiating temperature above about 1200° C. at a rate sufficient to avoid formation of any appreciable amount of chromium carbide during such temperature rise.

13. A method of producing chromium metal according to claim 8 in which the temperature of the mixture is raised from the degassing temperature to a reaction initiating temperature above about 1200° C. at a rate sufficient to avoid formation of any appreciable amount of chromium carbide during such temperature rise, and the temperature of the mixture during the remainder of the reaction is maintained between about 1200° and 1425° C.

14. A method of producing chromium according to claim 8 in which the partial pressure of non-condensable gas in said chamber is brought below about 400 microns of mercury during the course of the reduction reaction, the temperature of the mixture is maintained between about 1200° and 1425° C., and substantially the last defined conditions of temperature and pressure are then maintained until reduction of the oxide is substantially ly complete.

15. A method of producing chromium metal according to claim 8 in which the degassing temperature is between about 800° and 925° C. and the degassing pres-

sure is at least as low as 400 microns of mercury, the temperature of the mixture during the reduction reaction is maintained between about 1200° and 1425° C., the partial pressure of non-condensable gas in said chamber is brought below about 400 microns of mercury during the course of the reduction reaction, and substantially the last defined conditions of temperature and pressure are then maintained until reduction of the oxide is substantially complete.

16. A method of producing chromium metal from chromium oxide by reduction of the oxide with carbon, comprising intimately mixing finely divided chromium oxide and finely divided carbon in substantially stoichiometric proportions for combination of all of the oxygen of the oxide with all of the carbon to produce carbon monoxide, subjecting the mixture, in a closed reaction chamber, to a temperature between about 800° C. and 925° C. while evacuating evolved gas released from the mixture until the pressure in the chamber is reduced to as low as 400 microns of mercury, raising the temperature of the mixture to a reaction initiating temperature between about 1200° C. and 1425° C., and maintaining such temperature while removing carbon monoxide generated by the reaction and maintaining a partial pressure of non-condensable gas inert to chromium in said chamber between about 400 microns of mercury and the partial vapor pressure of chromium at the prevailing temperature to drive the reaction toward

completion, reducing said partial subatmospheric pressure to within about 100 microns of mercury of the partial vapor pressure of chromium at the prevailing temperature, and maintaining substantially the last defined conditions of temperature and pressure in said reaction chamber until reduction of the oxide is substantially complete.

17. A method of producing chromium metal according to claim 16 in which the temperature of the mixture is raised from the degassing temperature to the reaction initiating temperature at a rate sufficient to avoid formation of any appreciable amount of chromium carbide during such temperature rise.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,850,378   September 2, 1958

Hugh S. Cooper

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 37, strike out 'and under a "high vacuum," in order to determine the".

Signed and sealed this 28th day of July 1959.

(SEAL)

Attest:

KARL H. AXLINE   ROBERT C. WATSON
Attesting Officer   Commissioner of Patents

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