

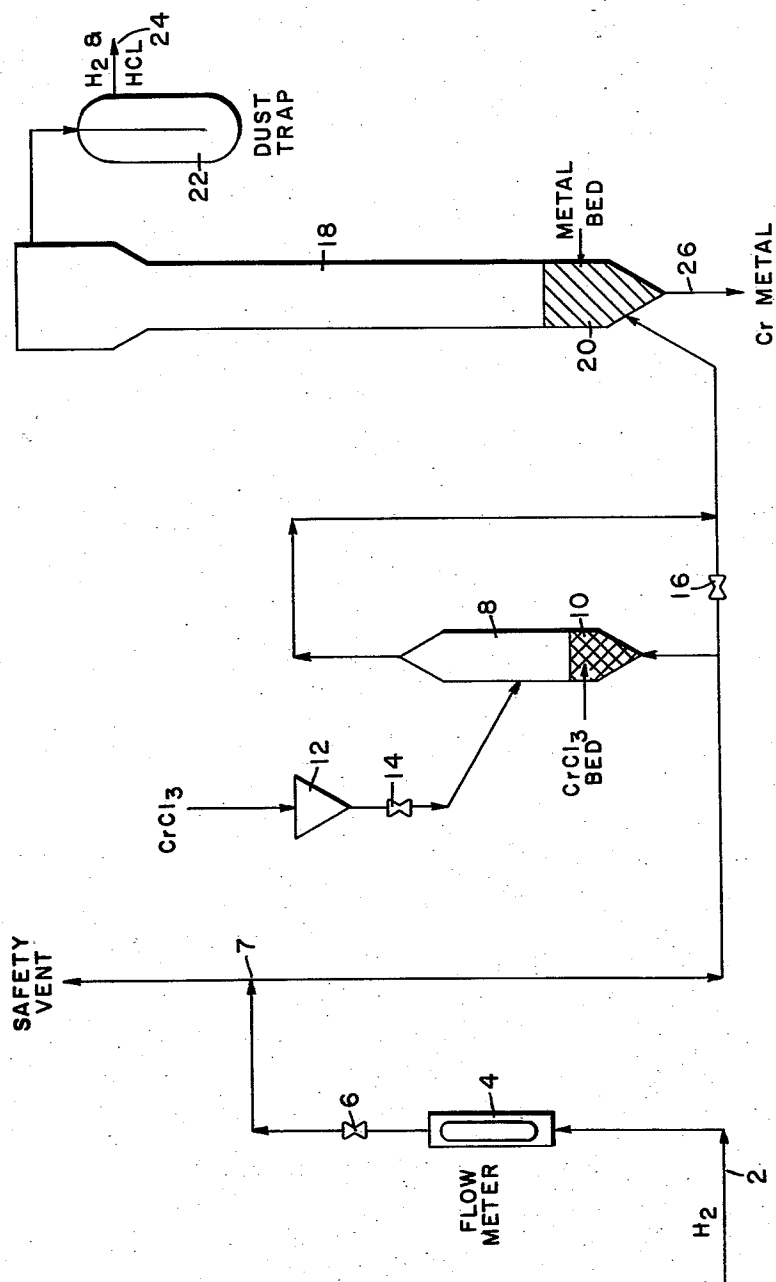
July 10, 1962

I. E. CAMPBELL ETAL

3,043,679

METHOD OF PRODUCING CHROMIUM

Filed Oct. 20, 1958



INVENTORS

IVOR E. CAMPBELL

JOSEPH H. OXLEY

BY *Warburton & Cross*

ATTORNEY

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3,043,679

METHOD OF PRODUCING CHROMIUM

Ivor E. Campbell, New Albany, and Joseph H. Oxley, Columbus, Ohio, assignors, by mesne assignments, to Diamond Alkali Company, Cleveland, Ohio, a corporation of Delaware

Filed Oct. 20, 1958, Ser. No. 768,223

4 Claims. (Cl. 75-26)

This invention relates to a method for producing chromium of high purity and in particular to a method for producing chromium of high purity by the hydrogen reduction of chromium chloride in a fluidized bed-type reactor.

Until recently, chromium metal was produced commercially, primarily, by either the aluminum or silicon reduction of chromium oxide, which methods are commonly known as the aluminothermic or silicothermic processes. Chromium produced by these processes is generally about 99% pure and as such, is sufficiently pure to meet most metallurgical requirements. However, alloys containing more than about 55% of chromium made by either of the above processes, are found to have very poor hot and cold working properties as well as being extremely brittle, i.e., having low impact resistance. While, for most alloy uses, a chromium content of between 15 and 50% is sufficient, in many recent high temperature applications, such as gas turbine rotor blades, the outstanding resistance to oxidation and high temperature deformation of higher chromium alloys would offer great promise, were it not for their disadvantageous characteristics of difficult workability and extreme brittleness.

It has now been found, that when a chromium metal is used having a purity appreciably greater than 99%, upwards to 10% or more additional chromium may be added to the alloy without encountering the above disadvantageous characteristics. In view of this, numerous processes have been developed in an attempt to produce such a high purity chromium metal. However, none of these processes have been able to produce chromium of an appreciable higher purity than that of the present commercial processes, at a commercially feasible cost.

In this regard, as a third commercial process, an aqueous solution containing trivalent chromium ions has been electrolyzed to produce chromium metal. Although the cost of such a process is competitive with the aluminothermic and silicothermic processes, the chromium thus produced, commonly called electrolytic chromium, still has an impurity content of about 1% as shown in Table III. However, unlike the chromium from the other commercial process, wherein aluminum, iron and silicon are the major impurities, the major impurity here is oxygen. In view of this, electrolytic chromium has been further purified by reducing it with hydrogen, thus producing a chromium metal containing impurities of only about a tenth of a percent. The respective ranges of impurities for this process are shown in Table III wherein the process is identified as "H₂ Reduced Electrolytic." However, the cost of such a process coupled with the original cost of the electrolytic chromium makes it commercially unattractive.

Similarly, processes in which chromic oxide is reduced with carbon, calcium, magnesium, and hydrogen, although

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producing chromium of a significantly higher purity than the aluminothermic and silicothermic processes, have all proved to be too expensive to be used commercially. Other processes which have been examined and discarded on like grounds have included the reduction of chromium chloride using magnesium, sodium, manganese, zinc, calcium and hydrogen.

Of these, this last process, i.e., the hydrogen reduction of chromium chloride, has been investigated extensively and the results reported in both the patent and non-patent literature. In the Bureau of Mines Bulletin #436, "Sponge Chromium," by C. G. Maier, and in U.S. Patents 2,142,694 and 2,341,844, it is proposed to heat chromic chloride in shallow pans to about 850° C. while passing hydrogen over the pans, thereby reducing the chromic chloride to chromium metal. At this temperature, however, there is considerable decomposition of the chromic chloride and the free chlorine formed attacks the materials of the apparatus, forming chlorides which in turn contaminate the chromium. Thus, the purity of the product is not appreciably higher than that of the present commercial process. Additionally, the chromium so produced is not readily recoverable and the process itself is not readily adaptable for continuous operation, thereby, materially increasing the cost of chromium produced so it is not a commercially competitive process.

In U.S. Patent 2,837,420, it is proposed to coat particles of powdered chromium metal with liquid chromous chloride and pass the thus coated particles countercurrent to a stream of hydrogen, thereby reducing the chromous chloride to chromium metal. Here again, at the temperature required to maintain the chromous chloride in the liquid state, considerable contamination of the product occurs due to corrosion of the reactor by the molten chromous chloride. Thus, although this process can be operated continuously and the product chromium is more easily recoverable, the purity of the product is no higher than that of the commercial processes.

In considering and evaluating the prior art methods, it must be kept in mind, that although one major objective of such methods is the production of chromium of high purity, this is not the final consideration. If such were the case, iodide chromium produced by the thermal dissociation of chromous iodide, would be the solution to the problem, inasmuch as it contains only about .01% impurities. Cost, however, is also an important factor and iodide chromium's price of about \$128 a pound causes it to fall far short of being commercially competitive. It can thus be seen that none of the prior art processes have been able to fulfill both the criteria of high purity and reasonable cost.

It has now been found, in the practice of the present invention, that solid, particulate chromium chlorides can be reduced with hydrogen in a fluidized bed reactor to produce chromium having a purity of about 99.9%. It has further been found that such a process can be operated on a commercial scale to produce a product costing considerably less than hydrogen reduced electrolytic chromium.

It is therefore an object of the present invention to provide a method for producing high purity chromium from chromium chlorides.

A further object of this invention is to provide such

a method which can be operated as a commercially feasible process.

These and other objects will become apparent to those skilled in the art from the description of the invention which follows.

Referring now to the drawing which is attached hereto and made a part hereof, the single FIGURE is a schematic flow diagram of the process of the present invention.

The present invention envisions the reduction of a chromium chloride with a stream of hydrogen gas in a fluidized bed type reactor, wherein the hydrogen acts not only as the reducing agent but also as a carrier for the chromium chloride and as the fluidizing medium for the bed in the reactor. More particularly, the method of the present invention envisions introducing solid, particulate chromic chloride and hydrogen, as the fluidizing media, into a fluidized bed type reactor, maintained at a temperature sufficiently high to cause the chromic chloride to be reduced, by the hydrogen, to chromium metal.

In the present process, solid, particulate chromic chloride is introduced, with hydrogen, into the bottom of a fluidized bed type reactor, as a suspension of finely-divided chromic chloride entrained in the hydrogen. Alternatively, chromous chloride can be used instead of chromic chloride. In the latter instance, however, the chromous chloride is generally formed by reducing chromic chloride thus adding an additional step to the process and for this reason it is preferred to use chromic chloride. It has been found that excellent results are obtained when using chromic or chromous chloride having a particle size of less than 60 mesh, i.e., having particles of a size which will pass through a screen having about 60 openings per linear inch.

The fluidized bed in the reactor is maintained at a temperature between about 700°-1000° C., and preferably between 800°-950° C. At this temperature, the chromic chloride or chromous chloride is reduced to metallic chromium, which material is deposited on the particles of the fluidized bed.

The fluidized bed in the reactor is preferably finely-divided, high purity chromium metal, and has a particle size within the range of 20 to 100 mesh, i.e., of a size such that the particles will pass through a screen having about 20 openings per linear inch but will be retained on a screen having about 100 openings per linear inch. A bed made up of particles within this range is found to be readily fluidizable by the hydrogen gas which is introduced into the reactor with the chromium chloride. It will be appreciated, that the method of the present invention is applicable to the production of various alloys of high purity chromium and another metal as well as to the production of high purity chromium, itself. Thus, although where the desired product of the reaction is high purity chromium metal, the fluidized bed is preferably made up of high purity chromium, where a chromium alloy is desired, the fluidized bed may be formed of similarly small particles of the metal with which it is desired to alloy the chromium. In this instance, the chromium metal produced is deposited upon the metal particles in the bed and the thus-coated particles are periodically removed from the reactor and remelted to form the desired chromium alloy. Examples of metal which may be so used are: iron, nickel, and molybdenum, although other metals which will alloy with chromium and which have a melting point sufficiently above the reduction temperatures in the reactor may also be used.

It has been found, that as the chromium metal is deposited upon the particles of the fluidized bed, some nucleation also occurs, i.e., new particles of chromium are formed. In this manner, the fluidized bed is, for the most part, self-sustaining and no additions of fluidizable material are generally necessary. However, where the nucleation is not sufficient to maintain the desired quantity of material in the fluidized bed, and in particular where a chromium alloy is being produced, the bed may

be replenished by periodically or continuously by adding finely-divided particles thereto, such as, a portion of the product which has been ground to the desired size.

As would be expected, the purity of the chromium product of the method of the present invention will depend to a great extent on the purity of the reactants which are used. For this reason, the chromium chloride and hydrogen should be relatively free of all impurities and in particular, oxygen, nitrogen and hydrocarbon impurities. The chromic chloride can be purified by any suitable methods, as for example, by resublimation, while electrolytic hydrogen which has been dried after converting the oxygen therein to water, has been found to be sufficiently pure for the present process. Additionally, recirculation of the hydrogen which has not been used up in reducing the chromium chloride, has been found to reduce the impurity content thereof on subsequent passes through the reactor.

By means of the entrainment feed of the chromium chloride, in the hydrogen, contamination of the product chromium by the corrosion of the material of the apparatus with which the reactants come in contact, is eliminated. Because, there is no heating of the chromium chloride until it is introduced into the reduction reactor, no decomposition of the chromium chloride occurs and hence no chlorine corrosion and subsequent contamination of the product. Within the reduction reactor, some chromium metal is deposited on the walls as well as on the particles of the fluidized bed so that contamination from corrosion of the reactor is prevented. However, the reactor is preferably constructed of a material which is resistant to high temperature corrosion, as for example a high nickel stainless steel or any other material commonly used in high temperature applications.

Unlike the prior art processes, wherein the chromium chloride is deposited on the particles of chromium metal prior to reduction thereby necessitating the use of high temperatures which decompose the chromium chloride with resulting corrosion of the apparatus and contamination of the product, in the present process, reduction occurs at least simultaneously and generally prior to deposition. In this manner, the problems of contamination are overcome.

While theoretically, an excess of hydrogen of about 50 times that of the stoichiometric amount required in order to obtain substantially complete conversion of the chromium chloride to chromium metal in the present process, it has been found that, generally, somewhat greater excess hydrogen ratios are required to obtain 100% conversion to metallic chromium. Thus about 100 to as high as 400 or 600 times the stoichiometric amount of hydrogen is required. Inasmuch as the percent conversion of chromium chloride to chromium, for any given contact time in the reactor is greatest at higher reduction temperatures, e.g., 950°-1000° C. as lower reduction temperatures are used, e.g., 800° C., greater excess hydrogen ratios must be used in order to obtain substantially complete reduction of the chromic chloride without lengthening the time of contact within the reactor. Thus, at these lower reduction temperatures, excess hydrogen ratios of about 400 have been found to be necessary. Conversely, at reduction temperatures of about 950° C., excess hydrogen ratios of somewhat less than 400 are sufficient.

While, theoretically, it would be possible to use reduction temperatures in excess of about 1000° C., thereby further reducing the excess hydrogen ratio required, it has been found that at such higher temperatures, particles of the fluidized bed agglomerate, thereby preventing the fluidization of the bed and adversely affecting the conversion of the chromic chloride to chromium metal.

Referring now to the drawing, hydrogen, which is substantially free from oxygen, nitrogen and hydrocarbon impurities, is introduced into line 2 where it flows through flow meter 4. The rate of hydrogen flow past the flow meter 4 is controlled by valve means 6, with suitable

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safety venting means for relieving excess pressures as shown at 7. From the flow meter 4, hydrogen flows into the chromic chloride bed 10 in the chloride feeder 8. The chromic chloride is added to the chloride feeder 8 by means of hopper 12, the flow of chromic chloride being controlled by valve means 14. As the hydrogen passes through the chromic chloride bed 10, the chromic chloride becomes entrained in the hydrogen stream and is carried into the fluidizable metal bed 20 in the reduction reactor 18. Within the reduction reactor 18, the chromic chloride is reduced by the hydrogen to metallic chromium, which latter material is deposited upon the metal particles of the fluidized bed. As the chromium metal is deposited upon the particles of bed 20, the larger particles fall to the bottom of the reactor 18 and are removed therefrom as the final product as shown at 26. The excess hydrogen gas and the gaseous HCl which is formed in the reduction reactor are drawn off at the top of the reactor and pass into dust trap 22 wherein any solid materials contained therein are removed. The hydrogen and gaseous HCl are removed from the dust trap as at 24 and are passed through separators, purifiers and recirculators (not shown) whereby the hydrogen is reconditioned for reuse in the process.

It will be appreciated that passing the hydrogen through a bed of chromic chloride is only one means of entraining the chromic chloride in the hydrogen and other methods may also be used, e.g., feeding particulate chromic chloride directly into the hydrogen stream by means of a screw conveyor. It is the entrainment of the chromium chloride in the hydrogen which is important and not the manner in which entrainment is achieved.

Similarly, although the reduction reactor has been described as containing a fluidized bed, the product chromium metal can be collected in any other suitable manner, as for example, in a fixed bed, in a moving bed, or it can be deposited on the walls of the reactor itself. However, because of the problems of recovery and for simplicity of operation, the fluidized bed is preferred.

In actual operation, high purity chromium having a particle size of about 60 mesh is placed in the reduction reactor 18 to form the metal bed 20 and the entire system is purged with argon gas to remove any impurities from the system. Reduction reactor 18 is then heated, by any suitable heating means (not shown), to within the range of 800° to 950° C., preferably about 900° C., while the metal bed 20 is fluidized by passing purified hydrogen through the system. During this time, the flow of hydrogen is bypassed around the chloride feeder by means of valve 16. If desired, prior to the reduction of the chromic chloride, all or part of the hydrogen may be heated to about 300° C. in order to improve the heating efficiency of the reactor 18. When the reactor and bed have obtained the desired temperature, bypass valve 16 is adjusted so that all or any part of the hydrogen is directed into the chromic chloride bed 10 and the chloride feeder 8. Chromic chloride is constantly added from hopper 12 to the chloride feeder 8, the rate of addition being controlled by valve 14 so as to maintain the level of the chromic chloride bed 10 in the chloride feeder at a substantially constant level. The chromic chloride suspended in the hydrogen stream is introduced through the bottom of reactor 18, where in contact with the fluidized bed of chromium metal 20, it is reduced to metallic chromium, which is deposited upon the particles of the bed. The flow of hydrogen is regulated at all times by means of valve 6 so as to maintain an excess hydrogen ratio in reactor 18 of about 400. As the particles of metal bed 20 become coated with chromium, they drop to the bottom of the reactor and are removed as the final product at 26, the bed being replenished by nucleation and internal grinding or by the continuous or periodic addition of new particles. The excess hydrogen and HCl formed in the reactor are

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discharged into a dust trap 22 wherein the solid materials contained therein are removed and the gases discharged, as at 24, to be treated in any well-known manner so as to make the hydrogen reusable in the process. By this process, upwards to 97% conversion of chromium is obtained with the chromium deposition rates being as high as 1.2 lbs. of chromium per hour per square foot of reactor cross sectional area, the average being about .9 lb. of chromium per hour per square foot of reactor cross sectional area.

In order that those skilled in the art may better understand the method of the present invention and manner in which it may be practiced, the following specific examples are given.

In all of the following examples, the reduction reactor used is 4 feet in length and constructed of high nickel stainless steel. The upper fourth of the reactor has an internal diameter of 4 inches, constricted to an internal diameter of 2 inches for the remaining three-quarters of its length. The remaining parts of the system, including the chloride feeder, are of glass and flexible rubber tubing. Additionally, the chloride feeder system is mounted on a balance so that periodical checks on the feed rate of chromic chloride are easily made during the reaction. The chromic chloride used is purified by resublimation, while the hydrogen is electrolytic hydrogen in which the oxygen impurities have been converted to water and the hydrogen subsequently dried. The entire system is purged with argon and then the reactor heated to the desired temperature, while the purified hydrogen is passed into the reactor after bypassing the chloride feed. When the reactor has attained the desired reduction temperature, the hydrogen feed is diverted through the chromic chloride bed so as to carry chromic chloride into the reactor wherein it is reduced to metallic chromium. The chromium coated bed particles are not removed from the reactor during the reaction but a weight determination of the bed is made before and after the reaction, the difference in weight being the amount of chromium which is deposited on the bed particles. Using this procedure and apparatus, several determinations are made under varying conditions with the following results:

Table I

Example	Bed Temp., ° C.	Excess Hydrogen Ratio	Length of Run, Hours	Weight of Bed in grams		Weight of Deposit, grams	Cr Conversion, Percent
				Initial	Final		
I.....	800	463	17.5	1,000	1,132	132	99
II.....	800	647	32	1,296	1,442	146	97
III.....	800	448	10.5	1,398	1,462	64	86
IV.....	800	374	15	1,000	1,144	144	97
V.....	800	545	31	1,000	1,161	161	95
VI.....	950	2,150	9	1,000	1,015	15	96
VII.....	800	422	14.5	1,000	1,138	138	93

The bed from each of the above experiments is analyzed to determine the impurity content in the chromium contained therein. The results obtained are as follows:

Table II

Product from—	Impurities—p.p.m.					
	O ₂	H ₂	N ₂	C	Fe	Ni
Example I.....	—	—	730	—	600	10
Example II.....	446	2	570	280	50	30
Example III.....	593	4	630	380	70	40
Example V.....	—	—	860	790	—	—
Example VI.....	—	—	870	550	—	—

In order to compare the results of the present process with those obtained in other methods for producing chromium, the impurity content of chromium produced in the longest run by the present method, as taken from the above table, is compared with the impurity content of

chromium produced by various other methods. This comparison can be seen in the following table:

Table III

Chromium Process	Impurities—p.p.m.											Total Impurities, percent
	C	N ₂	O ₂	H ₂	Fe	Ni	Al	Si	S	Cr	V	
Electrolytic.....	30-100	70-100	5,400-6,000	-----	200-600	-----	-----	10-100	250	50	-----	.6-.72
H ₂ Reduced Electrolytic.....	5-100	30-200	88-300	1-10	200	-----	-----	40	-----	50	-----	.04-.09
Iodide.....	80	10	50	-----	-----	-----	-----	-----	10	-----	-----	.01
Alumino-thermic.....	300	450	-----	-----	4,100	-----	3,700	4,700	180	40	-----	1.35
Silico-thermic.....	400	-----	-----	-----	7,900	-----	800	7,100	100	-----	400	1.67
Present Process (Ex. II).....	280	570	446	2	50	30	-----	-----	-----	-----	-----	.13

From the above results, it is seen, by the method of the present invention, chromium metal is produced having a purity of about 99.9% which purity is at least as high as that of chromium produced by other methods, with the exception of iodide chromium and electrolytic chromium which has been further purified by reducing it with hydrogen. Chromium produced by these prior known methods, however, is very costly to produce and, as such, is not commercially feasible. Additionally, the present method is a continuous process which is operated with chromium conversions as high as 97 or 98% and as a continuous process, it is readily adaptable for commercial production.

While there have been described various embodiments of the invention, the methods described are not intended to be understood as limiting the scope of the invention as it is realized that changes therewithin are possible and it is further intended that each element recited in any of the following claims is to be understood as referring to all equivalent elements for accomplishing substantially the same results in substantially the same or equivalent manner, it being intended to cover the invention broadly in whatever form its principle may be utilized.

What is claimed is:

1. The method of continuously producing high-purity chromium metal which comprises entraining finely divided solid chromic chloride having a particle size of less than 60 mesh in hydrogen gas, introducing the hydrogen gas and entrained chromic chloride into a reactor containing a bed of finely-divided high-purity chromium metal having a particle size within the range of 20 to 100

mesh, the hydrogen gas and entrained chromic chloride being introduced at a velocity sufficient to fluidize the bed

15 of chromium metal, maintaining the fluidized bed at a temperature in the range of about 890° to 950° C. such that the chromic chloride is reduced to chromium metal having an impurity content no greater than that of the chromic chloride and hydrogen gas, depositing the thus produced chromium on the particles of chromium metal in the fluidized bed and removing the coated particles from the reactor, the ratio of hydrogen gas to entrained chromic chloride being such that the hydrogen is at least 50 times the stoichiometric amount required to completely reduce the chromic chloride to chromium metal.

2. The method of claim 1 wherein the ratio of hydrogen gas to entrained chromic chloride is at least 100 times the stoichiometric amount required to completely reduce the chromic chloride to metallic chromium.

3. The method of claim 1 wherein the ratio of hydrogen gas to entrained chromic chloride is in the range of 400 to 600 times the stoichiometric amount required to completely reduce the chromic chloride to metal chromium.

4. The method of claim 1 wherein the excess hydrogen gas is removed from the reactor, purified and recycled.

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