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METHOD OF REDUCING METAL OXIDES

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This invention relates to a process for the reduction of metallic oxides and more particularly to a method of reducing the oxides while alloying the reduced metals with other metals. It is known that many oxides can be reduced by hydrogen but that in order to effect reduction of some oxides the hydrogen must be practically free from all traces of oxygen and of water vapor. The purification of hydrogen is effected by passing the hydrogen over incandescent platinum or copper turnings and the like to convert the oxygen to water and thereafter over moisture absorbing materials and finally through suitable liquid air traps to absorb and to condense the water vapor. This cleaning process made the reduction process with hydrogen considerably more expensive than other methods.

The applicant has found that it is possible to effect the reduction of metal oxides, and in particular the oxide compounds of those metals of the 5th and 6th groups of the periodic system of the elements which have a melting point of more than 1000° C. with ordinary technically pure hydrogen, provided that the reduction reaction is carried on in the presence of a "receiver" for the reduced metal.

It is, of course, also possible to reduce a mixture of oxides simultaneously and consequently to reduce into the basic metal serving as "receiver" simultaneously several constituents.

By "technically pure hydrogen" it is understood that the hydrogen still contains slight impurities of water vapor (steam), oxygen and the like such as, for example, commercially pure hydrogen that is commonly sold compressed in tanks.

By the word "receiver" is meant a metal or alloy comprised wholly or in part of a constituent adapted to combine physically or chemically with the reduced metal to form therewith an intermetallic compound or alloy adapted to be dissolved in the main body of the receiver.

Specifically the "receivers" or "absorbers" of the present invention comprise for example one or more of the elements of the so-called iron group of metals including iron, nickel, cobalt, manganese, and chromium. While nickel chromium and iron are preferred as "receiver" or "absorber" elements, any other metal or any alloy with which the reduced metal in turn can be combined with or alloyed may be used. The elements referred to herein of the 5th and 6th group of the periodic system are the metals, vanadium, niobium, tantalum, chromium, molybdenum, tungsten and uranium.

For the carrying out of the present invention it is advisable to place a layer of the oxide or ore to be reduced on a molten bath of the metal or alloy which serves as a "receiver" and to pass over the same a current of hydrogen. The reduced metal alloys with the molten metal serving as a "receiver", and there results an alloy which is free from impurities and especially free from carbon. In this specification the word oxide is to be understood to include chromium or other ores with or without the admixture of other substances which aid in the liquefaction of the oxide material.

When metal oxides are reduced without the presence of a "receiver" to absorb or to alloy with the reduced metal the reduction ceases as soon as the hydrogen has absorbed even small quantities of water vapor. When a "receiver" or "absorber" is employed the reduction proceeds much more easily. It is only necessary therefore to let the hydrogen circulate over the heated metal oxides and to free it from the water vapor during or after the circulation.

The freeing of the hydrogen from water vapor can take place either outside of the furnace in any convenient manner such, as for example, by the use of suitable freezing coils over which the moist hydrogen is passed, or by the provision of suitable freezing coils in the furnace itself in the places which are not affected by the heat energy of the reduction process. The freezing coils may be cooled by means of brine solutions and the like passed through the same in a manner heretofore practiced in the art.

As a specific embodiment of the practice of the present invention the method devised

for the production of carbon free chromium, ferro-chromium, or ferro-nickel-chromium alloys will be described.

It has been known that chromic oxide can be reduced by hydrogen to metallic chromium if the hydrogen used is exceptionally pure and especially free from all traces of oxygen and a water vapor. On account of this, it has not been heretofore possible to economically reduce chromic oxide with the customary technically pure hydrogen as it was necessary to first of all free the hydrogen from oxygen, for instance, by passing it over incandescent platinum, and to free it from water vapor (steam) by passing the same over suitable moisture absorbing substances such as KOH, $CaCl_2$, P_2O_5, etc. and finally by freezing the residual moisture out with liquid air. The cost of the reduction process is thus increased so that it could only be used in individual special cases, while the manufacture of pure chromium on a technical scale by this method is prohibitive. On the other hand, there is great interest in producing chromium alloys which are free from impurities, especially from carbon. Such a demand exists in the industry both in connection with raw materials, for instance, ferro-chromium and in connection with finished alloys, for instance, stainless (rust-free or corrosion resisting) steels, chrome nickel alloys and the like.

In accordance with the present invention the applicant has found that it is possible to produce chromium and chromium alloys, with iron and/or nickel, of an exceptionally high degree of purity, if one conducts technically pure hydrogen over chromic oxide, and at the same time provides a "receiver" to absorb or to alloy with the reduced chromium. As a "receiver" there can be used, for instance, iron, nickel, cobalt, chromium or manganese, or admixtures of any or all of the metals to form a fusible alloy. While, as stated above, the reduction of chromic oxide up to the present time was only possible with especially purified hydrogen, the reduction in accordance with the present invention can be carried out with the customary technically pure hydrogen without difficulty. In accordance with the present invention a layer of chromic oxide is preferably placed on a molten bath of the "receiver" metal and an atmosphere of hydrogen is maintained over the same. The chromium thus formed alloys with the molten metal and there results a very pure chromium alloy substantially free from carbon. The reduction reaction is facilitated by maintaining the molten bath in a superheated condition.

The production of high percentage chromium alloys is facilitated by especially purifying the hydrogen before it comes in contact with the chromic oxide placed on top of the molten metal bath.

Where chromic oxide is reduced without the presence of a so-called "receiver", the reduction reaction is stopped as soon as the hydrogen has absorbed even small quantities of oxygen (as far as is definable, approximately below 0.1%) so that large quantities of hydrogen must be continuously used and continuously freed from steam (water vapor). Where the reduction of chromic oxide is made in the presence of a "receiver" in accordance with the present invention, the reduction reaction takes place much more easily and the moisture content of the gas may be much higher so that much smaller quantities of hydrogen need to be used in the operation. The hydrogen is freed from moisture outside of the furnace by any of the well known agents and may be returned to the reduction furnace. To avoid the rather troublesome repumping of the hydrogen, means may be provided within the furnace to absorb the water vapor from the hydrogen as it is generated. Such means may comprise, for example, suitable cooling or freezing coils disposed within the furnace itself at places remote from the heat of the reduction reaction. Such coils may be cooled by brine solutions and the like conducted through the same to such a temperature that the steam formed by the reduction reaction deposits directly on the coil in a frozen condition. Chemical absorption means may be provided however if desired. In general the more pure the hydrogen the more readily the higher percentages of alloyed chromium are obtained in the molten metal bath.

An especially important field of application for the process described is the making of corrosion resisting alloys.. It is known that the corrosion resistance of iron-chromium, chrome-nickel and chrome-nickel-iron alloys is very unfavorably influenced by even small quantities of carbon. This is especially true in stainless (corrosion resisting, rust free) steels adapted for use in chemical apparatus. It is found necessary to subsequently heat the apparatus, produced by welding or the like, to a high temperature and to thereupon quench them, in order to bring the carbon contained therein into solution, in such a manner that the corrosion resistance of the alloy is not affected thereby. For this reason cumbersome processes have been developed in order to produce stainless (corrosion-resisting) steels with such a low carbon content in order to make superfluous such a refining heat treatment, which, in connection with large apparatus, is frequently not technically possible at all.

The present invention makes it possible in a simple and economic manner to produce substantially carbon free stainless (rust free corrosion resisting) steels or alloys comprised, for example, of about 18–20% chro-

mium, 8–9% nickel and the balance mainly iron.

While the present invention has been specifically disclosed with respect to the production of carbon free chromium, ferro-chromium or of ferro-nickel-chromium alloys, it is apparent that the same process can also be advantageously used for the production of other carbon free ferro or ferro-nickel or ferro-nickel-chromium alloys such as; ferro-vanadium, ferro-tantalum, ferro-uranium, ferro-nickel-vanadium, ferro-chromium-vanadium, etc.

Having broadly and specifically disclosed the present invention, it is apparent that many modifications and departures may be made without departing essentially from the nature and scope thereof as may be included within the following claims:—

What I claim is:

1. The method of reducing metal oxides which comprises placing the metal oxide upon a molten bath of metal adapted at least in part to alloy with the metal constituent of said oxide, and thereafter circulating substantially pure hydrogen over said oxide while maintaining said bath in a molten state.

2. The method of reducing metal oxides which comprises placing the metal oxide upon a molten bath of metal composed at least in part of a constituent adapted to combine with the reduced metal constituent of the oxide to form therewith a compound soluble in said metal bath, and thereafter passing substantially pure hydrogen over said oxide while maintaining the bath in a molten state.

3. The method of reducing the metal oxides of those elements of the 5th and 6th group of the periodic system of elements having melting points above about 1000° C., which comprises reducing said oxides at elevated temperatures with hydrogen while said oxides are in contact with a metallic substance adapted to absorb, combine and/or to alloy therewith at the temperature of reduction.

4. The method of forming alloys of those elements of the 5th and 6th group of the periodic system of elements having melting points above about 1000° C., which comprises reducing the oxide compounds of said elements at elevated temperatures with hydrogen while said oxides are in contact with a metallic substance adapted to alloy therewith at the temperature of reduction.

5. The method of forming alloys of those elements of the 5th and 6th group of the periodic system of elements having melting points above about 1000° C., which comprises reducing the oxide compounds of said elements at elevated temperatures with hydrogen while said oxides are in contact with a metallic substance comprising at least one of the elements of the iron group and adapted to alloy with the reduced metal.

6. The method of forming alloys of those elements of the 5th and 6th group of the periodic system of elements having melting points above about 1000° C., which comprises reducing the oxide compounds of said elements at elevated temperatures with hydrogen while in contact with a molten bath composed at least in part of one of the elements of the iron group and adapted to alloy with the reduced metal.

7. The method of forming alloys of chromium which comprises reducing chromium oxide with hydrogen at elevated temperatures while said oxide is in contact with a metallic substance adapted to alloy with the chromium at the temperature of reduction.

8. The method of forming alloys of chromium which comprises reducing chromium oxide with hydrogen at elevated temperatures while said oxide is in contact with a metallic substance comprising at least one of the elements of the iron group and adapted to alloy with the chromium at the temperature of reduction.

9. The method of forming alloys of chromium which comprises reducing chromium oxide with hydrogen at elevated temperatures while in contact with a molten bath of a metallic substance adapted to alloy with the chromium at the temperature of reduction.

10. The method of forming alloys of chromium which comprises reducing chromium oxide with hydrogen at elevated temperatures while in contact with a molten bath of a metallic substance comprising at least one of the elements of the iron group and adapted to alloy with the chromium at the temperature of reduction.

11. The method of forming ferro-chromium which comprises reducing chromium oxide with hydrogen at elevated temperatures while the oxide is in contact with a molten bath of iron.

12. The method of forming ferro-chromium-nickel alloys which comprises reducing chromium oxide with hydrogen at elevated temperatures while the oxide is in contact with a molten bath comprising iron and nickel.

13. The method of forming nickel-chromium alloys which comprises reducing chromium oxide with hydrogen at elevated temperatures while the oxide is in contact with a molten bath of nickel.

14. The method of forming substantially pure chromium which comprises reducing chromium oxide with hydrogen at elevated temperatures while the oxide is in contact with a molten bath of chromium.

15. The method of forming substantially carbon free chromium alloys which comprises melting down a bath of metal composed in part of at least one metal adapted to combine with chromium, adding thereto a proportion of chromium oxide, sealing the same from the

atmosphere and maintaining enough hydrogen thereover to reduce the chromium oxide, maintaining the metal bath molten during the reducing process.

16. The method of forming substantially carbon free chromium alloys which comprises melting down a bath of metal composed in part of at least one of the metals of the iron group, adding thereto a proportion of chromium oxide, sealing the same from the atmosphere and maintaining enough hydrogen thereover to reduce the chromium oxide, maintaining the metal bath molten during the reducing process.

17. The method of forming substantially carbon free chromium-nickel-iron alloys which comprises melting down a bath comprising nickel and iron, adding thereto chromium oxide in the desired proportion, sealing the same from the atmosphere and maintaining enough hydrogen thereover to reduce the chromium oxide, maintaining the metal bath molten during the reduction of the chromium oxide.

18. The method of claim 15, removing water vapor and the like from the effluent gases and again passing the hydrogen, thus purified over the oxide, the metal bath taking up the chromium as it is separated from its oxide and making it possible to continue the reduction of the remaining oxide by the continuous maintenance of a hydrogen atmosphere until practically all the chromium desired is thus received.

19. The method of claim 16, removing water vapor and the like from the effluent gases and again passing the hydrogen, thus purified over the oxide, the metal bath taking up the chromium as it is separated from its oxide and making it possible to continue the reduction of the remaining oxide by the continuous maintenance of a hydrogen atmosphere until practically all the chromium desired is thus received.

20. The method of claim 17, removing water vapor and the like from the effluent gases and again passing the hydrogen, thus purified over the oxide, the metal bath taking up the chromium as it is separated from its oxide and making it possible to continue the reduction of the remaining oxide by the continuous maintenance of a hydrogen atmosphere until practically all the chromium desired is thus received.

In witness whereof, I have hereunto signed my name.

WILHELM ROHN.