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PROCESS OF FORMING CHROMIUM IRON ALLOYS

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My invention relates to a process for the production of chromium iron alloys from chrome ores of many different kinds, but especially from chrome ore known as chromite.

The object of my invention is to provide a process of converting chrome ores into chromium iron alloys having many advantages over previous processes of producing chromium iron alloys. Another object is to produce alkali chromates more cheaply than was hitherto possible. Still another object is to produce chromium iron alloys without the addition of such large quantities of iron as were hitherto found necessary in process of producing such alloys.

When a mixture of chrome ore and alkali carbonate and a refractory material, such as lime, is roasted to produce an alkali chromate the reaction proceeds rapidly in the beginning and then slows down as the oxidation progresses. For example, a furnace which will convert 60% by weight of the chromium to chromate in one hour will usually take approximately four hours for the oxidation of 90% by weight of the chromium and eight hours for oxidizing substantially all of the chromium present. In accordance with my process, a roasted ore mixture is removed as soon as it reaches an oxidation of from 60 to 70% by weight of the chromium, thereby greatly increasing the daily capacity of the furnace and also economizing on the amount of the alkali carbonate added which, in accordance with my invention, is added in an amount merely sufficient to combine with 60 to 70% by weight of the chromium present. The insoluble residue, after lixiviation, contains the oxides of chromium and iron, Cr_2O_3 and Fe_2O_3, together with the refractory materials present, as well as any impurities that were contained originally in the chrome ore. The refractory materials present are of such a nature that they will not melt at the roasting temperatures, which are approximately from 1800 to 2000° F., but are of such a character as to fuse readily at the temperature applied for producing the molten metal in the smelting stage of the process, that is to say from approximately 3000 to 3500° F., and should be of such a nature, also, as to react chemically at these temperatures so as to remove the impurities present, such as phosphorus, silica, etc. Also, the quantity of the refractory materials should be such as to prevent fusing of the roasting mixture during the roasting operation but at the same time not sufficient in quantity to produce an unnecessarily large amount of slag in the smelting operation, as otherwise the capacity of the furnace would be cut down, thus causing loss of the chromium which is taken up in the molten slag. I have found that a mixture of burned lime and fluorspar gives the desired results, as above referred to. The smelting operation above referred to may be carried out in an electric arc furnace of any known type, or it may be carried out still more advantageously in an ordinary electric induction furnace. This operation is conducted while the materials are in contact with the reducing agent, such as hydrogen or hydrocarbon gases, coke or silicon, or in such a manner that the coke is present for the first portion of the smelting operation and the silicon is thereafter added, until the oxides are reduced and the chromium iron alloy collects as a molten mass at the bottom of the furnace while the materials that have been added, as above referred to, as refractory materials, to provide a non-molten mass in the roasting operation, now fuse and act as a slag to purify and protect the molten metal.

This method is of particular importance in view of the fact that there has been no effective method known of separating iron and chromium by a metallurgical process and as in actual practice it has been the custom, in producing chromium iron alloys, to first make the chromium from a salt of chromium, as, for example, a bichromate, after which the chromium is added to the iron.

While my invention is capable of being carried out in many different ways, by way of example I shall describe hereinafter only certain ways of carrying out the same.

For example, 100 parts by weight of finely ground chrome ore (containing, for instance, 50% of chromium oxide, Cr_2O_3, that is to say about 35% by weight of chromium and 15 to 30% by weight of iron, in the form of iron oxides) are mixed with 42 parts by weight of sodium carbonate (that is to say, sufficient to combine theoretically with 60% by weight of the chromium present in the ore), 8 to 15 parts by weight of ground burnt lime, (the amount of the lime being thus extremely small, in view of the fact that the mass is to be maintained porous during the oxidation, in the presence of excess air, which takes place during the roasting operation and because the loss of the chromium in the slag formed in the subsequent smelting operation is to be reduced to a minimum), and 10 parts by weight of fluorspar (which remains powdery and which assists in keeping the mass porous during the roasting operation without combining with the chrome ore or sodium carbonate, but which

will readily become fused to form a slag in the subsequent smelting operation). This mixture is roasted in the strongly oxidizing atmosphere at a temperature of 1000° C. until about 60% by weight of the chromium has become converted into sodium chromate, $Na_2Cr_2O_4$. This generally requires about one hour. The roasting operation may be conducted, for example, in a rotary furnace of any desired type, The hot mass is then allowed to cool somewhat, that is to say, to a temperature of about 200° F., after passing out of the furnace, and is then lixiviated with water to remove the soluble salts consisting mainly of the sodium chromate. The residue will be found to contain about 13.6% by weight of the original percentage of chromium present and a varying amount of iron which may be, for example, the original 30% by weight of iron, the chromium and iron being present in the form of oxides comprised principally of Cr_2O_3 and Fe_2O_3, together with the lime and fluorspar originally present. This residue is then mixed with a reducing agent, as, for example, coal, coke, silicon, ferrosilicon or calcium, or subjected to a gaseous reducing agent, such as hydrogen or hydrocarbon gases, while heated, so as to raise the materials to a smelting temperature of approximately 3100° F. until the mass becomes liquid, at which point the reaction is substantially complete. The oxides of chromium and iron thus become reduced into the metallic form comprising molten metal containing approximately 25% chromium and 75% iron, some of the chromium, usually in an amount equal to about 5% of the chromium in the molten metal, being lost by being taken up in the slag, which also contains the sulphur and phosphorus which were present as impurities. Scrap iron may then be added to adjust the proportions of metals present to the desired extent. Usually the final alloy desired contains from 10 to 12% by weight of chromium, as, for example, when intended for use as a stainless or rustless iron or steel. Also, additional metals of any desired kind may be added at this point, as, for instance, nickel, tungsten, molybdenum, etc., to produce special alloys.

The scrap iron or steel added is preferably such as to have a low carbon content, that is to say, approximately from 0.1% to 0% by weight of carbon. Preferably it would also be low in phosphorus and sulphur but in actual practice the usual commercial scrap iron or steel can be used.

In the reducing operation the process may, if desired, be conducted by first adding a smaller amount of carbon and following this by adding an amount of silicon or ferrosilicon or calcium. In this manner the carbon present is kept as low as possible, which is desirable, as in order to produce rustless or stainless iron or steel the more carbon there is present the greater must be the percentage of chromium present. When carbon alone is used as a reducing agent an excess amount of carbon must be present to obtain complete reduction, but when the operation is started with carbon and completed by the addition of the silicon, ferrosilicon or calcium, this excess carbon is not present at the end of the smelting operation. Thus, when proceeding in this way less than the theoretical amount of carbon is added and as soon as the temperature of 3100° F. is reached the other reducing agent is added to eliminate the remaining oxides.

Furthermore, in the roasting operation, if desired, I may substitute some of the refractory materials, such as lime and fluorspar, by an amount of the slag obtained after the smelting operation, which should be finely ground if used for this purpose. This slag could thus be used over again a number of times but not indefinitely in view of the accumulation of the impurities therein.

It will of course be understood that many changes and variations may be made in carrying out the above process, in the materials used, their percentages and temperatures, etc. For example, instead of the sodium carbonate there may be used potassium carbonate.

While I have described my invention above in detail I wish it to be understood that many changes may be made therein without departing from the spirit of the same.

I claim:

1. The process which comprises producing a chromium iron alloy directly from chrome ore, involving the removal of a part of the chromium from the ore by roasting the ore with a material adapted to combine with some of the chromium and calcium fluoride while avoiding fusing the latter to form a chromate and reducing the residue by smelting to form a liquid slag with the calcium fluoride.

2. The process which comprises producing a chromium iron alloy directly from chrome ore by roasting the ore with a material adapted to combine with some of the chromium to form a chromate and calcium fluoride while avoiding fusing the latter, removing the chromate therefrom, reducing the residue by smelting to form a liquid slag with the calcium fluoride and then adding scrap to increase the content of iron therein.

3. The process which comprises producing a chromium iron alloy directly from chrome ore by roasting the chrome ore in the presence of an alkali carbonate and calcium fluoride while avoiding fusion thereof, then leaching, and smelting the residue in the presence of a reducing agent involving the formation of a slag with the calcium fluoride.

4. The process which comprises producing a chromium iron alloy directly from chrome ore by roasting the chrome ore in the presence of an alkali carbonate and calcium fluoride while avoiding fusion thereof, then leaching, smelting the residue in the presence of a reducing agent involving the formation of a slag with the calcium fluoride and then adding scrap to increase the content of iron therein.

5. The process which comprises producing a chromium iron alloy directly from chrome ore by roasting the chrome ore in the presence of an alkali carbonate in an amount to combine with only approximately 60% of the chromium present, and calcium fluoride while avoiding fusion thereof, then leaching and smelting the residue in the presence of a reducing agent involving the formation of a slag with the calcium fluoride.

6. The process which comprises producing a chromium iron alloy directly from chrome ore by roasting the chrome ore in the presence of an alkali carbonate in an amount to combine with only approximately 60% of the chromium present and calcium fluoride while avoiding fusion thereof, then leaching, smelting the residue in the presence of a reducing agent involving the formation of a slag with the calcium fluoride and then adding scrap to increase the content of iron therein.

7. The process which comprises producing a chromium iron alloy directly from chrome ore by roasting the chrome ore in the presence of an alkali carbonate and an insoluble refractory ma-

terial, comprising lime and fluorspar while avoiding fusion thereof, then leaching and smelting the residue in the presence of a reducing agent involving the formation of a slag with the refractory material.

8. The process which comprises producing a chromium iron alloy directly from chrome ore by roasting the chrome ore in the presence of an alkali carbonate and an insoluble refractory material, comprising lime and fluorspar while avoiding fusion thereof, then leaching, smelting the residue in the presence of a reducing agent involving the formation of a slag with the refractory material and then adding scrap to increase the content of iron therein.

9. The process which comprises producing a chromium iron alloy directly from chrome ore by roasting the chrome ore in the presence of an alkali carbonate and an insoluble refractory material, comprising lime and fluorspar while avoiding fusion thereof, the refractory material being present in an amount such as to prevent fusing in the roasting operation but not sufficient to remove more than 5% of the chromium in the form of slag in the subsequent smelting operation, then leaching and smelting the residue in the presence of a reducing agent involving the formation of a slag with the refractory material.

10. The process which comprises producing a chromium iron alloy directly from chrome ore by smelting with a reducing agent after roasting the chrome ore in the presence of an alkali carbonate and an insoluble refractory material, comprising lime and fluorspar, the refractory material being present in an amount such as to prevent fusing in the roasting operation but not sufficient to remove more than 5% of the chromium in the formation of a slag in the subsequent smelting operation.

11. The process which comprises producing a chromium iron alloy directly from chrome ore by roasting the chrome ore in the presence of an alkali carbonate and calcium fluoride while avoiding fusion thereof, then leaching and smelting the residue in the presence of carbon in less than the theoretical quantity for complete reduction, followed by a non-carbonaceous reducing agent, involving the formation of a slag with the calcium fluoride.

12. The process which comprises producing a chromium iron alloy directly from chrome ore by roasting the chrome ore in the presence of an alkali carbonate and calcium fluoride while avoiding fusion thereof, then leaching, smelting the residue in the presence of carbon in less than the theoretical quantity for complete reduction, followed by a non-carbonaceous reducing agent, involving the formation of a slag with the calcium fluoride and then adding scrap to increase the content of iron therein.

13. The process which comprises producing a chromium iron alloy directly from chrome ore by roasting the chrome ore in the presence of an alkali carbonate and calcium fluoride, as well as some slag obtained from the subsequent smelting operation while avoiding fusion thereof, then leaching and smelting the residue in the presence of a reducing agent, involving the formation of a slag with the calcium fluoride.

14. The process which comprises producing a chromium iron alloy directly from chrome ore by roasting the chrome ore in the presence of an alkali carbonate and calcium fluoride, as well as some slag obtained from the subsequent smelting operation while avoiding fusion thereof, then leaching, smelting the residue in the presence of a reducing agent involving the formation of a slag with the calcium fluoride and then adding scrap to increase the content of iron therein.

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