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[54] PROCESS FOR MAKING CHRIMIUM ALLOYS

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[30] **Foreign Application Priority Data**

Apr. 2, 1969 Germany .... P 19 16 945.0

[52] **U.S. Cl.** **75/49**, 75/52, 75/60, 75/130.5

[51] **Int. Cl.** **C21c 5/34**

[58] **Field of Search** 75/49, 51, 52, 59, 75/60, 130.5

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[57] **ABSTRACT**

A process for making a chromium alloy containing from about 10 percent to about 30 percent chromium and the remainder essentially iron comprises refining a pig iron melt containing chromium in a converter by blowing oxygen jets into the melt under the melt surface in the converter, the oxygen jets each being surrounded by a sheath of a jacket gas such as propane which is slow to react with the melt in order to protect the lining of the converter and the nozzles through which the oxygen jets are blown. The pig iron itself may contain the chromium or the chromium may be added to the melt in the form of a chromium alloy after an initial refinement of the pig iron melt in the converter and in this case further refinement by the introduction of the jacketed oxygen jets into the melt takes place after the chromium has been added. After the oxygen blowing there may be a final blow using jets of argon in place of the oxygen.

4 Claims, No Drawings

PROCESS FOR MAKING CHRIMIUM ALLOYS

The invention relates to processes for making chromium alloys containing from 10 to 20 percent chromium, the remainder essentially iron, in which a pig iron melt containing chromium, preferably pig iron of the "Stahleisen" type is refined in a converter.

Highly alloyed steels, such as ferritic and austenitic chromium steels are usually made by melting in an electric furnace. The charge, consisting of scrap with a little pig iron, is oxidised to remove the phosphorus. After drawing off the slag, the sulphur is removed. To the usually non-alloyed melt, the alloy constituents are added in the form of ferrous alloys. In another process pig iron containing 14 to 20 percent chromium is melted in a cupola furnace, in a blast furnace or in an electric arc furnace. The melt is then refined in a converter, by means of surface blown oxygen, to produce steel. During the refining undesired impurities in the iron, particularly phosphorus, sulphur and manganese are oxidised by the surface blown oxygen and go over into the slag. A characteristic of this process is that the surface blown oxygen does not reach the melt directly. A large quantity of ferrous oxide is first formed and thus explains the high concentration of ferrous oxide in the slags produced by this process. Ultimately the ferrous oxide in the slag oxidises the undesired impurities in the iron, but at the same time oxidises part of the chromium in the melt. At the usual refining temperatures the comparatively high affinity for oxygen of chromium brings a large fraction of the chromium into the slag, resulting in a high loss of chromium.

Consequently, in order to limit the amount of chromium passing into the slag, the refining of melts containing chromium is preferably conducted at very high refining temperatures, that is to say at approximately 1,800° C. At these temperatures the free enthalpy of chromium oxide is only a little less than the free enthalpy of ferrous oxide. The loss of chromium can be still further decreased by interrupting the refining when the carbon has been brought down to approximately 1.10 percent. After the refinement, silicon is added to the slag. The silicon reduces part of the oxidised chromium again, increasing the chromium concentration in the melt. However, this slag reducing process has the disadvantage that other elements, for example phosphorus, have less affinity for oxygen than silicon has, and consequently these elements are also reduced to some extent and pass back into the melt. This applies particularly to phosphorus and manganese, and consequently chromium steels which have been refined by the oxygen surface blow process contain not only a comparatively high percentage of carbon but also more than average concentrations of phorphorus and manganese. Finally, the high refining temperature used considerably accelerates destruction of the refractory converter lining, making it necessary to rebuild the converter more often.

In order to minimize the chromium losses, very pure pig iron is preferably used for the oxygen surface blown process, the pig iron, containing for example only small quantities of phosphorus, sulphur and silicon. Due to the low concentrations of the impurities, less oxygen is required and consequently the chromium losses are reduced. However this advantage has to be paid for in that the process requires high quality and correspondingly costly pig iron, as the raw material.

In another known process for refining pig iron containing chromium, a mixed gas containing argon and oxygen is blown into the melt through nozzles installed in the converter bottom. This method has the disadvantage that approximately 20 Normal Cubic metres of argon are required per metric ton of pig iron. Argon is expensive and the process is comparatively uneconomical.

The object of the present invention is to provide a process for making chromium alloys containing 10 to 30 percent chromium, the remainder essentially iron, in which chromium losses are comparatively low, in which a lower refining temperature gives the converter lining a longer working life.

According to this invention, in a process for making chromium alloy containing from 10 to 30 percent chromium, the remainder essentially iron, in which a pig iron melt containing chromium, for example pig iron of the Stahleisen type, is refined in a converter, the refinement is brought about by introducing at least one oxygen jet through a nozzle into the melt under the melt surface in the converter, the oxygen jet being surrounded by a sheath of a jacket gas which is slow to react with the melt in order to protect the nozzle and the lining of the conveter.

This invention is based on the surprising discovery that if the oxygen required for refining the pig iron is introduced into the melt from under its surface in this way considerably less chromium goes over into the slag. This low loss of chromium to the slag allows a pig iron to be used which already contains part or all of the chromium content of the alloy before the refining process begins.

The process thus enables the pig iron melt to be refined with little loss of chromium, at a temperature of approximately 1,700° C, the carbon being brought down to a final concentration of 0.10 percent. If it is desired to bring the carbon down still further, and to lose even less chromium to the slag, the fraction of comparatively inert jacket gas around the oxygen jet can be increased towards th end of the refining process and/or the oxygen may be mixed with an inert gas such as argon. This hardly influences the economics of the process, because the oxygen mixed with inert gas, for example argon, is blown only briefly, for example for approximately 10 percent of the total refining time.

In those cases where it is desired to produce a melt containing very little final carbon the reaction gases may be drawn away from the melt by means of a vacuum pump so that the pressure applied to the surface of the melt is less than atmospheric, for this purpose, it is sufficient to bring the pressure above the melt down to approximately 10 percent of atmospheric. The carbon can also be brought down by subjecting the melt after refinement to a vacuum treatment, in which case it is advantageous to leave all or at least part of the slag on the melt. A subsequent vacuum treatment should be conducted under a more extreme vacuum than that which prevails during refining, preferably 1 percent of atmospheric pressure.

The process in accordance with the invention may be conducted as follows. A pig iron of the usual kind is refined and then, after drawing off the slag, the necessary chromium is added in the form of a chromium alloy, for example ferrochrome, containing approximately 6 percent of carbon and an above average concentration of silicon that is at least 3 percent silicon. The high concentration of silicon in the alloy added delivers, during the oxidation, the quantity of heat necessary for melting the alloy, The refining of the pig iron is preferably allowed to proceed until the melt contains only 0.05 percent carbon, 0.15 percent manganese, 0.012 percent Phorphorus and 0.014 percent sulphur.

Some examples of processes in accordance with the invention will now be described in greater detail.

EXAMPLE I

In order to make a ferrite chromium steel containing approximately 0.10 percent carbon and 14 percent chromium, pig iron of the Stahleisen type, that is to say a pig iron containing approximately 3 to 4 percent carbon, up to 1 percent silicon, 2 to 6 percent manganese, 0.08 to 0.12 percent phosphorus and up to 0.04 percent sulphur was refined in a converter, oxygen being blown into the melt through compound nozzles installed in the converter bottom, each compound nozzle consisting of an oxygen pipe surrounded concentrically by a jacket gas pipe, to the effect that each oxygen jet was surrounded by a sheath of jacket gas which in this example was propane. The non-alloyed pig iron was initially refined to give a melt containing 0.05 percent carbon, 0.010 percent phosphorus, 0.010 percent sulphur and 0.010 percent manganese. During this refinemeent the melt temperature was 1,740° C. After drawing off the slag and reducing the melt with a 2 kg of aluminum per metric ton of steel, 23 percent of ferrochrome, based on the total weight of the finished melt, and 50 kg of lime per metric ton of steel were added to the melt. The ferrochrome consisted of 64 percent chromium, 6 percent carbon and 5 percent silicon, the remainder iron. After adding the ferrochrome and the lime, refining took place again for a further five minutes, altogether 25 Normal Cubic metres of oxygen being blown per metric ton of steel through the converter bottom. Analysis showed a carbon concentration of 0.15 percent and chromium 15.4 percent. The blow was therefore repeated for 20 seconds. The steel was then tapped off at a temperature of 1,640° C and showed on analysis 0.10 percent carbon and 14 percent chromium.

In the example it is not necessary to add all the chromium just after drawing off the slag. If desired the ferrochrome can be added in several successive portions during the second refining process. Particularly good results are obtained by blowing the lime, in the form of a fine dust, into the melt with the oxygen.

EXAMPLE II

Using a similar converter, a melt was refined for the purpose of making a ferrite chromium steel containing 17 percent of chromium. For this purpose pig iron containing 7 percent of chromium was refined. This pig iron had been prepared in a 30 metric ton converter from pig iron of the Stahleisen type containing 4.2 percent carbon, 0.5 percent silicon, 0.1 percent phosphorus and 0.04 percent sulphur to which were added per metric ton of pig iron 200 kg of scrap containing 17 percent of chromium by weight and 65 kg of ferrochrome containing carbon and containing 64 percent of chromium by weight. During the refining of this pig iron melt, lime dust was blown with the oxygen. At the end of the 15 minute blow with oxygen jets jacketed with propane during which a total of 55 Normal Cubic metres of oxygen were consumed per metric ton of melt, the temperature was 1,680°C and analysis of the melt showed 0.15 percent carbon, 7.1 percent chromium, 0.015 percent phosphorus and 0.012 percent sulphur.

After drawing off all the slag, 18 percent of ferrochrome based on the total weight of the finished steel melt was added to the melt, the ferrochrome containing 63 percent chromium, 6 percent carbon and 4 percent silicon by weight. After a further blow lasting for 4 minutes and consuming altogether 20 Normal Cubic metres of oxygen per metric ton of steel, the melt had a temperature of 1,620° C and showed 0.13 percent carbon, and 17.4 percent chromium. A further blow was then applied for 90 seconds, blowing through the oxygen pipe a mixture containing 50 percent oxygen and 50 percent argon, pure argon being blown through the jacket gas pipe. The melt which was tapped off contained 0.05 percent carbon and 16.8 percent chromium.

These two examples show that the process according to the invention allows chromium steels to be made containing 0.10 percent of carbon, or less, with very little chromium loss to the slag, and this without using a reduced pressure over the melt. Still lower carbon contents can easily be obtained by refining under reduced pressure, or by giving the refined steel a subsequent vacuum treatment.

We claim:

1. In a process for making chromium alloy containing from about 10 percent to about 30 percent chronium and the remainder essentially iron, including the steps of (1) refining a pig iron melt in a convertor by introducing at least one oxygen jet into said melt through a compound nozzle located in the bottom of said convertor and discharging said oxygen jet into said melt below the surface of said melt and surrounding each said oxygen jet with a sheath of protective gas which is slow to react with the melt and which is discharged into said melt simultaneously with each said oxygen jet, in order to protect said compound nozzle and the lining of said convertor and (2) thereafter drawing slag off from said refined pig iron melt, and (3) then introducing a chromium alloy containing at least 3 percent of silicon into said pig iron melt to form a pig iron melt containing chromium (4) thereafter further refining said melt by repeating step (1) by introducing said oxygen jet into said pig iron melt containing chromium and (5) recovering the produced alloy containing 10 percent to 30 percent chromium.

2. A process as claimed in claim **1**, further comprising the step of applying a pressure less than atmospheric pressure to the surface of said melt during said step of introducing said oxygen jets into said melt.

3. A process as claimed in claim **1**, wherein said pig iron melt contains not more than 50 percent of the chromium content of said alloy and further comprising the steps of drawing off slag from said melt after said step of introducing said oxygen jet into said melt and adding the remainder of said chromium content of said alloy to said melt after said slag has been drawn off.

4. The process of claim **1** in which the protective gas is propane.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,751,242 Dated August 7, 1973

Inventor(s) Helmut Knuppel et al.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

On the Title page Item 19, "Helmut et al" should read -- Knuppel et al. --; Item 54, "CHRIMIUM" should read -- CHROMIUM --; Item 75, "Knuppel Helmut" should read -- Helmut Knuppel --; Item 56, "Osorzaly et al" should read -- Ogorzaly et al --; Item 73, "Eisenwek" should read -- Eisenwerk --; Item 73,

"Maximilian-shutte" should read -- Maximilianshutte --;

"Attorney - Lawrence J. Field" should read -- Attorney - Lawrence I. Field --. Column 1, line 4, "20" should read -- 30 --. Column 2, line 19, "Stahleisen" should read -- "Stahleisen" --; line 41, "th" should read -- the --. Column 3, line 6, "Phorphorus" should read -- phosphorus --; line 1 of Example 1, "ferrite" should read -- ferritic --; line 3 of Example 1, "Stahleisen" should read -- "Stahleisen" --; line 2 of Example 2, "ferrite" should read -- ferritic --; line 6 of Example 2, "Stahleisen" should read -- "Stahleisen" --.

Signed and sealed this 1st day of January 1974.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

RENE D. TEGTMEYER
Acting Commissioner of Patents

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