PROCESS FOR REFINING ALLOY STEELS CONTAINING CHROMIUM AND INCLUDING STAINLESS STEELS

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ABSTRACT
An alloy steel containing chromium is refined by blowing fluids into the molten steel through double or triple feed tuyeres. Each tuyere first provides a flow of an oxidizing fluid, a second flow of a fluid for diluting the carbon monoxide in the bath and a third peripheral flow of a carbon make-up liquid.

21 Claims, 3 Drawing Figures
This invention relates to the refining of alloy steels containing chromium, particularly but not exclusively stainless steels.

It is impossible to decarburise steel containing chromium without appreciable chromium loss in the slag unless decarburisation is either carried out at an elevated temperature or at a reduced pressure (to keep the partial carbon monoxide pressure low). The temperature must be higher, or the partial carbon monoxide pressure must be lower, in proportion as the carbon content of the steel is lower and/or its chromium content is higher. It is well known to work at an elevated temperature in an electric furnace, but this procedure has a number of disadvantages, for example heavy consumption of furnace refractories and a furnace utilisation level which is reduced by the necessity of frequent repairs.

Operation at a reduced carbon monoxide pressure is also known and there are two different ways of achieving the reduced pressure in conventional processes. One method involves blowing the metal with oxygen in vacuo, and the other method involves blowing into the bath oxygen diluted with a neutral gas such as argon which, unlike nitrogen (although more expensive than nitrogen), does not lead to the formation of nitrides. In the oxygen and neutral gas method, it is known to blow a mixture of oxygen and argon into the metal through one or more single tuyeres. It is also known to use separate double feed tuyeres to blow into the metal oxygen (or a mixture thereof with argon) at the centre of each tuyere and argon at the tuyere periphery.

Unfortunately, tuyere life is short in the latter method, since the argon gives very little protection against corrosive wear at the tuyere outlet by hot iron oxides. Another disadvantage inherent in this technique is that the argon is required to perform two different functions, namely to protect (as much as possible) the tuyeres and to dilute the carbon monoxide evolved in refining so as effectively to reduce the partial pressure of the carbon monoxide, and these two effects do not always proceed in the same direction at the same intensity. Thus, it is unnecessary to reduce the carbon monoxide partial pressure above a 0.400 percent carbon content melt at about 18 percent chromium content and approximately 1,600°C, but at carbon contents of this order a very appreciable flow of argon is needed to protect the tuyere against serious wear.

We have now devised a process for refining steel which overcomes or mitigates these disadvantages.

According to the invention, there is provided a process for refining an alloy steel containing chromium, which comprises blowing fluids into the molten steel through at least one double or triple feed tuyere, the or each tuyere providing a first flow of an oxidising fluid, a second flow of a fluid for diluting the carbon monoxide in the bath, and a third peripheral flow, which is separate from the said first and second flows, of a carbon make-up liquid.

Apparatus for carrying out the process of the present invention is shown in the accompanying drawings in which:

FIG. 1 shows a tuyere of concentric tubes with the protecting liquid admitted between the tubes and the oxidising and diluent fluid admitted to the inner tube;

FIG. 2 shows a triple concentric tuyere with the oxidising fluid admitted to the central tube; the diluent fluid admitted to the next outer tube; and the protecting fluid admitted to the outer tube; and

FIG. 3 is a variant of FIG. 2 in which the tubes for admission of the diluent fluid and the oxidising fluid are reversed.

In one embodiment of the process, at least one double tuyere is used, to the inner circuit of which is supplied a mixture of the diluent fluid and oxidising fluid. In another embodiment, at least one triple tuyere is used and the oxidising fluid and the diluent fluid are introduced separately into two separate inner circuits of the or each triple tuyere. In this embodiment, either a primary flow of the oxidising fluid is supplied to the centre of the tuyere, a secondary flow of the diluent fluid is supplied in a separate circuit around the primary flow, and a tertiary flow of the carbon make-up liquid is supplied at the periphery of the tuyere, or a primary flow of the diluent fluid is supplied to the centre of the tuyere, a secondary flow of the oxidising fluid is supplied in a separate circuit around the primary flow, and a tertiary flow of the carbon make-up liquid is supplied to the periphery of the tuyere.

The diluent fluid can be a neutral gas such as argon or a fluid (such as water vapour) which dissociates, associates or reacts upon contact with the molten metal, to produce a diluent gas. The diluent fluid can be an emulsion or an aerosol. In one embodiment, the diluent fluid is a spray of water droplets in a vehicle gas, which can be the oxidising gas itself or a diluent gas or any other appropriate gas.

The oxidising fluid may be, for example, industrially pure oxygen, air or oxygen-enriched air.

In one method of carrying out the process of the invention, the steel is refined in two stages, and in the first stage the flow of diluent fluid is zero being replaced by an oxidising fluid flow, and, in the second stage, the diluent fluid flow increases until it is more than twice the oxidising fluid flow. Towards the end of the second stage when the carbon content is low, the proportion of diluent may be, for example, 70 percent and the proportion of oxidising fluid (correspondingly) 30 percent.

The carbon content of the metal at the end of the first stage of refining (i.e., before the introduction of any diluent fluid) is preferably from 0.150 to 0.700 percent, more preferably approximately 0.400 percent, and the temperature of the metal approximately 1,600°C and a chromium content of the metal approximately 18 percent.

The carbon make-up liquid may be any liquid which reduces the corrosive wear on the tuyeres. It is preferably a hydrocarbon-containing liquid, one example of such a liquid being fuel oil. An emulsion or argon or water vapour or water droplets in fuel oil may also be used. The proportion by weight of fuel oil flow relative to the oxygen flow is preferably from 1 to 10 percent, more preferably from 2.5 to 4 percent. This proportion may be either constant or may be varied during the refining process.

The vessel in which the refining process according to the invention is performed may be in vacuo or under a reduced pressure, or at atmospheric pressure.
One of the main advantages of the process of the invention is that the task of tuyere protection (performed by the carbon make-up liquid) is divorced from the function of diluting the bath decarburization carbon monoxide (the latter being performed either by a neutral gas or by a dissociation product of a fluid). In the first place, therefore, the working life of the tuyeres can be substantially improved, e.g., up to several times longer than that of tuyeres blowing only oxygen and argon. Secondly, since tuyere outlet protection is provided by a small flow of carbon make-up liquid the invention makes it possible in the first stage of a refining operation to blow pure oxygen without a neutral gas, for much of the time of the refining operation, for instance, in the case of an 18 percent bath chromium content, for as long as the bath carbon content does not drop below 0.400 percent, for instance, at a temperature of 1,600°C.

Another advantage of the invention is that a heavy concentration of a neutral gas, such as argon, and hence a low concentration of oxygen can be used at the end of the decarburization, thus reducing chromium losses still further without greatly impairing the overall thermal balance of refining, since pure oxygen without argon can be blown during the first stage of refining and thus pave the way for a good thermal balance.

Another advantage of the invention is that argon consumption is much less than in known processes using argon and oxygen all the time even though, according to the invention, about 70 percent argon is used at the end of refining. The reason for this reduction is that oxygen is blown pure without argon during a relatively long first stage of refining. An intermediate phase using ordinary air or, preferably, oxygen-enriched air can be included; it must be fairly brief, otherwise nitriding may become excessive.

Another advantage of the invention is that argon can be completely omitted and water vapour or water spray used instead of argon, for the non-dissociated portion of water vapour or water spray and the hydrogen evolved from the dissociated portion both help to dilute the carbon monoxide and (effectively) reduce the partial pressure thereof.

Another advantage of the invention is that, as starting material, an alloy of high carbon content, even cast iron, can be used without a heavy consumption of diluent fluid, since there is no consumption of diluent fluid in the first stage, which may continue until the carbon content is 0.400 percent or even 0.300 percent.

Another advantage of the variants of the invention in which the oxidising fluid and the diluent fluid are not mixed prior to introduction but are introduced into each tuyere separately, is that they make the process very easy to operate and make it very easy to check the rates of flow of each fluid at any time, since each individual fluid remains uniform as it flows through each tuyere. For instance, if the diluent fluid is water vapour, there is no risk of the vapour condensing in the zone where it is mixed with cold oxygen, and so the actual water vapour flow through the tuyere can be controlled much more accurately than previously.

In order that the invention may be more fully understood, the following Examples are given by way of illustration only.

The first two Examples illustrate the use of separate double-feed tuyeres and the third and fourth Examples illustrate the use of separate triple feed tuyeres.

The first three Examples start from a metal of approximately 0.9 percent carbon content, and the fourth Example starts from cast iron having 6 percent carbon content. In all four cases, nickel and chromium are present to start with.

Example 1
This Example uses a 20-ton converter having two separate double feed tuyeres; the oxidising gas flow is at the centre of each tuyere and the fuel oil flow at the tuyere periphery. The converter is charged with 20 tons of liquid steel at 1,540°C from an electric furnace, the steel having the following composition:

<table>
<thead>
<tr>
<th>C</th>
<th>Ni</th>
<th>Si</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.9%</td>
<td>10.6%</td>
<td>0.2%</td>
<td>17.7%</td>
</tr>
<tr>
<td>Mn</td>
<td>0.85%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Pure oxygen is blown through the centre of each tuyere in the first stage and, in two periods of the second stage, a mixture of argon and oxygen is blown in the following proportions:

<table>
<thead>
<tr>
<th>Argon in</th>
<th>Oxygen in</th>
<th>Argon %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nm3/min.</td>
<td>Nm3/min.</td>
<td></td>
</tr>
<tr>
<td>1st period</td>
<td>30</td>
<td>0%</td>
</tr>
<tr>
<td>2nd period</td>
<td>15</td>
<td>50%</td>
</tr>
<tr>
<td>3rd period</td>
<td>9</td>
<td>70%</td>
</tr>
</tbody>
</table>

A carefully controlled flow of domestic fuel oil is provided at the periphery of each tuyere at a rate of 1 litre/minute/tuyere, i.e. a total of 2 litres/minute for the two tuyeres together.

Blowing times are as follows:

<table>
<thead>
<tr>
<th>Period</th>
<th>Time (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st period</td>
<td>6</td>
</tr>
<tr>
<td>2nd period</td>
<td>6</td>
</tr>
<tr>
<td>3rd period</td>
<td>6</td>
</tr>
<tr>
<td>TOTAL</td>
<td>18</td>
</tr>
</tbody>
</table>

At the end of blowing, the bath analyses as follows:

<table>
<thead>
<tr>
<th>C</th>
<th>Ni</th>
<th>Mn</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.020%</td>
<td>10.6%</td>
<td>0.550%</td>
<td>16.6%</td>
</tr>
</tbody>
</table>

Temperature: 1,670°C, due to an appropriate addition of stainless scraps to the converter to aid the thermal balance.

Fluid consumptions for 20 tons of steel are as follows:

<table>
<thead>
<tr>
<th>Oxygen:</th>
<th>324 Nm3</th>
<th>i.e. 16.2 Nm3/t</th>
</tr>
</thead>
<tbody>
<tr>
<td>Argon:</td>
<td>218 Nm3</td>
<td>i.e. 10.8 Nm3/t</td>
</tr>
<tr>
<td>Fuel-oil</td>
<td>36 litres</td>
<td>i.e. 1.8 litre/t</td>
</tr>
</tbody>
</table>

Example 2
In this second example, a 20-ton converter is used having two separate double feed tuyeres. In each tuyere, the oxidising gas flow is at the centre and the fuel oil flow at the periphery.

The converter is charged with molten steel at 1,540°C from an electric furnace, the steel composition being as follows:

<table>
<thead>
<tr>
<th>C</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.85%</td>
<td>10.5%</td>
</tr>
</tbody>
</table>
Pure oxygen is blown through the centre of the tuyere in the first stage, and a mixture of water vapour and oxygen is blown in the two periods of the second stage, in the following proportions:

<table>
<thead>
<tr>
<th>Vapour in Nm³/min.</th>
<th>O₂ in Nm³/min.</th>
<th>Vapour volume %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st period</td>
<td>15</td>
<td>30%</td>
</tr>
<tr>
<td>2nd period</td>
<td>15</td>
<td>50%</td>
</tr>
<tr>
<td>3rd period</td>
<td>9</td>
<td>70%</td>
</tr>
</tbody>
</table>

Refining is carried out in three consecutive periods. In stage 1 (i.e. period 1), pure oxygen is blown in both the primary and secondary circuits, and in stages 2 and 3 (periods 2 and 3) oxygen is blown in the primary circuit and argon in the secondary circuit at rates of flow given in the following table:

<table>
<thead>
<tr>
<th>Argon in Nm³/min</th>
<th>Oxygen in Nm³/min</th>
<th>Argon %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Secondary circuit</td>
<td>Primary circuit</td>
<td>Secondary circuit</td>
</tr>
<tr>
<td>1st period</td>
<td>0</td>
<td>15</td>
</tr>
<tr>
<td>2nd period</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>3rd period</td>
<td>21</td>
<td>9</td>
</tr>
</tbody>
</table>

At the end of blowing, the bath analyses as follows:

| C = 0.020% | Ni = 10.7% | Mn = 0.600% | Cr = 16.7% |

Temperature: 1,650°C due to an appropriate addition of stainless scraps, with allowance for the cooling effect of the blown water vapour, to achieve thermal balance. Consumptions for 20 tons of steel are as follows:

Oxygen: 333 Nm³ — i.e. 16.6 Nm³/t
Argon: 237 Nm³ — i.e. 11.8 Nm³/t
Fuel oil: 38 litres — i.e. 1.9 litre/t.

Chromium loss in the slag is slight, namely a 1.2 percent reduction corresponding to 7 percent of the total chromium content of the bath. Some of this “lost” chromium can, of course, be recovered by ferro-silicon reduction.

Example 4
The starting material is a 6 percent carbon cast iron.
The rate of fuel oil flow in each of the four tuyeres is kept constant at 1 litre/minute, corresponding to 4 litres/minute for all the tuyeres together.

At the end of blowing, the chromium loss is 1.9 percent and upon completion of refining, the metal analyses as follows:

\[
\begin{align*}
C &= 0.021\% \\
Mn &= 0.35\% \\
Ni &= 11.05\% \\
Cr &= 18.15\%
\end{align*}
\]

Temperature: 1,660°C, due to the addition of stainless scraps.

Fluid consumptions for 20 tons of metal are as follows:

- \(O_2\) = 1344 Nm\(^3\) = 67 Nm\(^3\)/t
- Argon = 216 Nm\(^3\) = 10.8 Nm\(^3\)/t
- Fuel-Oil = 104 litres = 5.2 l/t

The economic advantage of separating the diluent agent from the cooling agent is clearly apparent in this case. Argon is introduced for only 6 minutes of a total refining time of 26 minutes.

What we claim is:

1. A process for refining an alloy steel containing chromium, which comprises blowing fluids into the molten steel through at least one feed tuyere, each tuyere providing a first flow of an oxidising fluid, a second flow of a fluid for diluting the carbon monoxide in the bath, and a third peripheral flow, which is physically distinct and separate from the said first and second flows in the tuyere, of a hydro-carbon containing liquid, said third flow remaining in the liquid state until after leaving the tuyere.

2. A process according to claim 1, wherein at least one double tuyere is used, to the inner circuit of which is supplied a mixture of the diluent fluid and oxidising fluid physically distinct and separate from said third fluid.

3. A process according to claim 1, wherein at least one triple tuyere is used and the oxidising fluid and the diluent fluid are introduced separately into and maintained physically distinct and separate in two separate inner circuits of each triple tuyere and physically distinct and separate from said third fluid.

4. A process according to claim 3, wherein a primary flow of the oxidising fluid is supplied to the centre of the tuyere, a secondary flow of the diluent fluid is supplied in a separate circuit around the primary flow, and a tertiary flow of the hydro-carbon containing liquid is supplied to the periphery of said tuyere the three flows being maintained physically distinct and separate in said tuyere.

5. A process according to claim 3, wherein a primary flow of the diluent fluid is supplied to the centre of the tuyere, a secondary flow of the oxidising fluid is supplied in a separate circuit around the primary flow, and a tertiary flow of the hydro-carbon containing liquid is supplied to the periphery of said tuyere said flows being maintained physically distinct and separate in said tuyere.

6. A process according to claim 1, wherein the oxidising fluid is industrially pure oxygen.

7. A process according to claim 1, wherein the oxidising fluid is air or oxygen-enriched air.

8. A process according to claim 1, wherein the diluent fluid is an inert gas.

9. A process according to claim 8, wherein the inert gas is argon.

10. A process according to claim 1, wherein the diluent fluid dissociates or reacts to produce a diluent gas on contact with the molten metal.

11. A process according to claim 10, wherein the diluent fluid supplied to the tuyere is water vapour.

12. A process according to claim 10, wherein the diluent fluid supplied to the tuyere is a spray of water droplets in a vehicle gas.

13. A process according to claim 1, wherein the steel is refined in two stages, and in the first stage the flow of diluent fluid is zero, being replaced by an oxidising fluid flow, and, in the second stage, the diluent fluid flow increases until it is more than twice the oxidising fluid flow.

14. A process according to claim 13, wherein the carbon content of the molten metal at the end of the first stage is from 0.150 to 0.600 percent, the molten metal temperature is approximately 1,600°C and the chromium content of the metal is approximately 18 percent.

15. A process according to claim 14, wherein the carbon content of the molten metal at the end of the first stage is approximately 0.4 percent.

16. A process according to claim 1, wherein the hydro-carbon containing liquid is fuel oil.

17. A process according to claim 1, wherein the carbon make-up liquid is an emulsion of a component selected from the group consisting of argon, water vapour and water droplets in fuel oil.

18. A process according to claim 16, wherein the proportion by weight of fuel oil flow relative to oxygen flow rate is controlled during the refining operation and is from 1 to 10 percent.

19. A process according to claim 18, wherein the said proportion is from 2.5 to 4 percent.

20. A process according to claim 1, which is performed in vacuo or at a reduced pressure.

21. A process according to claim 1, wherein the alloy steel is stainless steel.