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N.B. Use International abbreviation for country (See Schedule 4)

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THE THERMAL REDUCTION OF AGGLOMERATED METALLURGICAL FEED MATERIALS WITH METALLIC COATINGS
### COMPLETE SPECIFICATION

(Section 30(1) - Regulation 28)

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<th>Full Name(s) of Applicant(s)</th>
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<th>72</th>
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<td></td>
<td>Nicholas Adrian BARCZA, Robert Christopher NUNNINGTON</td>
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<td>THE THERMAL REDUCTION OF AGGLOMERATED METALLURGICAL FEED MATERIALS WITH METALLIC COATINGS</td>
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ABSTRACT

A process is provided for the reduction, in particular the prereduction of metallurgical materials to be reduced such as chrome and iron containing materials, for example chromite ore, by the action of solid reductants such as solid carbonaceous reductants, wherein finely sub-divided materials, reductant and any fluxes or other ingredients are formed into agglomerated units. The agglomerated units are coated with a layer of material which contains at least 50% by mass metallic material and preferably substantially purely metallic material (such as ferrochrome) and the coated agglomerate is then dried and heated to effect the required reduction. The heating can be effected in process gases comprising 50% or more of CO₂, air, or a mixture thereof and even upwards of 75% of such process gases.
FIELD OF THE INVENTION

THIS INVENTION relates to the solid state thermal reduction of agglomerated metallurgical feed materials and, more particularly, relates to agglomerated metallurgical feed materials in which the material to be reduced is sub-divided and mixed with a solid reductant, and optionally any required fluxes or other additives, prior to agglomeration.

More particularly, but not exclusively, the invention is concerned with the reduction of agglomerated feed materials comprising chromium oxides, iron oxides such as hematite, and mixtures thereof, manganese oxide, vanadium oxide, or any other carbothermally reducible oxide, using a carbonaceous reductant such as coal, preferably in the form of anthracite, char or other carbonaceous reductant.

/...
in a step which is usually referred to as a pre-reduction step preparatory to effecting smelting or melting and slag-metal separation in a suitable furnace.

**BACKGROUND TO THE INVENTION**

In the solid state reduction of agglomerated finely sub-divided oxide material to be reduced, together with a carbonaceous reductant, and any required fluxes or other additives, the agglomerated material is generally, after being prepared and cured, subjected to the action of off-gases from a combustion process in order to heat and/or reduce them. Such off-gases contain, in various different proportions, carbon-monoxide and carbon dioxide and can even contain free oxygen. The performance of the reduction reaction may be seriously affected by the gas composition.

In particular, oxidation of carbon reductant in the pellet can occur as a result of reaction with carbon dioxide contained in the process gases to produce carbon monoxide by the so-called Boudouard reaction.

/...
ie. \[ \text{C(pellet)} + \text{CO}_2 \rightleftharpoons 2\text{CO} \]

(process gases)

The consequences of this reaction are two-fold. Firstly, removal of carbon from the pellet diminishes the amount of potential reductant available for prereduction and metallisation of, for instance, chromium and iron species contained in the chromite or iron oxide present in the pellet and, secondly, an incompletely combusted gas (carbon monoxide) is generated which must be either rerouted elsewhere for combustion to realise the available sensible and thermochemical energy, or be flared off to waste.

In addition, reoxidation of the metallised ferrochromium may occur as the conditions become less reducing within the pellet as the carbon is oxidised. The oxidised ferrochromium is often identified microstructurally by the presence of sesquioxide laths \((\text{Al}_2\text{O}_3\cdot\text{Cr}_2\text{O}_3)\) adjacent to residual metallic blebs that are present.

It is the object of this invention to provide a process whereby the adverse effects of such Boudouard reaction between carbon and the \(\text{CO}_2\) in the
process gases which are in close contact with the agglomerated material can, at least to some material extent, be diminished.

**SUMMARY OF THE INVENTION**

In accordance with this invention there is provided a process for the solid state reduction of agglomerated metallurgical feed material composed of a sub-divided material to be reduced in admixture with a sub-divided solid reductant, the process being characterized in that the units of agglomerated material are coated with a layer of material chosen to at least inhibit contact between the components of the agglomerate and any component of heating gases employed for heating same which may react in a deleterious manner therewith, the material forming the said layer comprising a subdivided metal, alloy, metal carbide, alloy carbide, or mixtures thereof to render such layer essentially metallic in nature.

Further features of the invention provide for the reduction to be a prereduction step carried out at temperatures of from 1200 to 1500°C, preferably about 1300°C; for the agglomerate to be in any suitable
form such as pellets, briquettes or the like: for the material to be reduced to be finely sub-divided oxides of chromium, iron or both, and in particular for such material to be a chromite ore; for the reductant to be a carbonaceous reductant, in particular anthracite, coal, coke, coal char, or charcoal; for the agglomerate to optionally include required flux additions; for the material coating the units of agglomerate to be either purely metallic in nature or a mixture of at least 50% by mass metallic material with oxide coating material; and for the heating to be carried out in process gases containing:

0 - 100% of a mixture of CO₂ and CO in the ratio of CO₂:CO of at least 1:1 and optionally 3:1 or even greater;
0 - 100% air, oxygen or a mixture thereof;
and wherein the balance consists of other combustion products, nitrogen, and impurities.

It is to be noted that existing processes are limited in this regard to some extent. Generally, rotary furnaces are operated with a CO₂:CO ratio of about 2:1 whilst a shaft furnace is operated at a CO₂:CO ratio of about 1:10. The process of this invention can, on the other hand, be operated at

/...
CO$_2$:CO ratios upwards of 3:1 and even up to 100:1. This enables a process gas containing large amounts of CO$_2$ to be used, with or without excess oxygen (air) being present and allows substantially complete combustion of the heating fuel to take place whilst conserving reductant.

Preferably the metallic material comprises ferrochromium, a chromium-iron alloy or other ferroalloys, or mixtures of ferrochromium or iron chromium alloy or other ferroalloys and oxide coating materials such as Andalusite. Many of these materials are conveniently available in suitable inexpensive forms, for example ferrochromium scrap is produced as a normal product during smelting processes producing same.

The material used for forming the coating is usually finely sub-divided and can be mixed with a suitable binder prior to formation of the layer thereof on the outside of the units of agglomerate. The formation of such a layer may conveniently be carried out by, for example, pneumatically conveying
the powdered material and spraying it onto the surface of the agglomerate or by simply adding the coating material to a conventional pelletizing apparatus together with preformed pellets where the agglomerate is in the form of pellets. Coatings may be obtained by any other convenient means for example dipping the agglomerate in a slurry or dusting the coating material onto the surface.

The thickness of the coating layer is preferably of the order of up to 1.5mm and most preferably about 1mm or less. In any event the quantity of coating material will usually not be more than 50% by mass of the total weight of the coated pellet and will usually be of the order of 15 to 20% and preferably about 10%.

In the case of preformed agglomerates of chromite together with a carbonaceous reductant (such as anthracite) and fluxes, preferred coating materials, based on research carried out to date, are ferrochromium fines mixed with a suitable binder or a mixture thereof with an oxide material namely refractory grade and andalusite employed together with a binder, which was preferably a bentonite clay binder.
Other oxide materials could also be employed. Such materials include tabular alumina, Portland cement, used alumino-silicate brick, and refractory alumino-silicate cements.

Tests conducted to date have indicated that the mixture of coating materials must be chosen carefully as some materials operate better than others and some are difficult to form into an unbroken layer on the agglomerate units without excessive cracking or peeling, or otherwise without resulting in adverse effects during the processing of the agglomerate such as, fusion for example. Purely metallic coatings such as ferrochromium, however, generally do not exhibit such difficulty.

In order to demonstrate the operation of this invention, the results of a few selected tests will now be described with reference to the accompanying drawings.

**BRIEF DESCRIPTION OF THE DRAWINGS**

In the drawings :-

/...
FIGS. 1 & 2 are each graphs of the individual metallization of iron (Fe) and chromium (Cr) after treatment for 180 minutes at 1300°C of a pelletized chromite feed material without a coating of this invention in a gaseous atmosphere composed of various ratios of carbon dioxide and carbon-monoxide;

FIG. 3 is a similar graphical illustration wherein coated pellets according to the invention are heated in a similar range of carbon monoxide to carbon dioxide ratios to those shown in Fig. 2; and,

FIG. 4 is a graph of temperature as % metallisation of pellets of hematite mixed with anthracite and coated with ferrochromium when heated for 180 minutes in 100% CO₂ atmospheres.

/...
Initially tests were carried out on two somewhat different recipes of a chromite ore with finely sub-divided anthracite as a reductant, the chromite, anthracite and fluxes having a particle size such that approximately 75% passed through a 74µm (ie a 200 mesh) sieve. The two recipes are detailed in Table 1 and it will be noted that they include granite and fluorspar fluxes which have been found to give enhanced reduction of chromite and have been described fully in our Patent No. 87/5774 entitled "Process for enhanced reduction of Chromite". However, these pellets do not necessarily have to contain the fluxes for the coatings to operate effectively.

The recipes were mixed by tumbling them in plastic drums with a light ball charge. Pellets were then formed in a disc pelletizer by the addition of a controlled amount of water followed by 8 - 12 hours air drying and oven drying at 110°C for approximately 12 hours.
### TABLE 1
Pellet Compositions (expressed as % by mass and as recipe proportions)

<table>
<thead>
<tr>
<th></th>
<th>Recipe 1</th>
<th></th>
<th>Recipe 2</th>
<th></th>
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<tr>
<td>% (Proportions)</td>
<td>% (Proportions)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Mooinooi chromite</td>
<td>65.4 (100)</td>
<td>56.6 (100)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Grinaker anthracite</td>
<td>19.6 (30)</td>
<td>28.3 (50)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Granite</td>
<td>9.8 (20)</td>
<td>8.5 (20)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fluorspar</td>
<td>3.3 (20)</td>
<td>2.8 (20)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Bentonite</td>
<td>1.9</td>
<td>3.8</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>+ Moisture (%)</td>
<td>10.1</td>
<td>11.8</td>
<td></td>
</tr>
</tbody>
</table>

NB. Figures in brackets relate to proportions of anthracite and total fluxes to chromite (100)

The uncoated pellets were then heated isothermally in various different gas mixtures of carbon monoxide and carbon dioxide at 1300°C and the process was monitored with an on-line data logging facility. The various different gas mixtures that...
were used are as follows:

\[
\begin{array}{cccccccc}
\text{Vol} \% \text{ CO} & 100 & 95 & 85 & 75 & 50 & 25 & 0 \\
\text{Vol} \% \text{ CO}_2 & 0 & 5 & 15 & 25 & 50 & 75 & 100 \\
\end{array}
\]

and the results are illustrated graphically in Figs. 1 and 2 for the two pellet compositions after heating for 180 minutes in the above gas atmospheres. It will be noted that, in both cases, the metallization of both iron and chromium were extremely low at gas compositions in which there was less than about 60 to 70\% of carbon monoxide (i.e. more than 30 to 40\% carbon dioxide) when compared to the case in which a concentration of 100\% carbon monoxide was employed.

Pellets of the Recipe type 1 described above were then coated with two different materials in order to test the operation of the present invention. The following materials were tested as coating layers.

(i) 98\% by mass clean ferrochromium fines (75\% - 74\,\mu m) and 2\% by mass bentonite binder; and,
(ii) A mixture of 56% by mass clean FeCr fines combined with 38% by mass andalusite and 6% Bentonite clay binder.

All the coated pellets were produced from one batch of standard recipe 1 pellets which were sized to approximately 9mm in size in order to minimize coating thickness variations.

The coating materials were premixed, where applicable, and gradually added to the sized preformed pellets in the rotating pelletizing disc. A small amount of water (or sodium silicate) was added to re-wet the pellet surfaces before adding the coating material.

The coating additions were chosen to give a coating thickness of approximately 1mm. The pellets were then dried at 110°C for approximately 12 hours. In the case of the substantially pure ferrochromium coating layer (i) the coating amounted to about 30% by mass of dry coated pellets whilst in the case of the mixed coating layer (ii) the coating amounted to about 36% of the dry coated pellets.

/...
The coated pellets were then heated, as in the case of the uncoated pellets, at 1300°C and the compositions determined after heating had taken place for 180 minutes. In addition the coated pellets were heated in air as well.

Both coating materials namely the ferrochromium and the ferrochromium and andalusite mixture gave suitable layers with respect to their physical integrity and with respect to the metallization of chromium and iron as is shown in Fig. 3. (Calculation of % metallisation for Cr and Fe taking cognisance of the Fe and Cr in the coating was carried out as follows :-

/...
Metallization and mass balance calculations

\[
\text{Cr metallization (\%)} = \frac{(CL \times FM/LM) - (IM \times B)}{IM \times A} \times 100 \quad \text{(E)}
\]

\[
\text{Fe metallization (\%)} = \frac{(FL \times FM/LM) - (IM \times D)}{IM \times C} \times 100 \quad \text{(F)}
\]

\[
\text{Total metallization (\%)} = \frac{(CL \times FM/LM) - (IM \times B) + (FL \times FM/LM) - (IM \times D)}{(IM \times A) + (IM \times C)} \times 100
\]

\[
\text{Cr recovery in residue (\%)} = \frac{CR \times RM \times 0.01 \times FM/LM}{IM \times A} \times 100 \quad \text{(G)}
\]

\[
\text{Fe recovery in residue (\%)} = \frac{IR \times RM \times 0.01 \times FM/LM}{IM \times C} \times 100 \quad \text{(H)}
\]

Deviation from closed mass balance:

\[
\Delta \text{Cr (\%)} = [E + G] - 100
\]

\[
\Delta \text{Fe (\%)} = [F + H] - 100
\]

where CL = mass of dissolved Cr (Metal) in leach solution (g)
FL = mass of dissolved Fe (Metal) in leach solution (g)
FM = final mass of sample
IM = mass of sample used for leaching
IM = initial mass of sample (g)
RM = mass of residue (g)
CR = \% Cr in residue
IR = \% Fe in residue
A = mass of Cr from chromite in base pellet/g coated pellet (g)
B = mass of Cr from FeCr or mixed coating/g coated pellet (g)
C = mass of Fe from chromite in base pellet/g coated pellet (g)

\[
D = \text{mass of Fe from FeCr or mixed coating/g coated pellet (g)}
\]

It is to be noted this technique assumed that only a negligible amount of the FeCr coating is oxidised and reported to the residue. This assumption is justified even in 100% CO\textsubscript{2} atmospheres from SEM (Scanning Electron Microscopy) analysis, which indicated that only up to 50 - 100 µm of the FeCr material in the outer coating surface is oxidised on a 1mm thick coating.

It will be observed that, for a coating of ferrochromium approximately 90% of the iron and 73% of the chromium were metallized even in a 100% carbon dioxide atmosphere. In comparison with results for the uncoated pellets, chromium metallization is only slightly less than in 100% carbon monoxide atmosphere. Iron metallization was almost independent of gas composition.
Furthermore, experimental work has indicated that decreasing the nominal particle size of both base pellets and coating below 75% to pass a 74 µm screen does not significantly enhance the final levels of metallization achievable.

In the case of the coating made from a mixture of ferrochromium and andalusite, it will be noted that the extent of metallization was somewhat more dependent on the gas composition than in the case of the ferrochromium coated pellets. Iron metallization is, as with the ferrochromium coated pellets, virtually independent of carbon monoxide to carbon dioxide ratio.

Accordingly it will be appreciated that extremely advantageous results can be achieved using the present invention but that the coating material must be chosen carefully.

In general, tests carried out to date indicate that metallic coatings are more effective than mixed metallic and oxide based coatings in preventing carbon dioxide ingress into the pellet core. Pellets coated
with ferrochromium appear to rapidly form a chromium oxide based outer film which, although it is only about 25 - 50 μm thick, probably plays an important role in sealing the pellets from the carbon dioxide in the atmosphere. Once the protective skin has formed, metallization can proceed in the inner pellet core with 100% carbon dioxide gas compositions or even with uncombined oxygen present. The carbon monoxide gas which is a product of the carbothermic reduction of the chromite ore can nevertheless escape through this protective layer and can itself be combusted to CO₂ by introducing air to provide additional oxygen thereby increasing the thermal energy available to the process (i.e. decreasing the need to supply this amount of energy from another source).

Further experiments have shown that the ferrochromium coatings are effective even in the presence of free oxygen in the furnace atmosphere. When ferrochromium coated Recipe 1 pellets were heated for 2 hours in air at 1300°C and metallization levels of 92% iron and 70% chromium were achieved. The results after 180 minutes and 120 minutes (broken lines) are shown in Fig. 3 at the left hand side.
With regard to iron oxide reduction, experiments have been conducted at temperatures of between 800°C and 1000°C where hematite and anthracite base pellets, without fluxes, were coated with ferro-chromium and heated in a 100% CO₂ atmosphere. The pellet composition is indicated in Table 2, while iron (Fe) metallisations are indicated in Fig. 4. The latter shows that 85% Fe metallisation was achieved after 180 minutes at 800°C, whilst 100% Fe metallisation was achieved after 180 minutes at 1000°C.

TABLE 2

FeCr coated hematite pellet composition

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<tr>
<th>Component</th>
<th>Percentage</th>
<th>Comments</th>
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<tr>
<td>Hematite</td>
<td>71.6</td>
<td>1) All material sized</td>
</tr>
<tr>
<td>Anthracite</td>
<td>26.4</td>
<td>to 75% - 74 μm</td>
</tr>
<tr>
<td>Bentonite</td>
<td>2.0</td>
<td>2) Coating addition =</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30% by mass of dry coated pellets.</td>
</tr>
</tbody>
</table>

Coating
FeCr fines    98
Bentonite     2

/...
The invention therefore provides a highly effective expedient for use in the solid state reduction of pelletized feed materials mixed with a solid reductant and wherein contact between such solid reductant and the gases being used to heat same, in a solid state reduction process, is inhibited, at least to some measurable extent.

Furthermore the useful sensible energy in hot oxidising gases and the chemical energy in combustible gases which hitherto could not be used for heating and reducing oxide materials can now be employed and complete combustion of fuels (gaseous, liquid or solid) to the fully oxidised form can be carried out thereby utilizing all the available energy of combustion. Even the presence of free oxygen with the combustion gases should not result in any significant loss of reduction with the protection of such metallic or mixed coatings.

A further advantage of such coatings is that they can inhibit pellets from sticking and enhance the physical strength of the agglomerate (eg. up to a six-fold increase in the pellet drop number using a standard drop test).
WHAT IS CLAIMED IS:-

1. A process for the solid state reduction of agglomerated metallurgical feed material composed of a sub-divided material to be reduced in admixture with a sub-divided solid reductant, the process being characterized in that the units of agglomerated material are coated with a layer of material chosen to at least inhibit contact between the components of the agglomerate and any component of heating gases employed for heating same which may react in a deleterious manner therewith, the material forming the said layer comprising a subdivided metal, alloy, metal carbide, alloy carbide, or mixtures thereof to render such layer essentially metallic in nature.

2. A process as claimed in claim 1 in which the reduction is a prereduction step and heating is carried out at temperatures from 1200\(^\circ\) - 1500\(^\circ\)C.
3. A process as claimed in claim 2 in which heating is effected at about 1300°C.

4. A process as claimed in any one of claims 1 to 3 in which the heating is carried out in process gases containing:
   0 - 100% of a mixture of CO₂ and CO in the ratio of CO₂:CO of at least 1:1 and optionally 3:1 or even greater;
   0 - 100% air, oxygen or a mixture thereof;
   and wherein the balance consists of other combustion products, nitrogen, and impurities.

5. A process as claimed in claim 4 in which the process gases are obtained by the substantially complete combustion of a heating fuel optionally with excess air (oxygen) therein.

6. A process as claimed in any one of the preceding claims in which the units of agglomerated material are pellets, briquettes or the like.

/...
A process as claimed in any one of the preceding claims in which the material to be reduced is formed, together with sub-divided solid reductant and any other ingredients such as fluxes, into agglomerated units which are dried, followed by coating of the layer into the formed agglomerated units and drying of the coating layer prior to reduction being effected.

A process as claimed in any one of the preceding claims in which the sub-divided material to be reduced is a sub-divided oxide of chromium, iron, or both and the sub-divided solid reductant is a carbonaceous reductant.

A process as claimed in claim 8 in which the material to be reduced is a sub-divided chromite ore and the sub-divided reductant is a sub-divided coal, anthracite, coke, char or charcoal.

A process as claimed in any one of the preceding claims in which the coating layer is substantially purely metallic.
11. A process as claimed in claim 10 in which the coating layer is substantially ferrochromium, chromium iron alloy, or other ferrochromium alloy together with a suitable binder.

12. A process as claimed in any one of claims 1 to 9 in which the coating layer is at least 50% by mass (on a dry basis) metallic admixed with oxide coating materials.

13. A process as claimed in claim 12 in which the oxide coating material is Andalusite.

14. A process as claimed in any one of the preceding claims in which the sub-divided material to be reduced, and the solid reductant has a particle size such that about 75% passed a 74 μm sieve.

15. A process as claimed in any one of the preceding claims in which fluxes are admixed with the material to be reduced and its solid reductant.

/...
16. A process as claimed in any one of the preceding claims in which the thickness of the coating layer is up to 1.5 mm.

17. A process as claimed in claim 16 in which the thickness of the coating layer is about 1 mm.

18. A process as claimed in any one of the preceding claims in which the material forming the coating constitutes less than 50% by mass of the coated agglomerate.

19. A process as claimed in claim 18 in which the material forming the coating constitutes less than 30% by mass of the coated agglomerate.

20. A process substantially as herein described and exemplified in the description of tests carried out with reference to either of Figs. 3 or 4 of the accompanying drawings.
Figure 1. Metallization of chromium and iron in reduced pellets made according to recipe 1.
Figure 2. Metallization of chromium and iron in reduced pellets made according to recipe 2.
Figure 3. Metallization of chromium and iron in reduced (recipe 1) pellets coated with ferrochromium or a mixture of ferrochromium and andalusite.
Conditions - Duration of test: 180 min.
Gas: CO₂

Figure 4. Metallization of Fe in reduced Hematite/Anthracite pellets coated with Ferrochromium
Conditions - Duration of test: 180 min.
Gas: \( \text{CO}_2 \)

Figure 4. Metallization of Fe in reduced Hematite/Anthracite pellets coated with Ferrochromium