

REPUBLIC OF SOUTH AFRICA

REPUBLIEK VAN SUID-AFRIKA



72/6389.

No. DEPARTMENT OF COMMERCE—DEPARTEMENT VAN HANDEL

LETTERS PATENT—PATENTBRIEF

NATIONAL INSTITUTE FOR METALLURGY

WHEREAS
NADEMAAL

has/have pursuant to the Patents Act, 1952, made application for Letters Patent for an invention for
ingevolge die Wet op Patente, 1952, aansoek gedoen het om 'n Patentbrief vir 'n uitvinding vir

IMPROVEMENTS IN OR RELATING TO THE PRODUCTION OF FERROCHROMIUM
ALLOYS

and has/have made a declaration that he/they
en 'n verklaring gedoen het dat hy/hulle

are the assignees of PETER ROBERT JOCHENS

who claim/claims to be, the inventors thereof and that there is no lawful ground for objection to the grant of a Patent to him/them and has/
wat aanspraak maak, die uitvindere daarvan is en dat daar geen wettige rede vir beswaar daarteen bestaan dat 'n Patent aan hom/hulle toe-
have by a complete specification fully described and ascertained the invention;
gestaan word nie en deur middel van 'n volledige spesifikasie die uitvinding volledig beskryf en vasgestel het;

NOW, THEREFORE,
SO IS DIT DAT AAN

NATIONAL INSTITUTE FOR METALLURGY

(hereinafter called the patentee/s) is/are granted full power, sole privilege, and authority that the said patentee/s by himself/themselves
(hieronder the patenthouer/s genoem) volmag, alleenvoorreg, en magtiging verleen word dat genoemde patenthouer/s self, sy/hulle agente
his/their agents, or licensees, and no others, may at all times hereafter, during the term mentioned herein, make use, exercise and vend the
of lisensiehouders, en niemand anders nie, te alle tye hierna gedurende die termyn hierin genoem, genoemde uitvinding in die Republiek van
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enjoy the whole profit and advantage from time to time accruing by reason of the said invention during the term of 16 years from
tydperk van 16 jaar met ingang van
die volle wins en voordeel het en geniet wat van tyd tot tyd deur genoemde uitvinding opgelewer word.

19.3.1974

PROVIDED ALWAYS that these Letters Patent shall be granted subject to the provisions of the said Act.
MET DIEN VERSTANDE ALTYD dat hierdie Patentbrief behouders die bepalinge van genoemde Wet toeges aan word.

IN WITNESS WHEREOF these Letters Patent have been sealed as from the
TEN BEWYSE WAARVAN hierdie Patentbrief geseel is met ingang van die

NINETEENTH

day of
dag van FEBRUARY

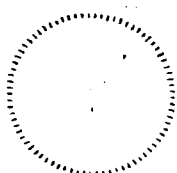
One Thousand Nine Hundred and
Eenduisend Negenhonderd

SEVENTY-THREE

Dated this
Geslateer op hede die SEVENTH

day of
dag van OCTOBER, 1974.

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Patent Office
Patentkantoor

Handwritten signature and stamp of the Registrar of Patents/Registateur van Patente

See overleaf
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P. 6138

Application No. 72/6389

Completion Filed 19th March, 1974.

REPUBLIC OF SOUTH AFRICA

The Patents Act, 1952

COMPLETE SPECIFICATION

(a) Here insert title verbally agreeing with that in the application form.

(a) "IMPROVEMENTS IN OR RELATING TO THE PRODUCTION OF FERROCHROMIUM ALLOYS"

(b) Here insert (in full) name, address, and calling of applicant(s) as in application form.

(b) We, NATIONAL INSTITUTE FOR METALLURGY of: 1 Yale Road, Milner Park, Johannesburg, Transvaal Province, Republic of South Africa,

do hereby declare this invention, the manner in which and the method by which it is to be performed, to be particularly described and ascertained in and by the following statement :—

THIS INVENTION relates to the production of ferrochromium alloys and more particularly to the production of ferrochromium alloys having carbon contents of less than 4% which is the lowest value that is generally obtainable in the high-carbon range of ferrochromium alloys

High-carbon ferrochromium is at present produced in a single stage smelting operation in a submerged electric arc furnace. The alloy produced has carbon contents varying between 4 and 8% and silicon contents varying between 0 and 10%

As far as applicants are aware, it has not been possible to produce ferrochromium alloys having a carbon content of less than 4% carbon directly from the ore in a process involving only one smelting stage.

Several smelting processes exist for the products of ferrochromium alloys with low carbon contents but these processes rely on the production of an intermediate alloy namely ferrochromium silicide which alloy can be produced directly from the ore or it can be produced from a high-carbon ferrochromium alloy. This ferrochromium silicide alloy reacted with a melt consisting of chromite ore and lime. In this reaction the silicon in the ferrochromium silicide alloy (containing very low carbon contents) acts as a reducing agent

for the iron and chromium oxides in the chromite ore-lime melt. These processes therefore, although specifically designed to produce a final alloy of ferrochromium with low carbon content, are inherently expensive to operate. The low-or medium-carbon alloy is considerably more expensive than high-carbon ferrochromium. It would therefore be of considerable advantage to produce directly an alloy of ferrochromium with relatively low contents of carbon and silicon.

The reduction of Cr_2O_3 to the carbide Cr_7C_3 has a negative free energy above 1130°C while the reduction of Cr_2O_3 to chromium metal has a negative free energy only above 1240°C and at all practical temperatures the carbide is thermodynamically more stable. Hence high-carbon ferrochromium is produced when chromite ore is reduced with a carbonaceous reducing agent in a submerged electric arc furnace.

However, it has now been found that it is possible to produce ferrochromium alloys having a carbon content below about 4% by a process involving only a single melting step.

In accordance with this invention there is provided a process for the production of ferrochromium alloy having a carbon content of less than about 4% comprising prereducing a mixture of finely subdivided chromite ore and a carbonaceous

reducing agent in a solid state process and at a temperature above 1100°C for a time sufficient to ensure that at least 40% pre-reduction takes place and wherein the amount of carbonaceous reducing agent is limited to a maximum of 50% excess carbon and thereafter melting the pre-reduced ore in the absence of further carbonaceous reducing agents in a furnace together with any required fluxing agents and separating the alloy produced from the slag.

Further features of the invention provide for the pre-reduction to be effected at a temperature of from about 1300°C to about 1700°, and for the excess carbon to be limited to a maximum of 20%.

Better recoveries are often available if an amount of ferrochromium silicide is added to the pre-reduced ore at the melting stage and in this case a pre-reduction of only about 50% can give good results. However, if this addition is not made then the pre-reduction should preferably be carried as far as possible and to at least 70% in order to produce results which at present ^{are} acceptable economically.

Applicants believe the theory behind the present invention to be as follows:

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It has been shown that the iron oxides in the chromite ore are the first to be reduced. The free energy of formation of the iron carbide, Fe_3C from the oxide FeO is negative above 393°C and has values of approximately -173 and -207 K calories (592 and 828 K joules) at 1400°C and 1600°C respectively. Applicants believe that initially the low melting Fe_3C is formed and this provides a vehicle for the transport of carbon through the chromite ore until a carbon ferrochromium alloy is formed as reduction progresses which alloy then functions in a similar manner.

The reaction that should be considered therefore is



As the reduction proceeds the carbide of iron becomes a mixed carbide of iron and chromium. The carbon from the reducing agent dissolves into this alloy and the alloy continues to act as a reducing agent to the ore.

Thus it is feasible by control of the reduction subsequent and / melting process to react chromite ore with a carbonaceous reducing agent in a solid state to produce ferrochromium alloys which contain lower amounts of carbon than those normally obtained in high-carbon ferrochromium alloys.

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The required control of the reduction and smelting process can be defined in the following manner.

The chromite ore fines or ground chromite ore is reduced with controlled amounts of solid carbonaceous reducing agent at such temperatures and for such periods, that preferably high degrees of reduction are obtained but relatively little fusion of the gangue occurs. Under such conditions the ferrochromium alloy particles in the pre-reduced material has a carbon content of less than 4 per cent and it can be controlled below 2 per cent provided that additions of carbonaceous reducing agent have been controlled with respect to the carbon requirement for reduction of iron and chromium oxides and losses.

This reduction process can be achieved in a similar manner to existing processes where pre-reduction of the chromite ore is carried out up to the values of generally 50 to 65 per cent. However, at present this pre-reduced product is subjected to smelting with the addition of more carbon and under those conditions the thermodynamics are such that high-carbon ferrochromium alloys are produced.

In our invention, however, the reduced material containing small particles of ferrochromium alloy of lower carbon content is melted in such a manner that as little as possible extra carbon is added for example in an open arc operation.

However, because it is not practically feasible to obtain 100 per cent pre-reduction without using a large excess of reducing agent and thereby obtaining high carbon values in the alloy, this process aims at achieving as high a degree of reduction as possible without excessive carbon contents in the alloy. During the melting step, the alloy separates from the gangue and unreduced oxides of iron and chromium (predominantly chromium oxide) enter the slag phase. This causes a lowering of the Cr-to-Feratio in the final alloy. Also, depending on the chemical constitution of the gangue in the chromite ore, fluxing additions may be made to facilitate phase separation between alloy and slag at optimum operating temperatures. This loss of chromium oxide to the slag can be decreased considerably by reacting the slag with a reducing agent and assisting this reaction by adding oxides to the slag to increase the activity coefficient of the Cr_2O_3 . If the reducing agent contains carbon then the alloy may very readily increase in carbon content and this depends to some degree on the temperature. However, if the reducing agent is silicon, introduced as, for example, ferrochromium silicide, then the carbon content of the original alloy is unaffected and the final carbon content is decreased by dilution with the iron and chromium derived from the ferrochromium silicide. Obviously the amount of reducing agent required, predominantly depends on the degree of pre-reduction of the chromite ore.

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A process is contained in a U.S. patent held by M.J.Udy in which initial reduction of the chromite is carried out by smelting in a submerged arc furnace using only sufficient carbon to reduce the Fe oxides and up to 80% of the chromium oxides. The resulting metal (low in Cr) and slag (high in Cr oxide) are poured into an open arc furnace to which ferrochromium silicide is added. Alloys containing between 1 and 5% C may be produced and recoveries of Cr are of the order of 95%. The major difference between this process and the present invention lies in the fact that different techniques are employed to prereducer the chromite. This is important since at high degrees of pre-reduction Udy could only produce an alloy containing a minimum of 4.8%C while in the new process: high degrees of pre-reduction still enable alloys containing less than 2%C to be produced. Udy, in order to obtain lower carbon values only pre-reduced to approximately 50% at which stage 25% by mass of a 50% Si, ferrochromium silicide alloy had to be added to win back the Cr, from the slag.

It should be pointed out that the chromite ore can be subjected to preconcentration to remove a proportion of the gangue prior to the pre-reduction step. Also, it is feasible to achieve some concentration of the metal in the pre-reduced material by ore dressing techniques applied to the pre-reduced material. The former concentration reduces the amount of material that has to be pre-reduced and also by removing some low melting components decreases the possibility

of excessive sintering. The latter concentration step will reduce the final volume of slag, thereby decreasing metal losses and facilitate melting of the pre-reduced material. Concentration of the pre-reduced material renders it more amenable for direct production of stainless steel.

The following examples carried out on a small scale in the laboratory indicate the essential features of the new process and the results obtained.

The degree of reduction is calculated on the basis of the ratio between actual mass of oxygen removed to that mass of oxygen that is combined with the iron and chromium in the chromite ore.

Analysis of the materials used:-

Ferrochromium silicide

Fe - 23%, Cr-37%, Si-40%, C-0,05%

	<u>Transvaal Ore</u>	<u>Rhodesian Ore</u>
Cr	31,2	35,7
Fe	19,9	11,8
Si	0,54	1,10
MgO	9,8	15,3
Al ₂ O ₃	14,4	11,1
Cr/Fe Ratio	1,57	3,03

Anthracite:

6,61 Ash, 10,18 Volatiles, 2,55 Moisture, 0,9 Sulphur, 79,75 Fixed Carbon.

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Size analysis of anthracite:-

100% - 100 mesh (Tyler)

Size analysis of Transvaal ore used in examples 1, 3a and 3b:-

<u>+ 65 mesh</u>	<u>+ 100 mesh</u>	<u>+ 150 mesh</u>	<u>+ 200 mesh</u>	<u>- 200 mesh</u>
50%	72%	89%	96%	4%

Size analysis of Transvaal ores used in examples 2 and 3 except 3a and 3b:-

<u>+ 100 mesh</u>	<u>- 100 mesh + 200 mesh</u>	<u>-200 mesh</u>
1%	8,2%	91%

Size analysis of Rhodesian ore used in example 2:-

<u>+ 100 mesh</u>	<u>- 100 mesh + 15 mesh</u>	<u>- 150 mesh + 200 mesh</u>	<u>-200 mesh</u>
0,13%	20%	12,9%	66,75%

Example 1

In this example the object was to obtain an analysis of the metal in the prereduced ore as a function of temperature

The reductant used was anthracite, the analysis of which is given above and the reaction time was 2 hours.

The results are given in Table 1 below.

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TABLE 1

Temperature (°C)	Excess carbon	<u>Rhodesian chromite</u> alloy concentrate analysis				<u>Transvaal chromite</u> alloy concentrate analysis			
		C	Cr	Si	Fe	C	Cr	Si	Fe
1450	0	4,86	66,82	0,39	20,83	1,92	48,52	1,83	39,48
1550	0	1,59	68,83	1,01	22,22	1,30	49,91	1,96	38,98
1650	0	0,05	70,05	1,45	22,78	1,67	50,19	1,79	38,80

It has been found that the degree of pre-reduction can be controlled by variation in reaction time, temperature, amount, type and size of the carbonaceous reducing agent and particle size and type of chromite ore and thus the optimum values of these parameters must be chosen by conducting suitable tests in each case.

Example 2

This example was conducted to ascertain the final ferro-chromium alloy composition after subsequent melting of the pre-reduced material. In this case pre-reduced alloys were used which were obtained similarly to example 1 and which were known to have low carbon contents. Ferroalloys of the following composition were obtained. Fluxes such as CaO and SiO₂ were added to assist in the melting operation. The results are given in Table 2 below.

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TABLE 2

pre-reduction %	charge % relative to prereduced ore		alloy composition %				Cr	Cr/Fe
	CaO	SiO ₂	Cr	Fe	Si	C	recovery %	
81,3	10	15	49,18	47,30	0,83	2,15	67,8	1,04
89,1	10	15	50,05	44,32	0,65	3,13	77,2	1,13
75,2	10	15	73,1	24,8	0,98	1,01	67,8	2,95

Example 3

To indicate the effect of addition of Si derived from additions of ferrochromium silicide in subsequent melting, smelting tests were performed in which the prereduced material was reacted with predetermined amounts of ferrochromium silicide and flux additions. The material used was Transvaal ore and the results are given below in Table 3.

TABLE 3

Run	charge % relative to prereduced ore			Alloy composition %				Total Cr recovery	Cr/Fe
	FeCrSi	CaO	SiO ₂	Cr	Fe	Si	C		
1,5	25,2	10	Nil	50,46	45,26	1,37	2,1	75,9	1,12
1,7	25,0	10	Nil	51,87	41,76	1,45	2,56	89,5	1,27
4,8	15,0	10	10	53,28	41,84	2,06	0,92	85,6	1,27
4,8	20,0	10	10	53,43	40,23	2,98	1,34	89,8	1,33
3,9	13,0	10	10	53,29	40,56	2,89	0,40	86,5	1,32
3,2	13,0	10	12	53,58	40,87	2,39	0,86	86,6	1,31
2,1	16,0	10	10	53,70	39,46	2,89	1,21	91,3	1,36
2,1	10,0	10	15	53,72	39,68	3,00	0,86	91,0	1,35
1,0	11,1	10	14	54,15	39,29	2,22	2,31	93,5	1,38
3,7	20,0	10	5	53,66	39,55	2,82	1,73	94,0	1,36

These results confirm that the chromium oxide losses in the slag can be decreased i.e. higher ratios of Cr/Fe in the final alloy are obtained which in turn indicates improved recoveries of chromium in cases where ferrochromium silicide is added.

Example 4

The following conditions obtained to produce the various degrees of pre-reduction using Transvaal chromite and anthracite of analysis previously indicated. These tests show that a variety of degrees of pre-reduction are obtainable depending on the conditions used. The results are given in Table 4 below.

TABLE 4

Temp °C	Time, min.	excess carbon %	Reduction %
1650	120	15	81,3
1650	300	20	89,1
1600	120	0	51,5
1600	120	0	51,7
1650	120	0	74,8
1650	120	0	74,8
1650	120	5	78,9
1650	120	10	78,2
1650	120	0	72,1
1650	120	10	82,1
1650	120	15	81,0
1650	120	0	66,7
	For Rhodesian ore using anthracite		
1650	180	0	75,2

From the above examples it will be appreciated, therefore, that ferrochromium alloys having carbon contents less than 4% may easily be produced according to the invention with only a single melting stage being employed.

Having now particularly described and ascertained our said invention and in what manner the same is to be performed, we declare that what we claim is:

1. A process for the production of ferrochromium alloy having a carbon content of less than about 4% comprising pre-reducing a mixture of finely subdivided chromite ore and a carbonaceous reducing agent in a solid state process and at a temperature above 1100°C for a time sufficient to ensure that at least 40% pre-reduction takes place and wherein the amount of carbonaceous reducing agent is limited to a maximum of 50% excess carbon and thereafter melting the pre-reduced ore in the absence of further carbonaceous reducing agents in a furnace together with any required fluxing agents and separating the alloy produced from the slag.

2. A process as claimed in claim 1 in which pre-reduction is effected at a temperature of between 1300°C and 1700°C .

3. A process as claimed in claim 2 in which the temperature is about 1450°C to 1650°C .

4. A process as claimed in any of claims 1 to 3 in which carbonaceous reducing agent is used in an amount such that there is only 20% or less excess carbon.

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5. A process as claimed in any of the preceding claims in which non-carbonaceous reducing agent is added to the pre-reduced ore prior to melting thereof.
6. A process as claimed in claim 5 in which the non-carbonaceous reducing agent is ferrochromium silicide.
7. A process as claimed in either of claims 5 or 6 in which the degree of pre-reduction is at least 50%.
8. A process as claimed in any of claims 1 to 4 in which no additional reducing agent is added and the degree of pre-reduction is at least 70%.
9. A process substantially as herein described or exemplified.
10. Ferrochromium whenever produced by a process as claimed in any of claims 1 to 9.

DATED this 19th day of March, 1974.

W.E. JOHN & KERNICK
Patent Agents for the Applicants