

Complete Specification

(Section 30(1) - Regulation 28)

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54	Title of invention "PROCESS FOR THE ENHANCED REDUCTION OF CHROMITE ORES"		

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ABSTRACT

A process is provided for the solid state reduction of chromite ores in which a finely divided chromite ore is heated, in which intimate admixture, and preferably agglomerated form, with a solid carbonaceous reductant, an alkali metal aluminium silicate, silica and calcium fluoride, to a temperature generally between 1200°C and 1400°C, such that a liquid flux phase is formed in contact with adjacent solid particles of chromite and reductant. The alkali metal aluminium silicate, silica and calcium fluoride are conveniently present in the form of granite and fluorspar.

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reword

"PROCESS FOR THE ENHANCED REDUCTION OF CHROMITE ORES"

FIELD OF THE INVENTION

THIS INVENTION relates to a process for the reduction of chromite ores and particularly to the solid state reduction of these ores.

BACKGROUND TO THE INVENTION

Chromite is a spinel solid solution the composition of which may be represented by the general formula $(\overset{\text{Fe, Mg}}{\text{Fe}}, \overset{\text{Cr}}{\text{Al}}, \overset{\text{Fe}}{\text{Fe}})_2 \overset{\text{O}_4}$. The solid state reduction of such spinel using carbonaceous material is complicated and is generally associated with a high degree of metallisation of the iron present and a substantially

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lower reduction of the chromium for a given time and at a given temperature.

In the context of this specification the degree of metallisation of iron or chromium is based on the ratio of the mass of iron or chromium present in non-oxide form after reduction to the total mass of iron or chromium respectively initially present in the ore in all its forms.

By way of example, in a mixture of finely divided solid chromite and carbon the degree of metallisation of the iron will generally be almost complete and that of chromium just over 50% where the mixture has been heated for two hours at 1300°C. This low chromium reduction (or metallisation) is postulated to be the result of the formation of a stable magnesium, chromium, aluminium oxide spinel which forms as reduction and metallisation of the iron takes place. Obviously the rate of reduction increases with temperature leading to improved metallisation of the chromium but at increased expense and accompanied by problems often associated with high temperatures such as softening and fusion of the material which occurs at temperatures in excess of about 1500°C.

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Krupp does not consider it a process

4.

Such softening is an integral part of a process

~~Practical problems of this type are associated with a~~
~~process~~ referred to herein as the Krupp process in which a mixture of finely divided chromite, silica and carbon in large excess of the stoichiometric amount required for reduction is subjected to temperatures of 1500 - 1600°C to give a chromium metallisation in excess of 80%. This process is more fully described in South African Patent No. 84/0101 to Fried Krupp Gesellschaftt and entitled "Process for the production of Ferrochromium".

A more recent breakthrough in solid state chromite reduction has shown that the reduction rate may be increased significantly by the addition of small amounts of sodium salts and fluospar to the chromite and reductant mix. More specifically a 10% addition of fluospar and a 1% addition of a sodium salt results in an increase in the chromium metallisation from just under 50% to just under 100% after being held at 1200°C for 90 minutes. The reduction under these conditions is so fast that, in practice, the rate of reduction is likely to be determined by the rate of heat transfer to the pellets.

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It is postulated that components of the hitherto stable spinel (see above) are soluble in the liquid calcium fluoride-sodium fluoride phase formed and that the non-reducible oxides precipitate as $MgAl_2O_4$ thereby allowing the reducible ^{species} phases (ie. including chromium) to transport through the liquid to the reductant where reduction of such components takes place.

Even though the reduction rate for the chromium may be increased up to four times, this process would probably not be economically viable because of the high costs of the fluorspar and sodium salts.

It is thus an object of the invention to provide a method for the solid state reduction of chromite ores which may provide a high degree of chromium oxide reduction on an economically viable basis.

SUMMARY OF THE INVENTION

According to the invention a process for the solid state reduction of chromite ores comprises heating finely divided chromite ore in intimate admixture with a finely divided carbonaceous reductant and a flux

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comprising at least one alkali metal aluminium silicate, silica and calcium fluoride at a temperature and for a time chosen to cause the formation of a substantially liquid flux phase in contact with adjacent solid particles of chromite and carbonaceous reductant.

Further according to the invention the carbonaceous reductant preferably comprises at least one of coke, anthracite or char. Other carbonaceous reductants may also be used, either alone or together with other forms of carbonaceous reductant. It is considered that even sewage sludge could be employed as at least part of the reductant.

Still further according to the invention the alkali metal aluminium silicate is a compound having a comparatively low melting point with the alkali metal being potassium, sodium or calcium. Such compound is preferably a naturally occurring compound in the form of a feldspar, feldspathoid or syenite. The feldspar could even be a lithium bearing feldspar such as lepidolite.

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part of reductant
 this is possible
 - this is a
 patent on it
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 IS this
 kinetic?
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Still further according to the invention the calcium fluoride is a naturally occurring compound in the form of fluorspar.

Still further according to the invention the alkali metal ^{aluminum} silicate and the silica are added in the form of a naturally occurring material such as a granite.

Still further according to the invention the carbonaceous reductant is present in at least, and preferably more than, the stoichiometric amount necessary to effect reduction of all the chrome ^{iron} and iron oxides in the chromite to metal together with the accompanying formation of some chromium and iron carbides, *and silicides at the higher temperatures.*

Still further according to the invention, where a feldspar is used, the ratio of feldspar to fluorspar may vary from 0,5:1 to 5:1 (usually from 1:1 to 3:1) and the ratio of feldspar to silica may vary from 0,5:1 to 5:1 (usually from 1:1 to 2:1). The exact ratios will depend to a large extent on the objective to be achieved and the nature and composition of the starting materials. *the flux mix may be designed to minimize degradation of the furnace refractories, while optimizing metallization of the ore...*

Still further according to the invention the alkali metal aluminium silicate, silica and calcium fluoride account for between ~~10%~~^{5%} and about 35% by mass of the mixture, preferably from ~~15%~~^{10%} to 25%, and most preferably about ~~20%~~^{15%}.

Still further according to the invention the mixture is agglomerated prior to carrying out the reduction and the heating is carried out in a reducing atmosphere, ~~an initially reducing and then oxidising atmosphere.~~

this is in conflict with para p 21

Technically the mixture does not have to be agglomerated so long as it is, and remains during the solid state reduction process intimately mixed ~~and as long as good inter-~~
particle contact is maintained.
However, on the practical side, the homogeneity of the mixture is most easily maintained during reduction by ~~agglomerating~~^{agglomerating} it into pellets, briquettes or other agglomerated units. *agglomerating material is essentially very heterogeneous.*

Any suitable binder may be used for the agglomeration but sodium silicate and bentonite binders, used either individually or jointly are considered to provide good, strong agglomerated most suited to continuous processing. The particular agglomerated composition

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will also depend on whether induration of the agglomerate is necessary and practical before the agglomerated units can withstand the stresses imposed during processing without fracturing and collapsing.

It is also of importance that the different materials be sufficiently finely sub-divided to give best effect to the aforesaid reduction process being carried out.

In this regard the materials are preferably ^{INDIVIDUALLY} milled so that ^{the chromite} is as fine as, economically practical. and preferably about 75% pass-a 75 μ m sieve.

prior to mixing,

BRIEF DESCRIPTION OF THE DRAWINGS

In the drawings :-

FIG. 1 is a set of graphs illustrating % reduction against time for four different chromite mixtures and a comparative test not using the invention;

FIG. 2 is a set of graphs illustrating the effect of reduction at different temperatures; and,

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Fig. 3 is a set of graphs illustrating the effect of different compositions resulting in different flux quantities.

DETAILED DESCRIPTION OF EXPERIMENTS CARRIED OUT TO
EXEMPLIFY THE INVENTION

An experimental programme was conducted with the object of ascertaining the reduction behaviour of four chromites from different sources when reduced in accordance with the process of this invention. The four chromites are denoted A, B, C, and D for convenience and were of the compositions shown in Table 1.

TABLE 1

Average chemical analyses of the four chromites tested

Component	Composition in mass, %			
	Chromite A	Chromite B	Chromite C	Chromite D
Cr ₂ O ₃	46,60	44,62	45,50	45,35
Fe ₂ O ₃	7,1	6,77	7,23	7,85
FeO	19,5	19,95	19,9	19,10
MgO	9,83	9,57	9,14	9,17
Al ₂ O ₃	13,8	14,53	14,50	14,60
CaO	0,20	0,25	0,26	0,27
SiO ₂	0,50	1,64	0,95	1,02
TiO ₂	0,53	0,54	0,57	0,52
Total analysed components	98,06	97,87	98,02	97,88
Cr/Fe ratio	1,58	1,51	1,52	1,53

Samples of the four chromites were milled to approximately 75 μ m and mixed with similarly finely divided carbonaceous reductant in the form of anthracite or char having the analyses shown in Table 2, bentonite as a binder, and a flux comprising a granite and fluorspar, the granite providing the feldspar and silica additions required by the invention. The compositions of the granite and fluorspar are shown in Table 3 and the compositions of the mixes for 10%, 20% and 30% flux additions in Table 4.

TABLE 2

Chemical analyses of the two reductants, % by mass.

<u>Reductant</u>	<u>Moisture</u>	<u>Ash</u>	<u>Volatiles</u>	<u>Fixed Carbon</u>	<u>Sulphur</u>
Anthracite	1,3	12,9	8,0	77,8	1,4
Char	1,6	17,8	3,4	77,3	0,4

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TABLE 3Chemical analyses of the flux components*to by mass*

Component	Granite	Fluorspar
CaF ₂		87,6
SiO ₂	71,86	5,9
Al ₂ O ₃	13,97	
MgO	0,27	
CaO	1,23	
Fe ₂ O ₃	1,32	
Na ₂ O	4,13	
K ₂ O	3,91	
	96,69	93,5

In terms of mineral composition:

Granite approx, 75 percent feldspar

25 percent SiO₂

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TABLE 4

Individual component additions
for the various batches of pellets

Component	Net component addition, % by mass		
	10% Flux	20% Flux	30% Flux
Chromite	70,1	65,33	61,25
Carbon	21,0	19,60	18,37
Granite	5,25	9,80	13,78
Fluorspar	1,75	3,27	4,59
Bentonite	2,00	2,00	2,00

After thorough mixing, the mixtures were pelletised and the pellets air dried under forced draught conditions for a period of 24 to 36 hours, and thereafter placed in a thermobalance. A further minor quantity of moisture (1 - 2%) was driven off during a preliminary purge period, with sample temperatures reaching in excess of 120°C in the cool zone of the furnace under a nitrogen atmosphere. Once the mass had stabilised, the sample was raised into the hot zone of the thermobalance and reacted. The reaction temperatures used were 1200°C, 1300°C and 1400°C. The apparatus was monitored with an on-line data logging facility.

Data gathered by the data logger was processed off-line to establish the actual mass for each run, with corrections being applied to the measured sample mass loss figures for devolatilization of the carbonaceous reductant and any possible flux boil-off or other mass loss. The final corrected mass loss pertaining to chromite reduction was then calculated in terms of per cent reduction of each of chromium and iron against time.

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On removal of the reduced sample from the thermobalance, detailed observations were made on the form and agglomeration characteristics of the pellets. Portions of the sample were then taken for microscopic examination and chemical analysis.

In order to determine the actual degree of metallisation, samples were leached for 18 to 24 hours in a 50% HCl solution and the resulting leach liquor and residue analysed to determine the fraction of soluble (metallised) chromium and iron. The mass balances obtained in this way were always found to be in close agreement with that expected from the mass loss.

The results of the experiments may be summarised as follows:

Evidence of a marked improvement in the net reduction rate (ie. of iron and chromium combined) obtainable through the addition of flux was noted. Fig. 1 shows the percentage reduction against time for the four ores reacted at 1300°C and using 20% flux. A reduction of at least 80% of the chromium and iron is achieved

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after heating for 120 minutes at this temperature. Also illustrated is a graph of a similar solid state reduction carried out on similar pelletised materials but without the addition of the flux forming constituents. The improvement made by the invention is quite clearly illustrated.

The marked effect that temperature has on the reduction kinetics using chromite A as an example, is shown in Fig. 2. This curve also indicates the reduced spread in reduction rate that occurs as temperature is increased.

It will readily be appreciated that the standard reduction curve is a composite, comprising the individual iron and chromium reduction curves, and in order to obtain a more accurate assessment of the influence of different parameters analysis was conducted on the basis of the individual iron and chromium metallisation rates.

Accordingly, in order to establish the individual rates of metallisation, the iron-chromium metallisation envelopes had to be established for the various sets of conditions experienced. ~~It was found that~~ these curves indicate that, ~~while~~ temperature ~~does~~ have a ~~has~~ the effect

significant effect on the shape of the metallisation envelope, ^{SEE FIG 4 + FIG 5} particularly at the higher temperature,

Within the narrow range of compositions tested, ore type was not found to have a significant effect.

Accordingly, one set of ^{metallisation} curves was found to be applicable to all four ores at 1200°C and 1300°C, while a slightly narrower set of curves was found to be applicable for all ores at 1400°C.

An investigation of the influence that various parameters have on the rates of iron and chromium metallisation indicates that the rates of chromium reduction of the four ores shows the distinct order A-D-B-C, which is supported by the results on the pelletised material which show A and D as the best performers at flux additions of 20% - 30%. In each case, the major difference in reduction rate may be attributed mainly to differences in the rate of chromium reduction from the ore.

A specific comparison of the effect of variables such as reductant type and flux addition was made in terms of the time taken to achieve a particular degree of either iron or chromium metallisation as presented in Table 5, highlighting the difference between these various factors.

TABLE 5

TYPE B

A comparison of results for ~~two different~~ ore reduced under various conditions. Expressed in terms of the time required to achieve a particular degree of iron or chromium metallisation.

Pm	ta/min								Unpelletized 1300°C	Char 20% flux 1400°C	Char 20% flux 1200°C	Approx. error
	Char 20% flux 1300°C	Anthracite 20% flux 1300°C	Char 10% flux 1300°C	Char 30% flux 1300°C	Char 20% flux 1200°C	Char 20% flux 1400°C	Unpelletized 1300°C					
Cr - 30	20	26	25	19	53	12	60				±2	
Cr - 50	33	46	42	33	96	20	146				±5	
Cr - 70	62	91	82	62	184	41	290					
Cr - 90	131	180	190	131	-	99	-				±8	
Fe - 30	7	7,5	8	6,5	14	4,5	18				<1	
Fe - 50	10	12	11	9,5	22	. 6	43				±1	
Fe - 70	14	18	16	14	34	10	92				±1	
Fe - 90	25	34	31	24	72	21,5	202				±2	

ta = time to achieve specified degree of metallisation (minutes)

Pm = extent of chromium or iron metallisation (per cent)

An example of the curves obtained is shown in Fig. 3 in which the percentage reduction of chromium in chromite A is plotted against time using 10%, 20% and 30% flux at 1300°C.

The results as summarised in Table 5 indicate that increasing the flux addition above 20% results in a small, relatively insignificant increase in reduction rate, while decreasing the flux addition from 20% to 10% has more significant effect in decreasing the overall reduction rate. This decrease does not appear to diminish with increasing temperature as seen with other effects such as reductant type. However, the most significant effect that altering flux addition had was in terms of the physical properties of the pellet, which effectively set an upper limit on the quantity of flux which may be added to approximately 20%. Above this level the amount of liquid phase produced adversely effected the physical properties of the pellets ^{ed}flux indicating the probability of poor performance under load, that is, pellets sticking to one another.

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Electron microscope analysis of reaction products where 20% flux was used revealed that a quantity (20% - 30%) of the magnesia and alumina in the chromite spinel remained undissolved after the 1 - 2 hour reaction period.

Accordingly, it seems feasible that the quantity of flux phase could be reduced without significantly altering the reduction rate.

Where the inert nitrogen blanket was removed from samples undergoing reduction, thereby enabling the partial presence of oxygen to rise slightly, both pellets at high and relatively low extents of reduction were enveloped in a ceramic glass layer of 0,5 to 1mm thick. Investigation of this outer glass layer showed it to be composed of three phases, the bulk matrix being the common slag, with low MgO content, containing laths of recrystallised sesquioxide ($\text{Cr}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$ containing more than 60% Cr_2O_3) and at high extents of reduction, recrystallised spinel ($\text{Mg}(\text{Cr} \cdot \text{Al})_2\text{O}_3$ containing approximately 6% Cr_2O_3).

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It is important to note that the experiments were conducted without the presence of components of heating gases generated by combustion and the action of such gases must be taken into account when carrying out reduction in the presence of such gases as CO₂, for example.

The experimentation described indicates the highly beneficial results of the use of fluxes as defined in the solid state reduction of chromite ores. The constituents of the fluxes are freely available as abundant naturally occurring materials. It should be noted that depending on the composition of these materials it may be necessary to supplement them with other materials. Thus while granites will normally provide the feldspars and silica necessary, materials such as nepheline syenite may necessitate additions of silica.

It is the intention of this patent that the flux as specified should be used for the promotion of the rate and extent of reduction in a device in which material (preferably in agglomerated form), is treated under

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controlled conditions of atmosphere and temperature so as to ensure an optimum amount of reduction. Such devices include a rotary kiln, a rotary hearth furnace sometimes referred to as a pancake type of furnace and a vertical shaft kiln. Such a device is preferably one in which the rate of heat transfer to the material undergoing reduction is commensurate with the rate of reduction enabled by inclusion of the flux.

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WHAT IS CLAIMED IS :-

1. A process for the solid state reduction of chromite ores comprises ⁱⁿ heating finely divided chromite ore in intimate admixture with a finely divided carbonaceous reductant and a flux comprising at least one alkali metal aluminium silicate, silica and calcium fluoride at a temperature and for a time chosen to cause the formation of a substantially liquid flux phase in contact with adjacent solid particles of chromite and carbonaceous reductant.
2. A process as claimed in claim 1 in which the alkali metal aluminium silicate is a naturally occurring compound selected from a feldspar, feldspathoid or syenite.
3. A process as claimed in claim 2 in which the alkali metal aluminium silicate and the silica

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are added in a naturally occurring mixture thereof in the form of a granite.

4. A process as claimed in any one of the preceding claims in which the calcium fluoride is added as a naturally occurring fluorspar.
5. A process as claimed in any one of the preceding claims in which the mixture includes feldspar and fluorspar, the ratio of feldspar to fluorspar being in the range of 0,5:1 to 5:1.
6. A process as claimed in claim 5 in which the ratio of feldspar to fluorspar is in the range of 1:1 to 3:1 and the ratio of feldspar to silica is in the range of 1:1 to 2:1.
7. A process as claimed in any one of the preceding claims in which the combined mass of the alkali metal aluminium silicate, silica and calcium fluoride is between $\frac{5}{10}$ % and about 35% of the total mass of the intimate mixture.

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*Wider range of the
the m. number
patent*

8. A process as claimed in claim 7 in which the said combined mass is between about 15 and 25% of the total mass of the intimate mixture.
9. A process as claimed in any one of the preceding claims in which the carbonaceous reductant includes coke, anthracite or char.
10. A process as claimed in any one of the preceding claims in which the carbonaceous reductant is present in at least the stoichiometric amount necessary to effect reduction of all the chrom^{ium} and iron oxides present in the chromite together with the accompanying formation of some chromium and iron carbides *and silicides*.
11. A process as claimed in any one of the preceding claims in which the intimate admixture is agglomerated prior to heating thereof.
12. A process as claimed in claim 1 in which the mixture is formed into pellets or briquettes.

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13. A process as claimed in any one of the preceding claims in which the finely divided starting materials are ground to a fineness such that
14. A process as claimed in claim 13 in which the fineness is such that 75% pass a 75 μ m ~~60~~ mesh.
15. A process as claimed in any one of the preceding claims in which heating is effected at temperatures of between 1200°C and ~~1400°C~~.
1500°C
16. A process as claimed in claim 15 in which heating is effected at about 1300°C.
17. A process substantially as herein described and exemplified.

1. Should note figures be clear up?
2. Should figures have captions?

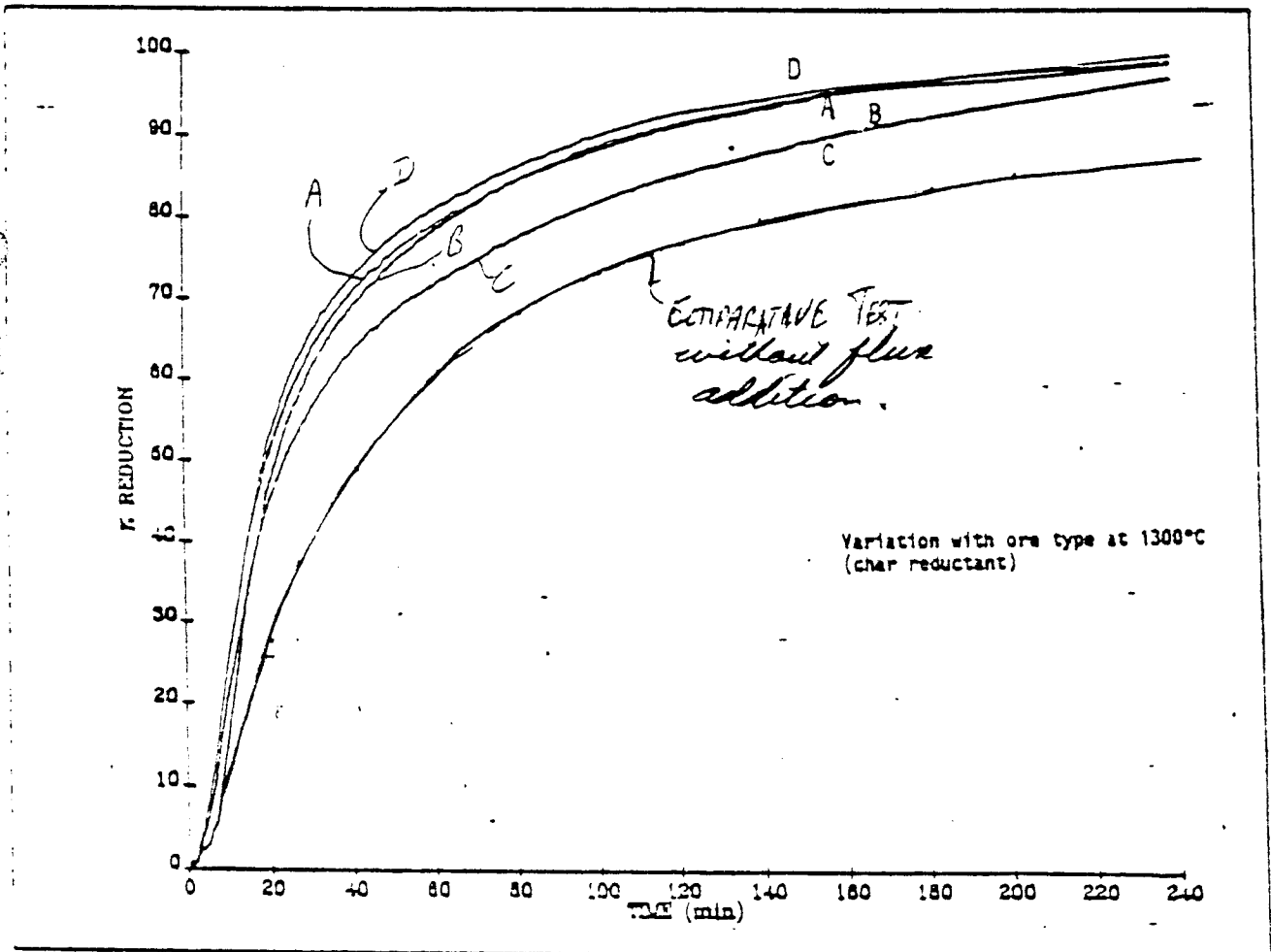


FIGURE 1. Curves showing percentage reduction of various ores with fluxes as compared with a typical ore without flux.

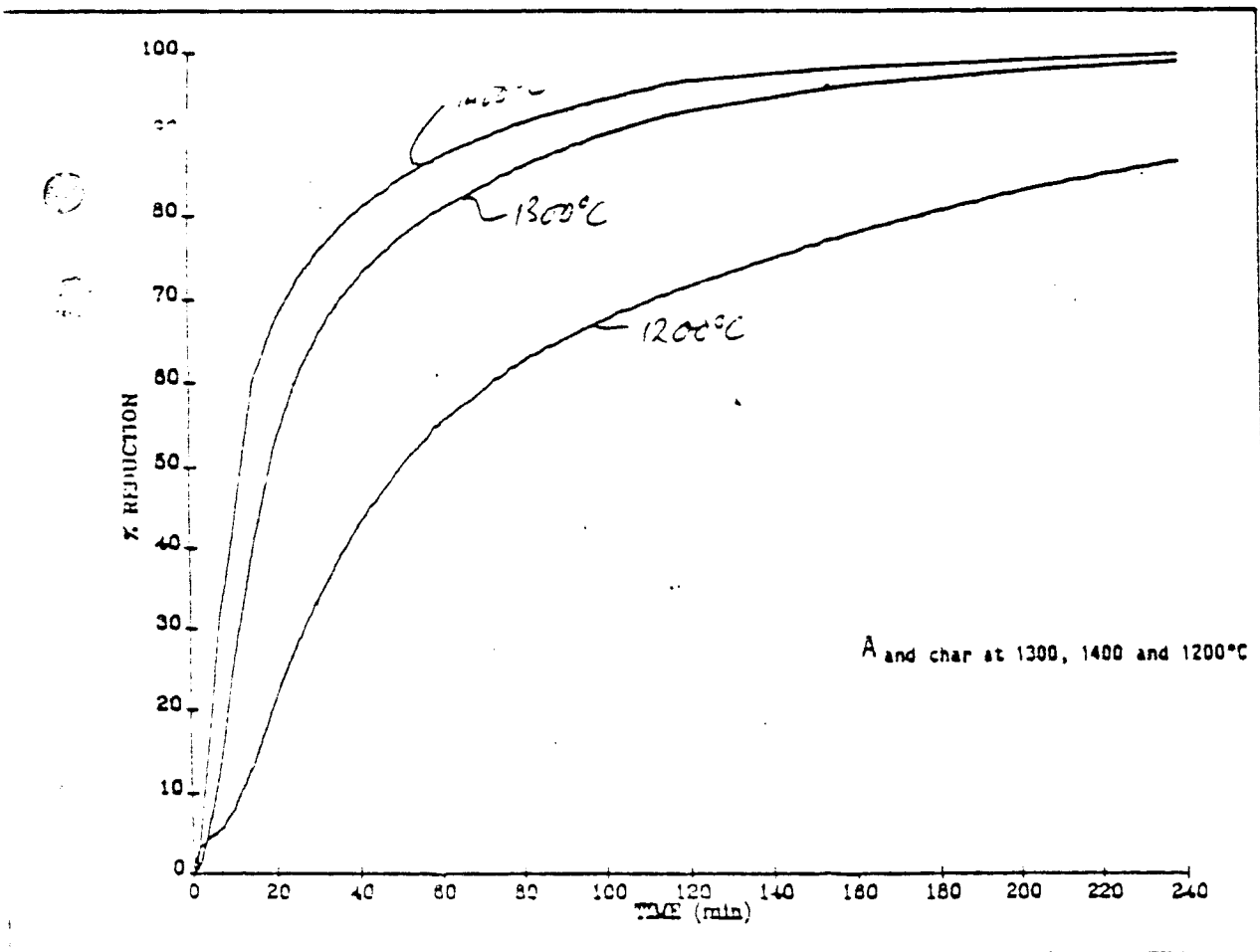
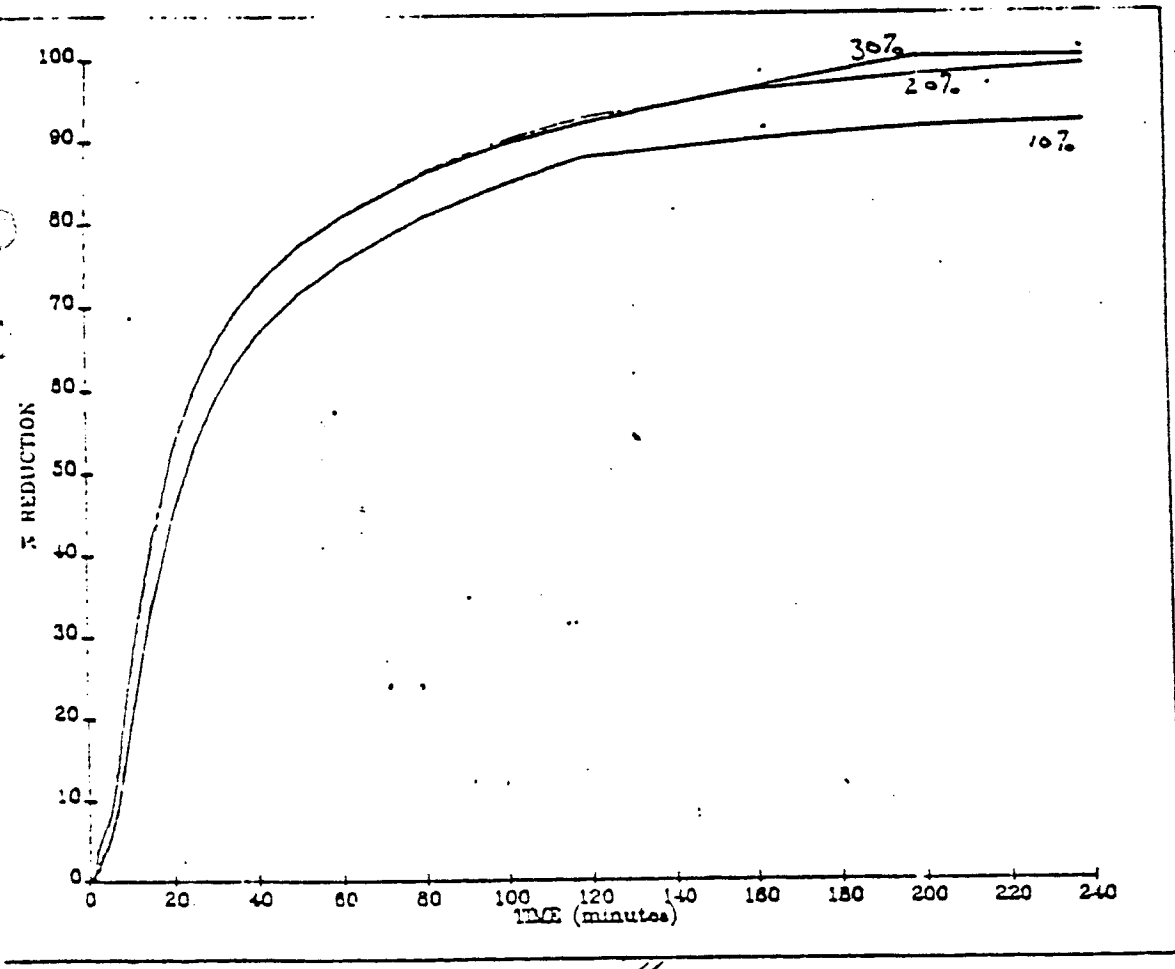


FIGURE 2. Curves showing effect of Temperature on reduction of ore type A with flux.

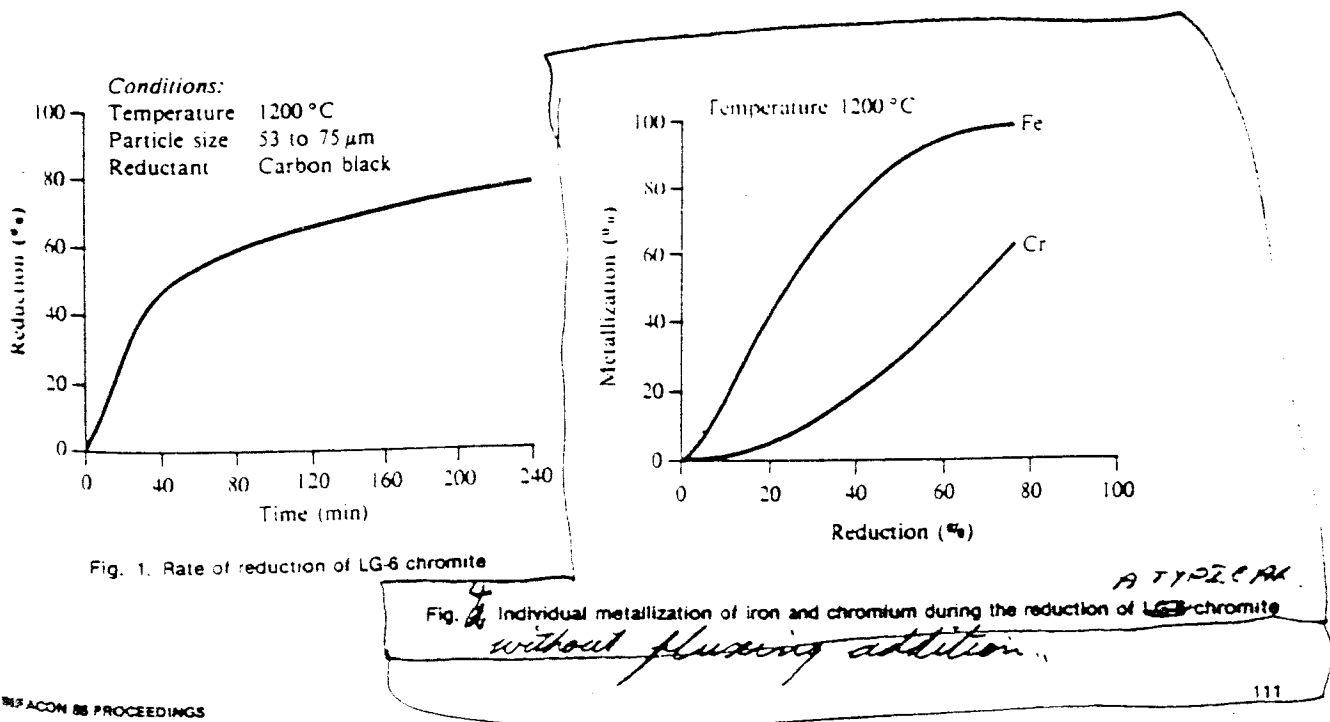


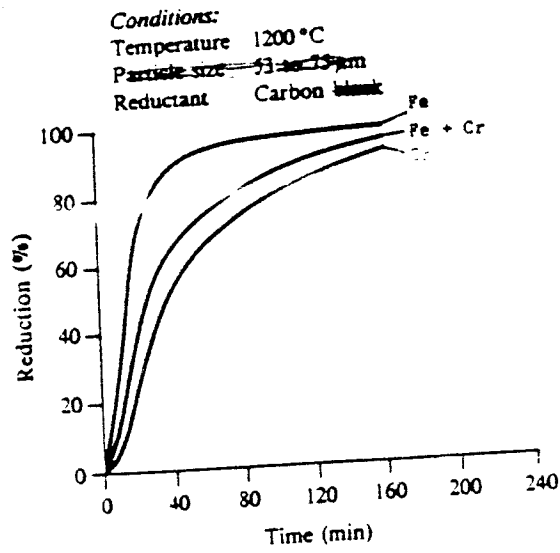
Effect of varying flux addition on Fe_2O_3 at 1300°C , char reductant ^{with}

FIGURE 3

TYPE B ORE

6. Y. Otsani and K. Ichikawa, "Manufacture and use of prereduced chromium ore pellets", pp. 31-37 in INFACON 74, Proceedings of the First International Ferro-Alloys Congress, H.W. Glen (ed.) The South African Institute of Mining and Metallurgy, Johannesburg, 1975.
 7. A.D. Barnes, C.W.P. Finn, and S.H. Algie, "The prereduction and smelting of chromite concentrate of low chromium-to-iron ratio", J. S.Afr. Inst. Min. Metall., 83(3) (1983) pp. 49-51.
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1. G. Schankter Haftung, "Process for the production of ferrochromium", Application for South African Patent no. 8 410 101 (1984).
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 3. W.L. Hunter and D.L. Paulson, "Carbon reduction of chromite", Report R16755, U.S. Bureau of Mines, Washington, 1966.
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Condit:
 Reductant
~~Carbon black~~
 & Particle
 Size

Fig. 5. Reduction of chromite ore with a 10 per cent fluxing addition of NaF-CaF₂

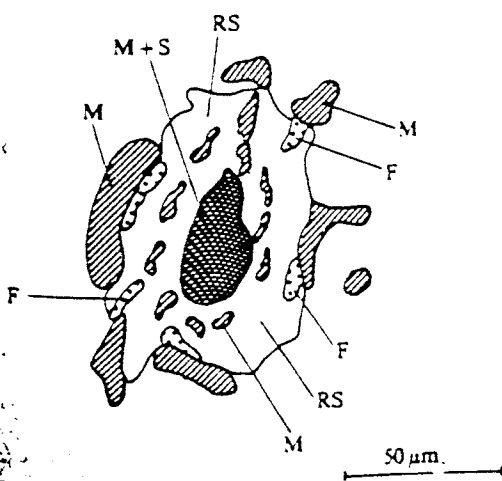


Fig. 6. Typical appearance of a chromite grain after reduction in the presence of a low-temperature flux phase. M = metal; S = spinel; RS = recrystallized spinel; F = flux

FIG 5.
 Technical method
 of iron - chromium line
 the reduction of a ferric
 chromite with ferrous
 addition.

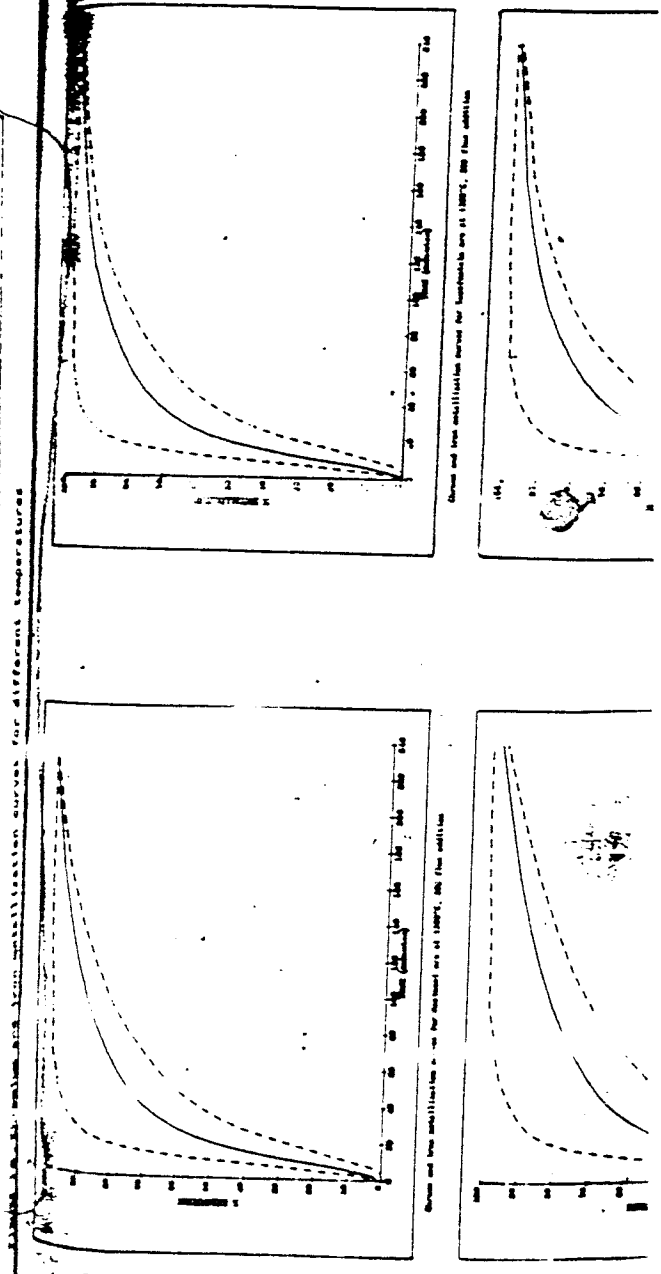
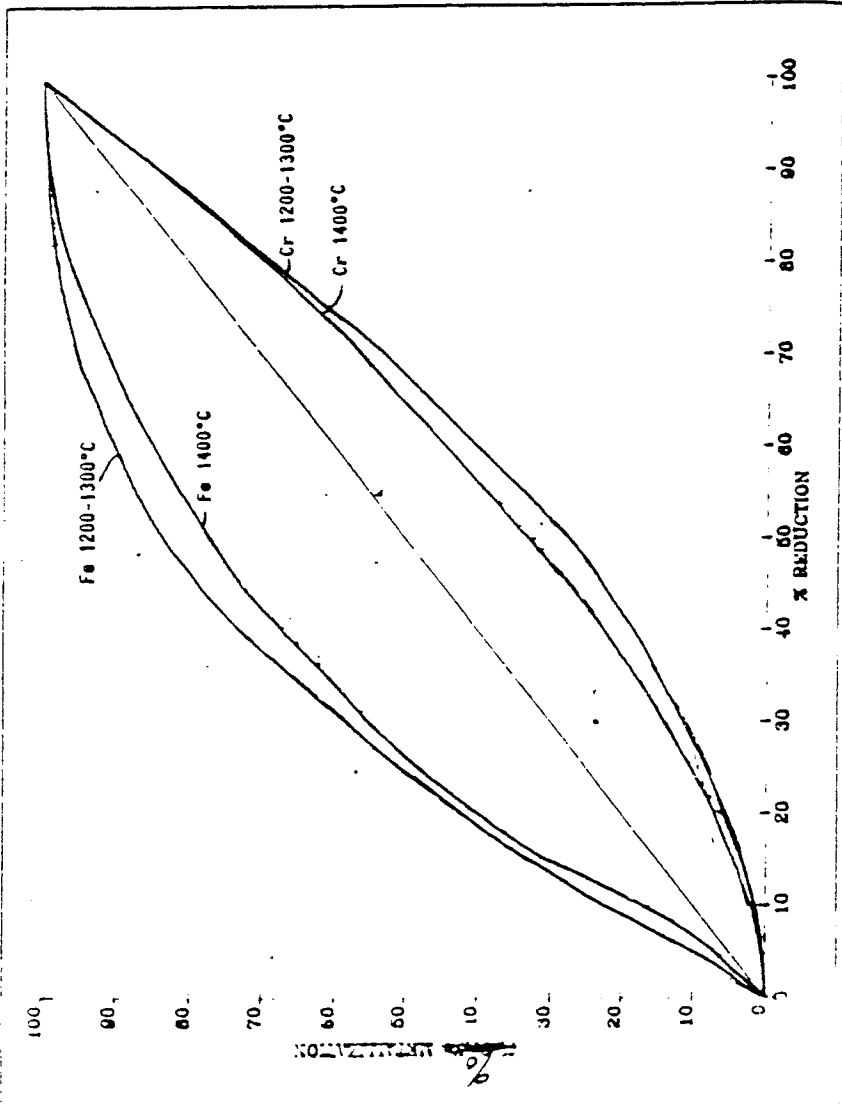


FIGURE 19