

The aluminothermic reduction of the oxide of reactive metals

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GUNTHER WERNER HEINZ DREIBRODT was born in 1920 in Berlin, Germany, and was apprenticed at OSRAM while receiving training as a technician at night school.

He received his Trade Test certificates in 1938, and was engaged in research work on short wave-radar before World War II. After the war he was employed by the Siemens-Halske Laboratory and, subsequently, by the laboratories of the Institute of Physics at the University of Würzburg. He moved to South Africa in 1962 and spent 11 years with Corner House Laboratories before joining Mintek in May, 1973. He was workshop foreman (services) for 8 years before joining the Pyrometallurgy Division as engineering draughtsman and designer (plasma-technology development).



JACOBUS ANDRIES THERON was born in September 1956 in Belfast, Transvaal and received his schooling and early university education in Pretoria, where the B.(Eng.) metallurgy degree was conferred on him in 1979. After completing his military training, he started a project at Mintek in October, 1980. In January, 1982 he was appointed a contract researcher at Mintek while completing his Masters degree. He resigned from Mintek to join Iscor in April, 1984. He is unmarried.

SYNOPSIS

A smelting process for the smelting of the oxides of reactive metals, together with subdivided aluminium is provided in which the furnace has a thermal plasma generating device for maintaining the slag on top of the furnace bath in a liquid condition. To achieve initial melting and subsequent stirring of the molten mass, the furnace is preferably also equipped with an induction heating coil which may be employed as and when required.

BACKGROUND TO THE INVENTION

This invention relates to the aluminothermic reduction of oxides of reactive metals by which term, in this specification, is meant the group consisting of titanium, zirconium, niobium, and tantalum to produce the metal or alloys of these metals with iron and aluminium.

The exothermic energy of reaction of the above defined reactive metals during an aluminothermic reduction, is generally insufficient to achieve the required objectives and, in particular, the required degree of reduction of the oxide materials being processed. As a consequence, it is necessary that thermal energy be added in some form or another to supplement the energy of the exothermic reaction and prevent the metal and slag from solidifying.

DISCUSSION OF THE PRIOR ART

Energy has, in the past, been added by conducting the reduction in an arc furnace which has been preheated, conveniently by melting down a charge of steel scrap. Alternatively, the processes have been conducted in an induction furnace in which case the optionally intimately mixed, finely divided reactants are fed to a molten susceptor metal together with any slag thereon in the furnace bath, at a controlled rate to ensure a reasonably constant temperature in the bath of liquid slag and metal.

The only other expedient employed, of which applicants are aware, is to add 'sustainers' such as barium peroxide, or sodium or potassium perchlorate which react vigorously with the aluminium to generate large quantities of energy, thereby overcoming the energy deficiency.

The latter procedure is generally regarded as being too costly and is not widely practised. The employment of an induction furnace leads to inefficient energy usage as a result of the poor conversion of electrical energy to thermal energy.

The conventional submerged arc furnace, on the other hand suffers from the fact that the resistive heating is carried out essentially within the slag and thus the metal can tend to freeze up and thus not participate in any further reaction. Furthermore the graphite electrodes are immersed in the slag and can react with the oxides of certain of the reactive metals in the slag to form unwanted metal carbides.

The induction furnace arrangement suffers additionally from the disadvantage that, as a result of the fact that the heating is carried out within the metal, the slag can acquire a substantially solid crust over the upper surface thereof. This is highly disadvantageous as reactants can no longer enter efficiently through the crust which must, indeed, sometimes be broken manually.

Also, where the crust or slag has been allowed to cool to any appreciable extent, the efficiency and rate of reaction will be impaired as the reactants are fed to the slag which defines the upper part of the reaction zone. A properly heated and, therefore, liquid slag thus reduces entrainment of formed alloy in the slag phase and assists in the proper heating and reaction of the reactants fed thereto.

Furthermore, aluminothermic reduction is characterised by large slag volumes, unlike the case of carbothermic reduction, since Al_2O_3 enters the slag whereas CO gas leaves the system. This Al_2O_3 requires larger amounts of fluxing additions to lower the liquidus of the slag thus further increasing the slag volume.

It is the object of this invention to provide an improved smelting process for effecting the aluminothermic reduction of reactive metals (as herein defined) in which supplementary energy is added in an improved manner which leads to at least some of the described disadvantages being obviated.

SUMMARY OF THE INVENTION

In accordance with this invention, there is provided a smelting process for effecting the aluminothermic reduction of reactive metals (as herein defined) comprising the contacting of at least one reactive metal oxide (intimately mixed) with sub-divided aluminium in a furnace under an inert atmosphere in which atmospheric oxygen and nitrogen are substantially eliminated, the process being characterised in that, as at least one heat source, there is employed a transferred thermal plasma arranged to effect heating of the upper surface of the reactants in the furnace.

A suitable transferred thermal plasma is generated by the passage of an electrical current through an ionized inert gas between two electrodes, one of which is normally the bath and the other is preferably a water cooled metallic electrode through which the inert gas is injected but which may also be a hollow graphite electrode.

Further features of the invention provide for an additional energy source to be employed in the form of an induction coil controllable separately from thermal plasma generating device; for the thermal plasma to be a direct current thermal plasma; and for the exclusion of atmospheric oxygen and nitrogen to be effected by suitably sealing the furnace.

Whilst pressures above atmospheric could be employed, as could atmospheric pressure itself, it has been found to be convenient to employ sub-atmospheric pressure of not more than 80 kPa in order to enhance the effect of certain types of seals which can conveniently be employed. However, with other seals or sealing arrangements other internal pressures could be employed.

In either event, the entire furnace arrangement could be enclosed in a housing which is subjected to the inert atmosphere or, alternatively, the plasma generating device and feeding device could be sealed to the furnace housing with the controls thereof on the outside. In either event it is essential that the exclusion of atmospheric oxygen and nitrogen be effective.

In the case where sub-atmospheric pressures are employed, the seals are of a type in which the sealing effect is enhanced by a sub-atmospheric pressure. In such a case it is preferred to use a pressure of about 50 kPa but pressures as low as 6 kPa may be employed without any noteworthy adverse effect on the energy transfer from the thermal plasma to the bath.

In each case, the intimately mixed reactants, being at least one subdivided reactive metal oxide and subdivided aluminium, are fed on to the top of the reaction zone in the furnace and the thermal plasma is directed at this surface. In this way, the slag which forms on top of the alloy is properly heated and no crust formation can take place. Where required, the induction furnace coils, where same are present, could be employed to provide a stirring action and to ensure that the metal which is underneath the slag does not freeze.

The power supplied by means of the thermal plasma generating device and the induction coils (where same are present) may be varied throughout the time period dur-

ing which the process is conducted. In particular, the power supplied by any thermal energy generating device can be different at a start up condition from what it is during normal operation of the furnace.

The process of this invention has been shown to be highly effective using a furnace fired primarily by a d.c. transferred thermal plasma with the exclusion of oxygen and nitrogen being assisted by using a pressure of about 50 kPa and seals having the characteristic that their effectiveness increases with decrease in pressure.

A typical flow rate of 2 to 4 NI/min of gas is required to sustain the plasma at 20 to 25 kW at this pressure.

In this application of the invention, the melting of a susceptor metal in the bottom of the bath of the furnace may be carried out as outlined in South African Patent No. 75/3447. In order to employ the invention effectively it has been found to be advantageous for an induction heating coil assembly to be arranged around the furnace bath in order to assist with certain aspects of the process. It will be understood that the plasma generally effects heating of the upper surface of the contents of the bath and, the induction heating coil can be used for ensuring that the metal does not freeze and also, if suitably designed, can create a stirring action. An initial quantity of susceptor metal can be melted by the plasma with or without the aid of the induction coil. The latter could, if required, be used alone.

The heating of the upper surface by means of the plasma has a number of advantages over the prior art induction furnace used alone. These include prevention of crust formation; maintenance of high slag temperature with improved reaction conditions; improved settling and collection of formed alloy; and improved immediate contact of feed materials with the interior of the slag.

The plasma device also has the advantage that it is possible to direct the plasma in a required direction, for example, to clean the pouring spout of the crucible or even melt any crust should it form, which is unlikely.

BRIEF DESCRIPTION OF THE DRAWINGS

In order that the invention may be more fully understood, two somewhat different furnaces which have been tested will now be described with reference to the accompanying drawings in which Fig. 1 is a schematic elevation of the furnace, and Fig. 2 is a similar view of an alternative arrangement of the furnace. Fig. 3 is a graph showing the relationship of voltage and current with pressure.

DETAILED DESCRIPTION WITH REFERENCE TO THE DRAWINGS

In the embodiment of the invention illustrated in Fig. 1, the furnace is of the type in which the entire furnace assembly is positioned within a housing 1 capable of withstanding the desired reduced pressure and fitted with seals of a type which are commonly known and the sealing effect of which increases with decreased internal pressure within the housing. The housing should preferably be made of a non-suscepting or weakly susceptible material such as stainless steel in view of the presence of the induction coils described below. This applies also to other components of the assembly as will be apparent to those skilled in the art. The furnace itself comprises a crucible 2 that is lined with a suitable refractory material, such as Al_2O_3 or CaO for example, and having

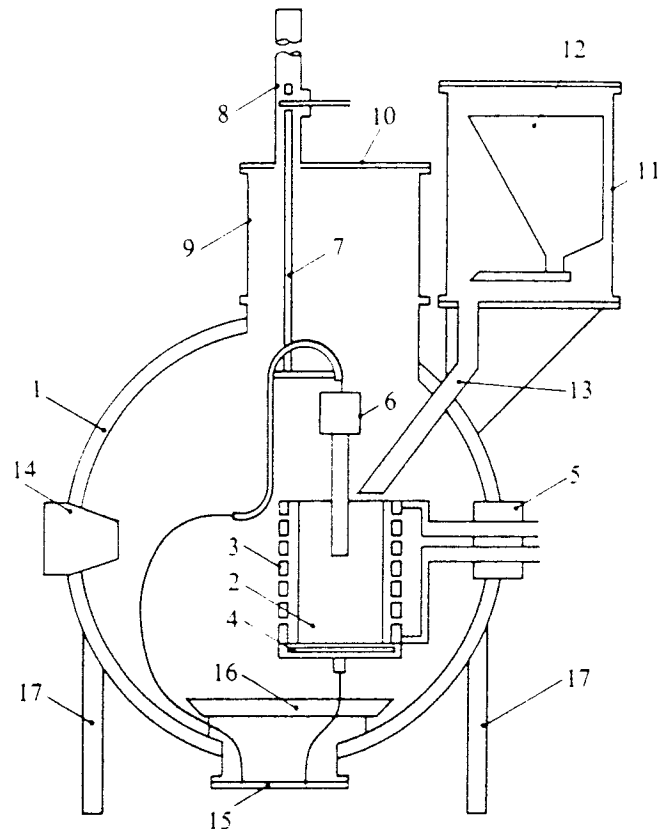


Fig. 1.

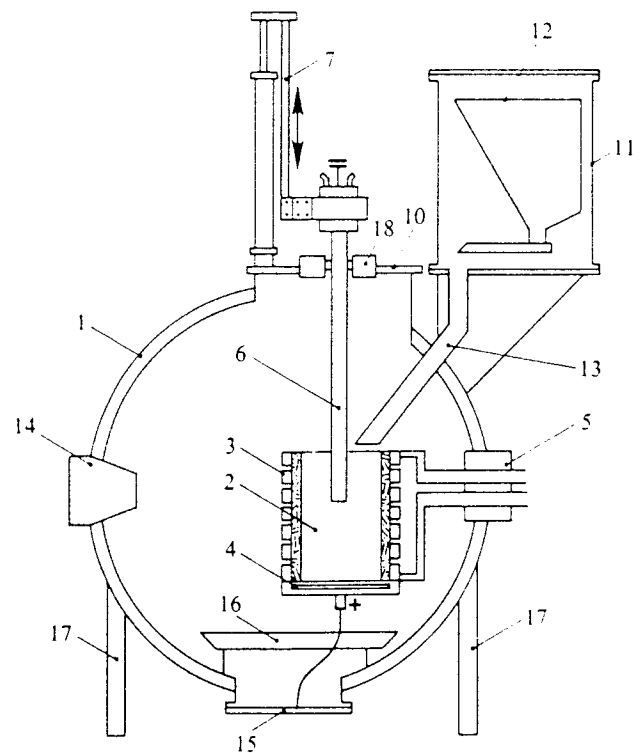


Fig. 2.

induction heating coils 3 on the outside thereof and a water cooled metallic bottom 4. The induction heating coils 3 have separate control means on the outside of the housing and access thereto is by way of suitable seals 5 of the general type described above.

A d.c. transferred arc type of plasma generating device 6 of the non-consumable electrode type is mounted on

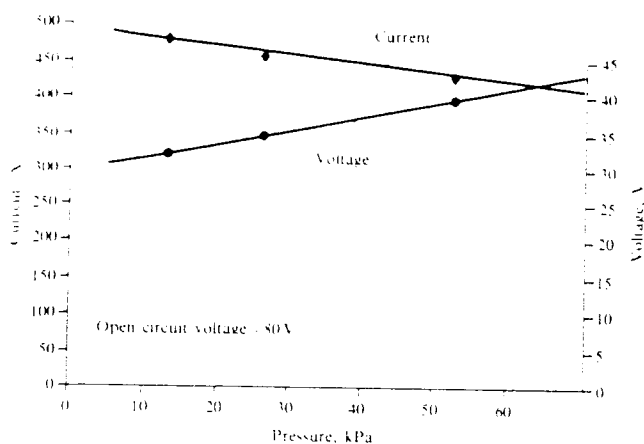


Fig. 3.

means 7 whereby it can be raised and lowered within the furnace by vertical drive means 8 which can be manually or motor driven. The connecting means 7 pass through a cylindrical portion 9 of the housing having a lid 10 and whereof the cylindrical portion 9 and lid 10 are sealed to the main housing 1 through the action of seals of the above described type.

An extension 11 to the housing, which is also adapted to be operated at the reduced pressure, defines a housing for a hopper and vibrator feeder assembly 12 adapted to feed into a water-cooled chute 13 and thence directly into the furnace bath. Again, seals of the above described type are employed for the top of the extension 11 and for intermediate connection of this extension to the main housing 1.

Clearly the plasma generating device has an inert gas supply, generally argon, for its operation and this argon is generally sufficient to maintain an argon atmosphere within the housing. It may, however, be advantageous to provide additional and auxiliary argon inlets for the initial flushing of the interior of the system with argon followed by repetitive applications of suction to a maximum extent in order to free the interior of the housing of oxygen and nitrogen.

In order to achieve the desired reduction in pressure within the housing a vacuum pump connection 14 is provided in one wall of the housing and a vacuum pump is connected thereto, in use.

In this particular embodiment of the invention, the electrical connections to the plasma generating device are effected by way of a closed access aperture 15 in the bottom of the housing and the argon gas may also be supplied through a suitable connection at this position.

A splash tray 16 is mounted within the housing beneath the bath, and the whole housing is mounted on legs 17 so that it can be free standing.

Fig. 2 shows a modified arrangement of the equipment in which the plasma generating device 6 is passed through a suitable seal 18 in the housing 1 of the apparatus instead of being completely housed within the housing 1. The plasma device could either be a water cooled metallic electrode or a hollow graphite electrode and the feed materials could be either fed via the hopper and vibrating feeder 12 and the feed chute 13 or down the hollow electrode, if this option was used.

It will be understood that, in use, the above described apparatus is employed by firstly charging the hopper with the optionally intimately mixed ingredients which are to be pyro-metallurgically treated in the furnace. These could be intimately mixed aluminium powder and oxides

of zirconium or titanium. In such a case a quantity of susceptor metal is introduced into the furnace bath and, prior to operation of the apparatus, the housing is sealed by means of the seals which have been described. The whole interior of the apparatus is then flushed two or three times with argon gas and evacuated each time to a maximum extent, in order to free the environment of atmospheric oxygen in the housing.

Thereafter, the plasma and/or induction heating coils can be operated in order to achieve melting of the susceptor metal which can most conveniently be an alloy of the type being produced in the furnace. If such an alloy is not available pure aluminium could be employed. The plasma generating device operation is then continued in the usual way and feeding of the intimately mixed reactants which are usually intimately mixed, but may be separate is commenced at a predetermined rate calculated to avoid freezing of the contents of the bath in any way. During this stage of the process the power to the induction heating coils can be substantially reduced as the major heat source will be the plasma gun. The process is then continued to completion in order to achieve the aluminothermic reduction of the reactive metal oxide. It will be understood that, whilst the reduction is indeed exothermic, it is insufficiently so to promote a self-sustaining aluminothermic reduction. For this reason a continuous power input, by way of the plasma generating device alone, or in combination with the induction heating coils, is necessary.

It must be borne in mind that the generation of a suitable thermal plasma depends on the ionisation of the gas present, and thus the pressure cannot be too low, as insufficient gas would be present for ionisation. Furthermore there is a decrease in the plasma arc voltage as shown in Figure 3 which causes a somewhat lower input of power for a given electrical current. Similarly, if the pressure is too high, say greater than 80 kPa, the effect of the decreased or sub-atmospheric pressure in the zone above the bath is diminished to an extent whereas the seals are not sufficiently affected to increase the sealing effect thereof adequately.

It will be understood that numerous variations may be made to the above described embodiment of the invention without departing from the scope thereof. In particular the furnace bath itself could be sealed, in which case the plasma generating device and, indeed, the other necessary passages and ducts, are sealed to the housing by seals having the characteristic that their sealing effect increases with decreased internal pressure. It will be understood that the interior of the feed hopper for reactants must, of necessity, be connected by way of extremely special flushing valve assemblies or, alternatively, other sealing arrangements could be employed which operate effectively at atmospheric or above atmospheric pressures.

The plasma generating device is an essential integer of this invention but, the induction heating arrangement is not. Thus, in another variation of the invention the induction heating coils could be entirely omitted.

The invention therefore provides an extremely simple yet highly effective process and apparatus for conducting the smelting of the oxides of reactive metals in an atmosphere which is substantially free of atmospheric oxygen and nitrogen and wherein disadvantages associated with crust formation can be entirely eliminated.

WHAT IS CLAIMED IS:

1. A smelting process for effecting the aluminothermic reduction of reactive metals (as herein defined) comprising the contacting of at least one intimately mixed reactive metal oxide and subdivided aluminium in a furnace under an inert atmosphere in which atmospheric oxygen and nitrogen are substantially eliminated, the process being characterised in that, as at least one energy source, there is employed a transferred thermal plasma arranged to effect heating of the upper surface of the reactants in the furnace.
2. A smelting process as claimed in Claim 1 in which an additional energy source in the form of an induction coil is employed for heating and optionally stirring the contents of the furnace during operation, such induction coil being controlled separately from the thermal plasma.
3. A smelting process as claimed in either of the preceding claims in which the thermal plasma is a direct current transferred thermal plasma.
4. A smelting process as claimed in any one of the preceding claims in which the smelting is carried out at sub-atmospheric pressures of not more than 80 kPa and not less than about 6 kPa.
5. A smelting process as claimed in claim 4 in which the pressure is preferably about 50 kPa.
6. A smelting process as claimed in either of claims 4 or 5 in which seals are employed which have the characteristic of an increasing sealing effect with decreasing pressure.
7. A smelting operation as claimed in any one of the preceding claims in which the feed materials are added at a rate commensurate with the maintenance of an energy balance being maintained in the system and the maintenance of a liquid condition of both the slag and alloy beneath the slag.
8. A smelting operation as claimed in Claim 1 and substantially as herein described or exemplified.
9. Metals and alloys whenever produced by a smelting process as claimed in any one of the preceding claims.

SUPPLEMENTARY DISCLOSURE

The process according to this invention may also be carried out at pressures above atmospheric.

In the embodiment of the invention illustrated in Figure 4, the furnace generally indicated by numeral 19, com-

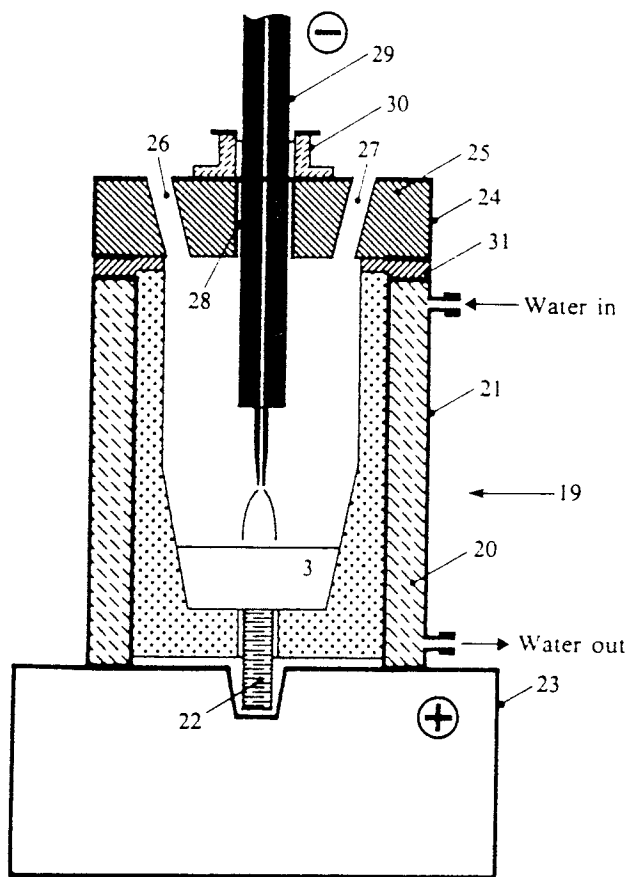


Fig. 4.

TABLE 1. The compositions of the furnace charges (in mass per cent)

| Test No. | Titania slag | Lime (burnt) | Al powder | CaF ₂ |
|----------|--------------|--------------|-----------|------------------|
| 1 | 44,7 | 36,2 | 19,2 | - |
| 2 | 50,8 | 27,5 | 21,7 | - |
| 3 | 56,3 | 19,6 | 24,1 | - |
| 4 | 70,0 | - | 27,0 | 3,0 |
| 5 | 72,2 | - | 27,8 | - |
| 6 | 72,2 | - | 27,8 | - |
| 7 | 74,5 | - | 25,5 | - |
| 8 | 76,9 | - | 23,1 | - |
| 9 | 79,5 | - | 20,5 | - |
| 10 | 70,0 | - | 30,0 | - |

The analysis of the metal and slag produced are given in Tables 2 and 3.

TABLE 2. Metal analysis (in mass per cent)

| Test No. | Ti/Al mass ratio | Si | Mn | Fe | Mg | Al | Ca | Ti | O | N | C | Total % |
|----------|------------------|------|------|------|------|-------|------|------|-----|------|------|---------|
| 1 | 2,16 | 3,03 | 1,6 | 9,42 | <0,1 | 25,6 | 0,52 | 55,4 | 1,3 | 0,95 | 0,57 | 98,39 |
| 2 | 2,51 | 2,85 | 1,98 | 13,7 | <0,1 | 21,7 | 0,55 | 54,4 | 1,8 | 0,30 | 0,19 | 98,97 |
| 3 | 2,69 | 1,63 | 1,54 | 10,0 | <0,1 | 21,3 | 0,84 | 57,2 | 2,7 | 0,26 | 0,06 | 95,93 |
| 4 | 4,65 | 1,18 | 1,56 | 9,65 | <0,1 | 12,9 | 0,25 | 60,0 | 5,2 | 0,84 | 0,15 | 91,73 |
| 5 | 4,12 | 0,95 | 1,54 | 10,6 | <0,1 | 14,0 | <0,2 | 57,6 | 2,9 | 0,52 | 0,06 | 88,20 |
| 6 | 4,23 | 0,89 | 1,36 | 10,1 | <0,1 | 13,9 | <0,2 | 58,9 | 3,9 | 0,84 | 0,09 | 89,98 |
| 7 | 5,65 | 1,11 | 1,81 | 11,9 | <0,2 | 10,41 | <0,2 | 58,8 | 3,6 | 0,29 | 0,08 | 88,00 |
| 8 | 5,85 | 1,91 | 1,86 | 11,9 | <0,2 | 9,78 | <0,2 | 57,2 | 2,8 | 0,42 | 0,13 | 86,00 |
| 9 | 5,65 | 1,99 | 1,32 | 15,0 | <0,2 | 9,76 | <0,2 | 55,2 | 2,9 | 0,98 | 0,25 | 87,4 |
| 10 | 3,06 | 1,89 | 1,62 | 11,5 | <0,2 | 17,9 | <0,2 | 54,8 | 2,5 | 0,42 | 0,09 | 90,72 |

TABLE 3. Slag analyses (in mass per cent)

| Test No. | SiO ₂ | MnO | FeO | MgO | Al ₂ O ₃ | CaO | TiO ₂ | CaF | Total % |
|----------|------------------|-------|-------|------|--------------------------------|------|------------------|------|---------|
| 1 | 0,88 | <0,05 | 0,12 | 6,99 | 37,2 | 36,7 | 22,6 | | 104,5 |
| 2 | 0,48 | <0,05 | <0,05 | 3,50 | 45,0 | 35,2 | 22,8 | | 105,6 |
| 3 | 0,23 | <0,05 | <0,05 | 3,11 | 54,5 | 27,3 | 24,2 | | 109,3 |
| 4 | 0,20 | <0,05 | 0,46 | 3,28 | 74,7 | - | 26,7 | 8,44 | 113,8 |
| 5 | <0,05 | <0,01 | 0,56 | 1,85 | 78,4 | <0,1 | 31,2 | | 112,0 |
| 6 | 0,20 | <0,01 | 0,62 | 1,41 | 79,0 | <0,1 | 32,6 | | 113,8 |
| 7 | <0,06 | <0,01 | 0,33 | 1,81 | 70,0 | <0,1 | 37,2 | | 109,3 |
| 8 | 0,21 | 0,28 | 0,63 | 1,99 | 64,8 | <0,1 | 41,53 | | 109,4 |
| 9 | 0,2 | 0,46 | 0,12 | 8,30 | 44,8 | <0,1 | 59,9 | | 113,6 |
| 10 | 0,1 | <0,05 | 0,38 | 2,25 | 73,5 | <0,1 | 30,8 | | 106,9 |

prises a magnesia refractory crucible 20 having a water cooled jacket 21, and a central steel anode 22 which projects through the floor of the crucible 20 and which is in electrical contact with an underlying graphite block 23.

In use, the crucible 19 is covered by a roof 24 which is made of mild steel and has a Söderberg electrode paste lining 25. The roof 24 has three openings 26, 27, 28 which are used for introducing raw materials to the furnace 19, for discharging gases, and for accommodating a central hollow graphite cathode 29 respectively. An electrode seal 30 is provided on the roof 24 and surrounds the cathode 29. Further, a refractory gasket 31 seals any gaps between the roof 24 and the walls of the crucible 20.

The following metallurgical tests were conducted in a furnace of the above-mentioned type. The reactive metal oxide being treated is titanium dioxide and is a component of a slag obtained from an industrial process in which ilmenite is smelted with carbonaceous reducing agents. The particular slag used in these tests was obtained from Richards Bay Minerals. The chemical analysis in mass per cent of the slag along with the analysis in mass per cent of the other raw materials used in this test are given as follows. It should be remembered that any convenient source of titanium dioxide (such as natural rutile) could in fact be used for this production stage.

The titania slag contained 87,2% TiO₂, 9,8% FeO, and 2,0% SiO₂. The aluminium powder contained 98,3% Al, 0,34% Fe, 0,16% Si, and 0,08% O, while the calcined (or burnt) lime and calcium fluoride were of reagent grade quality.

The attendant problems of forming nitrides or oxides of titanium was controlled by limiting the ingress of atmospheric gases into the furnace. This is achieved by providing the seals 30 and 31, and by narrowing the openings 26 and 27 in the roof 24, as required, by suitable means. This ensures that the internal gas pressure of the furnace from gases comprising reaction gases and any other inert gases used for flushing the feed materials or in the generation of the plasma arc exceeds atmospheric pressure.

It is to be mentioned that the use of a transferred arc thermal plasma, in addition to supplementing the en-

thalpy requirements of the reduction, has the advantage of providing a high temperature zone which will easily exceed the liquidus temperature of almost any slag. Consequently, it is possible to minimize fluxing additions to the feed and to reduce the volume of slag which is produced. This has the advantage of improving heat transfer to the underlying metal containing region of the furnace bath.

Although the use of a water cooled jacket surrounding the crucible has made it possible to use crucibles made of magnesia, applicants believe it would be preferable to use an alumina refractory which, if chemically reduced, will not contribute undesirable contaminants to the metal produced.

Further, it is to be mentioned that the presence of iron in the alloy phase during processing has the advantage of increasing the density thereof, thereby ensuring that the slag density is lower than the alloy density. It is particularly important in the case of reactive metals that the slag protect the metal from direct contact with any nitrogen or oxygen which may under some circumstances be present above the melt.

ADDITIONAL CLAIMS

10. A smelting process according to any one of Claims 1 to 7 wherein iron is present in the feed either in metallic form or as an oxide.
11. A smelting process according to Claim 10 wherein the source of reactive metal oxide contains a limited amount of iron oxide.
12. A smelting process according to Claim 11 in which the amount of iron oxide is less than 10 per cent by mass.
13. A smelting process according to any one of Claims 1 to 3, 7, 10, 11 or 12, wherein the smelting is carried out at pressures exceeding atmospheric pressure.
14. A smelting process according to Claim 10 substantially as herein described or exemplified.
15. A metal or alloy whenever produced by a smelting process according to any one of Claims 10 to 14.