

PATENT SPECIFICATION

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(72) Inventors JAMES WHITE and COLIN RICHMOND



(54) IMPROVEMENTS IN OR RELATING TO THE REMOVAL OF SILICA FROM MATERIALS CONTAINING SILICA

(71) We, GR-STEIN REFRACTORIES LIMITED, a British Company of Genefax House, Tapton Park Rd., Sheffield, S10 3FJ, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the production of zirconia from zircon, which process is capable of removing the silica content of zircon completely or to an appreciable degree.

According to the present invention a process for the production of zirconia from zircon comprises producing the zircon in particulate or pelletised form and heating the zircon under reducing conditions in an atmosphere containing sulphur, the reaction removing silica from zircon by producing a volatile sulphide of silicon.

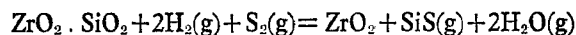
To produce the reducing conditions required the zircon may be mixed with carbon with the result that along with the volatile sulphide, carbon monoxide is formed. In certain instances the quantities of materials used when employing carbon may be controlled to ensure that the process is chemically balanced and that the whole of the carbon is contained in the carbon monoxide produced by the reaction so that there is no residual carbon remaining after the reaction is completed. If, however, an excess of carbon is used so that the reaction does leave residual carbon, then this can be removed by combustion. Alternatively, the reducing con-

ditions can be brought about by utilising a hydrogen atmosphere, when, in addition to the volatile sulphide of silicon, steam is produced.

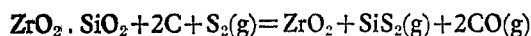
The sulphur essential to the process may be introduced as a powder or vapour entrained in a carrier gas and, advantageously, when hydrogen is required as the atmosphere the sulphur powder or vapour can be introduced in a stream of hydrogen or a mixture of hydrogen with an inert gas such as nitrogen. When carbon is used to create the reducing conditions, hydrogen may still be used as the carrier gas for the sulphur powder or vapour, or alternatively an inert gas such as nitrogen or argon may be used for the purpose. As a still further possibility, a sulphur bearing gas such as hydrogen sulphide can serve the double purpose of creating the reducing conditions and providing the sulphur required for the reaction. Another ready means of providing hydrogen to create the reducing conditions and provide carbon for the same purpose is to introduce the sulphide in a stream of hydrocarbon gas such as methane.

The invention will now be discussed by way of example in relation to the production of zirconia from zircon utilising hydrogen and carbon to create the reducing conditions, and using sulphur gas and then utilising a solid sulphide.

Thus, when hydrogen is used to create the reducing conditions the following reaction takes place:—



Alternatively, when carbon is used to create the reducing conditions, the following reaction takes place:—



In both cases the suffix (g) denotes that the compound is in gaseous form. In both examples, the sulphur has been introduced

either as a powder or vapour in a stream of carrier gas; in the first example the hydrogen required for the atmosphere serving

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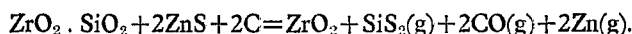
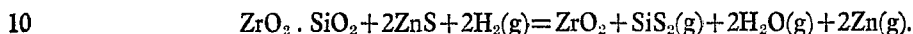
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to introduce the sulphur and in the second example an inert gas which takes no part in the reaction has been used for that purpose.

5 As an example of the use of a solid sulphide in the production of zirconia from



15 Preferably, the reaction is effected at a temperature in excess of 1,000°C. because below that level the rate of reaction becomes extremely slow and there is a progressive tendency for the reverse process to take place.

20 It has been found that there is an apparent optimum temperature range of 1,200°C. to 1,400°C. within which the process proceeds with greatest efficiency and speed.

25 In the case of the second alternative referred to above, i.e., when using a solid sulphide, it may be advantageous to operate the process such that the solid sulphide is reformed in the cooler part of the reaction chamber so that it can be re-used.

30 It is the case that zircon, from which the silica is to be removed to produce zirconia may also include a minor proportion of impurities or other undesirable matter which the process of the present invention is not capable of removing. However, the silica-free material may well be usable as such. In
35 any uses of the material formed by the invention where that material must be in a relatively pure form, then any suitable process to remove the undesirable matter can be employed.

40 In all cases it is very important that the atmosphere above the reaction is continuously removed to remove the gaseous products of the reaction and thereby prevent reversal of the process as the solid products of the reaction
45 are allowed to cool.

WHAT WE CLAIM IS:—

1. A process for the production of zirconia from zircon comprising producing the zircon in particulate or pelletised form and heating
50 the zircon under reducing conditions in an atmosphere containing sulphur, the reaction removing silica from zircon by producing a volatile sulphide of silicon.

2. A process as in Claim 1, wherein the
55 reducing conditions are produced by mixing the zircon with carbon when along with the volatile sulphide carbon monoxide is formed.

3. A process as in Claim 1 or Claim 2,
60 wherein the quantity of materials used when employing carbon is controlled to ensure that the process is chemically balanced and that the whole of the carbon is contained in the carbon monoxide produced by the reaction,

zircon, the following two reactions take place, firstly when the hydrogen is used to create the reducing conditions and, secondly, when carbon has been used for that purpose:—

whereby there is no residual carbon remaining after the reaction is completed.

65 4. A process as in Claim 1, wherein the reducing conditions are brought about by utilising a hydrogen atmosphere when, in addition to the volatile sulphide of silicon, steam is produced.

70 5. A process as in any of Claims 1 to 4, wherein the sulphur is introduced as a powder or vapour entrained in a carrier gas.

6. A process as in Claim 5, wherein the
75 carrier gas is hydrogen, which hydrogen also produces the required reducing conditions.

7. A process as in Claim 6, wherein the hydrogen may be mixed with an inert gas.

8. A process as in Claim 2 or Claim 3,
80 wherein the carbon required to produce the reducing conditions is introduced by way of a carrier gas.

9. A process as in Claim 8, wherein the
85 carrier gas is hydrogen.

10. A process as in Claim 8, wherein the
90 carrier gas is an inert gas.

11. A process as in Claim 1, wherein the atmosphere containing sulphur is produced by the introduction of a sulphur-bearing gas.

12. A process as in Claim 11, wherein the
95 sulphur-bearing gas is hydrogen sulphide, thereby serving the double purpose of creating the reducing conditions and providing the sulphur required for the reaction.

13. A process as in any of Claims 2 to
100 4, wherein a stream of hydro-carbon gas is utilised to provide the reducing conditions.

14. A process as in any of Claims 2 to 5,
105 wherein sulphur or a sulphide is introduced in a stream of hydrocarbon gas.

15. A process as in any one of Claims 1 to 14, wherein the reaction is effected at a temperature in excess of 1,000°C.

16. A process as in Claim 15, wherein the
110 temperature at which the reaction is effected is in the range 1,200°C. to 1,400°C.

17. A process as in any of Claims 1 to
115 16, wherein the atmosphere above the reaction is continuously removed to remove the gaseous products of the reaction, thereby preventing reversal of the process in the reaction zone as the solid products of the reaction are allowed to cool.

18. A process as in Claim 17, wherein the
115 products of the reaction are allowed to cool to provide a reversal of the process during

cooling at a point remote from the reaction zone, thereby enabling recovery of the solid products of the reaction.

- 5 19. Zirconia, when produced by the process of Claim 1, and substantially as hereinbefore exemplified.

HULSE & CO.,
Chartered Patent Agents,
Cavendish Buildings,
West Street,
Sheffield.
S1 1ZZ.

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