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Production of stabilized and non-stabilized ZrO_2 by carbothermic reduction of $ZrSiO_4$

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The kinetics of reduction of zircon by carbon have been investigated in the temperature range 1400–1650 °C. Volatilization of SiO permits production of zirconia of about 96% purity direct from zircon with 100% removal of the silicon content being achieved in less than 2 h at 1650 °C. Addition of MgO, Y_2O_3 or CaO stabilizers to zircon prior to the reduction permits direct production of partially stabilized zirconia from zircon by means of carbothermic reduction. The presence of such stabilizers has been found to produce a slight increase in the reduction of kinetics of zircon.

1. Introduction

The two major zirconium-containing minerals are baddeleyite (ZrO_2) and zircon ($ZrSiO_4$). Although baddeleyite is mined commercially in South Africa, the major source of zirconia (ZrO_2) is the mineral zircon.

The production and application of zirconia have continued to attract the interest of scientists and technologists and solid evidence of commercial application for this engineering ceramic is now available [1]. The main conventional ways for producing zirconia (ZrO_2) powder are wet chemical and dry methods. The wet chemical methods (extraction with caustic alkalis, fluorides and lime) can produce high-grade zirconia because the impurities can be separated by controlled precipitation from the solutions.

The dry methods or dissociation processes (electric-arc and plasma-arc furnace), use high temperature (around 2400 °C), where zircon can be completely dissociated to ZrO_2 and SiO_2. The silica (SiO_2) is then extracted by leaching with caustic soda. A rapid cooling rate is required for chemical extraction of silica to be effective. The use of plasma-arc furnace represents a significant improvement over the use of conventional electric-arc furnace because it permits a high-temperature operation with rapid quenching of the fused charge. However, the requirement for caustic soda (NaOH) leaching and disposal of filtrate may remain a major factor in limiting the use of dissociation processes [2]. There is also the cost of the reagent sodium hydroxide (NaOH) to be considered. According to the British patent [3], 183 lb (83 kg) dissociated zircon require 160 lb (73 kg) 50% sodium hydroxide solution to yield 122 lb (55 kg) zirconia and 212 lb (96 kg) sodium silicate penta-hydrate ($Na_2SiO_35H_2O$).

The present study investigates the extraction of silica from zircon by reduction and volatilization of silica (SiO_2) as silicon monoxide (SiO) at relatively low temperature (1600 °C). This has the potential advantage over other extraction techniques of producing technical grade zirconia without the need for wet chemical processing.

The purpose of this study was, therefore, to investigate kinetics and mechanism of the production of technical grade zirconia (96% ZrO_2) by the carbothermic reduction of $ZrSiO_4$ at relatively low temperatures (1400–600 °C).

Zirconia, when thermally cycled from room temperature to 2400 °C, undergoes a series of destructive phase changes provoking contractions and expansions because of the resultant changes of the density from monoclinic (density = 5.6 g cm^{-3}); tetragonal (density = 6.10 g cm^{-3}); to cubic (density = 5.8 g cm^{-3}). This characteristic has, until recently, prevented its use in engineering (mechanical applications) where unpredictable failure is unacceptable. The use of the additions of stabilizers (MgO, CaO, Y_2O_3, SeO, etc.) to zirconia introduces the toughness suitable for mechanical applications through the transformation toughening and microcracks mechanism, described elsewhere [4]. A further aim of the present study, therefore, was the investigation of the production of partially stabilized zirconia (PSZ) directly from zircon using MgO, CaO and Y_2O_3 as stabilizer additions. The overall aim of the work was the development of improved, lower temperature processing routes for the production of technical grade zirconia and partially stabilized zirconia directly from raw materials with a minimum number of process steps.

2. Experimental procedure

A schematic illustration of the experimental procedure utilized is shown in Fig. 1.

The carbothermic reductions were carried out with samples in the form of cylindrical briquettes approximately 10 mm in height made by pressing in a closed die of 10 mm diameter under constant load.

The main compounds of the zircon used in the experiments were ZrO_2 (65.0%) and SiO_2 (32.0% by weight). This was supplied by Magnesium Elektron Limited. The reducing agent used was Collie coal, which is an Australian coal of medium-high reactivity previously used in a number of reduction studies [5, 6], and its analysis is shown in Table I.

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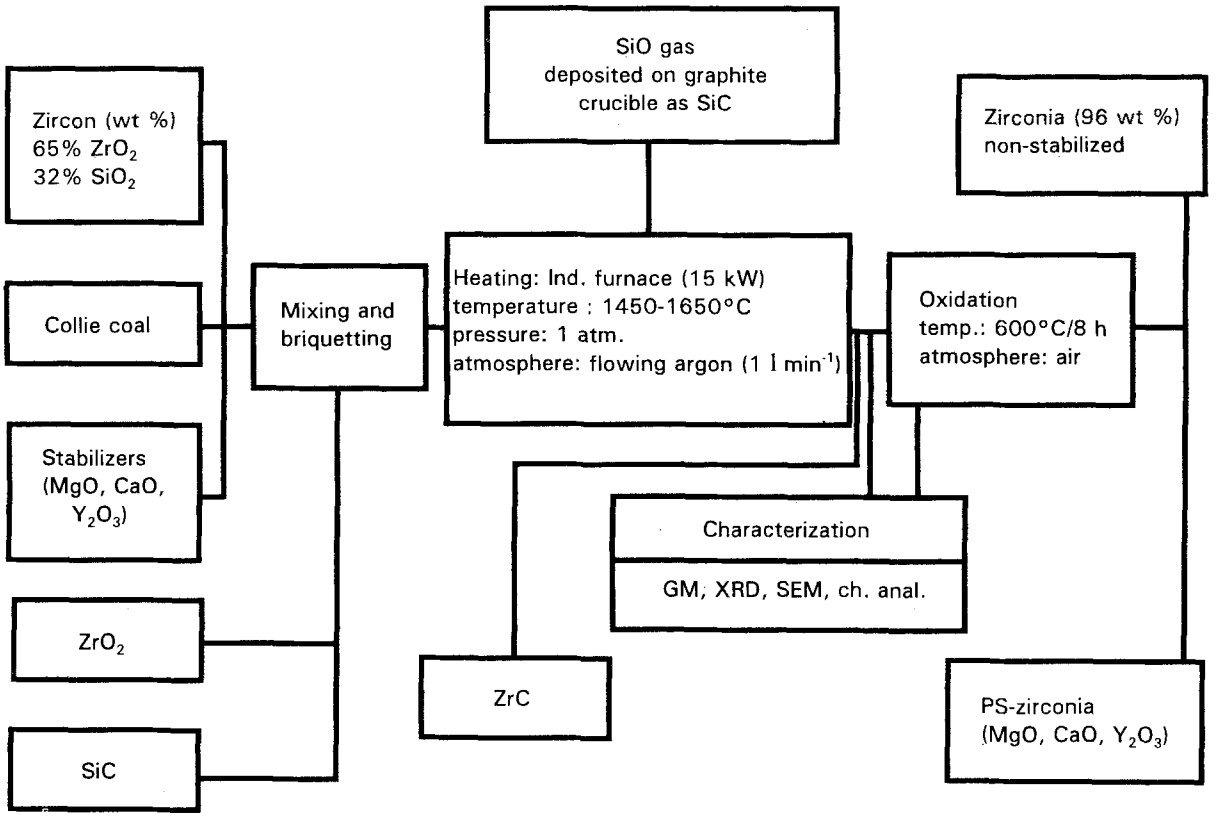

Figure 1 Experimental procedure utilized. GM, gravimetric method; XRD, X-ray diffraction; SEM, scanning electron microscopy; ch. anal., chemical analysis; PS-zirconia, partially stabilized zirconia.

TABLE I Chemical analysis of Collie coal

	(wt %)
Total carbon	59.50
Fixed carbon	48.40
Hydrogen	3.60
Sulphur	0.34
Ash	2.65
Loss at 105 °C	23.30

The zircon and the Collie coal were sieved into various size fractions using 300, 180, 125, 90, 63, 45 μm BS410 sieves and the fraction utilized in the experiments was in between 125 and 90 μm. The stabilizers used (MgO, CaO, Y_2O_3) were of Analar grade obtained from BDH. The experiments were carried out with mixtures of zircon and Collie coal with a molar ratio of C/SiO_2 between 1 and 2, with additions of stabilizers when required. Some experiments were carried out with a mixture of ZrO_2 and SiC, in order to investigate the SiO generation when SiC works as a reducing agent. The ZrO_2 was supplied by Magnesium Elektron Limited and the SiC was supplied by Ceramic Fibers Research Group. Samples were thoroughly mixed by keeping them on rolls overnight before briquetting in order to obtain a homogeneous mixture.

The experiments were carried out in a high-purity argon atmosphere and gravimetric measurements (GM) were made after different times of reaction. The SiO_2 contained in zircon was removed as silicon monoxide (SiO) gas which was deposited as SiC on the walls of the graphite crucible utilized as a susceptor in the induction furnace used. The products obtained after the carbothermic reduction were analysed by X-ray diffraction (XRD) using a diffractometer with CuK_α radiation. In some experiments, the products were X-rayed before and after the oxidation at 600 °C for 8 h. Samples where the percentage of weight loss of 42.0% was reached when all SiO_2 and carbon ($C/SiO_2 = 1:1$) are consumed to produce SiO, were chemically analysed by Cupferron Method [7]. Some samples were examined by scanning electron microscopy (SEM).

3. Results and discussion

3.1. SiO generation

The volatilization of silica as silicon monoxide has attracted the attention of scientists interested in understanding the high-temperature processing and high-temperature service of oxides, carbides and nitrides ceramics.

The volatility diagram for the system Si–O for different temperatures is shown in Fig. 2 as presented

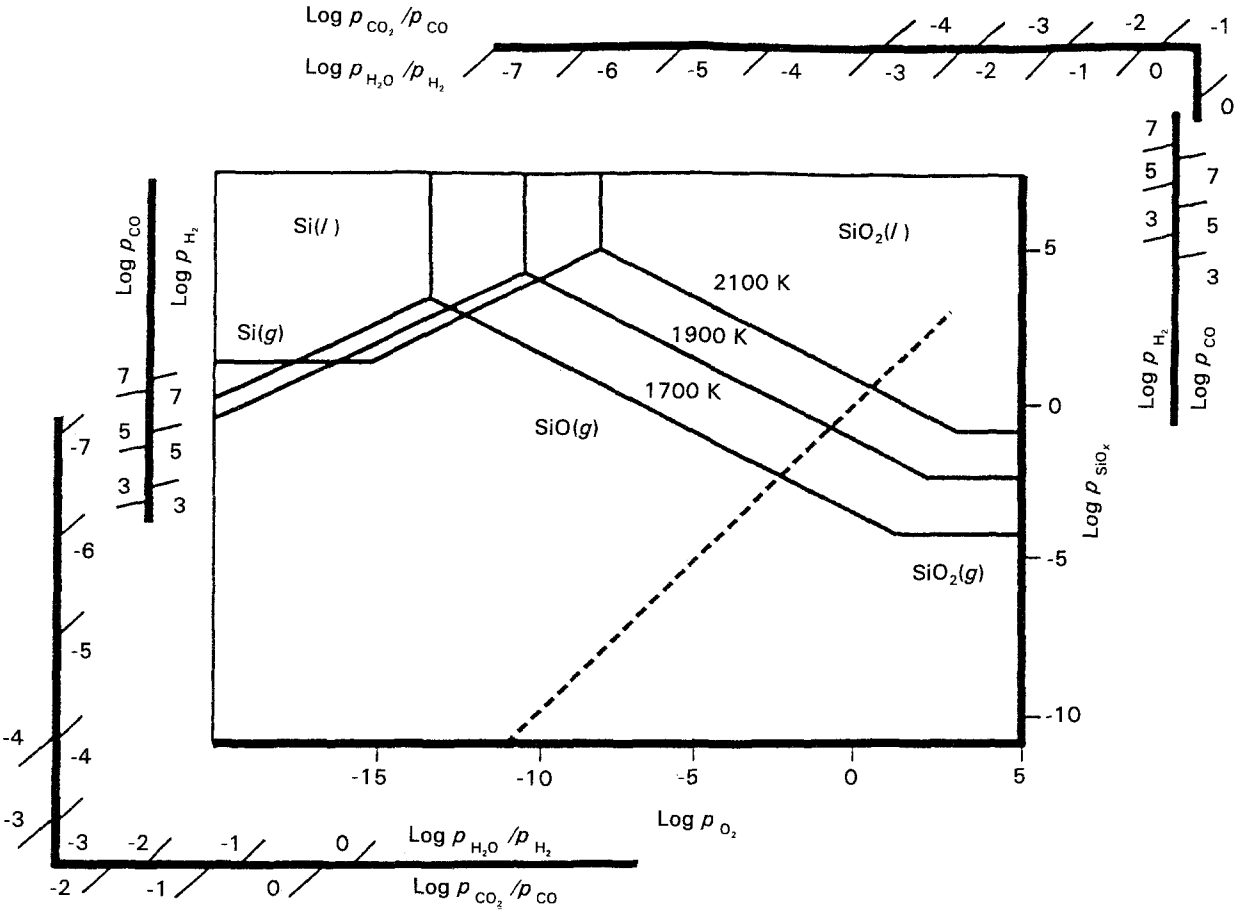

Figure 2 Volatility diagram for the Si–O system for 1700 (1527), 1900 (1727) and 2000 °C (1927 °C) (all pressures in the figure in Pa).

and discussed by Lou *et al.* [8]. The most volatile species is SiO(g), whereas Si(g) and SiO_2(g) are relatively unimportant, except at particularly low and high partial pressure of oxygen, (P_{O_2}), respectively, where they become the major vapour species.

Biernacki and Wotzak [9] have studied the stoichiometry of the C + SiO_2 reaction mainly focusing on the production SiO gas. They concluded that the reaction of SiO_2 and carbon when in the molar ratio one-to-one, proceeds via a two-stage reaction path in which SiC and some SiO are liberated during the first stage, while free carbon is present as a solid followed by liberation of SiO via the reaction of SiO_2 and SiC which dominates once the free carbon is consumed. The reaction path mechanism described was said to be evaluated in view of well-established thermodynamic data on the Si–O–C–Ar system and can be represented by the following global reaction stoichiometries

$$SiO_2 + C = SiO + CO \quad (1)$$

$$+$$

$$2C$$

$$SiO_2 + SiC = 3SiO + CO \quad (3)$$

$$+$$

$$CO$$

$$(2)$$

According to the free energy versus temperature

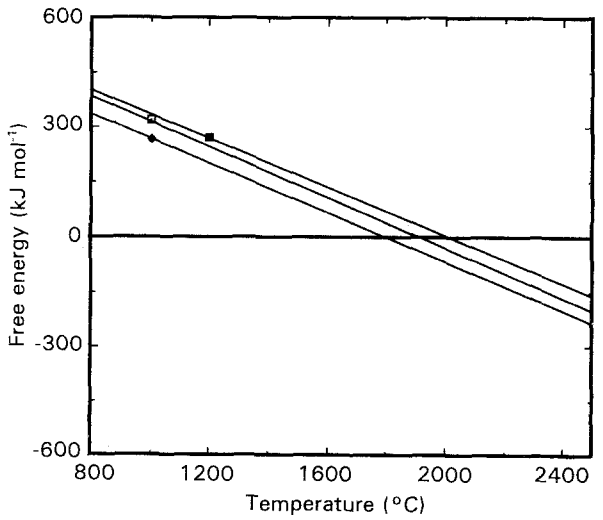

Figure 3 Diagram of free energy versus temperature. (⊡) $ZrO_2 + 3C = ZrC + 2CO$; (◆) $SiO_2 + 3C = SiC + 2CO$; (■) $SiO_2 + C = SiO + CO$.

diagram (Fig. 3) the reaction of formation of SiO from SiO_2 is the most difficult to occur when compared to the formation of SiC which is favoured by having a negative free energy at temperatures of about 1800 °C. However, thermodynamic calculations are insufficient to predict the reaction path and velocity without kinetic studies.

Some experiments were carried out with a molar ratio of $C/SiO_2 = 2:1$, where it was expected to form

a mixture of ZrO_2 and SiC by the overall reaction

$$ZrSiO_4(s) + 3C(s) = ZrO_2(s) + SiC(s) + 2CO(g) \quad (4)$$

However, the results of those experiments showed the formation of ZrC and SiO instead of ZrO_2 and SiC (Reaction 4). This observation could confirm the reaction path mechanism proposed in [9]. SiC could have formed while free carbon was present as a solid followed by liberation of SiO via the reaction of ZrO_2 and SiC, forming ZrC. Fig. 4 shows X-ray diffraction patterns for the phases present in the product obtained after 1.5 h reaction at 1650 °C. Only the presence of ZrO_2 and ZrC could be identified.

In order to confirm the observation that SiC could be reacting as a reducing agent, some experiments were carried out using mixtures of ZrO_2 and SiC. The amount of ZrO_2 and SiC in the mixture was according to stoichiometry to Reaction 5

$$2ZrO_2(s) + 3SiC(s) = 2ZrC(s) + 3SiO(g) + CO(g) \quad (5)$$

Fig. 5 shows curves representing the percentage of weight loss as a function of time with respect to SiO generation for two different temperatures. The percentage of weight loss expected by Reaction 5 is 44.0%. The reduction of ZrO_2 to ZrC and generation of SiO by SiC was found to be strongly temperature dependent. At 1550 °C almost all ZrO_2 was reduced to ZrC, while at 1450 °C about 10% of weight loss was reached after 3 h reaction. Miller *et al.* [10] and Pultz and Hertl [11] have studied the reduction of silica with carbon and SiC and they found linear rates of reaction varying with time. This behaviour was also observed for the reduction of ZrO_2 with SiC.

Fig. 6 shows the X-ray diffraction patterns for the products obtained at 1550 °C at different times of reaction. With increasing time, the peaks of ZrC become intense (Fig. 6a), and after 180 min reaction, all ZrO_2 is reduced by SiC to ZrC.

This information is important for the understanding of any processing which makes use of SiO generation as a method of concentration or purification of silicate materials and also for the understanding of failure of siliceous ceramic working at high temperatures.

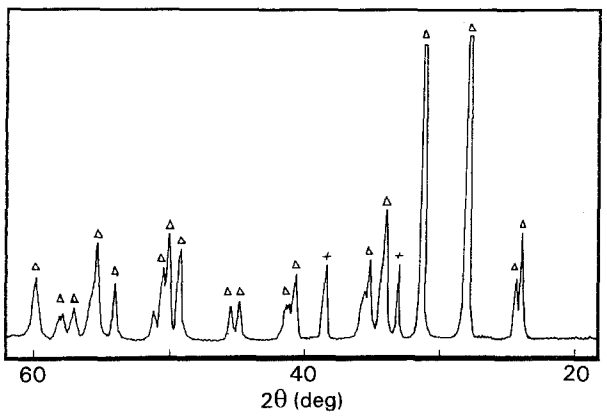

Figure 4 X-ray diffraction patterns of the products obtained after 90 min at 1650 °C (C/SiO_2 = 2:1). (△) ZrO_2 monoclinic, (+) ZrC.

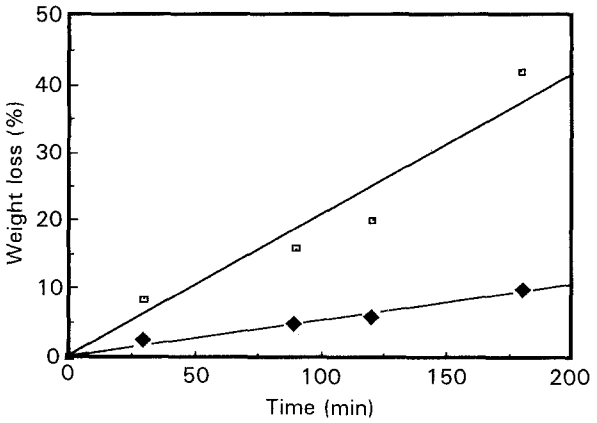

Figure 5 Percentage of weight loss versus temperature for the sample (C/SiO_2 = 2:1). (■) 1550 °C, (◆) 1450 °C.

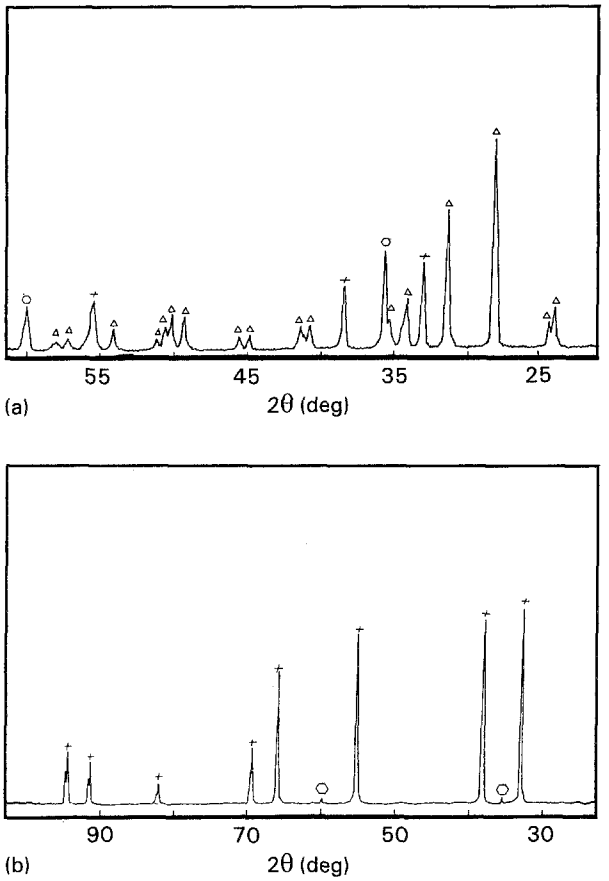

Figure 6 X-ray diffraction patterns at different times for the reaction of ZrO_2 with SiC at 1550 °C. (a) 90 min, (b) 180 min. (△) ZrO_2 monoclinic, (+) ZrC, (○) SiC.

3.2. Production of technical grade ZrO_2

Mixtures of zircon and Collie coal were prepared containing one-to-one molar mixtures of C and SiO_2, according to Reaction 6, which represents the global generation of SiO from zircon

$$ZrSiO_4(s) + C(s) = ZrO_2(s) + SiO(g) + CO(g) \quad (6)$$

Curves representing the percentage of weight loss as a function of time with respect to SiO generation from zircon with a C/SiO_2 ratio of 1:1 according to Reaction 6 are shown in Fig. 7 for different temperatures. When all SiO_2 and carbon are consumed to produce SiO the percentage of weight loss expected is 42.0%. Fig. 7 shows that the volatilization of silica as SiO is strongly temperature dependent. There was a significant increase in the SiO formation with increasing temperature. At 1650 °C all silica (100%) was volatilized as SiO in less than 2 h reaction, while about 50% of the silica (23% weight loss) was volatilized after 2 h reaction at 1450 °C.

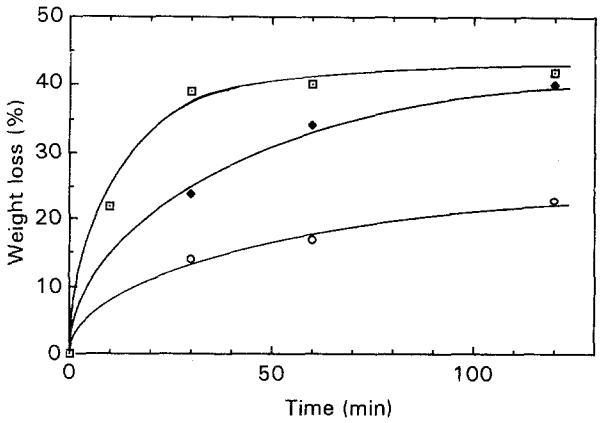

Figure 7 Percentage of weight loss versus time for the sample (C/SiO_2 = 1:1). (○) 1450 °C, (◆) 1550 °C, (⊡) 1650 °C.

X-ray diffraction analysis results are shown in Fig. 8 as a function of time and temperature. It can be confirmed that temperature plays an important role in the volatilization of silica. Fig. 8a shows X-ray diffraction pattern for the phase identified in the product obtained after 2 h reaction at 1450 °C. This shows peaks of $ZrSiO_4$ and monoclinic ZrO_2. The peaks of $ZrSiO_4$ are shown to be very intense, while at 1550 °C after 30 min (Fig. 8b) they show less intensity, and they almost disappear after 2 h reaction (Fig. 8c). In Fig. 8d, the X-ray diffraction pattern did not show any peak of $ZrSiO_4$, which could be identified in the product of the reaction obtained after 30 min at 1650 °C. The only phase present is monoclinic ZrO_2.

An Arrhenius plot of the initial slopes of the curves shown in Fig. 7 is given in Fig. 9. From the slopes of the Arrhenius plot, an activation energy of (176 kJ mol^{-1}) was calculated. The value of activation energy presented in the literature for the reaction of silica with carbon is higher than the value given by the Arrhenius plot in Fig. 9. Miller *et al.* [10] have for example presented an activation energy of (544 kJ mol^{-1}). This wide difference in values of activation energy might be attributed to the presence of zirconia or even because of other impurities present in zircon or in Collie coal, which could behave as a catalyst. Pultz and Hertl [11] and Miller *et al.* [10]

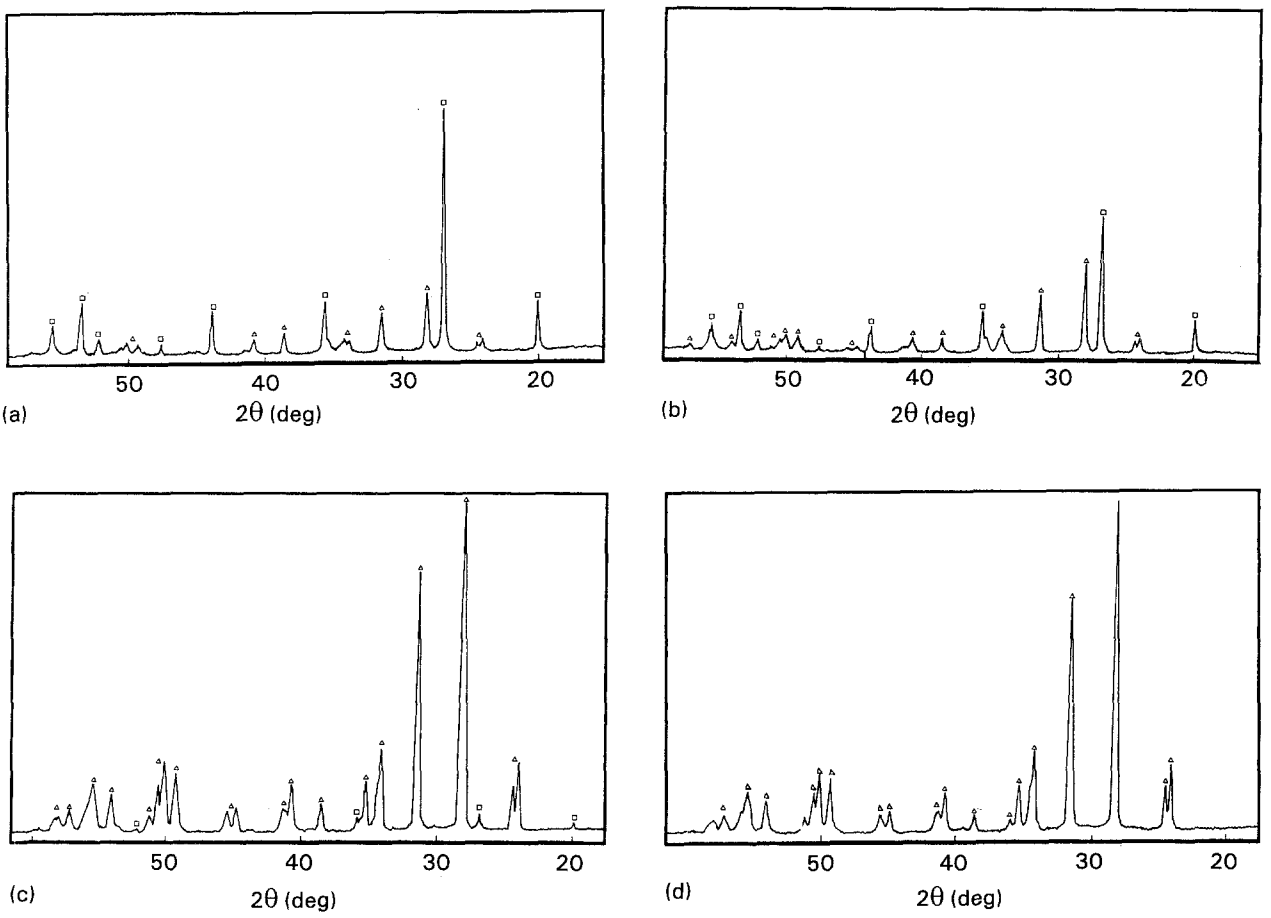

Figure 8 X-ray diffraction patterns for products obtained at different times and temperatures with C/SiO_2 = 1:1. (a) 1450 °C, 180 min; (b) 1550 °C, 30 min; (c) 1550 °C, 120 min; (d) 1650 °C, 30 min. (□) $ZrSiO_4$, (△) ZrO_2 monoclinic.

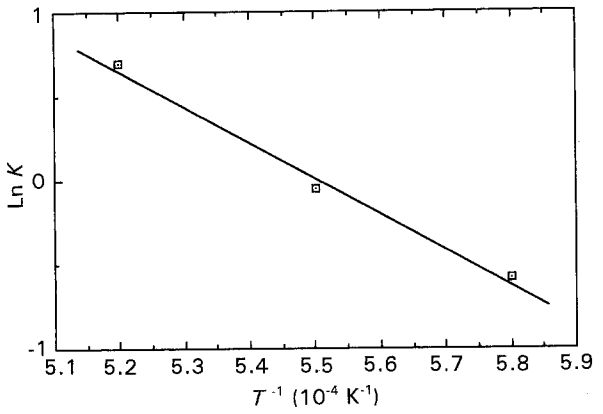

Figure 9 Arrhenius plot for SiO formation from zircon. $E_A = 176\ \mathrm{kJ\,mol^{-1}}$.

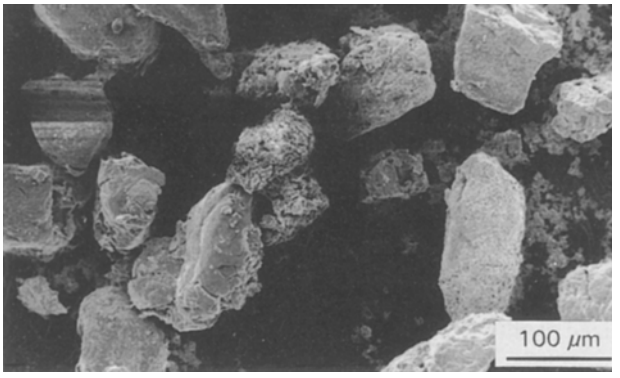

Figure 11 Scanning electron micrograph of the zirconia obtained after the carbothermic reduction.

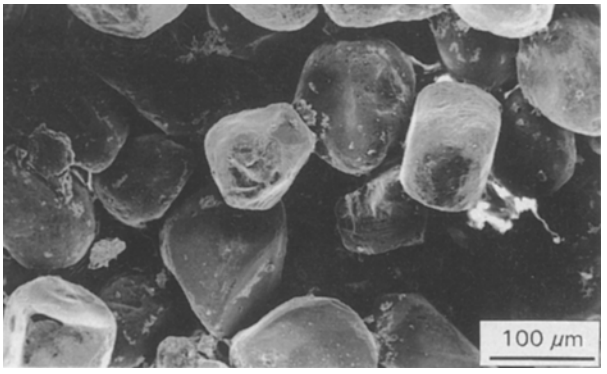

Figure 10 Scanning electron micrograph of zircon before the reaction.

pointed out the catalytic effect of iron of the volatilization of SiO_2 as SiO, and an activation energy of ($360\ \mathrm{kJ\,mol^{-1}}$) was calculated when 4% iron was utilized.

Chemical analysis of the products indicated that they contained about 95.0% ZrO_2 in samples where 42% weight loss was achieved. Therefore, there appears to be real promise in the proposed route for ZrO_2 production. The production of a technical grade ZrO_2 by any process which does not involve a wet chemical process would have significant economic and process advantages. The ZrO_2 produced here can be applied to the increasing requirement for technical grade ZrO_2 in the refractories and abrasives industries [2].

The technical grade ZrO_2 produced here can also be employed as a raw material for high-purity ZrO_2 powder production through a further wet chemical process. The amount of impurity disposal would be much smaller than that currently yielded by any of the conventional processes currently employed [2]. Alternatively, it may prove possible to achieve some removal of impurity content by performing the carbothermic reduction stage with the addition of fluxing reagents and the formation of a liquid slag phase.

Another potential advantage of the carbothermic reduction route is the potential for recovering SiO_2. In the present study, the SiO yielded was collected as SiC which was deposited on the walls of the graphite crucible utilized and was identified by X-ray diffraction as β-SiC. Appropriate processing of the SiO-bearing gas stream can permit the production of either SiO_2, SiC or Si_3N_4 as potentially marketable co-products.

Figs 10 and 11 show pictures of observations by scanning electron microscopy. Fig. 10 shows particles of zircon before being mixed with Collie coal and submitted to the carbothermic reduction and Fig. 11 shows the product obtained which was oxidized for 6 h after the carbothermic reduction. The particles are now porous because the silica was volatilized as SiO and leaving behind the ZrO_2.

3.3. Production of partially stabilized ZrO_2

The results of the experiments carried out using stabilizers are shown in Figs 12 and 13 for the reduction temperatures of 1450 and 1650 °C, respectively. The stabilizers used were MgO, CaO and Y_2O_3 and the amount utilized was 0.036 g. This amount represents 2.5 mol % Y_2O_3, 8.0 mol % CaO and 10.0 mol % MgO that, according to phases diagrams for ZrO_2–Y_2O_3 [12], ZrO_4–CaO [13] and ZrO_2–MgO [14], were at the stability fields of the tetragonal solid solution.

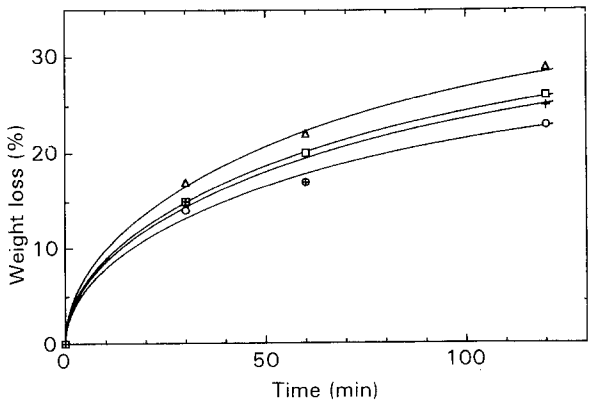

Figure 12 Percentage of weight loss versus time for the sample ($C/SiO_2 = 1:1$) at 1450 °C. (○) No stabilizer, (△) MgO, (□) Y_2O_3, (+) CaO.

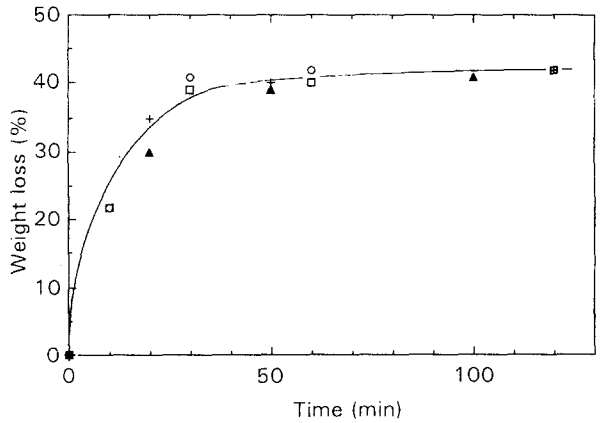

Figure 13 Percentage of weight loss versus time for the sample (C/SiO_2 = 1:1) at 1650 °C. (□) No stabilizer, (○) MgO, (+) Y_2O_3, (▲) CaO.

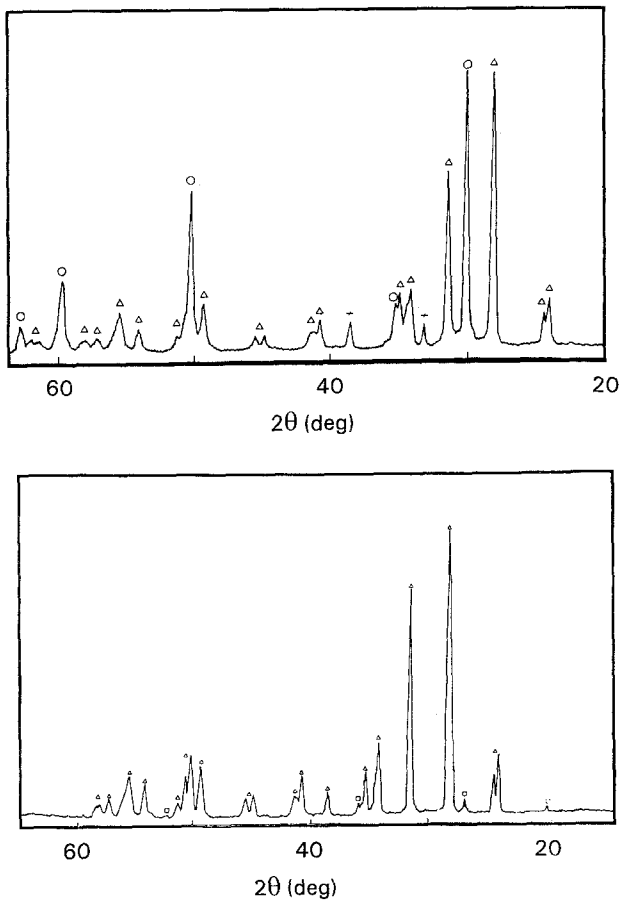

Figure 14 X-ray diffraction patterns of zirconia containing monoclinic and tetragonal phase. 1550 °C, 120 min, C/SiO_2 = 1:1. (△) ZrO_2 monoclinic, (○) ZrO_2 tetragonal, (+) ZrC, (a) with and (b) without 0.036 g MgO.

Fig. 12 indicates a small effect of the stabilizers on the percentage of weight loss. This might be attributed to the catalytic effect of the stabilizers used on the volatilization of silica. This small effect can also be attributed to the enhanced thermodynamic stability of the zirconia. Magnesium oxide seems to have a stronger effect than the other stabilizers.

Fig. 13 shows that the effect of temperature is much stronger on the rate of volatilization of silica than the catalytic effect of stabilizers. Once again, complete conversion to zirconia proved possible.

Using stabilizers it was possible to produce partially stabilized zirconia containing tetragonal phase which was identified according to the literature [15]. Fig. 14 shows the X-ray diffraction pattern of zirconia partially stabilized by magnesium oxide in comparison with the products obtained for similar experimental conditions but without stabilizer (at 1550 °C, 2 h reaction). Once again the beneficial effect of the stabilizer on the volatilization of silica can be observed, because no peak of zircon could be identified when the stabilizers were used. Some peaks of ZrC could be observed because this product was X-rayed before being submitted to oxidation. It can therefore be concluded that it is possible to produce partially stabilized zirconia directly from zircon by carbothermic reduction.

The partially stabilized zirconia could be applied in the refractory industries, preventing failures because of the phase changes promoted when thermally cycled.

The results presented represent a preliminary report on work on the direct utilization of zircon as a source for ceramic materials. Further work is currently underway, investigating the mechanism of the carbothermic reduction reaction in some detail, and it will be reported in due course.

4. Conclusion

Zirconia of about 96% purity was produced from zircon by carbothermic reduction at reasonably low temperature (1650 °C). Additions of stabilizers made it possible to produce partially stabilized zirconia which could be directly applied in the refractory industries.

Production of zirconia through the extraction of silica from zircon by carbothermic reduction represents a significant improvement over the use of the conventional processes, in not generating disposal material and consequently having less impact on the environment. The recovery of silicon content in a useful form is possible by further reaction of the SiO produced.

Acknowledgement

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References

1. R. STEVENS, "Zirconia and zirconia ceramics", Magnesium Elektron Ltd, July 1986.
2. J. D. HANCOCK, *Min. Sci. Eng.* **9**(1) (1977) 25.
3. HUMPHREYS CORPORATION, Brit. Pat. 1389 585, April 1975.
4. R. STEVENS, in "Proceedings of the first European Symposium on Engineerings Ceramics" 25–26 February, London (1985) pp. 97–110.
5. U. O. IGIEHON, Thesis, D Phil, University of London, Imperial College of Science, Technology and Medicine, November 1989.
6. D. AZUBIKE, Thesis, D Phil, University of London, Imperial College of Science, Technology and Medicine, October 1988.
7. N. HOWELL FURMAN (ed.) "Standard Methods of Chemical Analysis", 6th Edn, Vol. I The Elements (Krieger, Huntington, New York, 1975).

8. V. L. K. LOU, T. E. MITCHELL and H. HEUER, *J. Am. Ceram. Soc.* **68**(2) (1985) 49.
9. J. J. BIERNACKI and G. P. WOTZAK, *ibid.* **72**(1) (1989) 122.
10. P. D. MILLER, J. G. LEE and I. B. CUTLER, *ibid.* **62**(3–4) (1979) 147.
11. W. W. PULTZ and W. HERTL, *Trans. Faraday Soc.* **62** (1968) 2499.
12. V. S. STUBICAN, R. C. HINK and S. P. RAY, *Am. Ceram. Soc.* **61** (1–2) (1978) 17.
13. V. S. STUBICAN and P. RAY, *ibid.* **60**(11–12) (1977) 534.
14. D. VIECHNICKI and V. S. STUBICAN, *ibid.* **48**(6) (1965) 292.
15. T. K. GUPTA, J. H. BECHTOLD, R. C. KUZNICKI, L. H. CADOFF and B. R. ROSSING, *J. Mater. Sci.* **12** (1977) 2421.

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