JOURNAL OF MATERIALS SCIENCE 31 (1996) 4277–4288

Preparation of zirconia and silicon carbide whisker biphasic powder mixtures by carbothermal reduction of zircon powders

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Carbothermic reduction of zircon powders has been studied under argon and nitrogen gas pressures of 0.15 MPa in order to obtain biphasic composite powder mixtures containing zirconia and silicon carbide whiskers. The reduction has been carried out using different mole ratios of carbon and zircon. Carbon was used in the form of activated charcoal (specific surface area $\sim 1000\ m^2 g^{-1}$) or carbon black (specific surface area $\sim 300\ m^2 g^{-1}$). Whilst complete decomposition to m-ZrO_2 was obtained in the argon atmosphere at 1700 °C, under the nitrogen atmosphere the conversion was incomplete even at 1700 °C. However, the extent of conversion to zirconia at 1650 °C under nitrogen was found to be more than that under argon gas. In a few cases, particularly under the nitrogen atmosphere, minor amounts of other forms of zirconia e.g., tetragonal (t)-ZrO_2 or orthorhombic (o)-ZrO_2 were formed along with the major monoclinic (m)-ZrO_2 phase. The rate of reaction was found in general to increase with an increase in the carbon content. The studies particularly indicate that activated charcoal is a better reducing agent than carbon black owing probably to its enormous surface area. Further, it was also noted that cobalt chloride and sodium chloride act as a catalyst and a space forming agent respectively. They aid silicon carbide whisker formation and growth and hence the reaction is appreciably accelerated and reaches completion at 1650 °C in the argon atmosphere.

1. Introduction

Carbothermic reactions have been used for a long time as a preferred route to process oxidic ores [1], for the elimination of the silica component in mineral silicates [2–7] and for the preparation of carbides and nitrides of several elements, particularly those of silicon [3], which has been extensively studied by Bechtold and Cutler [1], Bishop *et al.* [4] and van Dijen and Metselaar [5].

There is considerable interest in producing ceramic whisker or ceramic fibre reinforced ceramic matrix composites with good high temperature capabilities. This has generated interest in the use of carbothermic reactions to generate carbides or nitrides *in situ* as second phase tougheners for an oxide ceramic matrix. An example of this is using a carbothermic reaction on aluminosilicate materials to yield a biphasic powder mixture of alumina and silicon carbide whiskers [3–6]. We present in this paper some preliminary results on the carbothermic reduction of zircon powders in order to obtain a mixture of m-zirconia and β-silicon carbide whiskers which could subsequently be directly hot pressed to obtain a $ZrO_2 + SiC$ (whisker) composite ceramic body.

2. Experimental procedure

2.1. Carbothermic reduction of zircon powders and selection of different reaction parameters

The overall chemical reaction of zircon with carbon can be stated as: [2]

$$ZrSiO_4(s) + 3C(s) \rightarrow ZrO_2(s) + SiC(s) + 2CO\ (g) \qquad (1)$$

i.e., zircon presumably decomposes into zirconia and silica and the latter then reacts with carbon to form SiC as per the reaction scheme shown in Equation 4 below. The reaction of silica with carbon could be conceived to proceed in two steps. Firstly, silica is reduced (as per the reaction scheme shown as Equation 2) to silicon monoxide (SiO), which in a subsequent step yields silicon carbide (SiC), by reaction

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with carbon (as per the reaction scheme shown as Equation 3).

$$SiO_2\,(s) + C\,(s) \rightarrow SiO\,(g) + CO\,(g) \qquad (2)$$

$$SiO\,(g) + 2C\,(s) \rightarrow SiC\,(s) + CO\,(g) \qquad (3)$$

$$SiO_2\,(s) + 3C\,(s) \rightarrow SiC\,(s) + 2CO\,(g) \qquad (4)$$

The reaction shown as Equation 3 which is a solid–vapour reaction is known to be responsible for the formation of the SiC mainly in whisker form. The morphology of the whiskers and the extent of reaction can be controlled by optimizing reaction parameters such as the SiO_2:C ratio, the temperature of the reaction and the duration of the reaction. The addition of space formers and the use of reaction catalysts is known to aid SiC whisker growth [8]. Due to the gaseous nature of SiO, it would be preferable not to carry out the experiments in a continuous flow of an inert gas since this would flush away a part of the SiO gas. Hence, in this study we performed the reactions in a closed reaction chamber filled with either an argon or a nitrogen gas atmosphere. A slight positive pressure (0.15 MPa) was maintained during the period of reaction with the aid of a relief valve rated to open beyond 0.15 MPa.

The ratio of SiO_2 to C and the extent of their mutual physical contact would obviously influence the reaction kinetics and hence the extent of formation of silicon carbide and zirconia. In case of an insufficient quantity of carbon, at high temperatures, the SiC formed would react with the released ZrO_2 and reduce it to ZrC as per the reaction scheme shown in Equation 5.

$$2ZrO_2(S) + 3SiC(s) = 2ZrC(s) + 3SiO(g) + Co(g) \qquad (5)$$

This reaction has been recently observed and reported by De Souza & Terry [2]. Some authors prefer to take a stoichiometric SiO_2:C ratio of 3 moles of carbon per mole of silica and increase their contact by pelletizing. While this method has the advantage that the loss of SiO gas can be minimized, it, however, might hinder extensive whisker growth by limiting a free permeation of SiO (g) and also the reaction might not go to completion. Yamada *et al.* [8] preferred in their efforts to produce Si_3N_4–SiC composites to start from a mixture of Si_3N_4, silica sol and carbon black. They took an excess of carbon to the extent of 5.5 moles of carbon per mole of silica in order to achieve a complete reaction in a loosely packed powder bed. Instead of producing a pellet they added NaCl as space forming agent and $CoCl_2$ as a reaction catalyst to produce better nucleation, growth and yield characteristics for the SiC whiskers. It has already been reported that the addition of $CoCl_2$ helps in the formation of SiC whiskers via the vapour–liquid–solid (VLS) growth process [1, 9].

In our experiments, we have studied the carbothermic reactions using 4.5, 5.5 and 9.0 moles of carbon for each mole of SiO_2 present in the zircon. We have investigated the temperature range of 1550–1700 °C at 50 °C intervals allowing 1 h of soaking in either a N_2 or an Ar atmosphere at the reaction temperature. In some of our experiments, we added NaCl and $CoCl_2$ to the precursor mixtures in order to study their effect on the progress of the reaction and also on the morphology of the SiC whiskers obtained.

2.2. Experimental conditions

Zircon powder (Indian Rare Earths, Chevara, Kerala, India) with a particle size distribution shown in Fig. 1 was directly used as the precursor for the reduction. Activated charcoal (S.D Fine Chemicals, India) and carbon black (Degussa, Germany) with surface areas of ~1000 and ~300 $m^2\,g^{-1}$ respectively were used as carbon sources. The zircon powder was mixed in ethyl alcohol with appropriate quantities of carbon to produce stoichiometries of 4.5, 5.5 and 9.0 moles of carbon per mole of silica content in the zircon. After a thorough mixing of the two powders, in some experiments, cobalt chloride (0.015 moles per mole of silica) and/or sodium chloride (0.6 moles per mole of silica) were also added to the precursor mixtures. The powders were loaded into graphite crucibles whose lids contained a small hole to allow atmospheric contact. The crucibles were initially sealed with an organic resin (araldite) and placed on the hearth of a graphite

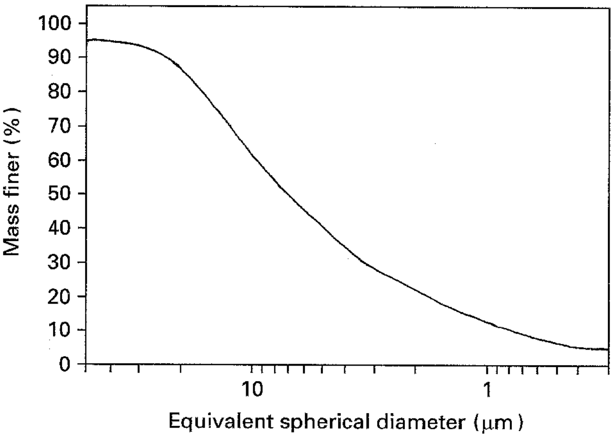

Figure 1 Typical particle size distribution of zircon powder used for the investigation.

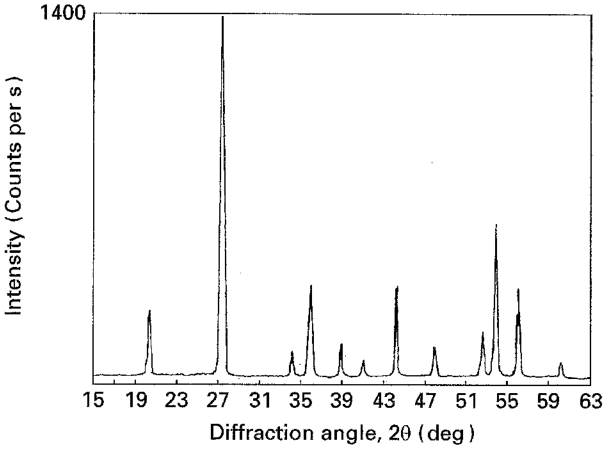

Figure 2 Typical XRD pattern of zircon powder used for the investigation.

furnace. The furnace chamber was then evacuated and back filled with an argon or nitrogen gas atmosphere to a positive pressure of 0.15 MPa. The graphite furnace was heated in a programmed manner, from room temperature to 1000 °C at 10 °C per min, from 1000–1250 °C at 5 °C per min and finally from 1250 °C to the desired temperature e.g., 1550 °C, 1600 °C, 1650 °C, or 1700 °C at 3 °C per min. The samples were held at any of these final temperatures for one hour before furnace cooling back to room temperature. The temperature in the furnace hot zone was measured by a freely suspended, unsheathed W–Re (5%)/W–Re (26%) thermocouple. The reaction products removed from the crucibles after cooling were decarburised at 700 °C for 2–3 h in air to remove any unreacted carbon. The decarburised powders which appeared powdery or

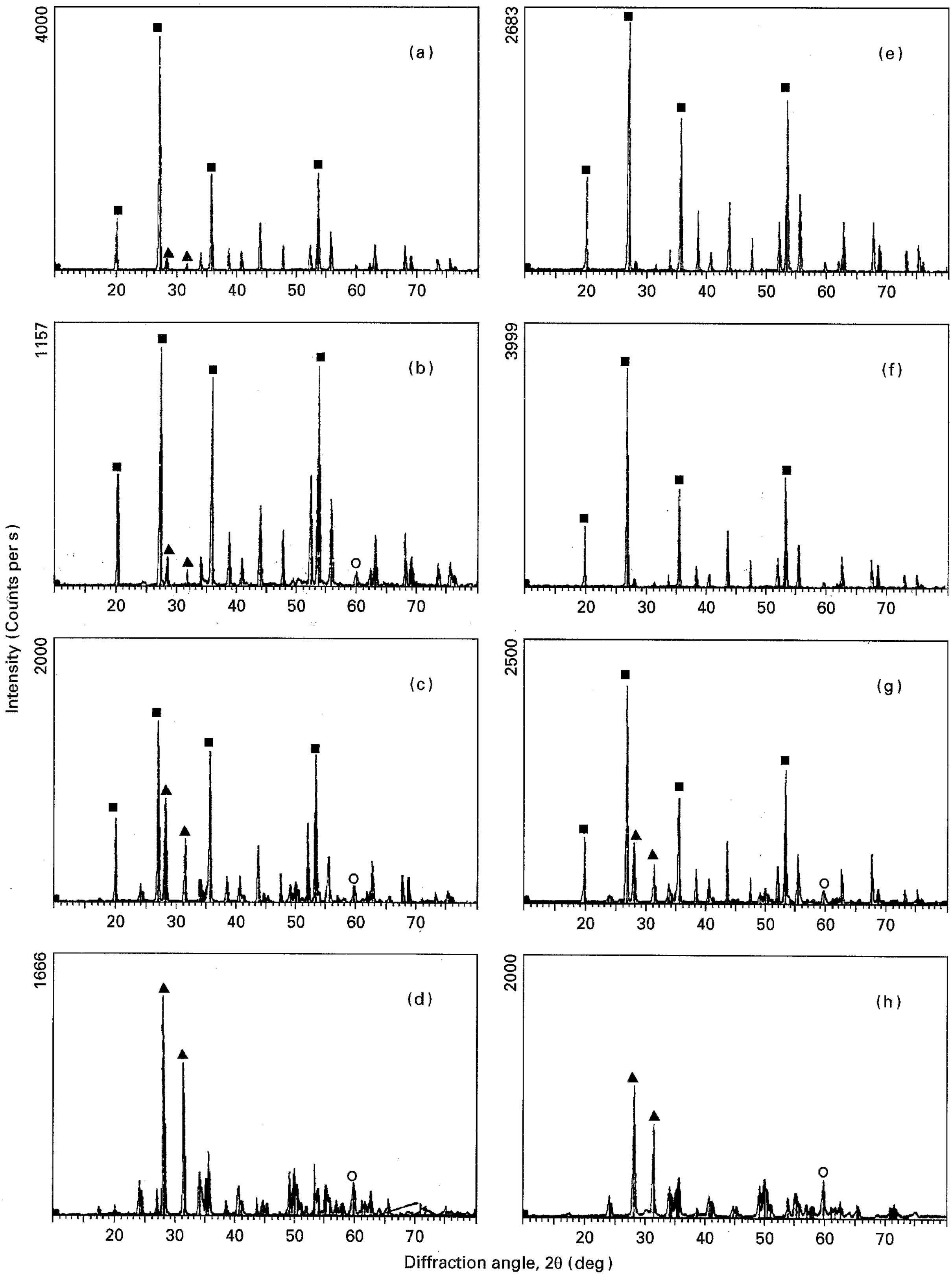

Figure 3 XRD spectra of products obtained at various temperatures in argon atmosphere from zircon by carbothermal reduction. (a) ZAC55A1550, (b) ZAC55A1600, (c) ZAC55A1650, (d) ZAC55A1700, (e) ZCB55A1550, (f) ZCB55A1600, (g) ZCB55A1650 and (h) ZCB55A1700. The phases observed in the patterns are; (■) Zircon, (▲) M-ZrO_2 and (○) β SiC.

woolly and ash-grey or greenish grey in colour were subjected to X-ray diffraction (XRD) using a Philips model 9902 X-ray diffractometer (Philips, Holland) equipped with a CuK_α radiation source. In addition scanning electron microscopic (SEM) investigations were performed using a JEOL JSM-35 electron microscope (JEOL, Japan).

3. Results and discussion

For clarity the samples prepared under different conditions are designated by the following notations: e.g., ZAC90A1650 denotes samples derived from the zircon (Z) precursor containing 9 moles (90) of activated charcoal (AC) per mole of silica (in the precursor) in an argon (A) atmosphere at 1650 °C for 1 h; similarly

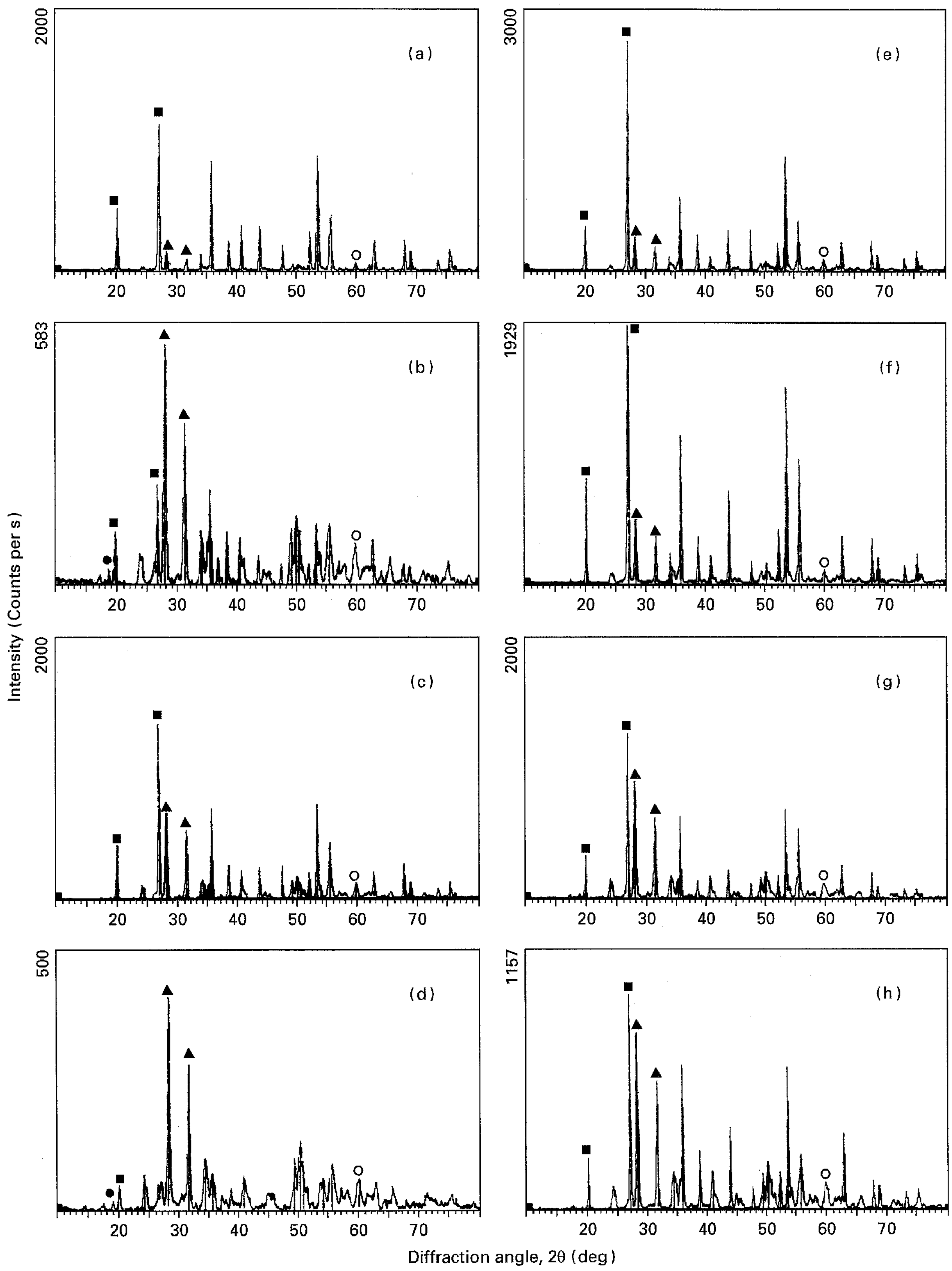

Figure 4 XRD spectra of products obtained at various temperatures in nitrogen atmosphere from zircon by carbothermal reduction. (a) ZAC90N1550, (b) ZAC90N1600, (c) ZAC90N1650, (d) ZAC90N1700, (e) ZCB45N1550, (f) ZCB45N1600, (g) ZCB45N1650 and (h) ZCB45N1700. The phases observed in the patterns are; (■) Zircon, (▲) m-ZrO_2, (○) β SiC and (●) Si_2N_2O.

ZCB45N1700 denotes samples derived from a zircon precursor containing 4.5 moles (45) of carbon black (CB) per mole of silica reacted in nitrogen (N_2) at 1700 °C for 1 h. Fig. 2 presents a typical XRD spectrum for unreacted zircon powder. Fig. 3(a–h) presents the typical XRD spectra of the samples obtained at 1550, 1600, 1650 and 1700 °C, in an argon atmosphere using activated charcoal (a–d) and carbon black (e–h) respectively. The corresponding XRD spectra of the samples obtained under a nitrogen atmosphere are presented in Fig. 4(a–h). All the XRD patterns were obtained on a constant weight of 100 mg of the decarburised products. In view of this point then, the intensity of the most intense peak of the various species present in the sample could be assumed to be representative of the quantity of that species present in the sample. This in turn could be assumed to represent the progress of carbothermic reaction under a given set of experimental conditions. Thus peaks at diffraction angles of 27.0° ($d = 0.330$ nm) and 28.2° ($d = 0.3165$ nm) were taken as the representative XRD peaks of zircon and m-ZrO_2 respectively in the samples. Unfortunately, the most intense peak of β-SiC located at a diffraction angle of 35.9° ($d = 0.251$ nm) was in most cases swamped by the peak of m-ZrO_2 at the same position. Hence, it was difficult to obtain a direct quantitative estimation of the amount of β-SiC formed in the reaction. It was indirectly measured in terms of the formation of an equivalent quantity of m-ZrO_2, since the carbothermic reduction of zircon produces equimolar proportions of m-ZrO_2 and β-SiC.

The qualitative XRD analysis of various phases present in the samples after reaction in argon and nitrogen atmospheres are presented in Tables I and II respectively.

An attempt was also made to broadly analyse the progress of the carbothermic reaction by evaluating the extent of m-ZrO_2 formation or the extent of zircon decomposition at the various temperatures for different silica: carbon ratios in the precursor mixtures. This was done by calculating the percentage of the relative intensity (%R.I.) of the most intense m-ZrO_2 ($d = 0.3165$ nm) or zircon peak ($d = 0.3300$ nm) at the temperature of reaction. The effect of carbon concentration and of the temperature on the progress of the reaction was also investigated. These results are presented in Fig. 5(a–d) and Fig. 6(a–d) for reactions performed respectively under argon and nitrogen atmospheres.

TABLE I Various phases identified (by XRD) in the products derived from the reduction of zircon under argon atmosphere

Composition	1550 °C	1600 °C	1650 °C	1700 °C
ZAC 4.5	Zn Zr	Zn Zr	Zn Zr	Zr, S –
ZAC 5.5	Zn Zr	Zn Zr	Zn Zr, S	Zr, S –
ZAC 9.0	Zn Zr	Zn Zr	Zn, Zr Zr, S	–
ZCB 4.5	Zn Zr	Zn Zr	Zn Zr, S	Zr, S –
ZCB 5.5	Zn Zr	Zn Zr	Zr, Zn S	Zr, S –
ZCB 9.0	Zn Zr	Zn Zr	Zn Zr, S	Zr, S –

CODES:
Zn–Zircon 1st line indicates major phases
Zr–m-Zirconia 2nd line indicates minor phases
S–Silicon carbide

TABLE II Various phases identified (by XRD) in the products derived from the reduction of zircon under nitrogen atmosphere

Composition	1550 °C	1600 °C	1650 °C	1700 °C
ZAC 4.5	Zn Zr	Zn Zr, S	Zn, Zr S, SiON	Zr, Zn S, SiON
ZAC 5.5	Zn Zr, S	–	Zr Zn, S Zr (t/o)	Zr, Zn S Zr (t/o)
ZAC 9.0	Zn Zr	Zn, Zr Zr (t/o)	Zn Zr, S, Zr (t/o)	Zr SiON, Zn, S Zr (t/o)
ZCB 4.5	Zn Zr, S	Zn Zr, S	Zn, Zr S	Zn, Zr S
ZCB 5.5	Zn Zr, S	–	Zn, Zr S Zr (t/o)	Zr Zr (t/o) Zn, S
ZCB 9.0	NA	Zn Zr, S	Zr Zr (t/o) SiON	Zr Zn, S Zr (t/o)

CODES:
S–β-SiC I & II Line denotes major phases
Zn–Zircon Last line denotes minor phases
Zr–m-Zirconia
SiON–Silicon oxynitride
Zr (t/o)–Tetragonal/orthorhombic zirconia

3.1. Studies using an argon atmosphere

It can be seen from Figs 5 and 6 that in both the activated charcoal and carbon black cases the reduction of zircon was slow upto 1600 °C, whilst between 1600–1650 °C a considerable increase in the rate of reaction was observed. The higher the mole ratio of carbon used the higher is the conversion in both activated charcoal and carbon black containing samples. Complete conversion to m-ZrO_2 and β-SiC is obtained at 1700 °C for both activated charcoal and carbon black as seen by the absence of zircon peaks in the XRD spectra. Fig. 7a shows the effect of initial carbon concentration on the extent of reaction, which is defined in terms of the percentage of m-ZrO_2 formed, at various temperatures. It is seen that the higher the carbon concentration the higher is the formation of m-ZrO_2 at any temperature. The reaction goes to near completion for 5.5 moles of carbon in the case of activated charcoal, as opposed to the case of carbon black where the reaction proceeds only when greater than 5.5 moles of carbon are used. This could be ascribed to the larger surface area of activated charcoal compared to that of carbon black. Fig. 8(a–d) shows SEM micrographs of some product powders obtained under argon at 1650 and 1700 °C. The formation of silicon carbide whiskers is quite evident

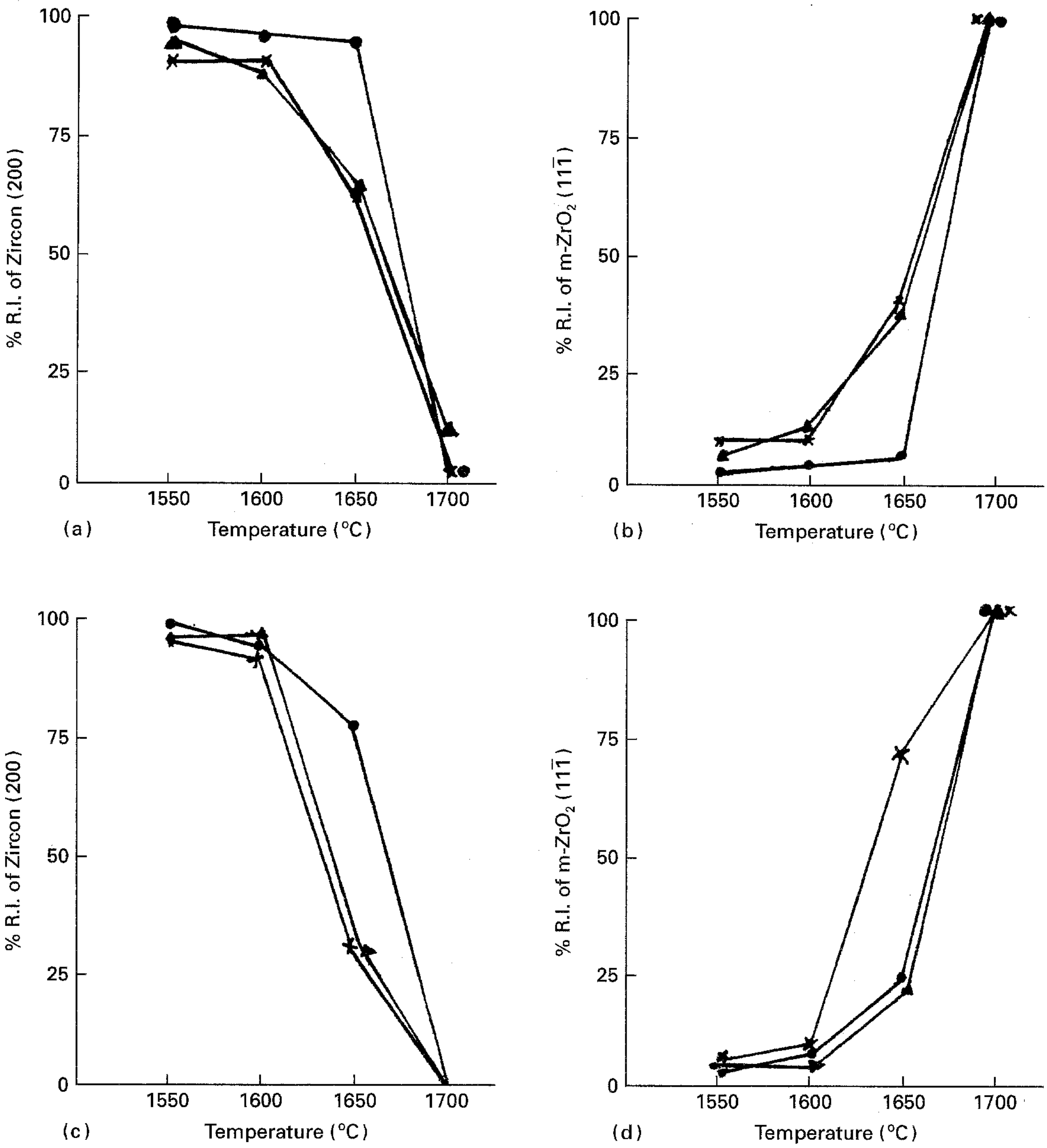

Figure 5 Relative intensity (R.I) of zircon (200) and m-zirconia (111) peaks in products obtained under argon atmosphere using activated charcoal (a and b) and carbon black (c and d) in the ratios of 4.5 moles (●), 5.5 moles (▲) and 9.0 moles (×) per mole of zircon.

from these micrographs. It is also clear that the whisker content is much higher in the case of products obtained from precursors containing the higher surface area charcoal than in the case of carbon black.

3.2. Studies using a nitrogen atmosphere

The percentage conversion of zircon to m-ZrO_2 appears to be much higher in a nitrogen atmosphere as compared to that in argon at lower temperatures (upto 1650 °C). However, the increase in the extent of conversion between 1650–1700 °C is rather slow and gradual and the reaction remains incomplete even at 1700 °C. This behaviour is in stark contrast to that observed in the case of the argon atmosphere where the reaction is completed at 1700 °C. The point that the reaction is incomplete is underpinned by the presence of zircon peaks in the XRD spectra even at 1700 °C as is shown in Fig. 4(a–h). At the outset, the nature of the reaction and the reaction products depicted in Figs 4 and 6 are quite different from those in Figs 3 and 5. The reaction at lower temperatures in nitrogen is dominated by the increasing tendency to form silicon oxynitride which possibly aids the decomposition of zircon. This could then effectively increase the formation of m-ZrO_2 by the reaction scheme shown in Equation 6. Evidence for the formation of Si_2N_2O is the observation of small XRD peaks present at diffraction angles of 19.6 ° (d = 0.443 nm), at 20 ° (d = 0.443 nm) and at 26.5° (d = 0.336 nm). However, at higher reaction temperatures (above 1650 °C), these peaks decrease in intensity or, even disappear due to the tendency of silicon oxynitride to decompose according to the reaction scheme shown as Equation 7, to solid silicon carbide and gaseous nitrogen and carbon monoxide.

$$2ZrSiO_4 + N_2 + 3C \rightarrow 2m-ZrO_2(s) + Si_2N_2O(s) + 3CO(g) \quad (6)$$

$$Si_2N_2O + 3C \rightarrow 2SiC(s) + N_2(g) + CO(g) \quad (7)$$

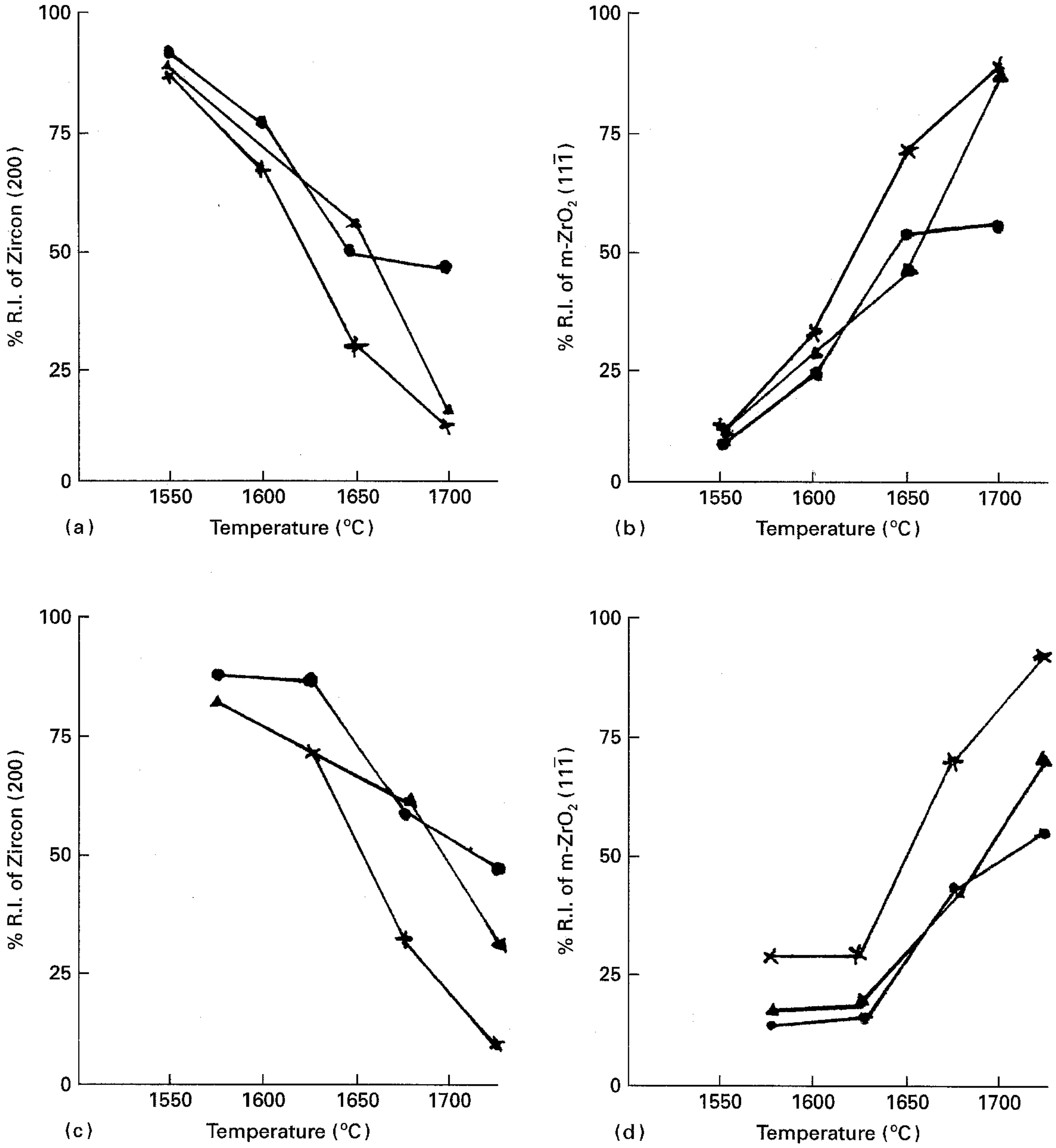

Figure 6 Relative intensity (R.I) of zircon (200) and m-zirconia $(11\bar{1})$ peaks in products obtained under nitrogen atmosphere using activated charcoal (a and b) and carbon black (c and d) in the ratios of 4.5 moles (●), 5.5 moles (▲) and 9.0 moles (×) per mole of zircon.

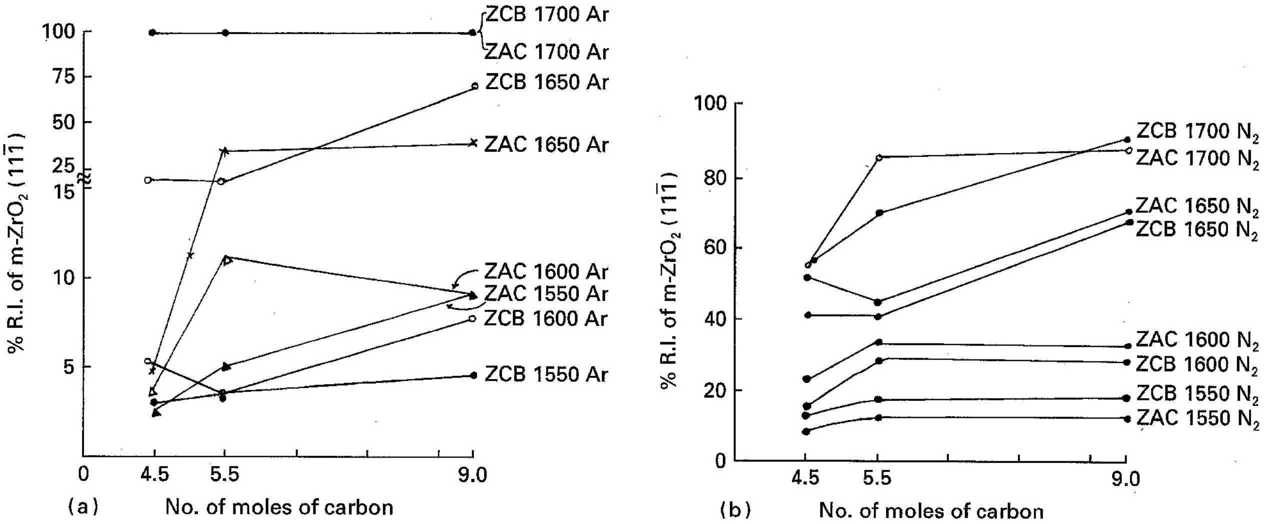

Figure 7 (a) Plot of relative (XRD) intensity (R.I) of $m\text{-}ZrO_2$ $(11\bar{1})$ phase as a function of number of moles of carbon in products obtained under argon atmosphere. (b) Plot of relative (XRD) intensity (R.I) of $m\text{-}ZrO_2$ $(11\bar{1})$ phase as a function of number of moles of carbon in products obtained under nitrogen atmosphere.

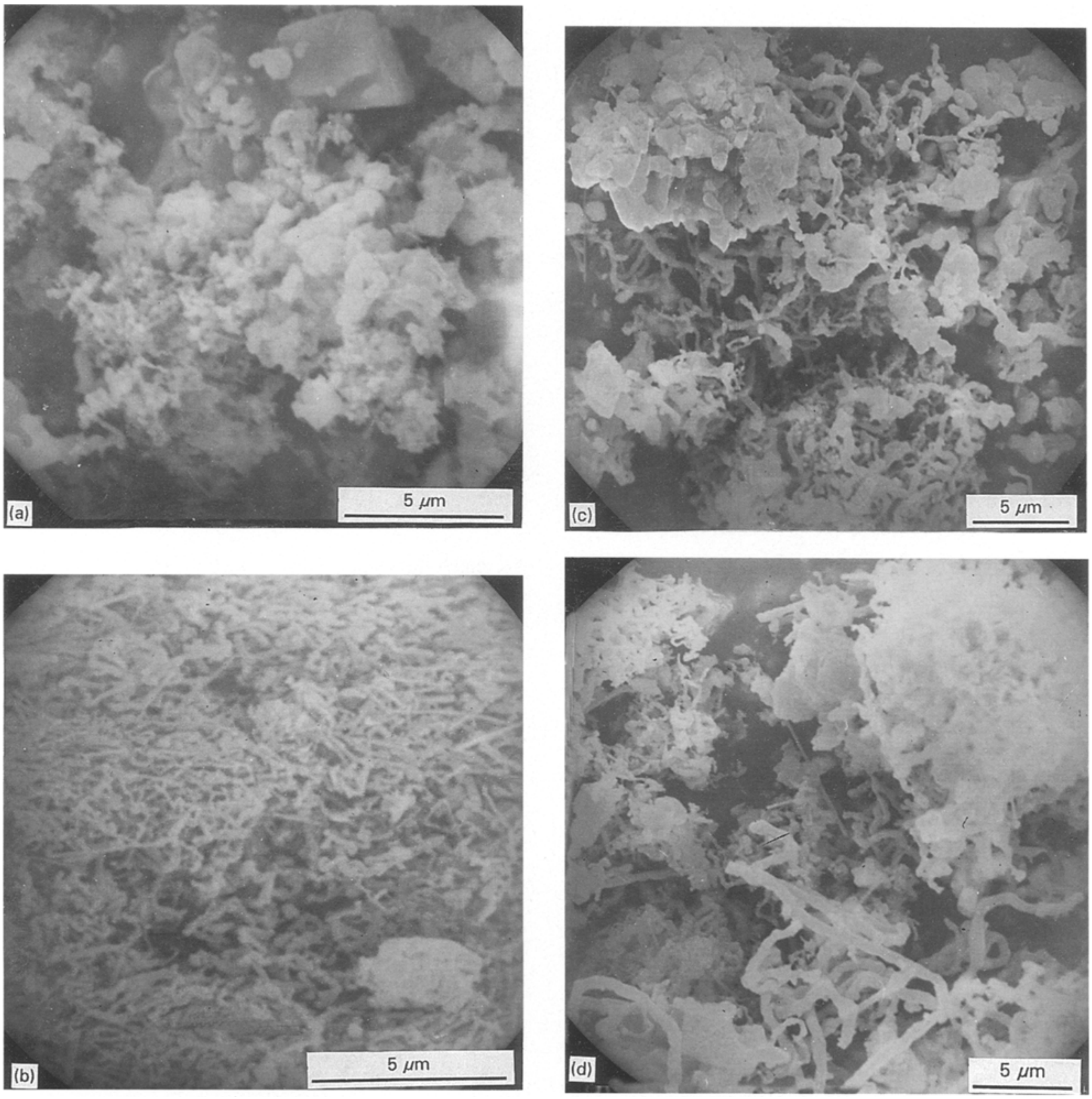

Figure 8 SEM of product powders containing zirconia, zircon and silicon carbide whiskers obtained by carbothermal reduction of zircon in argon atmosphere. (a) ZCB55A1650, (b) ZAC55A1650, (c) ZCB55A1700 and (d) ZAC55A1700.

Fig. 7(b) shows the extent of the reaction progress under nitrogen as a function of carbon content in the reaction mixture. It can be seen that in general there is an increase in the extent of reaction when the carbon content in the reaction mixture is increased. The extent of reaction in the case of activated charcoal is higher than that in the case of carbon black samples. The slight decrease in the extent of reaction at carbon content of 5.5 moles compared to other carbon contents was also observed in the case of reactions under the argon atmosphere. This could be ascribed to intermediate reactions in which ZrO_2 is bound into unstable species (as yet unidentified) which in turn decompose to yield ZrO_2 when the temperature is increased. The SEM pictures of some typical products prepared under the nitrogen atmosphere are shown in Fig. 9(a–d). The presence of silicon carbide whiskers can be clearly seen in these pictures.

3.3. Evidence for the formation of other forms of zirconia

Minor XRD peaks observed in the diffraction angle range of 29–30° indicate the formation of ZrO_2 phases other than m-ZrO_2 (which is formed as the major phase). The proportion of these other phases seems to increase with temperature in the case of argon and even more distinctly in the case of nitrogen as is illustrated in the X-ray patterns for samples ZCB90A1700 and ZCB90N1650 shown in Fig. 10 (a and b). The peaks are formed with appreciable intensities and could be assigned to either tetragonal and/or to orthorhombic forms of ZrO_2. The orthorhombic form of ZrO_2 was probably induced by the formation of the Si_2N_2O phase which also has an orthorhombic symmetry. However, it is interesting to note that while the Si_2N_2O phase decomposes at temperatures of $\sim$1700 °C, the t/o-ZrO_2 phases are

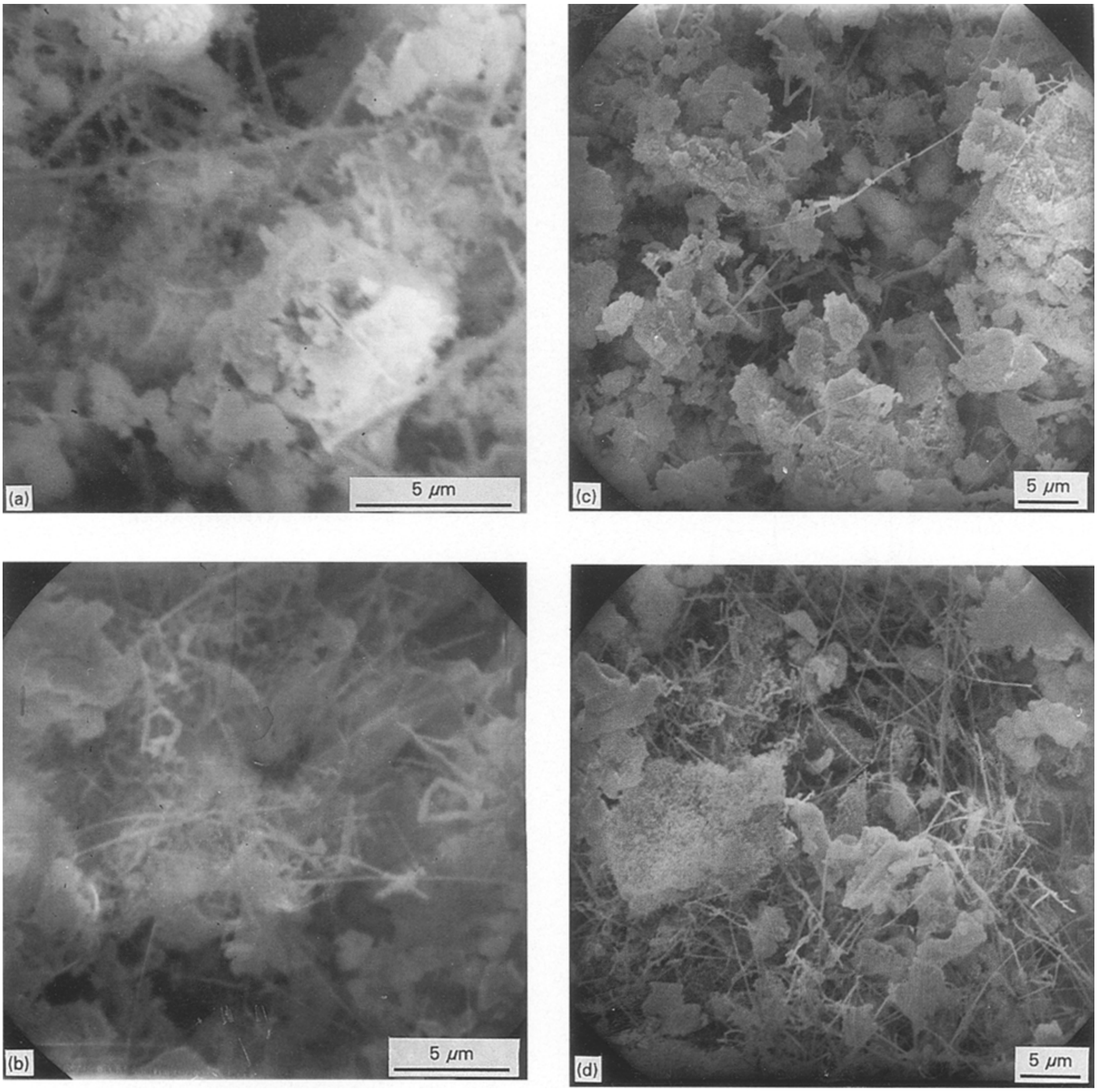

Figure 9 SEM of product powders containing zirconia, zircon and silicon carbide whiskers obtained by carbothermal reduction of zircon in nitrogen atmosphere. (a) ZCB55N1650, (b) ZAC55N1650, (c) ZCB55N1700 and (d) ZAC55N1700.

seemingly stable to and even beyond 1700 °C. The reason for the formation of these phases is under active study and the results will be published in a future paper.

3.4. Effect of the use of space formers and catalysts on the reaction kinetics

The carbothermic reaction generates a composite mixture of ZrO_2 and SiC whiskers which could be used to prepare ZrO_2–SiC(w) composite bodies. The strength and toughness of composites made from such powder mixtures are dependent on the quality and the content of SiC whiskers. Carbothermic reactions could be performed with catalysts and space former additives which could improve the quality and content of the SiC whiskers in the mixture. In this study, NaCl and $CoCl_2$ were chosen as the space former (SF) and catalyst (C) respectively.

From the study of the peak intensities of zircon and m-ZrO_2, it is seen that at 1650 °C the reaction under argon is complete (absence of zircon peaks) in case of the sample containing $CoCl_2$. However, in the other two cases where either no additives or only the SF additive were present the reaction was found to be incomplete at 1650 °C.

In the case of a nitrogen atmosphere, the reaction was found to be incomplete even when $CoCl_2$ was used. Significantly, $CoCl_2$ seemingly increased the percentage of t- or o-ZrO_2 in the sample. The representative XRD spectra to highlight these effects are presented in Figs 11(a–c) and 12(a–c). The role of $CoCl_2$ is that of a catalyst which accelerates the reaction to completion at a lower temperature (e.g., 1650 °C) as compared to cases where it was not used. When solely NaCl is used the reaction does not go to completion at 1650 °C but copious amounts of whiskers are still formed and the product appears woolly or spongy. In

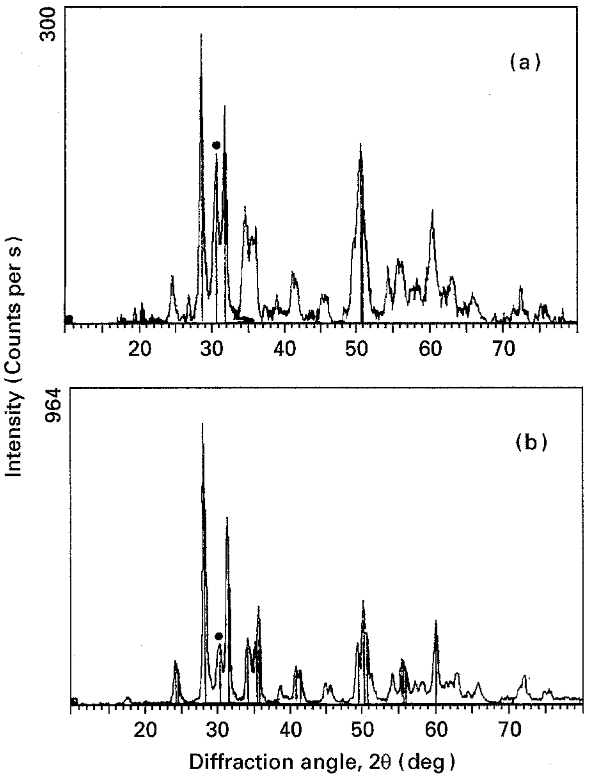

Figure 10 XRD spectra of products (a) ZCB90N1650 and (b) ZCB90A1700 showing considerable presence of t-/o-zirconia. The peak assigned to these phases is marked by (●)

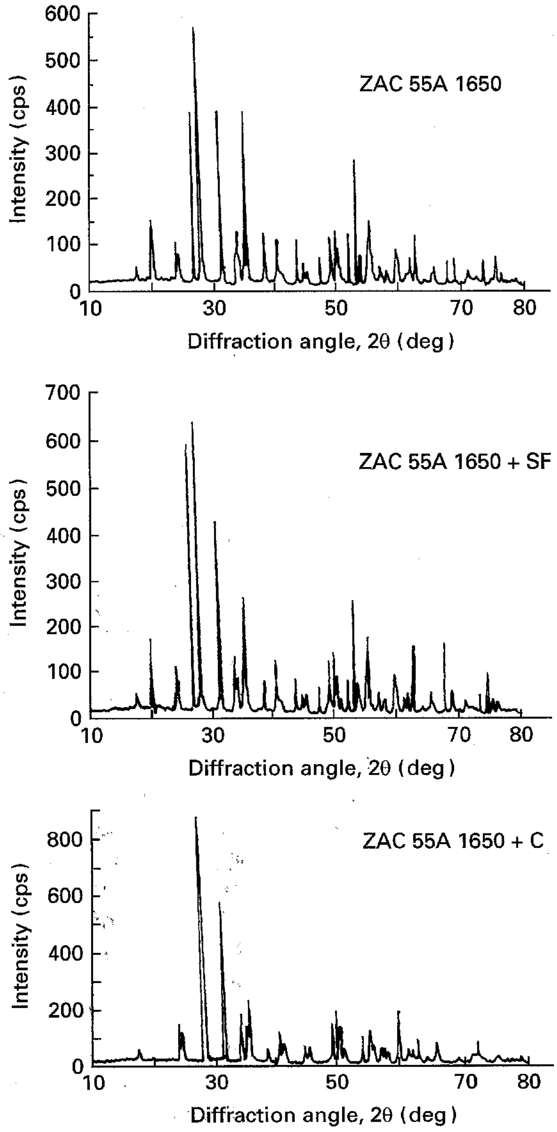

Figure 11 XRD spectra of products obtained under argon atmosphere using $CoCl_2$ as catalyst (C) and sodium chloride as space former (SF).

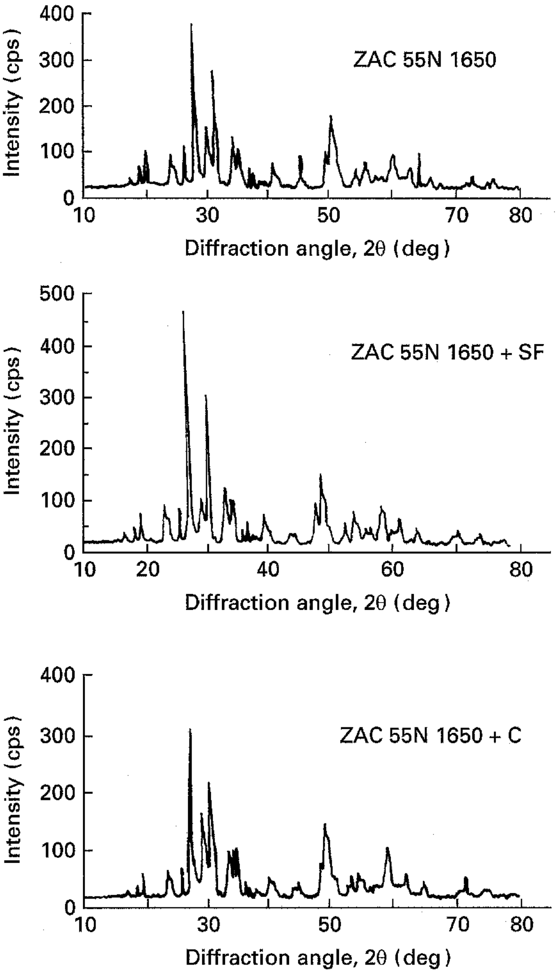

Figure 12 XRD spectra of products obtained under nitrogen atmosphere using $CoCl_2$ as catalyst (C) and sodium chloride as space former (SF). ● denotes t/o-ZrO_2 phases.

general more whiskers were obtained under nitrogen than under argon atmospheres whenever the additives (SF or catalyst) were used. Further studies are in progress both with and without the use of catalysts to enhance the content of t/o-ZrO_2 and SiC whiskers in the products.

3.5. Morphology of the silicon carbide whiskers formed in the reaction

From the SEM micrographs of the reaction products (Figs 8 and 9), it is clearly seen that silicon carbide whiskers are formed in quantity at temperatures beyond 1650 °C in both argon and nitrogen atmospheres. In general, our data suggests that activated charcoal is able to generate a larger quantity of whiskers that have a more uniform size distribution compared to carbon black. This could be ascribed to the very large surface area of activated charcoal. The minimum size of the whiskers is of the order of 0.2 μm in diameter and possess a length : diameter aspect ratio of 10 or more. In reactions carried out under both

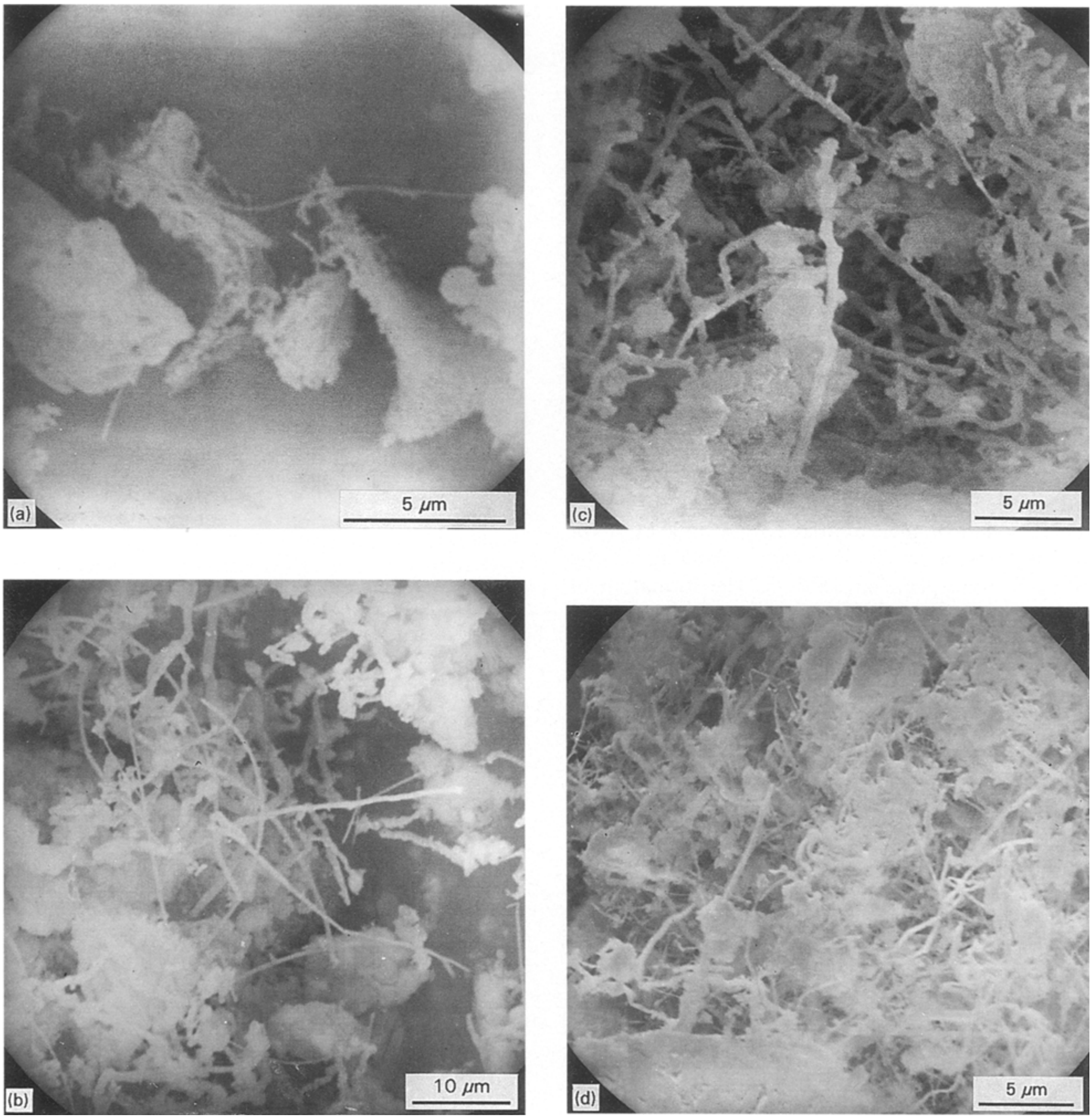

Figure 13 SEM pictures of products obtained under argon and nitrogen atmosphere using cobalt chloride as catalyst (C) and sodium chloride as space former (SF) products are from (a) ZAC55A1650 + C, (b) ZAC55N1650 + C, (c) ZAC55N1650 + C and (d) ZAC55N1650 + SF.

argon and nitrogen atmospheres at temperatures below 1650 °C, insignificant quantities of whiskers are formed. The XRD spectra of the samples indicate minimal decomposition at temperatures of 1550 °C and 1600 °C. However, the reactions, when carried out at 1700 °C, go to completion in the case of the argon atmosphere. Unfortunately in the nitrogen atmosphere, the reaction only goes to the extent of 70–80% in the best of the conversions. The SEM micrographs shown in Figs 8 and 9 indicate that many of the whiskers have grown to diameters (thickness) of 1 μm. The thicker whiskers are no longer straight and long but tend to become soft and coil-up or curl-up into irregular shapes and form clumps like woolly balls. There is presumably a strong vitrification effect seen at this temperature. From the point of view of utilization of these composite precursor powders to form ceramic composite bodies, it is preferable to avoid the formation of silicon carbide whiskers of this type. Thus utilization of the high temperature of 1700 °C to drive the reaction to completion and thus to obtain a 100% yield of $ZrO_2 + SiC$ (whisker) mixtures is not advantageous. However, the use of catalysts such as $CoCl_2$, $FeCl_3$, $NiCl_2$ etc. and space formers such as NaCl could lower the temperature for complete reaction to a level at which the whiskers would not become soft and deformable. Preliminary experiments in this direction performed in the present study indicate that the use of sodium chloride as a space former and of $CoCl_2$ as a catalyst do have beneficial effects namely the generation of a large quantity of uniform sized whiskers when NaCl is used and complete conversion effected at 1650 °C when $CoCl_2$ is added as a catalyst. Typical SEM pictures of products obtained at 1650 °C both in argon and nitrogen atmospheres with NaCl and $CoCl_2$ additions are presented in Fig. 13(a–d). Further studies on the optimization of the parameters to obtain acceptable composite precursor powders with or without the use of catalytic additives are in progress and these will be reported at a future date.

4. Conclusions

Carbothermic reduction of zircon has been carried out in both argon and nitrogen atmospheres in the temperature range of 1550–1700 °C. Three different mole ratios of carbon (4.5, 5.5 and 9.0 moles) per mole of silica in zircon have been used. The carbon was taken in the form of activated charcoal and carbon black powders with specific surface areas of $1000\,m^2\,g^{-1}$ and $300\,m^2\,g^{-1}$ respectively. Whilst complete decomposition to m-ZrO_2 was obtained at 1700 °C in the argon atmosphere, the conversion under the nitrogen atmosphere was incomplete even at 1700 °C. The extent of m-ZrO_2 formation was, however, greater under the nitrogen atmosphere at 1650 °C. The formation of minor quantities of t-ZrO_2 and o-ZrO_2 as well as of silicon oxynitride was also observed under the nitrogen atmosphere. The formation of silicon oxynitride could probably stimulate the formation of t/o-ZrO_2 in addition to aiding the decomposition of zircon at lower temperatures. The rate of reaction was in general found to increase with an increase in carbon content. Activated charcoal was also found to be a better agent (based on an increased yield of m-ZrO_2 and also a better yield of SiC whiskers) for decomposition of zircon in this study. Cobalt chloride catalyses the reaction by aiding the formation and growth of SiC whiskers and also accelerating the complete decomposition of zircon at 1650 °C. Sodium chloride gives rise to the formation of large quantities of silicon carbide whiskers with uniform sizes and a narrow size distribution.

Acknowledgments

The authors wish to thank A. Chelvaraju, R. Ramachandra Rao and H.N. Roopa of NAL for help received during the course of these studies. Thanks are also due to R.V. Krishan and T.A. Bhaskaran of NAL for help in the SEM observations and to A.K. Singh, Head Materials Science Division of NAL for kind encouragement during the course of this work. The authors gratefully acknowledge the Indo French Centre for Promotion of Advanced Research, New Delhi, India for the grant of a joint Indo-French collaborative research project to NAL and INSA de Lyon which made these studies possible.

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Received 8 August 1995
and accepted 13 February 1996