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The effect of various reaction parameters on carbothermal reduction of kaolinite

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Abstract

Preliminary studies on the carbothermal reduction of kaolinite ($Al_2O_3.2SiO_2.2H_2O$) in argon atmosphere are reported. The effect of various reaction parameters e.g. temperature (1550–1700°C) and time (1–3 h) of the reaction, nature and source of carbon, e.g. activated charcoal (sp. surface area, 1000 m^2/gm) and carbon black (sp. surface area, 300 m^2/gm), addition of reaction catalysts ($FeCl_3$, $CoCl_2$) and variation of mole ratios of carbon to silica (4.5–9) and state of mixing of carbon and kaolinite, etc., on carbothermal reduction have been investigated. It is observed that the reaction is completed at 1700°C in 1 h or at 1650°C in 3 h. Higher mole ratios of carbon, addition of catalysts, pelletisation of the reactants and longer reaction times accelerate the reaction rate at a given temperature. © 1999 Elsevier Science Limited and Techna S.r.l. All rights reserved

1. Introduction

The mechanical properties such as strength and toughness of monolithic ceramic materials, e.g. Al_2O_3, Si_3N_4, ZrO_2, etc., can be increased by introduction of a second ceramic phase in form of whiskers (w). For example, Al_2O_3–SiC(w) composites possess better room and high temperature strengths and toughness as compared to monolithic alumina [1,2]. In addition, composites display higher resistance to thermal shock and to high temperature creep [3,4].

Ceramic composite materials are generally prepared by physical mixing of the matrix powders, e.g. Al_2O_3, ZrO_2 or Si_3N_4, etc., with whiskers, e.g. SiC(w).They are not homogeneous due to their shape and size mismatch. The whiskers also cause self agglomeration and interlocking (like woollen balls) problems. The whiskers are expensive due to their preparation from costly organic precursors. On the other hand, in-situ preparation of SiC whiskers by carbothermal reduction of aluminosilicates is anticipated to be a simple and cheaper process besides better homogeneity and dispersion of SiC whiskers. For example, in-situ preparation of Al_2O_3–SiC whisker composite powders by carbothermal reduction of kaolin is anticipated to be a process for obtaining the homogeneous mixtures by a single step cheaper process as compared to the physical mixing individual components. This process has been studied by many workers [5–7].

In this study, we have presented the effect of various reaction parameters, e.g. temperature (1550–1700°C) and time of reaction (1–3 h), mole ratios of carbon to silica (4.5–9), nature and source of carbon (activated charcoal or carbon black) and addition of catalyst ($FeCl_3$, $CoCl_2$) on the carbothermal reduction of kaolin.

2. Experimental procedure

Kaolinite powder (M/s English India Clays, India) with a particle size distribution shown in Fig. 1 was directly used as the precursor for the reaction. Activated charcoal (M/s S.D. Fine Chemicals, India) and carbon black (M/s Degussa, Germany) possessing B.E.T. surface areas of 1000 and 300 m^2/gm respectively were the other reactants. 4.5, 5.5 and 9 mol of carbon per mol of silica content in kaolinite were mixed in ethyl alcohol medium. After a good mechanical agitation for 30 min the alcohol was evaporated to obtain homogeneous powder mixtures. Catalysts in the form of 2% solution of $FeCl_3$ or $CoCl_2$ was added to the extent of 2 and 4% by wt. of SiO_2 content present in the precursor. The powders were loaded into graphite crucibles whose lids

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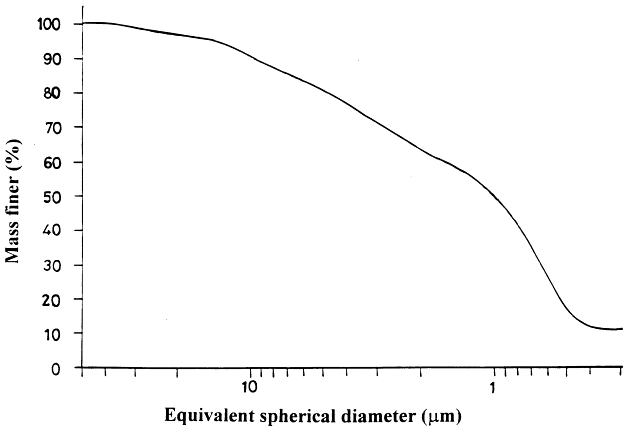


Fig. 1. Particle size distribution of kaolin.

contained small holes for the precursor powders to communicate and equilibrate with the outside furnace atmosphere at high temperatures. The crucibles and their lids after charging with the powders were initially sealed with an organic sealant (Araldite, M/s. Ciba Geigy, India) and placed on the hearth of a graphite furnace with internal graphite heating elements inside a carbon–carbon composite fibre board insulation. The furnace chamber containing the reactant crucibles was then evacuated to 1 m bar and backfilled with high purity argon gas to a positive pressure of 0.15 MPa. The temperature inside the furnace was measured by a bare W–5% Re/W–26% Re thermocouple. The furnace was equipped with an Eurotherm 414 thyristor powerpack and an Eurotherm 815 controller programmer to carry out the reactions at the desired temperatures and for desired durations. The graphite furnace was heated in a programmed manner e.g. from room temperature to 1000°C at 10°C/min, from 1000 to 1250°C at 5°C/min and finally from 1250°C to the desired temperature (e.g. 1550, 1600, 1650 and 1700°C) at 3°C/min while the reacting masses were soaked for 1 or 3 h, at the highest chosen temperatures. The product powders were removed and decarburised to get rid of excess unreacted carbon by heating in air at 700°C for 4 h.

To find the effect of heat on kaolin, it was heat treated at 1200 and 1500°C. XRD graphs of the products are presented in Fig. 2. It was observed that kaolin finally converts to mullite and cristoballite at high temperature (1500°C).

The products were subjected to X-ray diffraction (XRD) studies using CuKα radiation with nickel filters in a Rigaku X-ray Diffractometer (M/s Rigaku Corp., Japan) for phase analysis and to Scanning Electron Microscope (SEM) in a JSM-35 Scanning Electron Microscope (M/s JEOL, Japan) for morphological analysis of the products obtained.

3. Carbothermal reduction of kaolinite powders and selection of different reaction parameters

The overall chemical reaction of kaolinite with carbon (in an inert atmosphere such as argon) can be stated as follows.

$$\begin{aligned} Al_2O_3.2SiO_2.2H_2O + 6C \rightarrow {} & Al_2O_3 + 2SiC \\ & + 4CO + 2H_2O \end{aligned} \tag{1}$$

in which, silica part of the kaolinite would react with carbon to form SiC. The reaction of silica with carbon is known to proceed in the following two steps.

$$SiO_2(s) + C(S) \rightarrow SiO(g) + CO(g) \tag{2a}$$

$$SiO(g) + 2C(s) \rightarrow SiC(s) + CO(g) \tag{2b}$$

$$SiO_2 + 3C(s) \rightarrow SiC(s) + 2CO(g) \tag{2}$$

The standard free energy changes ($\Delta G^\circ{}_T$) and equilibrium constants (K_T) for the above reactions (2a), (2b) and (2) are now well characterised [8,9] and their values reproduced below.

Sl. No.	Reaction		Standard free energy changes (ΔG°) and equilibrium constants for the reactions at various temperatures			
		$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ in J mol^{-1}	$K_{1550^\circ C}$	$K_{1600^\circ C}$	$K_{1650^\circ C}$	$K_{1700^\circ C}$
1	Reaction 2a	$688354–344T$	0.02	0.06	0.19	0.56
2	Reaction 2b	$–132770 + 33.9T$	110.0	87.10	69.8	54.7
3	Overall reaction 2	$609023–351T$	7.60	22.10	60.9	159.4

From the changes of free energy values for the above reactions it could be seen that reactions (2a) and (2) are endothermic below 2000 and 1735 K, respectively, while reaction (2b) is spontaneous and exothermic at even much lower temperatures. Thus for the overall reaction to occur a minimum temperature of 1735 K (~1460°C) is required as per the thermodynamic criteria for formation of silicon carbide from silica.

The reaction (2b) which is a solid–vapour reaction is known to be responsible for the formation of SiC mostly in whisker form. The morphology and the extent of reaction could be controlled by optimising the various reaction parameters, e.g. C:SiO_2 ratio, temperature and duration of the reaction. Due to the gaseous nature of SiO, the experiments are carried out in a closed reaction chamber with a positive gas pressure of (0.15 MPa) of argon to minimise the loss of SiO gas from the crucibles. The reactions are carried out with loose powder mixtures with excess carbon for free whisker growth and completion of the reaction. Experiments were also carried out to find the effect of pelletisation of the reactants and the effect of catalyst on the reaction.

The ratio of carbon to silica and the intimacy of their mutual physical contact would obviously influence the reaction kinetics and the extent of formation of product mixtures of silicon carbide whiskers and alumina. In case of insufficient quantity of carbon at high temperatures the SiC formed could react with SiO_2 to form SiO and CO gas causing loss of SiC as claimed by Biernacki et al. [10]. Some earlier authors preferred to take C:SiO2 ratio stoichiometrically (3 mol of carbon per mol of silica) and increase their contact by pelletisation [5]. While this method has the advantage that the loss of SiO gas could be minimised, it however, might hinder extensive whisker growth. Sometimes the reactions might not be completed due to inhomogeneous distribution of carbon and the mineral in the compact at micro level. Some authors preferred the use of excess carbon (5.5 mol of carbon per mol of silica) for complete reaction along with space forming agent (e.g. NaCl) to create space for extensive whisker growth by the vaporisation of the latter (NaCl) at the high temperature of the reaction [11].

We preferred to carry out our experiments with excess carbon as was done in our earlier studies on carbothermal reduction of zircon and sillimanite [12,13]. In this study, we are presenting the effect of various parameters on carbothermal reduction of kaolinite.

4. Results and discussion

The product samples prepared under different conditions are designated by the following simple notations, e.g. KAC90A1650 denotes a sample derived from kaolinite (K) precursors containing 9 mol (90) of activated

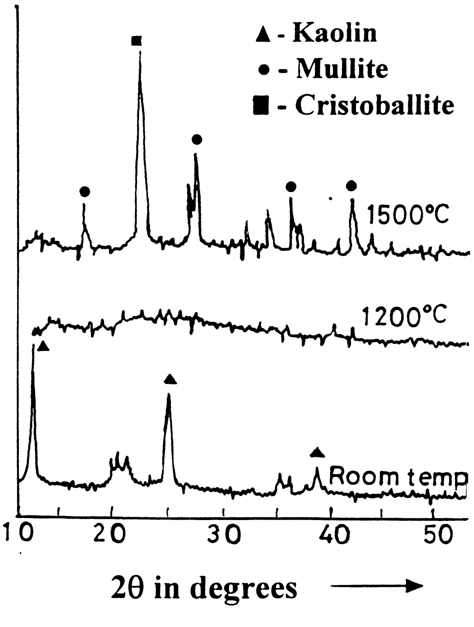


Fig. 2. XRD patterns of products obtained by beat treatment of kaolin at select high temperature.

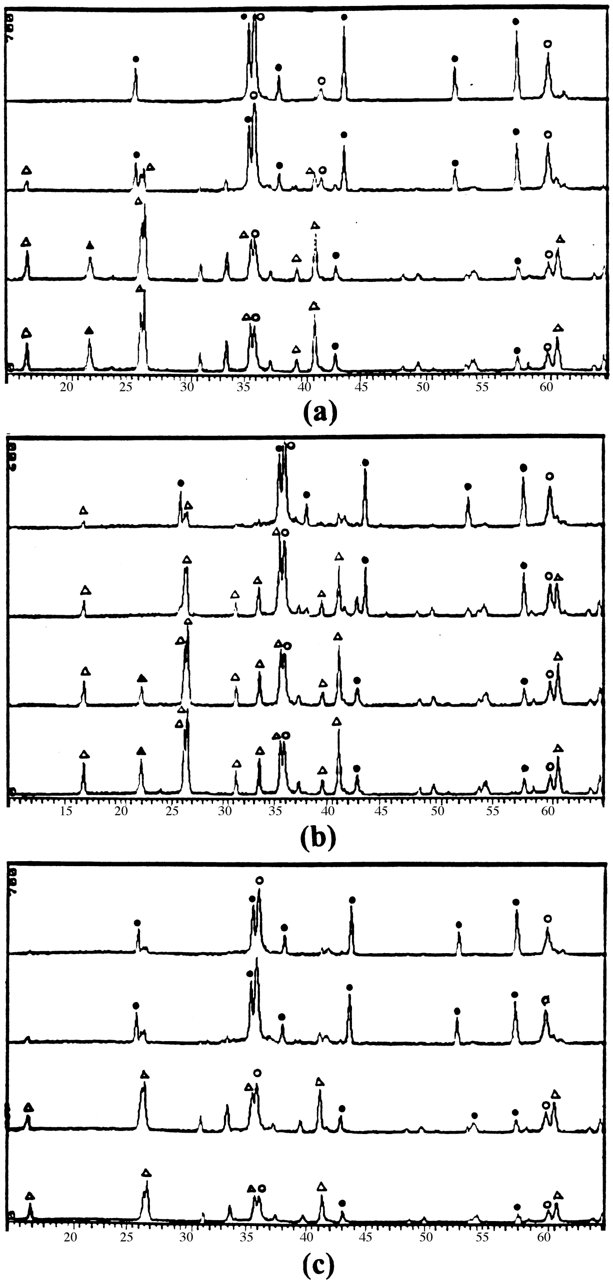


Fig. 3. (a)–(c). XRB patterns taken at 50°C intervals of the products obtained when (a) 4.5 (b) 5.5 (c) 9 mol ratios of activated charcoal are reacted between 1550°C (bottom trace) and 1700°C (top trace). (△) Mullite, (▲) cristoballite, (○) β-SiC (●), α-Al_2O_3.

charcoal (AC) per mol of silica (in the precursor) in argon (A) atmosphere at 1650°C for 1 h. Typical XRD patterns of the products obtained in argon atmosphere at 1650 and 1700°C using activated charcoal and carbon black of different mole ratios are presented in Fig. 3(a)–(c) and in Fig. 4(a)–(c) respectively. Since XRD patterns of all samples have been obtained taking a constant weight (100 mg) of the decarburised product, the peak height/intensity of the most intense non-overlapping peak of various species present in the product could be assumed to be representative of quantity of that particular species present in the product. Further the relative intensity of the most intense non-overlapping peaks of different species could also be assumed to be a measure of the extent of progress of carbothermic reaction under the given set of experimental conditions. Thus peaks at 43.3° of 2θ (d = 0.2085 nm) and 59.98° of 2θ (d = 0.1549 nm) were respectively taken as the representative (113) peak of α-Al_2O_3 and (220) peak of β-SiC for monitoring the progress of the carbothermal reactions. The qualitative XRD analysis of various products obtained for reaction durations of 1 and 3 h are presented in Tables 1 and 2 respectively.

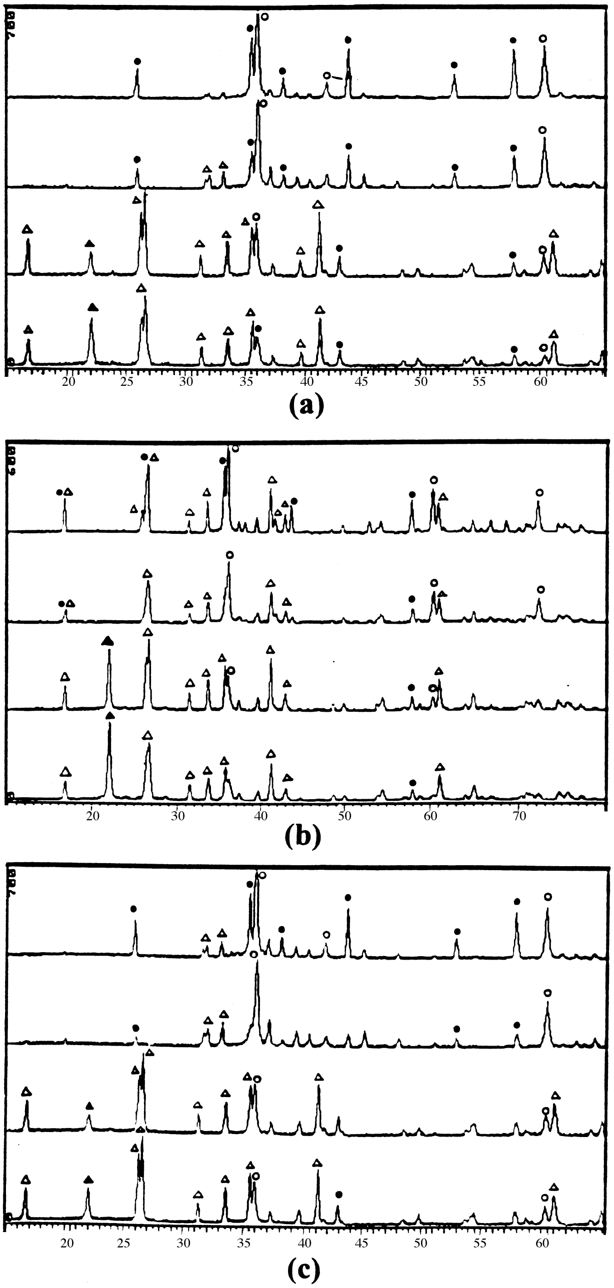


Fig. 4. (a)–(c). XRD patterns taken at 50°C intervals of the products obtained when (a) 4.5 (b) 5.5 (c) 9 mol ratios of carbon black are reacted between 1550°C (bottom trace) and 1700°C (top trace). (△) Mullite, (▲) cristoballite, (○) β-SiC, (●) α-Al_2O_3.

To broadly analyse the progress of the carbothermic reactions, plots of intensity of α-Al_2O_3 (113) and β-SiC (220) as a function of no. of mol of carbon and as a function of temperatures of reactions for cases of activated charcoal and carbon black were generated. To

Table 1
XRD results of various product phases obtained at different temperatures after 1 h reaction

Sl.no.	Reactants	C: SiO_2	Product phases (as analysed by XRD) at temperature			
			1550°C	1600°C	1650°C	1700°C
1	Kaolin + A. C.	4.5	M, C, S	M, C, S	M, A, S	A, S
		5.5	M, C, S	M, C, S	A, S, M	A, S, M
		9.0	M, S	M, S	A, S, M	A, S
2	Kaolin + C. B.	4.5	M, C, S	M, C, S	A, S, M	A, S
		5.5	M, C, S	M, C, S	A, S, M	A, S, M
		9.0	M, C, S	M, C, S	A, S, M	A, S

A. C. = activated charcoal.
C. B. = carbon black.
M = mullite.
S = β-silicon carbide.
C = cristoballite.
A = α-alumina.

Table 2
XRD results of various product phases obtained at different temperatures after 3 h reaction

Composition	1550°C	1600°C	1650°C
KAC55 loose	M, C, S	M, C, S	A, S
KAC55 pellet	M, S, A	M, S, A	A, S
KAC55 + 2% $FeCl_3$	M, A, S	M, C, A, S	A, S
KAC55 + 4% $FeCl_3$	M, A, S	M, A, S	A, S
KAC55 + 2% $COCl_3$	M, S	M, C, A, S	A, S
KAC55 + 4% $COCl_3$	M, A, S	M, A, S	A, S

M = mullite.
S = β-silicon carbide.
C = cristoballite.
A = β-alumina.

illustrate, the effect of carbon content on the reaction, graphs of intensity of β-SiC (220) of and α-Al_2O_3 (113) peaks vs no. of mol of carbon used for the reaction for different temperatures are presented in Fig. 5(a)–(c).

Typical SEM pictures of activated charcoal and carbon black used in the reaction are presented in Fig. 6 while that of typical final products are presented in Fig. 7.

The course of the reactions and the products formed at various stages could be followed through analysis of XRD patterns of products. XRD patterns of samples reacted at 1550 and 1600°C for 1 h contain peaks of mullite, cristoballite and β-SiC due to conversion of kaolinite to mullite and excess silica. A part of the excess silica converts to β-SiC while the rest remains in the form of cristoballite at low temperatures. The representative stoichiometric equations for the formation of above products could be represented as follows:

$$3(Al_2O_3.2SiO_2)(s) \rightarrow 3Al_2O_3.2SiO_2(s) + 4SiO_2(s) \qquad (3)$$

$$4SiO_2(s) + 12C(s) \rightarrow 4SiC(s) + 8CO(g) \qquad (4)$$

Note that Eq. (4) is the same as Eq. (2).

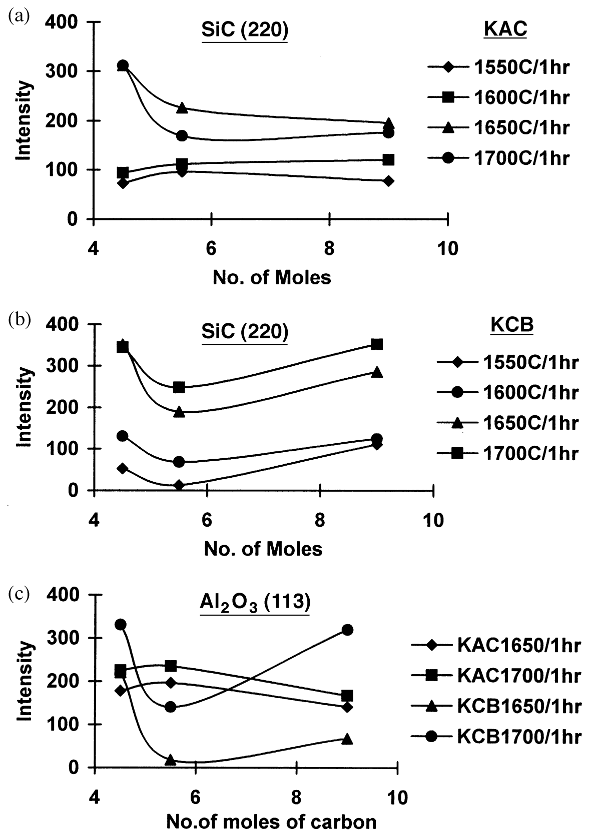


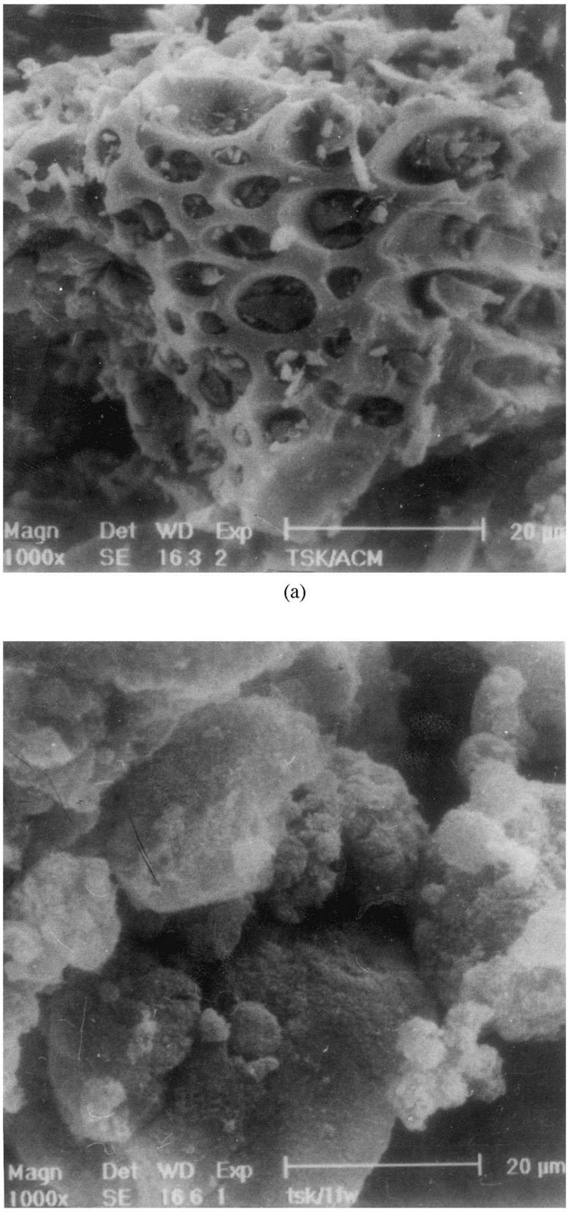
Fig. 5. (a)–(c). Intensity of XRD peaks of products vs mol ratios of carbon.

At 1650°C, from the presence of peaks of α-Al_2O_3 in the XRD patterns of the products, it is clear that the progress of reaction of mullite with carbon to form β-SiC and α-Al_2O_3 is as per the equation given below which justifies the disappearance of mullite content at higher temperatures.

$$3Al_2O_3.2SiO_2 + 6C \rightarrow 3Al_2O_3 + 2SiC + 4CO \qquad (5)$$

The overall reaction could be therefore represented as:

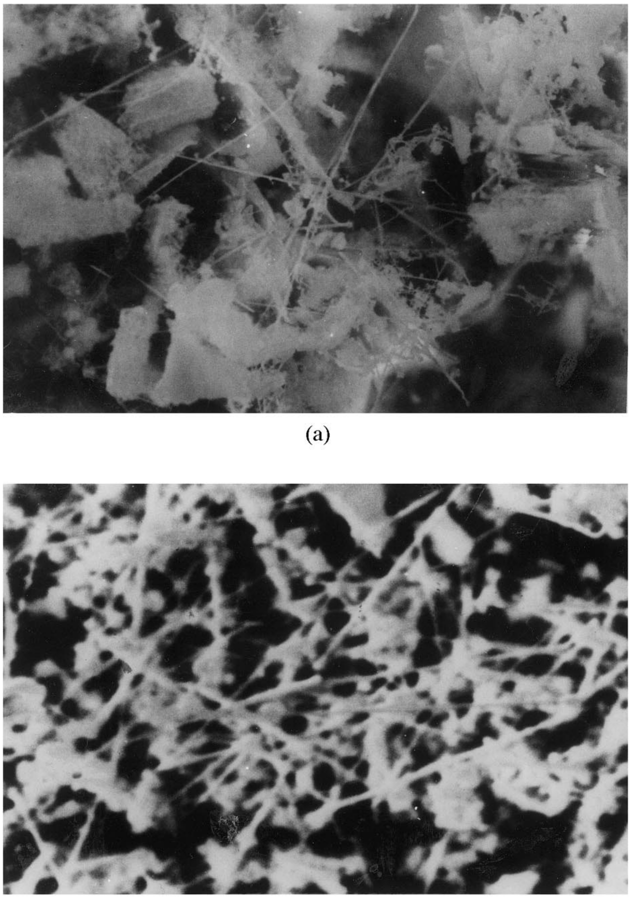
$$3(Al_2O_3.2SiO_2)(s) + 18C(s) \rightarrow 3Al_2O_3 + 6SiC + 12CO(g) \qquad (6)$$



(a)

(b)

Fig. 6. SEM micrographs of (a) activated charcoal and (b) carbon black used in the experiment.



(a)

(b)

Fig. 7. SEM micrographs of products obtained with (a) activated charcoal and (b) carbon black.

Note that Eq. (6) is the same as Eq. (1).

The free energy changes as well as the equilibrium constants for the reactions (3)–(6) could be calculated from the known free energy of formation [14] of the constituent components involved in these reactions. The values are given below.

Sl. no.	Reaction	Standard free energy change (ΔG°_T) and equilibrium constant (K_T) of reactions at various temperatures					
		$\Delta G^\circ_T = \Delta H^\circ_T - T\Delta S^\circ_T$ (in J mol^{-1})					
		$\Delta G^\circ_{1800\,K}$	$\Delta G^\circ_{1900\,K}$	$\Delta G^\circ_{2000\,K}$	$K_{1800\,K}$	$K_{1900\,K}$	$K_{2000\,K}$
1	Reaction 3	−1,84,300	−1,83,400	−1,77,700	2.13×10^5	1.06×10^5	4.2×10^4
2	Reaction 4	−4,000	−35,000	−66,600	1.31	9.09	52.17
3	Reaction 5	−5,500	−22,900	−39,000	1.44	4.24	10.35
4	Reaction 6	−65,100	−80,300	−94,600	76.40	158.30	289.50

The thermodynamic data for reactions (3)–(6) show clearly that the reactions are all exothermic and progress considerably as the temperatures are increased.

From Table 2, it can be seen that the reactions are complete for samples reacted at 1650°C for 3 h in all the cases. At 1600°C, cristoballite phase is present in samples taken in loose powder form containing 2% of $FeCl_3$ and $CoCl_2$. However, cristoballite is absent in the samples which are pelletised and in samples containing 4% of $FeCl_3$ and $CoCl_2$. At 1550°C, cristoballite is present only in the case of the sample reacted in the form of loose powder. This shows the rate of reaction is high either with addition of catalyst or with pelletisation. It is due to close contact of reactants in case of pelletisation and facility of formation of SiC whiskers due to VLS mechanism in case of samples containing catalysts.

The reappearance of cristoballite at 1600°C in samples taken as loose powder and containing less of catalysts is ascribed to the slow reaction rate for mullitisation and its decomposition to yield silica [15].

At 1700°C, the reactions are found to be complete except in the case of 5.5 mol where it is nearly complete due to reasons given in the subsequent section.

5. Effect of nature and amount of carbon

From Table 1, it is observed that the intensity of cristoballite decreases with increase in carbon content for both activated charcoal and carbon black. Hence, it is concluded that higher mole ratios of carbon increases the reaction rate. The samples reacted with 9 mol ratio of activated charcoal show absence of cristoballite peaks at 1550 and 1600°C while the corresponding samples containing carbon black show presence of cristoballite. It can be concluded that activated charcoal is more reactive than carbon black due to high surface area. In case of carbon black reacted samples. appreciable increase in intensity of Al_2O_3 and SiC at 1700°C was observed compared to that at 1650°C. However, there is only marginal increase in intensity in case of activated charcoal reacted samples. The reason could be ascribed to the high reactivity of activated charcoal which reacts further with Al_2O_3 and SiC leading to formation of $Al_4C_3.Al_4SiC_4$, etc., as per the equation given below.

$$2Al_2O_3 + 9C \rightarrow Al_4C_3 + 6CO \tag{7}$$

$$2Al_2O_3 + SiC + 9C \rightarrow Al_4SiC_4 + 6CO \tag{8}$$

In the cases of both activated charcoal and carbon black, the reaction is complete for 4.5 and 9 mol ratios. It is nearly complete (presence of small peaks of mullite) for 5.5 mol ratios owing to the inhomogenity of mixing at micro level.

6. Conclusion

It is concluded that carbothermal reduction of kaolin in argon produces Al_2O_3–SiC(w) composite powder. The rate of reaction is more for activated charcoal with higher surface area, high carbon ratios, longer soaking period. However morphology of whiskers and the extent of whiskerisation is better for carbon black reacted samples.

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