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Preparation of ceramic composite powders from waste colliery minestones

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An investigation was carried out to examine the potential for producing ceramic composites from waste colliery minestones. The nature of the raw materials had a marked influence on the kinetics and the product morphology. The product phases and product composition were dependent on the reaction temperature. Mullite–SiC composite powders could be formed at temperatures below 1300 °C while Al_2O_3–SiC was the final product of reduction at higher temperatures.

1. Introduction

Minerals which are associated with coal and are a by-product of coal-mining are known as colliery minestones. Large quantities of minestones are produced all over the world, most of which are deposited in landfill sites or discarded into the sea. Natural mineral resources are thus not only wasted, but also cause environmental problems. In recent years concern for the environment has increased and it would not be surprising if, for example within the European Community, governments were to enforce strict limitations on the discarding of minestones. It is therefore important to examine ways of recycling colliery minestones, as their composition makes them suitable raw materials for the production of ceramic composites based on Al_2O_3–SiC which is the subject of the investigation described here. Such composites have found uses as cutting tool materials.

The study of the production of ceramic powders and their sintering behaviour from low-cost aluminosilicate minerals or waste materials and their sintering behaviour has been the subject of a number of previous investigations. Lee and Cutler [1] showed that it is possible to prepare SiC using rice hulls as the raw material, as they contain SiO_2 and cellulose which acts as a source of carbon. It was shown that small amounts of iron had a catalytic effect on the reaction.

Subsequent studies [2–4] have led to a well-established process as well as a patent [5]. A similar investigation by Patel and Kumari [6] who used sugar-cane leaf and rice straw as raw materials led to the formation of SiC particles and whiskers. Sialon ceramics have also been obtained by carbothermic reduction of natural minerals like kaolinite and mullite under a nitrogen atmosphere [7–9]. The mechanical strength of densified sialon powders obtained from natural minerals showed a strong dependency on the nature of the raw material and the impurities present [9].

2. Experimental procedure

All reduction experiments were conducted in a horizontal tube furnace under a high-purity flowing argon atmosphere. The extent of reaction was monitored by measuring the weight loss of samples at specific intervals. All samples were reacted in the form of loose powder except in those cases where the effect of pre-compaction was examined. Raw material and product characterization was carried out by means of differential scanning calorimetry (DSC), X-ray diffraction (XRD) using CuK_{α_1} radiation, optical microscopy, and scanning electron microscopy (SEM) on a Jeol 6400.

Two kinds of minestones which were supplied by the British Coal Corporation were chosen for this study. They were both clay minestones which belonged to the kaolin group with kaolinite, $Al_2Si_2O_5(OH)_4$, being the major phase present as verified by XRD analysis. They also contained amounts of SiO_2 in the form of quartz and minor constituents like K_2O, MgO, Fe_2O_3 and TiO_2. The chemical compositions of the two minestones, M and N, are listed in Table I. A comparison of XRD peaks indicated that minestone M contained a greater ratio of $Al_2Si_2O_5(OH)_4$ to SiO_2 than minestone N. In Table II are presented results of the percentage weight loss on ignition in air at various temperatures as obtained by heat-treatment in a muffle furnace. Minestone M contained 25% carbon in the amorphous state which acted as the reducing agent. The weight loss of 45.4% in air at 1100 °C for this minestone accounted for carbon and water as well as other volatiles. It was deduced that the content of water and other volatiles was 20.4%. For the complete reduction/carburization of minestone M, a weight loss of 47.1% was expected.

Fig. 1 shows a typical micrograph of minestone M. It clearly shows particles or narrow seams of carbon embedded in a kaolinite particle. Minestone N con-

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TABLE I Minestone chemical composition

Minestone	Composition (wt %)							
	SiO_2	Al_2O_3	Fe_2O_3	K_2O	TiO_2	MgO	C	Moisture content
M	28.59	19.88	1.97	2.48	0.39	0.76	25	20.4
N	51.35	29.85	2.84	2.31	0.98	0.89	–	12.55

TABLE II Weight loss on ignition

Minestone	Weight loss (%)		
	200 °C	700 °C	1100 °C
Minestone M	5.31	45.38	45.35
Minestone N	2.84	12.06	12.55

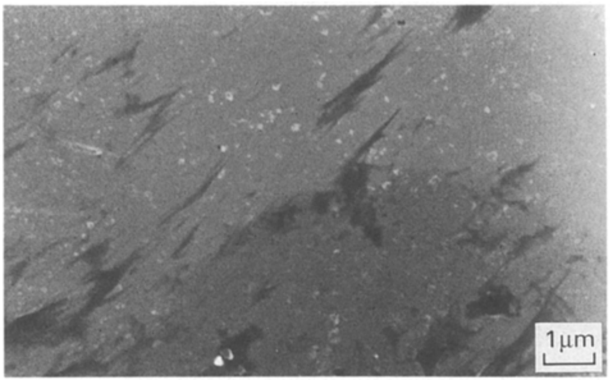

Figure 1 Micrograph of minestone M showing carbon embedded in a kaolinite particle.

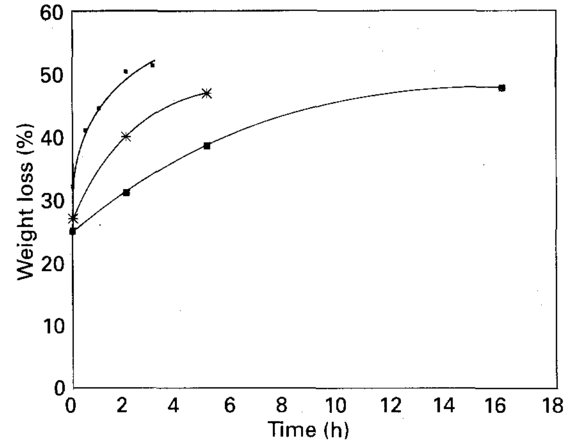

Figure 2 Plot of percentage weight loss with time for the reduction of minestone M at various temperatures: (■) 1300 °C, (*) 1400 °C, (□) 1450 °C.

tained no carbon so carbon black was added to it as a reducing agent. The required weight loss for complete carburization of a minestone N–carbon black (in a small excess) mixture was calculated to be around 46%.

3. Results

3.1. Carbothermic reduction of minestone M

A plot of percentage weight loss with time for the reduction of minestone M in the form of loose powder at various temperatures is presented in Fig. 2. Preliminary experiments had earlier shown that pre-compaction had no effect on the kinetics of reaction. A combination of DSC and XRD studies indicated that several changes occurred prior to the carbothermic reduction of the material. From the DSC data a small endothermic peak at about 100 °C was caused by the evolution of adsorbed water. The main endothermic peak occurred at about 600 °C and corresponded to the decomposition of kaolinite to metakaolin, $Al_2O_3{\cdot}2SiO_2$, and the elimination of the hydroxide group as water, according to the reaction

$$Al_2Si_2O_5(OH)_4 \rightarrow Al_2O_3{\cdot}2SiO_2 + 2H_2O$$

An exothermic reaction was observed at around 1000 °C and from XRD data this was attributed to the decomposition of metakaolin to mullite, $3Al_2O_3{\cdot}2SiO_2$ and quartz as shown by the equation

$$3(Al_2O_3{\cdot}2SiO_2) \rightarrow 3Al_2O_3{\cdot}2SiO_2 + 4SiO_2$$

This observation appears to be in contrast to earlier work by Brindley and Nakahira [10] who have claimed a reaction sequence leading to a spinel phase ($2Al_2O_3{\cdot}3SiO_2$) at 925 °C followed by pseudo-mullite at 1100 °C and finally mullite at 1400 °C. During the present study quartz was observed to transform to cristobalite at 1400 °C. The minimum temperature for the reduction of this minestone was about 1250 °C. Only SiO_2 could be reduced at this temperature, however, while for the reduction of mullite a temperature of at least 1300 °C was required. From mass balance calculations, reduction of all the free SiO_2 corresponded to a weight loss of 39.4%. Both of these temperatures of reduction were lower than those predicted by the available thermodynamic data [11]. As expected, SiO_2 (being thermodynamically less stable than mullite) could be reduced at a lower temperature.

The final products at and above 1300 °C consisted of β-SiC and Al_2O_3, while between 1250 and 1300 °C a weight loss of only about 40% was recorded and the products were β-SiC and mullite. At 1450 °C the reaction was complete after about 3 h while 5 h were required at 1400 °C. The rate of the reaction at 1300 °C was much slower and the reaction needed about 16 h for completion.

Two types of SiC grains were detected as a result of observations from micrographs obtained by SEM. SiC which was formed by the reduction of mullite had a strong association with Al_2O_3 in the product microstructure. This is evident in Fig. 3, which shows a particle obtained at 1450 °C the outer part of which is

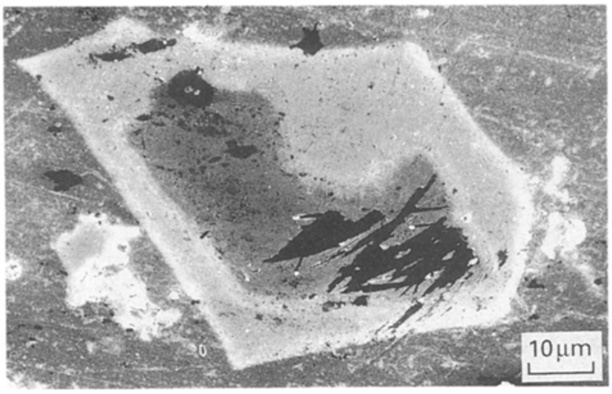

Figure 3 Particle obtained by reduction of minestone M at 1450 °C, showing SiC at the periphery and a core of Al_2O_3 containing unreacted carbon.

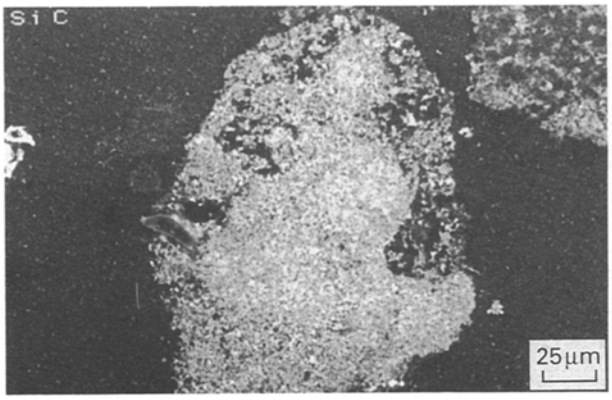

Figure 4 SiC particle obtained by reduction of minestone M at 1450 °C.

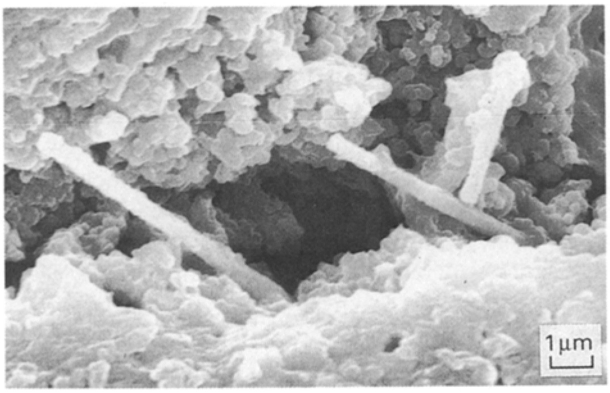

Figure 5 SiC whiskers produced by reduction of minestone M at 1450 °C.

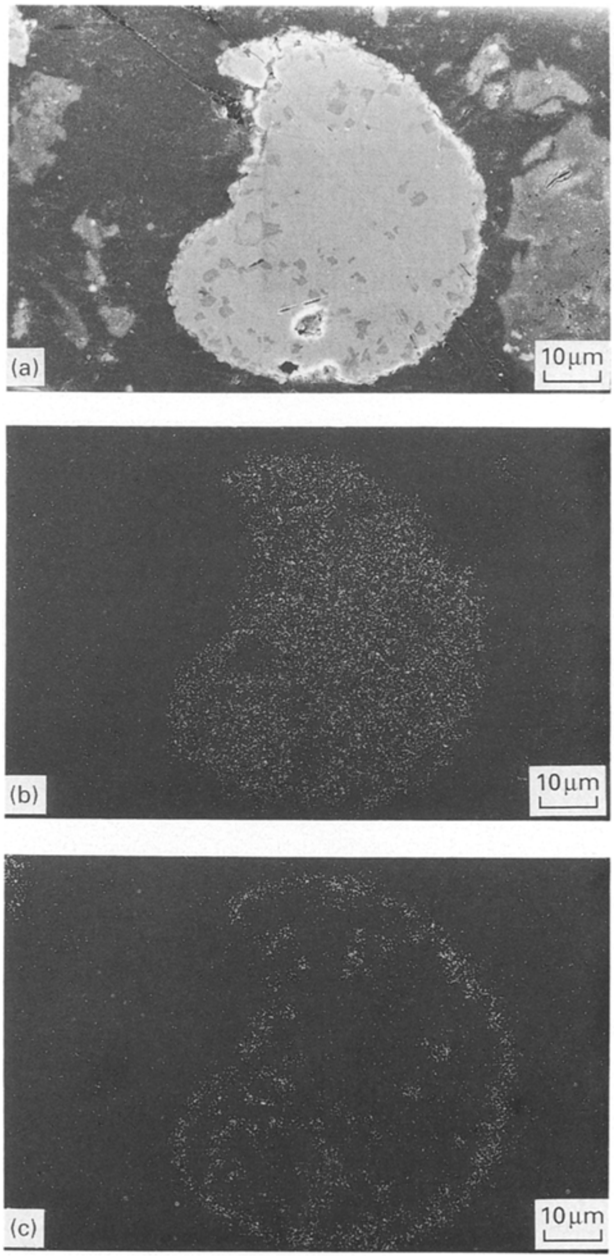

Figure 6 (a) Metallic iron grain containing TiC or Ti(O, C) produced at 1450 °C from minestone M, (b) elemental distribution map for Fe, (c) elemental distribution map for Ti.

SiC, while the core is Al_2O_3 containing unreacted carbon. Some free SiC particles were also present which were produced from the free SiO_2 in the raw material (Fig. 4). In addition some SiC whisker formation was also observed at 1450 °C (Fig. 5). The whiskers had a diameter of about 0.5 µm and an average length of about 10 µm. There was no evidence of SiC whisker growth at other temperatures.

According to the XRD results, metallic Fe (formed by the carbothermic reduction of Fe_2O_3) was among the product phases. Fig. 6a presents an iron grain produced at 1450 °C as deduced from the elemental distribution map for iron in Fig. 6b. Similar mapping for titanium in Fig. 6c shows areas of high titanium concentration within this grain. It is quite likely that titanium is in the form of TiC or Ti(O, C) which were produced by reduction of TiO_2 with carbon.

3.2. Carbothermic reduction of minestone N

Minestone N and carbon black were reacted at 1450 °C in the ratio of 1:0.4 compared to the theoretical 1:0.35. This ratio was chosen as the optimum by varying the amount of carbon black in the starting material and comparing the reaction rate. At ratios lower than 1:0.4 the kinetics of the reaction are slower, while little effect was observed above this value. The weight loss with time at 1450 °C is presented in Fig. 7. A maximum weight loss of about 46% resulted after 7 h, indicating completion of the reaction. As with minestone M, kaolinite was initially

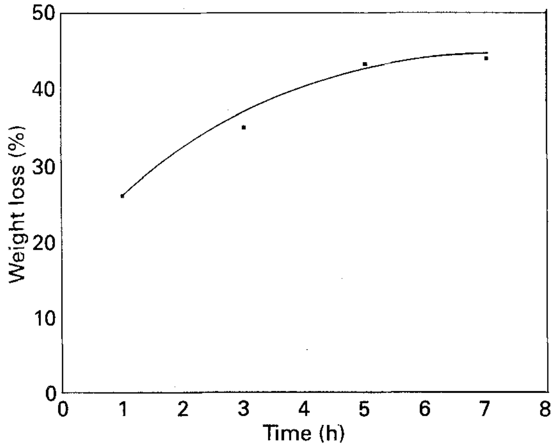

Figure 7 Percentage weight loss with time plot for minestone N at 1450 °C.

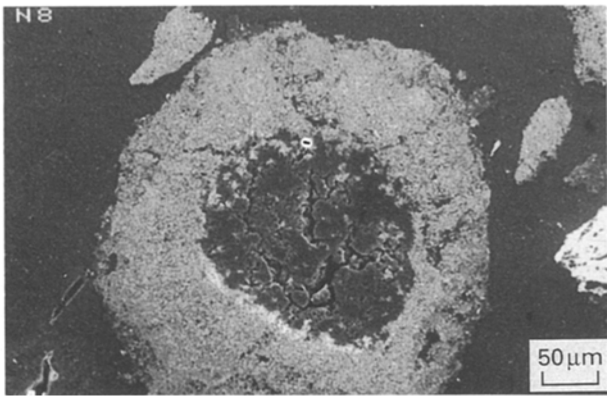

Figure 8 SiC particle formed around carbon black from the carbothermic reduction of minestone N at 1450 °C.

observed to decompose to metakaolin which subsequently transformed to mullite. Reduction of SiO_2 by carbon black was observed at temperatures above 1250 °C, while reduction of mullite was possible only at temperatures exceeding 1300 °C.

The product morphology obtained from minestone N was in marked contrast to that produced from M. The main difference was the observation of a significant number of SiC particles which were totally free from Al_2O_3, formed in some cases around a core of carbon black. A typical such microstructure is shown in Fig. 8. In all respects other than the product microstructure the two minestones behaved the same way.

4. Discussion

The effect of heat on pure kaolinite has attracted a great deal of attention over the years [12–14]. It is generally accepted [10] that kaolinite transforms to metakaolinite and water at about 450 °C by the reaction

$$Al_2Si_2O_5(OH)_4 \rightarrow Al_2O_3{\cdot}2SiO_2 + 2H_2O$$

However, the changes which occur at higher temperatures have been a matter of dispute. The most comprehensive study was carried out by Brindley and Nakahira [10] who described the entire heating process by the following chemical reactions:

$$\underset{\text{metakaolin}}{2(Al_2O_3{\cdot}2SiO_2)} \xrightarrow{925\,^\circ C} \underset{\text{silicon spinel}}{2Al_2O_3{\cdot}3SiO_2} + SiO_2$$

$$\underset{\text{silicon spinel}}{2Al_2O_3{\cdot}3SiO_2} \xrightarrow{1100\,^\circ C} \underset{\text{pseudo-mullite}}{2(Al_2O_3{\cdot}SiO_2)} + SiO_2$$

$$\underset{\text{pseudo-mullite}}{3(Al_2O_3{\cdot}SiO_2)} \xrightarrow{1400\,^\circ C} \underset{\text{mullite}}{3Al_2O_3{\cdot}2SiO_2} + SiO_2$$

However, during the present investigation metakaolin was observed to transform directly to mullite and SiO_2 at about 1000 °C without the formation of these intermediate phases. The contrast between these results may be due to the fact that Brindley and Nakahira [10] used pure kaolinite for their studies whereas the minestones used in the present study also contain substantial amounts of other oxides. Evidence of this has been provided by Glass [15] who emphasized the effect of impurities on the high-temperature transformations involving metakaolin and mullite. Moreover, Johns [16] has reported the importance of the degree of crystallinity of kaolinite by observing that well-crystallized kaolinite can develop mullite at a faster rate and at lower temperatures.

The overall reaction between SiO_2 and carbon can be expressed by the equation,

$$SiO_{2(s)} + 3C_{\text{graphite}} \rightarrow SiC_{(s)} + 2CO_{(g)} \qquad (1)$$

By using thermodynamic data as compiled by Turkdogan [11], the free energy for Reaction 1 is

$$\Delta G^\circ = 552\,000 - 310T \quad \text{J g-mol}^{-1}$$

and the minimum temperature for reaction is 1781 K or 1508 °C. The fact that the reaction was achieved at temperatures as low as 1250 °C is due to the high reducing ability of the coal contained in minestone M and of carbon black as compared to pure graphite. Both are metastable forms of carbon, which means that they are likely to be more reactive than graphite.

XRD data have established that SiO_2 and mullite are present in both minestones before reduction begins. The reaction between mullite and carbon can be described by the equation

$$\tfrac{1}{2}(3Al_2O_3{\cdot}2SiO_2)_{(s)} + 3C_{\text{graphite}} \longrightarrow$$
$$1\tfrac{1}{2}Al_2O_{3(s)} + SiC_{(s)} + 2CO_{(g)} \qquad (2)$$

The standard Gibbs free energy for this reaction is

$$\Delta G^\circ = 599\,705 - 330T \quad \text{J g-mol}^{-1}$$

indicating that under equilibrium conditions and when standard phases are used, the minimum reaction temperature is 1817 K or 1544 °C. Mullite is therefore more stable than SiO_2 and it requires higher temperatures for reduction to occur. This explains why below 1300 °C no mullite was reduced, but remained as one of the product phases. A choice of final products is therefore available; between 1250 and 1300 °C SiC and mullite can be formed, while at higher temperatures

SiC and Al_2O_3 are obtained. A greater than anticipated weight loss was recorded at temperatures exceeding 1500 °C. This was associated with the fact that some gaseous SiO which forms by the reaction

$$SiO_{2(s)} + C \rightarrow SiO_{(g)} + CO_{(g)} \qquad (3)$$

$$\Delta G^\circ = 688\,354 - 344T \quad \mathrm{J\,g\text{-}mol^{-1}}$$

escapes. The equilibrium constant for Reaction 3 is given by

$$K = p_{SiO}\, p_{CO}$$

and as the temperature increases a greater pressure of SiO is expected. During experiments at temperatures above 1500 °C small amounts of SiO_2 deposits were obtained on the inner furnace walls further away from the hot zone. This is likely to be the result of Reaction 3 becoming reversible at lower temperatures as SiO and CO travel to the lower-temperature zones in the furnace. Loss of silicon in the form of SiO is also one of the problems associated with the production of SiC by the Acheson process [17]. Some whisker growth was observed at 1450 °C from minestone M. This appears to be related to the reactivity of carbon and the supersaturation of SiO, as explained elsewhere [18].

Since the main phases present in the two minestones are the same, that is kaolinite and quartz, it is reasonable to assume that there will be little or no difference between their product morphologies. However, SEM has revealed a marked contrast in the microstructure of SiC produced from the two minestones. The reason for this observation is related to the nature of both the SiO_2 in the raw material and the reducing agent used. SiC obtained by reduction of minestone M tended to form around Al_2O_3 particles containing carbon as shown in Fig. 3. It must be stressed that this minestone in its raw state contained very little unbonded SiO_2. Therefore most of the SiO_2 which was present just prior to reaction was formed from the decomposition reactions of kaolinite and metakaolinite. The result of this is to create grains where mullite, SiO_2 and carbon are all present, leading to reaction within the grains, thereby establishing an association between SiC and Al_2O_3 in the final product. In addition to this the reduction of mullite by Reaction 2 will also result in composite grains of SiC and Al_2O_3. SiC is formed by reaction of SiO with carbon. This reaction takes place within the mullite particles since they contain carbon. As the SiO_2 content of mullite is gradually consumed, Al_2O_3 and unreacted carbon are left in the centre of these particles while SiC has formed around them. This unusual product microstructure is very interesting as it is likely to have a unique set of properties. Some free SiC particles were observed, but these occurred less frequently. The presence of carbon within the oxide grains suggests that shorter diffusion distances were required by the reducing agent and this may be partly responsible for the faster rate of reaction for minestone M than for N. In contrast to the product microstructure for minestone M, SiC formed from minestone N generally forms around carbon black. In this case contact between mullite and carbon black exists on the external surface of grains. As a result gaseous SiO has to diffuse out of them to encounter carbon black to form SiC. An SiC layer is thus produced around carbon black, resulting in a type of microstructure where SiC and Al_2O_3 are found separate from each other.

Minestone M is reduced faster than N in spite of the fact that it contains a greater mullite to quartz ratio. This can be attributed to the nature of the carbon in the minestone, which is probably also more reactive than carbon black.

One of the main concerns of this investigation was the behaviour of other oxides during reaction. It is almost impossible to examine the individual effect of each oxide because a large number of them were present. On examination of XRD patterns of reacted samples the only significant peaks other than SiC and Al_2O_3 were due to iron. This appears in all samples for both minestones. Iron was concluded to form by the reduction of Fe_2O_3 with carbon which can occur at much lower temperatures than the reduction of SiO_2. The easier than expected reducibility of the raw material may be aided by the catalytic effect of iron [1]. Perhaps surprisingly, impurities had no effect in nucleating SiC whiskers as observed in a previous study [18]. The reduction of TiO_2 is expected to produce TiC or a Ti(O, C) solid solution. Since both of these are known to be wetted by iron [19] they are observed to be associated with it in the microstructure. The alkali oxides are likely to be reduced at the processing temperatures with gaseous evolution of sodium and potassium. On the other hand the alkaline earth oxides CaO and MgO are thermodynamically stable at these temperatures and will not be reduced by carbon. Their presence may be beneficial as they are expected to promote the densification of these materials during sintering.

Reaction 1 is initiated by a solid–solid reaction and therefore compaction was expected to increase the contact between solid particles and favour the kinetics. However, it was observed that for minestone M, compaction only had a minor effect with regard to the reaction rate. The reason for this must be related to the already intimate mixing between the oxide minerals and carbon in the raw material, meaning that compaction will offer very little assistance in bringing the solid particles closer together. The high content of volatiles also plays an important part, the evolution of which results in the break-up of a compacted sample anyway. Very little effect can therefore be expected by compaction of the raw material. When pure SiO_2 and Al_2O_3 which contained no volatiles were mixed with carbon black, compaction increased the reaction rate at 1450 °C by 2.5 times. This provides further evidence in support of the above statements.

5. Conclusions

The investigation showed that it is possible to produce composite ceramic powders by the carbothermic reduction of waste materials like colliery minestone tailings. The maximum extent of reduction was related to the processing temperature. As a result, between 1250 and 1300 °C it is possible to produce composite powders of mullite SiC while above 1300 °C Al_2O_3–SiC can be formed. The kaolinite transformation to metakaolin which subsequently transformed to mullite and SiO_2 preceded the carbothermic reaction. Reduction then followed by reaction of carbon with SiO_2 and then mullite. Due to the nature of the raw materials, the product components from minestone M are in intimate contact with each other, producing a unique microstructure with SiC being formed around Al_2O_3. Minestone N produced a morphology where SiC and Al_2O_3 were formed separate from each other. Compaction had very little influence on the kinetics of the reduction of minestone M. This was due to its volatile content which had the effect of breaking up the compacted powder. The presence of iron as an impurity product from Fe_2O_3 was thought to have a catalytic effect on the reaction.

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References

1. J. LEE and I. B. CUTLER, *Ceram. Bull.* **54** (1975) 195.
2. N. K. SHARMA, S. WILLIAMS and A. ZANGUWILL, *J. Amer. Ceram. Soc.* **67** (1984) 715.
3. J. V. MILEWSKI, P. D. GAC, J. J. PETROVIC and S. R. SKAGGS, *J. Mater. Sci.* **20** (1985) 1160.
4. M. PATEL, C. B. RAJU, A. K. RAY and A. KARERA, Indian Patent INF/91/85 Pat. (1985).
5. M. PATEL and A. KARERA, *J. Mater. Sci. Lett.* **8** (1989) 955.
6. *Idem, ibid.* 9 (1990) 375.
7. Y. BIGAY, B. CALES and J. P. TORRE, in "Technical Ceramics", edited by H. Nosbusch and I. V. Mitchell (Elsevier, New York, 1988) p. 51.
8. F. L. RILEY and H. MOSTAGHACI, *ibid.* p. 65.
9. H. Le DOUSSAL, *ibid.* p. 59.
10. G. W. BRINDLEY and M. NAKAHIRA, *J. Amer. Ceram. Soc.* **42**, (1959) 319.
11. E. T. TURKDOGAN, "Physical Chemistry of High Temperature Technology" (Academic, New York, 1980) p. 5.
12. G. W. BRINDLEY and M. NAKAHIRA, *J. Amer. Ceram. Soc.* **42** (1959) 314.
13. J. F. HYSLOP and H. P. ROOKSBY, *Trans. Ceram. Soc.* **27** (1928) 93.
14. H. HINSLEY and R. H. EWELL, *J. Res. Natl Bur. Stand.* **14** (1935) 615.
15. H. D. GLASS, *Amer. Mineralogist* **39** (1954) 193.
16. W. D. JOHNS, *Mineral Mag.* **30** (1953) 186.
17. J. W. EVANS and L. C. De JONGHE, "The Production of Inorganic Materials", (Macmillan, New York, 1991) p. 382.
18. A. CHRYSANTHOU, P. GRIEVESON and A. JHA, *J. Mater. Sci.* **26**, (1991) 3463.
19. B. S. TERRY and O. S. CHINYAMAKOBVU, *Mater. Sci. Technol.* **8** (1992) 399.

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