Synthesis of Al_2O_3-SiC-ZrO_2 from kaolinite and zircon

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ABSTRACT

Advanced ceramic composites, based on alumina and silicon carbide have been synthesized by carbothermal reactions from inexpensive precursor materials such as kaolinite. Zircon is introduced as part of a ceramic composite to increase fracture toughness. The Al_2O_3-SiC-ZrO_2 powder could not be obtained directly by the carbothermal reaction due to zirconium carbide formation. A subsequent oxidation step to transform ZrC into ZrO_2 is needed. Very fine particles of ZrC formed during synthesis favour formation of tetragonal zirconia phase in the oxidation step which contributes to improve the fracture toughness. In contrast, coarse ZrC particles derive monoclinic ZrO_2 when oxidized. Formation of a passive layer which hinders ZrC oxidation is described. Studies have been focused in developing processes which help progress oxidation to obtain a mixture of tetragonal and monoclinic zirconia in the composite.

INTRODUCTION

Ceramic-ceramic composites have shown considerable improvement in the strength and fracture toughness with introducing of zirconia. Such studies have led to the belief that ceramic-ceramic composites are the best materials for high temperature structural applications, such as in automobiles, cutting tool bits, pump and valve components, seals, etc. One group of such composites are based on alumina (Al_2O_3) and silicon carbide (SiC) whiskers, which are very expensive (~$ 200/kg), not easily available and also considered to be carcinogenic.
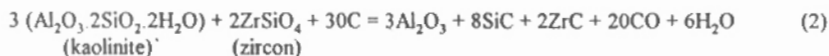
In a recent publication, Chaklader and his co-workers (1,2) have shown that advanced ceramic composites, based on alumina and SiC, can be synthesized by carbothermal reactions from cheap precursor materials such as kaolinite, kyanite, pyrophyllite, etc. Zirconia (ZrO_2) can also be introduced as part of the composite increasing fracture toughness.

In an initial approach, it was thought that zircon ($ZrSiO_4$), which is a common Zr mineral, could be introduced in the carbothermal reaction to form zirconia in the composite matrix. However, preliminary tests have shown that Al_2O_3-SiC-ZrO_2 cannot be obtained directly from carbon, kaolinite and zircon reaction. Formation of Al_2O_3-SiC-ZrC is always resulted in an inert atmosphere. A further oxidation step is necessary to transform ZrC into ZrO_2 (3,4) Reactions involved in the carbothermal process are derived and expressed by the following equations:

To obtain Al_2O_3-SiC

$$Al_2O_3.2SiO_2\ 2H_2O + 6C = Al_2O_3 + 2SiC + 4CO + 2H_2O \tag{1}$$
$$\text{(kaolinite)}$$

To obtain Al_2O_3-SiC-ZrC

$$3\ (Al_2O_3.2SiO_2.2H_2O) + 2ZrSiO_4 + 30C = 3Al_2O_3 + 8SiC + 2ZrC + 20CO + 6H_2O \tag{2}$$
$$\text{(kaolinite)}` \qquad \text{(zircon)}$$

Volatile silicon monoxide is an intermediate phase for SiC formation. Reaction of this gaseous phase with carbon produces silicon carbide according to the equation (3). The availability of SiO in the system is a parameter difficult to control. Part of forming carbon monoxide reduces more silica and part is lost in the fumes (5).

$$SiO\ (g) + 2C = SiC + CO\ (g) \tag{3}$$

Stoichiometric amounts of reactants as shown in equation (2) produce a composite with 37 wt% Al_2O_3, 38 wt% SiC and 25 wt% ZrC. However, this reaction assumes that SiO is not lost from the system.

This work presents results of an experimental investigation to synthesize Al_2O_3-SiC-ZrO_2 composite from kaolinite and zircon and a brief discussion about the relevant thermodynamic concepts related to carbothermal reactions.

EXPERIMENTAL PROGRAMME

Mixtures of zircon, kaolinite (Table I) and lamp black carbon were ground for 5 hours in a ceramic (porcelain) ball mill resulting in a homogeneous powder as fine as 1 μm. Around 32 g of the mixture were used to prepare pellets with diameter of 50.7 mm under a pressure of 6.4 kgf/mm^2. All pellets were put in a graphite crucible and heated in an induction vertical furnace which has operated with a maximum power of 13 kW, in an argon atmosphere. Temperatures used for synthesis ranged from 1460°C to 1600°C with different residence time (120, 150 and 180 min) in the induction furnace.

Table 1 - Chemical composition of kaolinite and zircon

Substance	Kaolinite (wt%)	Zircon (wt%)
Al_2O_3	38.74	0.01
SiO_2	44.54	33.76
CaO	0.19	0.03
Fe_2O_3	0.52	0.01
MgO	0.05	0.01
K_2O	0.16	0.01
Na_2O	0.05	0.01
P_2O_5	0.12	0.11
TiO_2	1.63	0.11
MnO	-	0.03
Ba	-	0.01
ZrO_2	-	65.23
H_2O	14.0	-

RESULTS AND DISCUSSION

Carbothermal Synthesis

The firing conditions were varied to determine the reaction steps to form Al_2O_3, SiC and ZrC composite. Table II shows the phases obtained with stoichiometric amounts of each reactant (51.6 wt% kaolinite, 24.4 wt% zircon, 24 wt% carbon).

Transformation of kaolinite ($Al_2O_3.2SiO_2.2H_2O$) into mullite ($3Al_2O_3.2SiO_2$), free silica (SiO_2) and subsequently gaseous SiO formation are assumed as the first step occurring at temperatures higher than 1300°C (6). At this temperature level, gaseous SiO reacts with carbon producing silicon carbide (SiC). Zircon is also transformed into zirconia at the same temperature range as observed by the presence of mullite and zirconia. The following intermediate reaction is proposed:
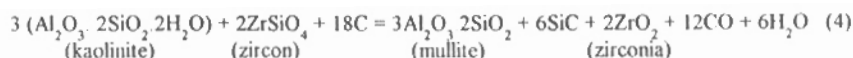
$$3 (Al_2O_3.2SiO_2.2H_2O) + 2ZrSiO_4 + 18C = 3Al_2O_3.2SiO_2 + 6SiC + 2ZrO_2 + 12CO + 6H_2O \quad (4)$$
$$\text{(kaolinite)} \qquad \text{(zircon)} \qquad \text{(mullite)} \qquad \text{(zirconia)}$$

Table II - Phases formed in carbothermal synthesis

Temperature (°C)	Time (min)	Phases Formed
1460	120 to 180	alumina, SiC, ZrC, zirconia, mullite
1490	120	alumina, SiC, ZrC, zirconia, mullite
1490	150 to 180	alumina, SiC, ZrC
1590	120 to 180	alumina, SiC, ZrC

Zirconium carbide is formed from the reduction of zirconia. At temperatures higher than 1500 °C, the products from the intermediate reaction (4) react with carbon to produce α-alumina (Al_2O_3), zirconium carbide (ZrC) and additional β-silicon carbide (SiC) :

$$3Al_2O_3.2SiO_2 + 2ZrO_2 + 12C = 2SiC + 2ZrC + 3Al_2O_3 + 8CO \qquad (5)$$
$$\text{(mullite)} \qquad \text{(zirconia)} \qquad\qquad\qquad \text{(alumina)}$$

Figure 1 is derived from thermodynamic data of intermediate reactions (eq. 4 and 5). At temperatures lower than 1560°C, mullite and zirconia are predominantly formed as confirmed by results of the tests shown in Table II. Alumina and ZrC are stable at temperature levels higher than 1560 °C. Partial CO pressure was not measured inside the induction furnace during the synthesis process. Assuming the partial pressure as 1 atm and temperature of 1400 °C in reaction (2), the free energy is -181 kcal/mole. However if Pco is considered hypothetically as 10^{-2} atm, the free energy of the resulting reaction decreases to -489 kcal/mole, indicating that the reaction becomes more thermodynamically favourable. Actually the partial pressure of CO is definitely lower than 1 atm as argon is injected into the synthesis chamber. The Pco controls the conditions of ZrC formation. This can be a plausible explanation for the formation of ZrC at temperatures below 1560 °C as observed previously (7).

The amounts of alumina, SiC and ZrC in the products were estimated by quantitative x-ray diffraction using fluorite as the internal standard. Products were obtained with a typical composition of 35 wt% Al_2O_3, 37.6 wt% SiC and 22.7 wt% ZrC which is close to that expected by equation (2) (37 wt% Al_2O_3, 38 wt% SiC and 25 wt% ZrC). Losses of SiO (gaseous) as well as the formation of amorphous SiO_2 are the main sources of error between the expected and analyzed compositions of products. The effect of changing composition of the precursors (carbon, kaolinite and zircon) was tested in further experiments and no other phase was produced, but rather, the same products with different compositions of Al_2O_3, SiC and ZrC were present.

Carbothermal reactions using others precursors such as kyanite, have been successfully tested and similar conclusions are being obtained.
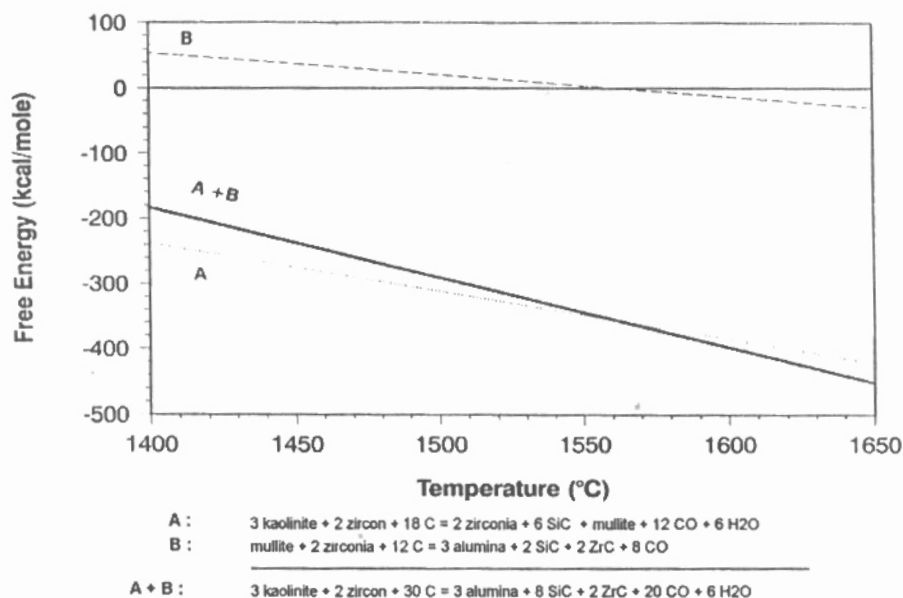
A :   3 kaolinite + 2 zircon + 18 C = 2 zirconia + 6 SiC + mullite + 12 CO + 6 H2O
B :   mullite + 2 zirconia + 12 C = 3 alumina + 2 SiC + 2 ZrC + 8 CO

A + B :   3 kaolinite + 2 zircon + 30 C = 3 alumina + 8 SiC + 2 ZrC + 20 CO + 6 H2O

Figure 1 - Free energy diagram of carbothermal reactions between kaolinite and zircon

Oxidation Tests

Oxidation of ZrC was studied in both an TGA equipment and electric furnace using analytical grade ZrC. Pure β-SiC (grain size of $0.5\mu m$) was also used to evaluate the degree of oxidation of this compound under oxidizing conditions (air and oxygen).

In a TGA equipment, no relevant oxidation was observed when SiC particles were heated up to 900 °C with oxygen (Figure 2). In contrast, 26 mg of pure ZrC increased 20% of weight when oxidized at temperatures higher than 600°C with oxygen forming monoclinic and tetragonal ZrO_2.

In an electric furnace at 700 °C, it was observed by x-ray diffraction and weight gain control that, 20 g of a thin layer of ZrC spread on an alumina tube were partially oxidized after 12 hours of heating with oxygen injection. Monoclinic zirconia was resulted together with an intermediate compound (supposedly zirconium oxi-carbide) which is likely formed as a thin layer onto ZrC particles that hinders oxidation progress. This phase, as previously observed by other authors (3,8), is formed as result of a poor diffusion of oxygen into ZrC particles. Complete oxidation of ZrC was only achieved introducing 20% of a strong oxidizing agent (KNO_3) in the system. In this case, the oxidation time was reduced to 5 hours, temperature to 500 °C and a mixture of tetragonal and monoclinic zirconia was obtained. Once oxidation step was completed, the excess oxidizing agent was easily removed from the final composite powder with hot water. No relevant oxidation was observed when pure β-SiC was oxidized under the same conditions as zirconium carbide.
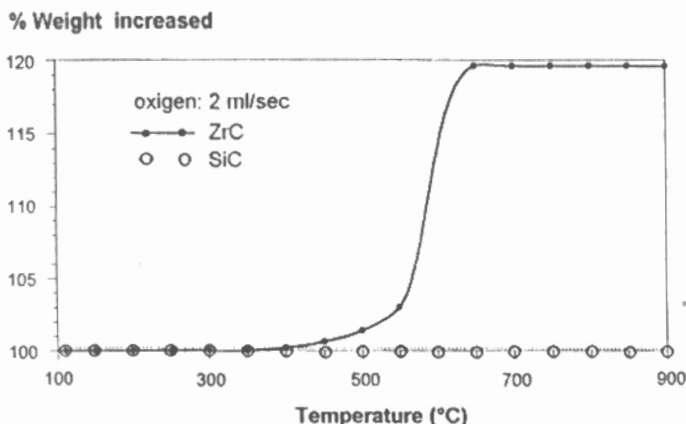
% Weight increased

Figure 2 - Oxidation of ZrC and SiC. Thermogravimetric Analysis

X-ray diffraction pattern of the composite powders oxidized with potassium nitrate, clearly indicated formation of both monoclinic and tetragonal zirconia (Figure 3). The concentration of the tetragonal phase in different powders varied from 30% to almost 100% of the total amount of zirconia. Even with the oxidizing agent, the more dispersed was the powder in the oxidation process, the more tetragonal zirconia was obtained (Figure 4).

X-ray Intensity (cps)

a = alumina
c = silicon carbide
zt = zirconia tetragonal
zm = zirconia monoclinic

2θ degree
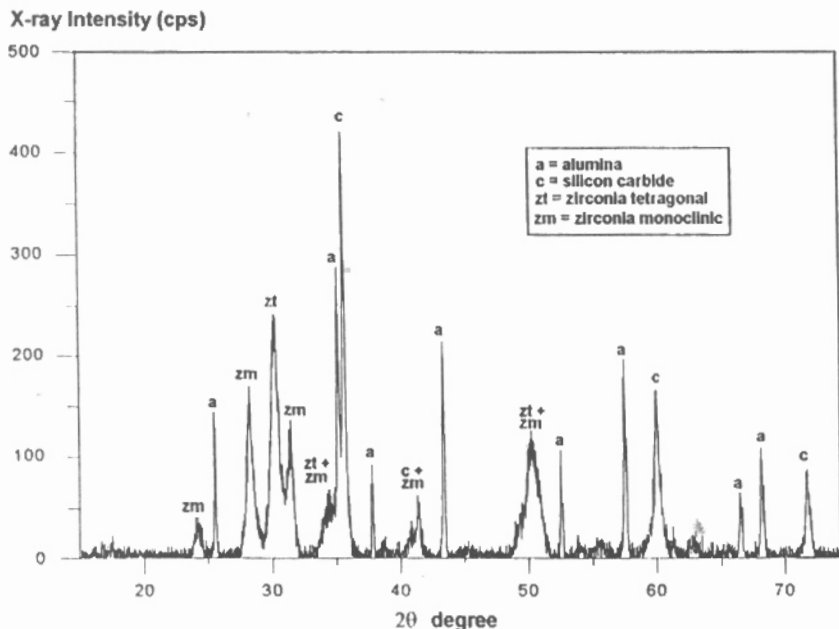
Figure 3 - X-ray pattern showing the presence of both tetragonal and monoclinic zirconia in the system alumina-silicon carbide-zirconia (after oxidation)
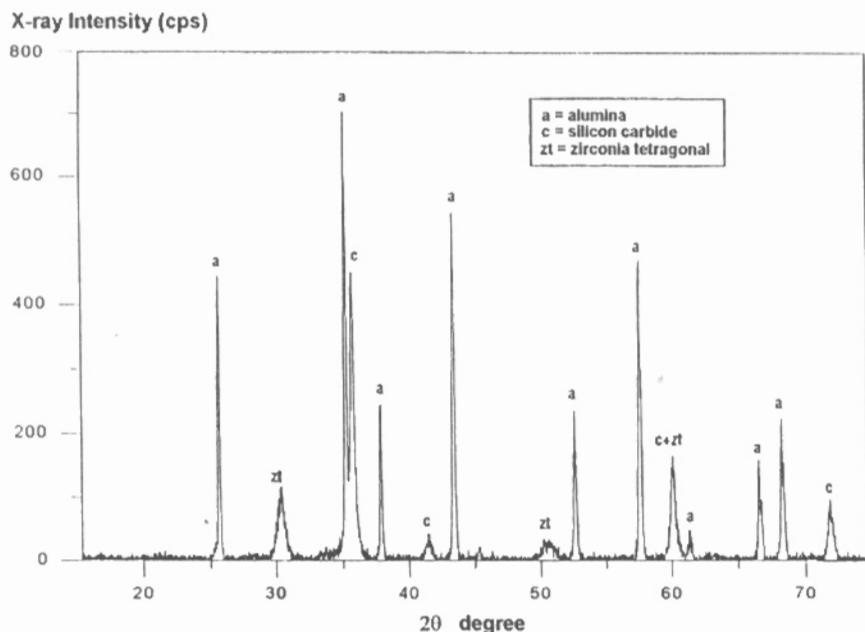
X-ray Intensity (cps)

a = alumina
c = silicon carbide
zt = zirconia tetragonal

2θ **degree**

Figure 4 - X-ray pattern showing the predominance of tetragonal zirconia in the system alumina-silicon carbide-zirconia (after oxidation).

Particle Analysis

It has been earlier reported (1,2) that the particles of SiC and Al_2O_3 formed from reduction of aluminosilicates are normally very small, in the range of below 1 µm. This is specially true if lamp black is used as the carbon source. Furthermore, it was also observed that the particle size and shape of SiC can be controlled by using morphologically controlled carbon powder in the carbothermal reduction process (6).

In this investigation it is also considered that particle size of the final phases, specially that of ZrC and ZrO_2, may have important bearings in developing tough ceramic composite materials. To enhance the fracture toughness by transformation toughening, the size and size-distribution of the ZrO_2 phase in the matrix are critical parameters. With this in view, particle size analyses were carried out on specimens containing ZrC and also on oxidized samples containing only ZrO_2 (in addition to SiC and Al_2O_3 being present in all systems). It is also well known that very fine particles of zirconia (< 0.2 µm) are normally in the metastable state of tetragonal form at ambient temperature.

Figure 4 shows the x-ray diffraction pattern of a sample in which all ZrO_2 is in the form of tetragonal phase. Particle size analyses carried out on the powders containing Al_2O_3, SiC and ZrC (before oxidation) have shown that 50% of particles before oxidation are smaller than 1 µm. The larger particles are identified as Al_2O_3 by SEM coupled with EDS. As a matter of fact, SEM photographs with EDS analysis showed that almost all ZrO_2 particles formed after oxidation are finer than 0.5µm (Figures 5, 6, 7 and 8). This suggests that finer particles of ZrC transform preferentially into tetragonal zirconia (9). Not infrequently, ZrC particles form agglomerates in the oxidation step. This favours formation of monoclinic ZrO_2.
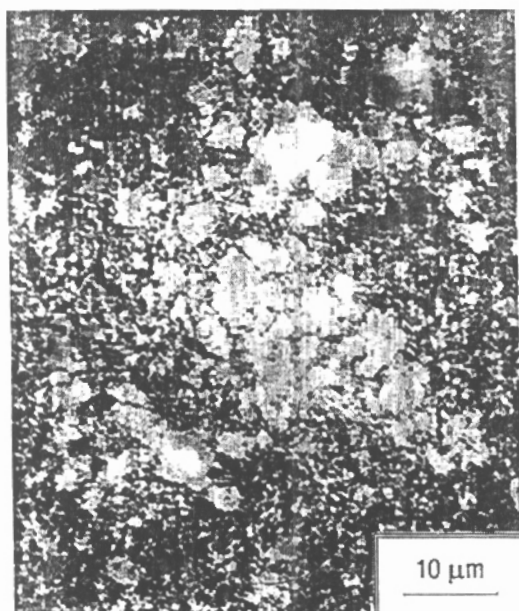
Figure 5 - SEM image showing microstructure of Al_2O_3 - SiC - ZrO_2 composite
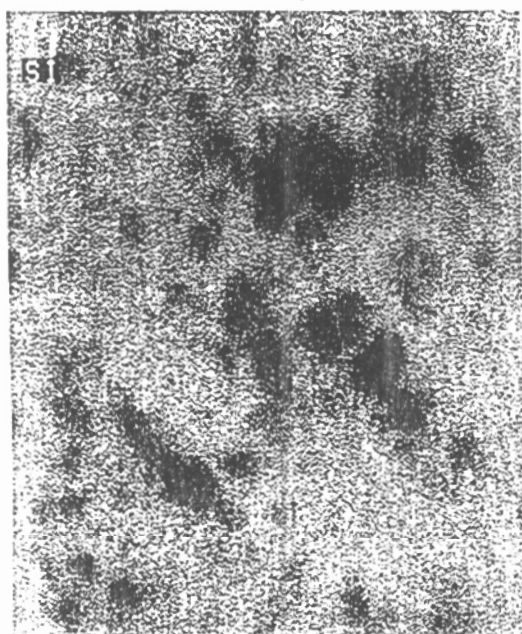(sample densified by hot pressing)

Figure 6 - X-ray image (EDS) of silicon distribution of Fig. 5

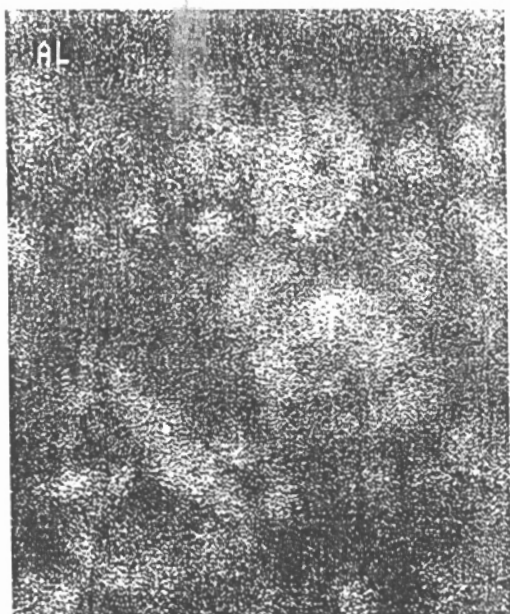Figure 7 - X-ray image (EDS) of aluminum distribution of Fig. 5

Figure 8 - X-ray image (EDS) of zirconium distribution of Fig. 5

CONCLUSIONS

Al_2O_3-SiC-ZrC is preferentially formed by carbothermal reaction of kaolinite and zircon in an argon atmosphere. An oxidation step, using a strong oxidizing agent, such as KNO_3, is needed to convert effectively ZrC into ZrO_2 to obtain powder of Al_2O_3-SiC-ZrO_2 as final products. Without potassium nitrate, a passive thin layer is likely formed onto ZrC particles hindering oxidation. It is inferred by SEM-EDS observations together with x-ray diffraction that tetragonal zirconia is formed preferentially from small particles of ZrC. Furthermore, in the oxidation process, monoclinic zirconia is predominantly formed from larger particles of ZrC or from agglomerates. Particles dispersion in the oxidation process is a key step in obtaining tetragonal zirconia in the composite powder.

Thermodynamic data have supported the test results, in which ZrO_2 and mullite are formed at temperatures below 1560 °C in the carbothermal synthesis. The Al_2O_3-SiC-ZrC composite powder is preferentially formed at temperatures above 1560°C at 1 atm. Variations in the amounts of kaolinite and zircon did not form different products but, always the same composite (Al_2O_3-SiC-ZrC) powder with different compositions.

ACKNOWLEDGMENT

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