Formation of an alumina–silicon carbide nanocomposite

N. J. WELHAM*, N. SETOUDEH
Extractive Metallurgy, Murdoch University, Perth WA 6150, Australia
E-mail: nicholas.welham@murdoch.edu.au

Alumina–silicon carbide ceramics have been increasingly studied in the past few years as the combination should provide a novel ceramic with chemical and oxidation resistance at high temperatures. Generally, the composite is made by separately manufacturing the powders, blending them in the desired ratio and sintering them to form a final monolith. Recently, Al_2O_3/SiC composites have been formed directly by carbothermic reduction of the polymorphic mineral precursors kyanite (Al_2SiO_5) [1] and andalusite (Al_2SiO_5) [2]. This route only allows a fixed composition of product, unless more SiO_2 or Al_2O_3 are added.

The properties of sub-micron grained composites are generally superior to those manufactured from larger particles and the importance of nanostructured materials will increase. High energy ball milling has been shown previously [3–6] to lead to the direct formation of nanocomposite high-value ceramics directly from comparatively inexpensive precursors, such as mineral concentrates.

In this paper high intensity ball milling of a mixture of silicon dioxide, aluminum and graphite powders is examined to determine whether the formation of a composite of alumina and silicon carbide can be achieved at a low temperature.

The feed powders consisted of amorphous, precipitated silicon dioxide, graphite and aluminum foil all of which were nominally >99% pure. Two mixtures, each of 7.00 g, were prepared in accordance with *reaction (1)* which was the thermodynamically predicted reaction. The foil was torn into <1 cm squares prior to use.

$$3SiO_2 + 4Al + 3C \Rightarrow 3SiC + 2Al_2O_3$$
$$\Delta G_{298} = -807\ \text{kJ} \quad \Delta H_{298} = -838\ \text{kJ} \qquad (1)$$

The mixtures were sealed under a pressure of $\sim 10^{-2}$ Pa in laboratory ball mills. The milling medium consisted of five 1″ (25.4 mm) diameter steel balls giving a ball: powder mass ratio of 43:1, the ball motion was controlled by an external magnetic field. The rotation speed used was 165 rpm. After 10 and 100 hr the powders were removed from the mill.

Differential thermal analysis (DTA) was performed on milled powders using approximately 20 mg of sample, which was heated in an argon atmosphere to 1200 °C and then cooled to 500 °C, both at 20 °C min^{-1} using a Shimadzu DTA-50 instrument. Thermogravimetric analysis (TGA) performed under identical conditions in a Shimadzu TGA-50 showed mass losses <0.5% confirming the solid-state nature of the reaction.

The DTA traces of the 10 hr milled powder is shown in Fig. 1. After 10 hr of milling there were three thermal events, the first of which was an endotherm at ∼660 °C due to the melting of the aluminum. The presence of aluminum indicates that little or no reaction had occurred during the initial 10 hr of milling. The second event was a large exotherm which occurred directly after the melting of the aluminum, indeed it is probable that there was some overlap between the final stages of aluminum melting and the exotherm beginning. Consequently, it is impossible to accurately deconvolute these peaks to obtain the energy involved and give any information about the consumption of aluminum during milling. The final event also overlapped the main exotherm and was somewhat wide, suggesting that the process had a large activation energy [7–9]. No further events were observed during the remaining heating and cooling, the absence of an exotherm for aluminum freezing would clearly indicate that all of the available aluminum had been consumed in the two thermal events.

The products were analyzed by X-ray diffraction (XRD) using monochromatic $Co_{k\alpha}$ radiation ($\lambda = 1.78896$ Å) using a count time of 1 s per 0.02 ° step. The crystallite size was estimated by applying the Scherrer equation to profile fits of all of the available identified peaks for each phase. The error reported in the crystallite size is 2σ for the available data.

The XRD trace for the powder milled for 10 hr is shown in Fig. 2a, the main peaks correspond to those of aluminum, the small, broad peak at ∼31 ° is the main graphite peak, this confirms the lack of reaction indicated by DTA. The breadth of the graphite peak is indicative of crystallite refinement due to milling, with a crystallite size of ∼10 nm estimated from the one available peak. In multiphase systems, the softer phases tend to amorphise more rapidly [10–13] and this would seem to be the case here with 100 hr milling of the same graphite, in the absence of other phases, showing a crystallite size of 26 nm [14]. The very broad peak (width >10 °) centred around 27 ° is typical of amorphous materials and was due to the silicon dioxide used with XRD of the feed powder only showing a similar peak.

XRD of the powder after DTA, Fig. 1b shows clearly that aluminum has been consumed with Al_2O_3 the only aluminum bearing phase present. There are also small

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*Author to whom all correspondence should be addressed.

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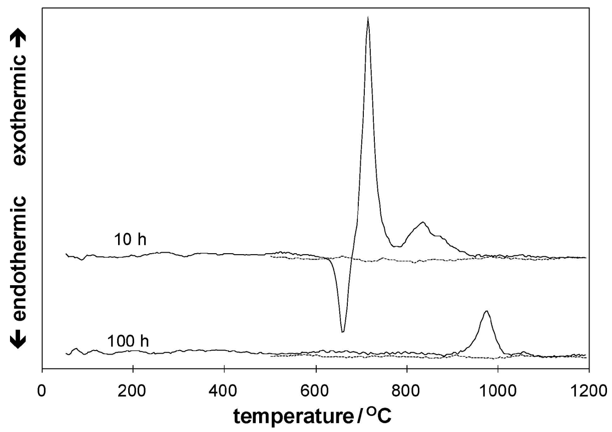

Figure 1 Differential thermal analysis traces for the powders milled for 10 and 100 hr, samples of 20 mg heated in argon at 20 °C min^{-1} to 1200 °C (solid lines) and then cooled at the same rate to 500 °C (dashed lines).

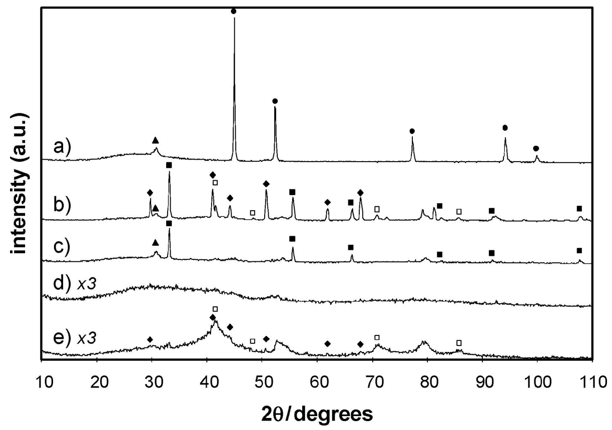

Figure 2 XRD traces for (a) as-milled 10 hr, (b) 10 hr milled powder after heating to 1200 °C, (c) 10 hr milled powder after heating to 780 °C, (d) as-milled 100 hr and (e) 100 hr milled powder after heating to 1200 °C. ■-Si, ♦-alumina, •-aluminum, ▲-graphite and □-SiC.

peaks for silicon carbide present indicating that reaction (1) had occurred. However, several peaks for elemental silicon are present indicating that reaction (2) occurred, which implies that reaction (1) may be composed of two separate stages—formation of silicon and alumina by reaction (2) followed by carburisation of silicon by reaction (3).

$$4Al + 3SiO_2 \Rightarrow 2Al_2O_3 + 3Si \qquad (2)$$

$$3Si + 3C \Rightarrow 3SiC \qquad (3)$$

DTA of a sample of powder up to 780 °C showed no freezing peak for aluminum on cooling indicating that the main exotherm was almost certainly due to reaction (2). XRD of this powder, Fig. 1c, showed no aluminum peaks, silicon was the major phase present and a small graphite peak was also evident. Very weak peaks for alumina were evident indicating that grain growth in alumina was slow at this temperature. No peaks for silicon carbide were observed, although their absence may be due to an extremely small crystallite size or a low abundance.

Integration of the areas of these two exotherms indicated that the main exotherm was ~3.0 times the area of the smaller exotherm. The area of the main exotherm did not account for any aluminum melting and a slightly greater ratio is probably more realistic. Calculation of the enthalpy of reaction at the peak temperatures gave values of −672 and −218 kJ for reactions (2) and (3) respectively—a ratio of 3.08. Silicon and graphite were both present at 1200 °C, Fig. 1b, indicating that carburisation was incomplete, thus giving a smaller exotherm and leading to a higher observed ratio. However, given that deconvolution of the energetic peaks is extremely difficult without knowing the rate determining step of all of the overlapping reactions [7–9], a better estimate of the ratio is impossible. However, the combination of thermal and XRD evidence would confirm that the reaction is two stage with reaction (2) occurring prior to reaction (3).

The average crystallite size of the silicon after heating to 780 °C (43 ± 2 nm) was slightly larger than that after heating to 1200 °C (37 ± 6 nm), indicating that crystallite growth was rapid for silicon at low temperatures. The decrease in crystallite size after heating to 1200 °C may be due to the break-up of the larger crystallites by reaction with the graphite to form SiC. The alumina and SiC peaks were barely evident at 780 °C, however, after heating to 1200 °C alumina and silicon carbide both underwent crystallite growth to form crystallites of 46 ± 6 nm and 27 ± 4 nm respectively. Powdered silicon diffracts very strongly when crystalline and is used as an internal standard, thus the fact that the major peak at both 780 and 1200 °C was for silicon is not an indication that it was the most abundant phase.

Annealing the powder for 1 hr at 1200 °C under a flowing argon atmosphere showed that both alumina and silicon carbide were present, a small peak for silicon was also present indicating that the reaction was incomplete. The smaller silicon peak would suggest that the carburisation of the silicon was a comparatively slow step requiring some time at 1200 °C to approach equilibrium.

DTA of the 100 hr milled powder, Fig. 1, shows a significant change from the 10 hr powder. There is no endotherm for aluminum melting and the absence of any exotherm below 660 °C indicated that all of the aluminum had been consumed during milling. The only feature of the DTA is an exotherm with an onset of ~920 °C.

The XRD trace of the as-milled powder, Fig. 2d showed few features. There are no major peaks and the broad peak for amorphous silica is absent. The almost complete absence of features is typical of a material which is either amorphous or composed of extremely small crystallites. The apparent absence of the silica would imply that it had been consumed during milling. The absence of graphite may be due to continuation of the crystallite size refinement observed in the 10 hr milled powder, or reactive consumption. It has been shown elsewhere [15] that aluminum milled with TiO_2, a phase of similar hardness to SiO_2, still showed its two main peaks even after 100 hr of milling. Thus, it seems that aluminum was no longer present in the elemental form confirming its consumption by reaction, presumably with the silica, to form alumina and either silicon carbide by reaction (1) or possibly silicon by reaction (2). However, the XRD shows that the phases formed were either amorphous, had an extremely small crystallite size or both.

XRD of powder annealed to 900 °C, just below the onset of reaction, showed no distinct changes when compared with the as-milled powder shown in Fig. 2d. Silicon cannot have been present as it would have been expected to have recrystallized during the excursion to 900 °C, as observed in Fig. 2c, therefore it must have been completely sequestered into the amorphous phase or nanocrystalline SiC. XRD of powder annealed to 1020 °C, the completion of the exotherm, showed the same XRD pattern as the powder annealed to 1200 °C shown in Fig. 2e. Thus, the exotherm would seem to be related to a crystallization process. Since peaks for both Al_2O_3 and SiC are present only above the exotherm it would seem that they were the phases recrystallized. The width of the peak at 71 ° indicates a crystallite size of ∼5 nm for SiC.

Clearly, these results indicate that the reaction between aluminum, silica and graphite is not complete after 10 hr of high energy milling but seems to be complete after 100 hr. Previous experiments [16–18] have shown that some reactions have an induction time before which no reaction occurs but beyond which the reaction is over within seconds or minutes. It is possible that this system also has an induction time, but further experiments are needed to determine the milling time required. For the shorter milling time the reaction was two stage with elemental silicon appearing as an intermediate prior to carburisation to SiC. The 100 hr milled powder did not show any evidence of thermally induced reaction with only an exotherm due to crystallization evident in the DTA trace. Indeed, the as-milled 100 hr powder showed no features at all on the XRD trace indicating the product was either amorphous or nanocrystalline. Even after heating to 1200 °C only very broad peaks for SiC and Al_2O_3 were evident confirming the nanocrystalline nature of the product.

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