PII: S0955-2219(97)00212-4

Ambient Temperature Formation of an Alumina–Titanium Carbide–Metal Ceramic

P. E. Willis,[a] N. J. Welham[a,b]* and A. Kerr[b]

[a]Petrochemistry and Experimental Petrology, Research School of Earth Sciences, Australian National University, Canberra ACT 0200, Australia
[b]Department of Electronic Materials Engineering, Research School of Physical Sciences and Engineering, Australian National University, Canberra ACT 0200, Australia

Abstract

The fabrication of a sub-micron sized powder composed of alumina, titanium carbide and iron in a single low temperature stage is reported in this paper. The starting materials were the mineral ilmenite ($FeTiO_3$), graphite and aluminium powder. A similar composite without iron was also produced using rutile (TiO_2) as the starting material. The powders were ball milled together for 100 h in a laboratory scale mill and subjected to annealing at up to 1200°C. X-ray diffraction showed that the phases formed during the milling step were nanocrystalline and underwent crystallite growth on annealing. Differential thermal analysis indicated that the reaction was complete within the mill with no evidence for residual elemental aluminium. Mixtures of the same composition showed only a slight reaction when heated to 1200°C. © 1998 Elsevier Science Limited. All rights reserved

1 Introduction

Oxide bonded hard materials have been produced for over 50 years for use in wear surfaces and cutting edges. Recently, there has been considerable interest in the reactive formation of the composite materials by reduction of titanium dioxide by aluminium in the presence of carbon.[1–13]

The general method of production is to mix the precursor powders, press them into a pellet and supply heat at one end to initiate the reaction, the consensus is that the reaction requires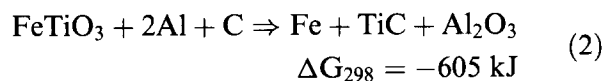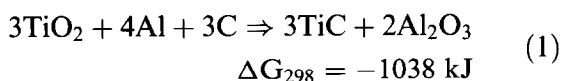 around 900°C for the onset of reaction. Once started, the mixture rapidly heats up and becomes self propagating with a high temperature reaction front moving throughout the pellet. The nature and type of the precursor powders affects the rate of reaction and has a bearing on the microstructure[10,11,13,14] as does the use of diluent phases designed to keep the temperature of synthesis down.[10,11] The use of comparatively inexpensive oxide as the source of titanium for the carbide has economic advantages over the direct reaction between elemental titanium and carbon which takes place at high temperatures.[15–17] Ball milling of the precursors is often carried out to enhance the rate of reaction by causing more intimate mixing of the components. Indeed, synthesis of titanium carbide from the elements has also been achieved by ball milling.[18–23] The addition of a metallic phase to a mixture of TiC and Al_2O_3 has been shown to lead to marked increase in toughness of the composite[24] and this advantage may lead to a new generation of cermets.

In this paper high intensity ball milling of a mixture of titanium dioxide, aluminium and graphite powders is examined to determine whether the formation of a composite of alumina and titanium carbide can be achieved at low temperature. The addition of a metal is also examined by the use of ilmenite ($FeTiO_3$) in place of rutile.

2 Experimental

The feed powders consisted of the ilmenite[25] and rutile[26] previously described. The aluminium and graphite powders were nominally >99%. Two mixtures, each of 7·00 g, were prepared in accordance with the stoichiometry indicated by eqns (1) and (2), which were the thermodynamically predicted reactions.

*To whom correspondence should be addressed. Fax: (61) (26) 249 0511; e-mail: nicholas.welham@anu.edu.au

$$3TiO_2 + 4Al + 3C \Rightarrow 3TiC + 2Al_2O_3$$
$$\Delta G_{298} = -1038 \text{ kJ} \quad (1)$$

$$FeTiO_3 + 2Al + C \Rightarrow Fe + TiC + Al_2O_3$$
$$\Delta G_{298} = -605 \text{ kJ} \quad (2)$$

The mixtures were sealed under vacuum in laboratory ball mills, as previously described.[27] The milling medium consisted of five 1″ (25·4 mm) diameter steel balls whose motion was controlled by an external magnetic field. The rotation speed used was 165 rpm. After 100 h the powders were removed from the mill and subjected to annealing under flowing argon for 1 h at 800 and 1200°C. The lower temperature is sufficient for crystallite growth, but is below the ignition temperature commonly used for pressed pellets. The higher temperature gives further crystallite growth and should provide an indication of possible reactions between the phases present during subsequent sintering. Powders of identical composition were loaded into identical mills without balls, rotated for 100 h and then treated in a similar manner to the milled powders. The ilmenite in the mixed powder was pre-milled to reduce the particle size from $> 100 \mu$m to $< 1 \mu$m to enhance mixing.

Differential thermal analysis (DTA) was performed on milled and mixed powders using approximately 30 mg of sample, which was heated in an inert argon atmosphere to 1200°C at a heating rate of 20°C min^{-1} using a Shimadzu DTA-50 instrument. Thermogravimetric analysis (TGA) was performed under identical conditions in a Shimadzu TGA-50.

The products were analysed by X-ray diffraction (XRD) using monochromatized Co$_{k\alpha}$ radiation ($\lambda = 0\cdot178896$ nm) using a count time of 2 s per 0·01° step. Estimation of the crystallite size was made using the Scherrer formula[28] on at least four peaks for each phase, except iron which only has three peaks in the range scanned.

Scanning electron microscopy (Jeol 2600) was used to examine the morphology and elemental composition of the as-milled powders. The powders were dispersed onto double sided conducting carbon tape and carbon coated prior to examination.

3 Results

It is obvious from the XRD traces given in Fig. 1 that the as-milled powder contains no discernible rutile, carbon or aluminium. This is due to a combination of consumption by reaction and the extremely small crystallite size caused by milling. The main peaks for TiC are clearly evident and there are broad peaks for alumina. The peak around 52° is coincident with the main peak for elemental iron and is due to abrasion of iron from the mill body and balls during milling. Annealing at 800°C caused a narrowing of peaks indicating crystallite growth was occurring and allowing confirmation that the phases present after milling were as expected from eqn (1). However, small peaks for rutile remained after milling, suggesting that a thermal reaction had not occurred at 800°C. The estimated crystallite size for the phases are presented in Table 1, it is clear that in the as-milled powder all of the phases are below 10 nm. The iron crystallite size was taken from the main peak only, the other peaks being too weak for fitting to be performed due to the low fraction of iron present. After annealing at 1200°C the peaks for the various phases were completely separated due to extensive crystallite growth, as indicated by Table 1. The same phases as at 800°C were present, suggesting that the thermal reaction did not occur. The absence of a complete reaction is almost certainly due to insufficient aluminium powder being present in the starting mixture. Aluminium has a thin surface layer of Al$_2$O$_3$ and the powder used would have had a high surface area. Thus a significant fraction of its mass would already have been oxide leaving insufficient metal for the complete reaction. The absence of aluminium was confirmed by the lack of any energetic events during heating of the milled powder up to 1200°C in a DTA, as shown in Fig. 2. Had aluminium remained then a melting endotherm would have been expected at 660°C, if a reaction involving aluminium had occurred at lower temperature then an exotherm would have been expected due to the high enthalpy of formation of aluminium oxide.

These features are present in the DTA of the mixed powder, Fig. 2, which showed two thermal events, an endotherm around 660°C due to the melting of the aluminium and a wider exotherm around 950°C due to reaction. The mass of the system remained constant throughout the entire temperature range, thus the exotherm could not have been the reaction between carbon and rutile to form CO, which has been shown to occur above 900°C.[25,29–34] XRD of the product showed that only a slight reaction had occurred with aluminium and graphite still present, although peaks for rutile were no longer present, Fig. 3. Part of the rutile had formed TiC, the remainder was, presumably, present as an intermediate reduction phase—most probably an oxide of the general formula Ti$_n$O$_{2n-1}$. These phases have been examined during the reduction of rutile by carbon and small amounts of
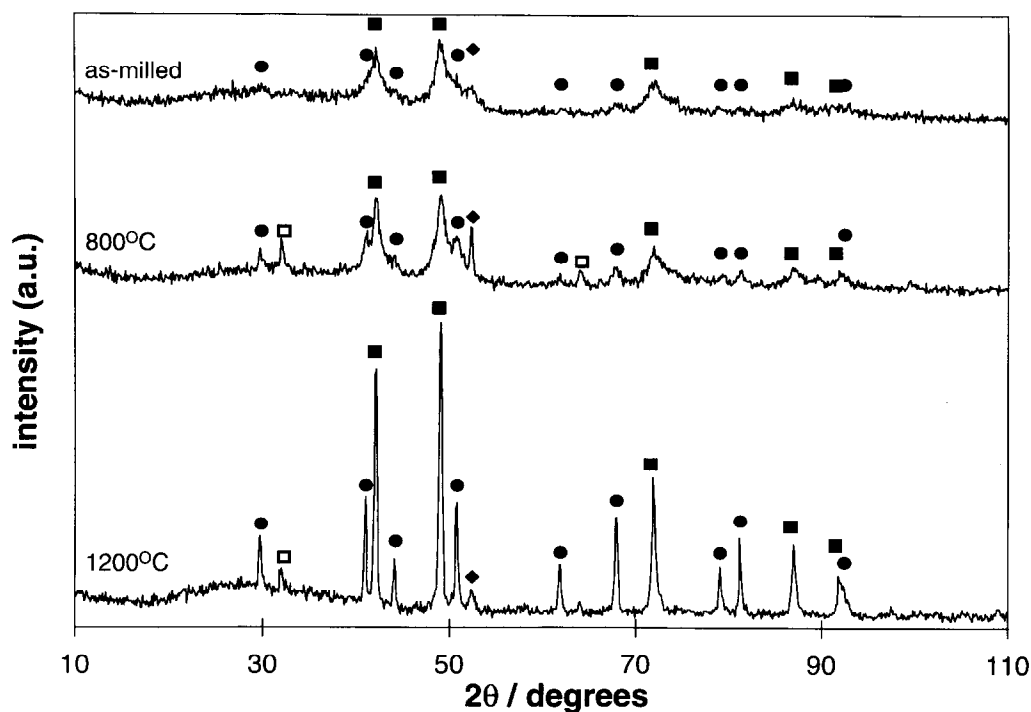
Fig. 1. Intensity—2θ traces for the rutile powder, of starting composition given in eqn (1). Traces are directly after 100 h of milling, after 1 h annealing in argon at 800 and 1200°C. ■, TiC; ◆, iron; ●, Al₂O₃; □, rutile.

Table 1. Estimated mean crystallite size (in nm) of the phases contained within the as-milled, annealed at 800 and 1200°C powders. The 2σ value for each series of peaks is given as subscripts. No errors could be calculated for iron, due to the weakness of the second and third peaks making fitting unreliable, except for the powder derived from ilmenite which was annealed at 1200°C

	Rutile			Ilmenite		
Phase	As-milled	800°C	1200°C	As-milled	800°C	1200°C
TiC	$6.2_{2.6}$	$8.7_{3.2}$	$30.1_{8.1}$	$9.7_{3.6}$	$10.3_{1.1}$	$29.9_{4.8}$
Al₂O₃	$7.8_{2.2}$	$12.1_{3.8}$	$43.2_{6.9}$	$8.1_{1.6}$	$13.1_{3.2}$	$39.4_{5.5}$
Fe	9.7	19.5	42.3	4.8	12.2	$32.4_{3.8}$

the numerous phases present preclude detection by XRD.[35] No reaction was observed after heating to 800°C for 1 h, as expected from the DTA results. XRD of the powder annealed for 1 h at 1200°C, above the exotherm in the DTA, showed the reaction was incomplete, some titanium carbide and alumina were present but rutile and reduced titanium oxides remained.

The XRD traces for the samples derived from ilmenite are shown in Fig. 4 and are similar to those in Fig. 1 except for the stronger iron peak at 52° and the slightly narrower and more intense peaks for alumina. On annealing at 800°C peaks for two new phases, rutile and haematite became apparent. Rutile is an intermediate phase during the reduction of ilmenite[25,29–34] and its presence implies an incomplete reaction during milling. The presence of haematite is somewhat surprising and could indicate the presence of adventitious oxygen during annealing. However, the length of the

annealing was such that both the elemental iron and titanium carbide would have reacted with the oxygen and it seems more probable that the haematite was another intermediate phase.

For the sample heated to 1200°C, both the haematite and rutile had been consumed by reaction and were absent. DTA of the as-milled powder, shown in Fig. 2, confirmed the absence of elemental aluminium indicating that another reductant was present in the system. The peaks for titanium carbide which were evident at 800°C had become doublets, this is most clearly shown for the peak at 72°. The position of the carbide peaks is known[16,36] to change with the stoichiometry, the peaks moving to higher 2θ as the value of x in TiC$_x$ decreases. Thus, the reductant phase would appear to be TiC which loses carbon to form CO and a carbon deficient TiC according to eqn (3).

$$\mathrm{TiC} + x\mathrm{Fe_2O_3} \Rightarrow 2x\mathrm{Fe} + \mathrm{TiC_{1-3x}} + 3x\mathrm{CO} \quad (3)$$
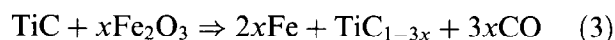
This reaction involves a mass loss due to CO evolution, thermogravimetric analysis of this sample, Fig. 2, showed a mass loss at temperatures in excess of 1000°, although no associated peak was observed on the DTA trace suggesting that reaction was not very energetic, limited in extent or slow. Profile fitting of the TiC peaks confirmed the presence of two distinct phases, both of which had a smaller unit cell size (i.e. contained less carbon) than the phase present at 800°C. This would seem to confirm that reaction (3) occurred. The absence of rutile can be explained by a similar reaction
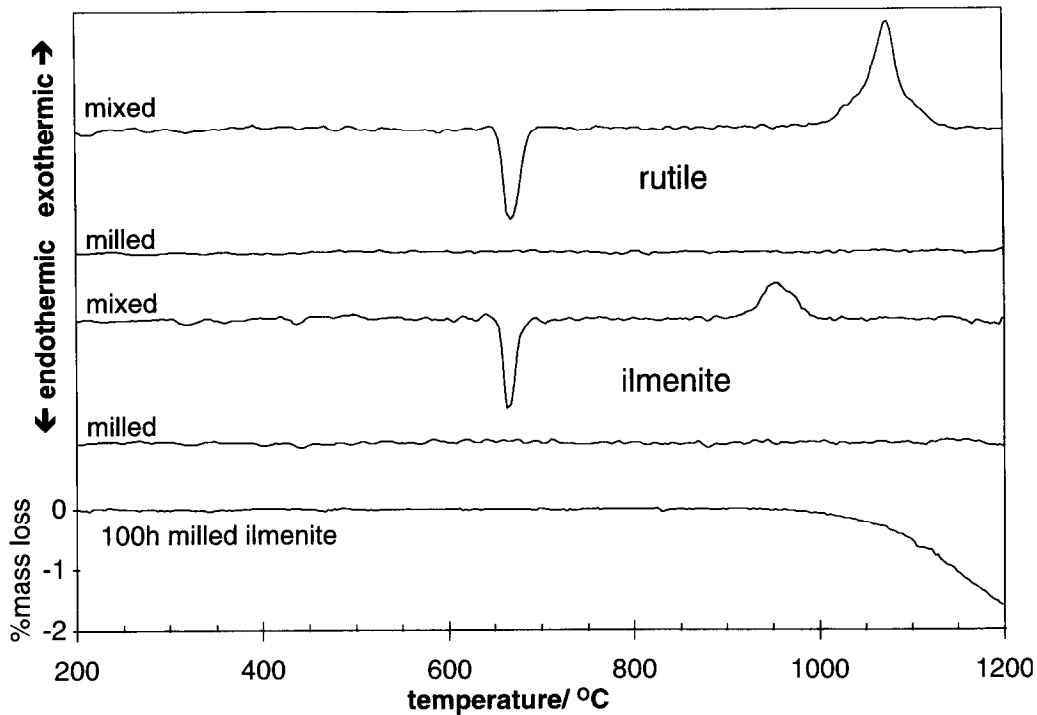
Fig. 2. Differential thermal analysis traces for powders heated at 20°C min^{-1} up to 1200°C under an argon ambient. The traces are for mixed and 100 h milled powder of stoichiometry according to eqns (1) and (2). The bottom trace is the TGA trace for powder for eqn (2) milled for 100 h.
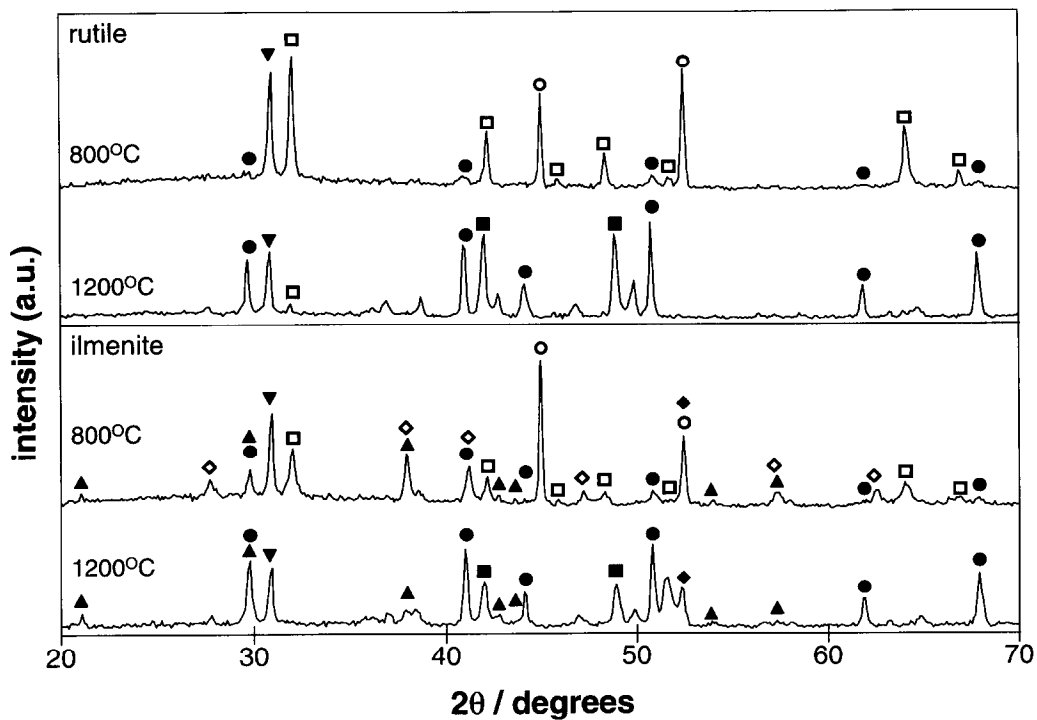

Fig. 3. Intensity—2θ traces for the unmilled powders, of starting composition given in eqns (1) and (2). Traces are after 1 h annealing in argon at 800 and 1200°C. ■, TiC; ◆, iron; ●, Al$_2$O$_3$; ▼, graphite; □, rutile; ◇, ilmenite; ○, aluminium; ▲, pseudobrookite.

involving TiC. The two reduction reactions may be the reason for the two distinct compositions of TiC observed.

The crystallite size of the phases derived from ilmenite were found to be similar to those of the phases obtained from rutile, Table 1. The TiC, Al$_2$O$_3$ and Fe all underwent crystallite growth on

annealing, although the growth during annealing at 800°C was small compared to that at 1200°C. The size for Fe was taken from the single peak which was evident which, although it was one of the major phases present it seemed to take more damage to its crystal structure than the other phases with only the main peak evident. A preferential
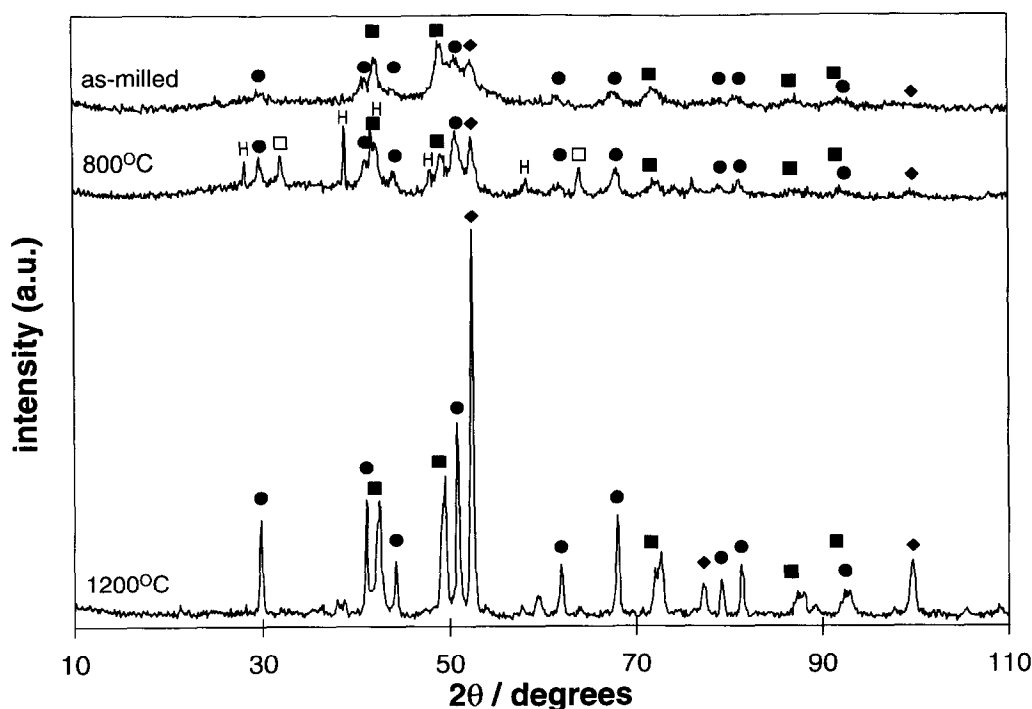
Fig. 4. Intensity—2θ traces for the ilmenite powder, of starting composition given in eqn (2). Traces are directly after 100 h of milling, after 1 h annealing in argon at 800 and 1200°C. ■, TiC; ◆, iron; ●, Al_2O_3; □, rutile and H, haematite.

decrease in the crystallite size of softer phases has been noted elsewhere[37–41] and the much softer iron could be expected to take more damage than the considerably harder Al_2O_3 and TiC.

XRD of the mixed powder, Fig. 3, showed intense, narrow peaks for each of the starting materials. DTA on the ilmenite powder mix, Fig. 2, showed two thermal events, an endotherm around 660°C and a wide exotherm around 950°C, neither of which involved a change in mass. The endotherm was due to the melting of the elemental aluminium, the exotherm was due to reaction. No mass loss was associated with the exotherm so it could not have been the reaction between carbon and ilmenite to form iron, TiO_2 and CO which is known to occur above 800°C.[25,29–34] XRD of the product showed that peaks for aluminium and graphite still remained, confirming that the reaction was incomplete. Ilmenite may have been present but the peaks were weak and partially overlapped by a new phase, Fe_2TiO_5—pseudobrookite. This phase has been shown to be formed by solid state reaction between rutile and elemental iron above 600°C[42,43] and by oxidation of ilmenite.[44,45] The absence of a mass gain during TGA would indicate that the oxidation route did not occur and the pseudobrookite was formed by the solid state route. This would indicate that reduction of ilmenite to iron and TiO_2 had occurred, presumably with the concomitant formation of Al_2O_3. Annealing for 1 h at 800°C showed that reaction had occurred, Al_2O_3, TiO_2 and pseudo-

brookite were all present in addition to the starting materials, iron could not be confirmed as present, as its peaks are coincident to those of alumina. The absence of an exotherm in the DTA indicated that the reaction is either not very exothermic, of low extent or slow. The aluminothermic reduction of ilmenite to form TiO_2 and Fe, reaction (4), is extremely exothermic ($\Delta H > -800\,kJ$) and would be expected to provide sufficient energy to show a peak during DTA.

$$3FeTiO_3 + 2Al \Rightarrow 3Fe + 3TiO_2 + Al_2O_3 \qquad (4)$$
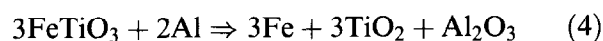
The extent of this reaction is less clear, aluminium and ilmenite were still present, although the rutile peak was of similar size to that of ilmenite which suggests around 50% of completion. The reaction which occurred was entirely solid state and can only have occurred at the interparticle contact points. The reaction would be controlled by diffusion, probably of oxygen from ilmenite to the reaction boundary,[35] and would be expected to be slow.

After 1 h at 1200°C, alumina, titanium carbide, iron and pseudobrookite were found to be present, neither aluminium nor rutile were found. There were also several peaks for reduced titanium oxides. Ilmenite may also have been present but sufficient distinctive peaks were not found. The peak at 51° is close to that of several iron–aluminium compounds (AlFe, $AlFe_3$) and alloys ($Al_{0.5}Fe_{0.5}$, $Al_{0.4}Fe_{0.6}$). The less intense peaks of these phases

coincide within data error and no conclusive attribution of this peak is possible. The formation of an iron–aluminium phase would explain the absence of aluminium despite the presence of graphite confirming the incomplete reaction.

Photomicrographs of the as-milled powders are shown in Fig. 5, it is clear that there is a significant size difference between the rutile and ilmenite powders in (a) and (b), respectively. The majority of the particles of the sample derived from rutile are below $0.5\,\mu m$, although there are a few particles of 2–$3\,\mu m$. The ilmenite sample, (b), contains a few submicron particles but the majority are $1–3\,\mu m$. The only significant difference between the two powders is the considerably greater iron content in the sample derived from ilmenite. Thus, it would seem that iron is acting as a binding agent causing particles to reach a larger steady-state size than the rutile derived particles. The malleable nature of the iron may be responsible for this, physical deformation of particles is more likely than brittle fracture during impact, whereas the opposite is true for the rutile sample which only contains TiC and Al_2O_3 after milling. There is little difference in the morphology of the large particles, both powders show rounded edges with few angular fragments which are typical of brittle fracture. The smaller particles in the rutile powder are more angular but still show rounded edges. Quantitative analysis of individual particles showed that aluminium and titanium (and iron for

Fig. 5. Scanning electron micrographs of as-milled powders of (a) rutile derived powder and (b) ilmenite derived powder.

the ilmenite derived particles) were present in all of the particles with only a small compositional variation between particles confirming their homogeneity.

4 Discussion

The effect of milling is clear, reaction takes place within 100 h and the thermal treatment only serves to cause crystallite growth. However, oxide contamination in the powder used led to a sub-stoichiometric amount of aluminium being used. For ilmenite, this insufficiency enabled the formation of the phases haematite and rutile, both of which were thermally reduced by the TiC formed during milling, forming two different carbon deficient TiC phases. For rutile, the effect of the aluminium deficiency was less clear, but rutile remained after milling and annealing. There was no evidence of elemental aluminium remaining after milling. The particle size of the final powder was dependent upon the iron content, the particle size was larger in the presence of a substantial fraction of iron indicating that iron was acting as a binder for the ceramic particles. A similar dependence of final particle size on the presence of a metal has been observed in other, similar systems.[46,47]

Work on the same system using magnesium in place of aluminium[48] has shown essentially identical behaviour with reaction occurring within the mill. The use of Mg in place of Al allows the removal of the oxide phase (and Fe) by selective chemical leaching, thus leaving TiC as the major phase. By using this procedure the size of the TiC particles was found to be < 100 nm and similar to the XRD estimated crystallite size. Presumably, similar particle sizes would be found in this material.

Mixtures of the same stoichiometry showed different characteristics during thermal treatment. DTA showed that aluminium remained up to its melting point at 660°C with XRD confirming that no reaction occurred in either system. The ilmenite system underwent a partial reaction after 1 h at 800°C which was not evident during DTA, the products were TiO_2, Al_2O_3 and Fe_2TiO_5. An exotherm was evident in both systems at 950°C for ilmenite and 1070°C for rutile after which titanium carbide became evident. Although the ilmenite and rutile had been consumed by reaction there was still a peak for graphite in both cases confirming that the reaction was incomplete, even after 1 h at 1200°C.

The mechanism of the thermally induced reaction appears to be the initial reduction of ilmenite to TiO_2 and Fe, the Fe then reacting with TiO_2 to form Fe_2TiO_5. Subsequent heating, above the exotherm, implied the reduction of rutile, apparently
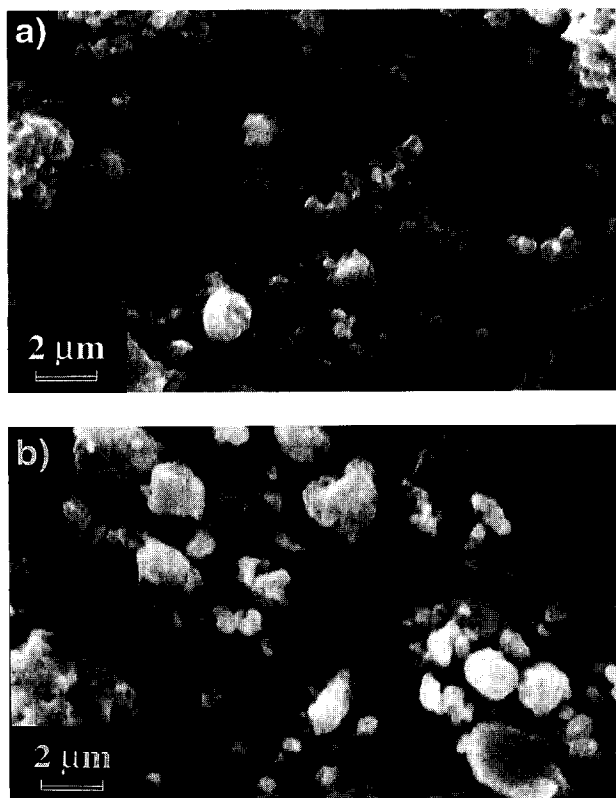
to TiC. Peaks for reduced titanium oxides were evident and it may be that these are intermediate phases in the reduction process, as has been demonstrated for carbothermic reduction[25,29–34,49,50] but conclusive evidence is lacking. The incompleteness of the thermal reaction could be attributed to the solid-state nature of the reaction, oxygen needs to diffuse out of the oxide and react with aluminium to form the oxide phase. This increases the diffusional path length slowing the oxygen removal reaction further. At some point, carbon also needs to enter the titanium phase to form the carbide and this needs to be accomplished through a thickening shell of alumina. Work elsewhere[50] has indicated that the formation of TiC is controlled by carbon diffusion into the system, although this was in the absence of a product oxide layer due to the use of carbon as reductant.

Milling would be expected to cause intimate mixing of the components, this would constantly expose unreacted surfaces to each other, leading to a reaction mechanism in which solid-state diffusion was of little or no importance. Thus, milling can produce an essentially complete reaction to occur at room temperature, comparatively, incomplete reaction was observed after thermal treatment at $> 950°C$ without milling. Thus, it would seem that milling causes a change in the rate-determining step of reaction from solid-state diffusion, however, the nature of the milling process does not allow the new rate-determining step to be elucidated.

5 Conclusions

Nanocrystalline, micronised composites of alumina, titanium carbide and iron can be formed by mechanochemical reaction between ilmenite, aluminium and graphite in a laboratory ball mill. A composite with contaminant levels of iron was also formed using a mixture containing rutile instead of ilmenite. The reaction was essentially complete directly after milling, despite the slightly sub-stoichiometric amount of elemental aluminium in the systems causing incomplete reduction. Identical unmilled powders showed less extensive reaction during annealing with the appearance of several intermediate phases which were absent from the milled powder.

References

1. Abramovici, R., *Materials Science and Engineering*, 1985, **71**, 313–320.
2. Bowen, C. R. and Derby, B., *Journal of Thermal Analysis*, 1994, **42**, 713–719.
3. Bowen, C. R. and Derby, B., *Journal of Materials Science*, 1996, **31**, 3791–3803.
4. Saidi, A., Chrysanthou, A., Wood, J. V. and Kellie, J. L. F., *Journal of Materials Science*, 1994, **29**, 4993–4998.
5. Saidi, A., Chrysanthou, A., Wood, J. V. and Kellie, J. L. F., *Ceramics International*, 1997, **23**, 185–189.
6. Chrysanthou, A., Saidi, A., Aylott, C. E. W. and Wood, J. V., *Journal of Alloys and Compounds*, 1994, **203**, 127–132.
7. Kunrath, A. O., Strohaecker, T. R. and Moore, J. J., *Scripta Materialia*, 1996, **34**, 175–181.
8. Kunrath, A. O., Strohaecker, T. R. and Moore, J. J., *Scripta Materialia*, 1996, **34**, 189–194.
9. Kunrath, A. O., Strohaecker, T. R. and Moore, J. J., *Scripta Materialia*, 1996, **34**, 183–188.
10. Choi, Y. and Rhee, S. W., *Journal of Materials Research*, 1993, **8**, 3202–3209.
11. Choi, Y. and Rhee, S. W., *Journal of Materials Science*, 1993, **28**, 6669–6675.
12. Choi, Y. and Rhee, S. W., *Journal of the American Ceramic Society*, 1995, **78**, 986–992.
13. Choi, Y. and Rhee, S. W., *Journal of Materials Science*, 1995, **30**, 4637–4644.
14. Choi, Y. and Rhee, S. W., *Journal of Materials Research*, 1994, **9**, 1761–1766.
15. Schwartzkopf, P. and Kieffer, R., *Refractory Hard Metals: Borides, Carbides, Nitrides and Silicides*. Macmillan, New York, 1953, p. 447.
16. Storms, E. K., *The Refractory Carbides*. Academic Press, New York, 1967, pp. 1–17.
17. Schwartzkopf, P. and Kieffer, R., *Cemented Carbides*, Macmillan, New York, 1960, p. 347.
18. Liu, L., Li, B., Ding, X., Ma, X., Qi, Z. and Dong, Y., *Chinese Science Bulletin*, 1994, **39**, 1166–1170.
19. Liu, Z. G., Ye, L. L., Guo, J. T., Li, G. S. and Hu, Z. Q., *Journal of Materials Research*, 1995, **10**, 3129–3135.
20. Liu, Z. G., Guo, J. T., Ye, L. L., Li, G. S. and Hu, Z. Q., *Applied Physics Letters*, 1994, **65**, 2666–2668.
21. Secondi, J. and Yavari, R., *Journal de Physique IV*, 1993, **3**, 1287–1292.
22. Vrel, D., Lihrmann, J. M. and Petitet, J. P., *Journal de Physique IV*, 1993, **3**, 743–746.
23. Vrel, D. L., Lihrmann, J. M. and Petitet, J. P., *Journal of Chemical and Engineering Data*, 1995, **40**, 280–282.
24. Bowen, P., Bonjour, C., Carry, C., Gonseth, D., Hofmann, H., Mari, D., Mulone, R. and Streit, P., *JOM Journal of the Minerals Metals and Materials Society*, 1995, **47**, 56–58.
25. Welham, N. J., *Minerals Engineering*, 1996, **9**, 1189–1200.
26. Welham N. J., *Journal of Materials Research*, in press.
27. Calka, A. and Radlinski, A. P., *Materials Science and Engineering*, 1991, **A134**, 1350–1353.
28. Warren B. E., *X-Ray Diffraction*. Dover, New York, 1990, pp. 251–314.
29. Becher, R. G., Canning, R. G., Goodheart, B. A. and Uusna, S., *Proceedings of the Australasian Institute of Mining and Metallurgy*, 1965, **214**, 21–44.
30. Jones, D. G., *Transactions of the Institution of Mining and Metallurgy*, 1974, **83C**, 1–14.
31. Grey, I. E., Jones, D. G. and Reid, A. F., *Transactions of the Institution of Mining and Metallurgy*, 1973, **82C**, 151–152.
32. Jones, D. G., *Transactions of the Institution of Mining and Metallurgy*, 1973, **82C**, 186–192.
33. Grey, I. E. and Reid, A. F., *Transactions of the Institution of Mining and Metallurgy*, 1974, **83C**, 39–46.
34. Welham N. J., *Proceedings of the Australasian Institute of Mining and Metallurgy*, in press.
35. Welham N. J., Carbothermic reduction of ilmenite and tile, to be submitted.
36. Albertsen, K. and Schaller, H. J., *Zeitschrift fur Metallkunde*, 1995, **86**, 319–325.
37. Weeber, A. W. and Bakker, H., *Physica B*, 1988, **153**, 93.
38. Koch, C. C., *Journal of Non Crystalline Solids*, 1990, **117/118**, 670.
39. Gaffet, E. and Harmelin, M., *Journal of Less Common Metals*, 1990, **157**, 201.

40. Shen, T. D., Koch, C. C., McCormick, T. L., Nemanich, R. J., Huang, J. Y. and Huang, J. G., *Journal of Materials Research*, 1995, **10**, 139–148.
41. Welham N. J., Mechanism of mechanical activation, (1998), to be submitted.
42. Schwertmann U., Friedi, J., Pfab, G. and Gehring, A. U., *Clays and Clay Minerals*, 1995, **43**, 599–606.
43. Welham N. J., Hwang, T. and Marsh, M. H., 1996, unpublished results.
44. Briggs, R. A. and Sacco, A., *Metallurgical Transactions A Physical Metallurgy and Materials Science*, 1993, **24**, 1257–1264.

45. Grey, I. E. and Merritt, R. R., *Journal of Solid State Chemistry*, 1981, **27**, 284–293.
46. Welham, N. J., Kerr, A. and Willis P. E., *Journal of the American Ceramic Society*, in press.
47. Kerr A., Welham, N. J. and Willis, P. E., *Nanostructured Materials*, submitted.
48. Welham N. J. and Llewellyn, D. J., Formation of nanometric hard materials, (1998), to be submitted.
49. McQuillan A. D. and McQuillan, M. K., *Titanium*. Butterworth, London, 1956, p. 466.
50. Welham N. J. and Willis, P. E., *Metallurgical and Materials Transactions*, in press.