JOURNAL OF MATERIALS SCIENCE 30 (1995) 3697–3703

Improving the uniformity in combustion-synthesized titanium carbide

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The effects of reactant dispersion and outgassing on the microstructure of combustion-synthesized TiC were investigated. Pressure filtration casting of Ti + C colloidal suspension was shown to be an effective reactant dispersion method to improve the homogeneity of the product. The relation between the nature of the outgassing atmosphere and the formation of titanium oxide and precombustion titanium carbide was investigated. The combination of the colloidal dispersion technique with outgassing was shown to provide TiC products with reduced defects and improved microstructure.

1. Introduction

As in other powder processing methods, particle size and dispersion uniformity play key roles in self-propagating high-temperature synthesis (SHS). An increase in the size of the reactant particles can lead to a decrease in the combustion wave velocity with attendant changes in the mechanism of the combustion process or the nature of the products [1, 2]. Expectedly, reduction of particle size alone is not a sufficient requirement for control of powder reactions. The degree of dispersion of the reactant particles is equally important. This is especially critical in self-propagating reactions due to their relatively short reaction times which favour short diffusion lengths and hence intimate contacts between reactants. The ideal situation would be one in which fine particles are packed in an ordered form, i.e. with one reactant particle surrounded by the appropriate number of particles of the other reactant, depending on stoichiometry. Recent computer simulation has shown that the combustion of an ordered array of particles produced steady-state waves while the combustion of random arrays gave rise to non-steady wave propagation [3].

The matter of contact between particles under a variety of powder processing methods (e.g. sintering) is dictated by the green density of the compact and hence is dependent on the compaction pressure. In the case of combustion synthesis, another effect can play a role in the degree of contact between adjacent particles. Volatile impurities contained in or adsorbed on the reactant powders can be released prior to the arrival of the combustion wave resulting in pore formation and hence reduction in contact between the particles. The role of impurities in the formation of porosity during combustion synthesis has been recently analysed [4]. In this paper, we investigate means of improving the uniformity of combustion-synthesized TiC by focusing on the two problems discussed above. To improve reactant uniformity, we use a colloidal approach to mix the titanium and carbon reactants, and to ameliorate the problem of volatile impurities we study the effect of outgassing on the synthesis of TiC. Theoretical as well as experimental aspects of the synthesis of this refractory have been previously investigated [5].

2. Experimental procedure

The characteristics of the reactant materials used to synthesize TiC in this study are summarized in Table I. The effect of reactant properties on the microstructure of the resultant TiC has been reported in a previous paper [6]. Particle size distribution was determined by gravity/centrifuge sedimentation or by light-transmission sedigraph. Densities were measured using helium pycnometry.

Titanium plus carbon or titanium plus graphite powder mixtures were proportionally weighed to produce a stoichiometric carbide, $TiC_{1.0}$. The reactants were mixed in 10–50 ml of methanol via an ultrasonic probe set at 75 W for 4–5 min. The mixture was then vacuum-filtrated to remove the methanol and cold-pressed by an axial pressure of 35 MPa. Colloidal pressure filtration was performed in a pressure casting cell schematically illustrated in Fig. 1. Solvents used in the pressure filtration of the reactants were methanol, cyclohexane, an azeotrope of methylethyl ketone and ethanol. Surfactants used in the colloidal consolidation process were Oloa 1200, L-4510 and menhaden fish oil.

Colloidal suspensions were ultrasonically mixed at 25 W for 2 min in a water-cooled bath prior to casting. Maximum solids loadings in each suspension were determined by visual observation with the maximum being resolved by a loss of fluidity in the slip. Casting pressure was maintained at 0.28 MPa for 23 h then increased to 0.5 MPa for 1 h in conjunction with a 6.66 Pa vacuum applied to the drain side during the last 15 min. Measurements using Archimede's principle, via force immersion in liquid mercury, were

TABLE I Titanium, carbon, and graphite reactant materials

Reactant	Particle sizes (μm)		Density ($g\,cm^{-3}$, He)	BET Surface area ($m^2\,g^{-1}$)
	50% below	100% below		
Carbon black (Monarch 700)	1	6	1.93	246
Carbon black (Monarch 1100)	3	8	1.97	250
Carbon black (Regal 250R)	6	34	1.88	6
Graphite powder (Alfa 00641)	25	80	2.28	8.3
Titanium powder (Micron Ti-020)	30	80	4.45	0.4

BET, Brunauer–Emmett–Teller.

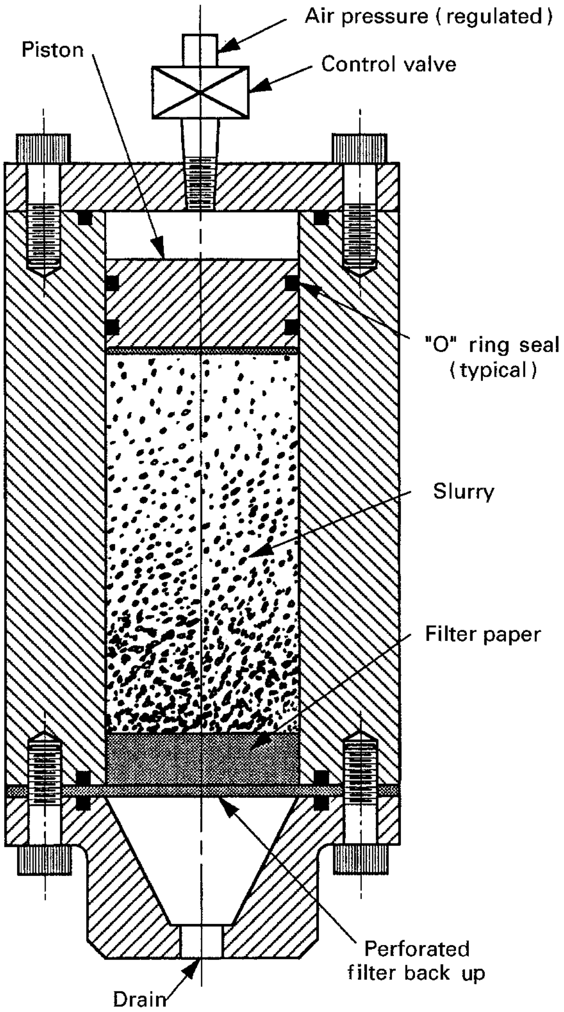


Figure 1 Schematic representation of colloidal pressure casting cell.

made on the pressure-cast bodies to determine their densities. The error in this method was ± 1.4–2.0%.

Thermal-vacuum outgassing was performed by heating the cold-pressed or pressure-cast bodies via a resistance-heated tantalum element that surrounded the part. Heating was maintained at a rate of $25\,K\,min^{-1}$. Ignition was initiated by a resistance heated tungsten coil with a heat-flux area of $1.2\,cm^2$ that reached 2700 K. Ignition occurred within 2–5 s after energizing the coil which was placed 0.3 cm above the sample. All combustion synthesis was carried out by igniting the sample in a vacuum of 3–8 Pa. Vacuum was selected as the synthesis environment to increase the conversion efficiency of the reactants [7].

3. Results and discussion

3.1. Colloidal consolidation studies

In this study three solvents were chosen, each with different hydrogen-bonding behaviour [8, 9]. These were: (1) a hydrocarbon solvent (cyclohexane), (2) a polar solvent (methanol) and (3) a 66:34 wt % methylethylketone/ethanol azeotrope that possesses hydrogen bonding qualities intermediate between (1) and (2). Organic hydrocarbon solvents are non-polar liquids with small intermolecular forces. The attraction of these liquids to surfaces is both small and non-specific, hence these solvents are often referred to as "non-wetting" solvents. In contrast, polar solvents have stronger intermolecular forces that promote their adsorption onto the surfaces of particles. Consequently, these are referred to as "wetting" solvents. These solvents alone, however, will not stop the attractive nature of the reactant particles to yield a "true" dispersion. Stable dispersions can only be achieved through the addition of a surface active agent (surfactant) that will impart a steric hindrance to the attractive forces inherent in the solvent–particle system.

In this work, three surfactants were also studied. These were: a polyisobutene succinamide (Oloa 1200), a fluorinated polymer (L-4510), and menhaden fish oil (MFO). Oloa 1200 is a head/tail copolymer used as a dispersant for paints and inks and also as a lubricating aid in motor oils. It has also been used effectively in organic solvents for the dispersion of carbon blacks [10, 11]. The L-4510 is a random fluorinated copolymer that is typically used as a lubricating aid in non-aqueous floor waxes and as a drilling additive [12]. It is soluble in most hydrocarbons and has been used as a lubricant to enhance particle–particle rearrangement during the colloidal processing of ceramics [13]. Menhaden fish oil is a fatty acid complex [14] commonly used in azeotrope solvents for the tape casting of electronic ceramics.

It should be noted that the L-4510 surfactant generally does not yield a steric-stabilized colloidal suspension. Rather, this unique polymer results in improved consolidation without colloidal stability. This is achieved through lubrication of reactant particle surfaces during the final stages of the compaction process. This makes its application very suitable for consolidating reactant particles with different theoretical densities (e.g. carbon with titanium). Because steric stabilization is not required, the faster settling rate of the heavier titanium particles does not have to be taken into consideration. Instead, both the sterically coated titanium and carbon particles rapidly settle through the solvent (after mixing) at nearly the same rate. Differential settling of titanium and carbon reactants can become a problem in steric-stabilized suspensions. This effect is amplified with low solids loadings, which is discussed next.

Before the codispersed reactant slips can be pressure-cast, their maximum solids loading must be determined. Solids loading is an indicator of the practical ability to obtain a stable suspension. This is particularly important when different density reactants are to be codispersed and differential settling is to be minimized. Conventional ceramic slips typically achieve solid loadings between 40–50 vol % [15]. With these high solid loadings differential settling can be substantially reduced due to the inability of the heavier particles to settle down through the suspended lighter particles. When solids loading is low, however, heavier particles can quickly fall to the casting filter resulting in the segregation of the reactants in the uncombusted sample.

Solids loading results are presented in Fig. 2 for the Ti + C mixtures made from the reactants of Table I and dispersed in methanol. Methanol was selected for this study because it was the most "wetting" solvent, thereby allowing each individual particle to be separated by a solvent layer. Solvent-only systems were used in the solids loading study because surfactants would have introduced additional particle–particle separation (repulsion), thereby further reducing the solids loading measurements. In Fig. 2 the solids loading values are plotted against the 50-percentile and 100-percentile particle sizes for the carbon and graphite reactants shown in Table I. The results indicate that larger carbon reactants allow for increased solids loadings for colloidal processing. The lines in the figure are linear regressions of the two sets of data, respectively.

Solids loading greatly influences the rheology of the slip to be cast. Reducing the particle size typically results in increasing the viscosity of the slip. This is due to increased particle–particle interaction as the particle size decreases for a given solids loading. Van der Waal's forces of attraction alone are generally strong enough to affect adjacent particles when their surfaces are within 2 nm of each other. Even in relatively dilute suspensions, such as those of the Ti + C codispersions of Fig. 2, considerable particle–particle interaction can occur. This interaction has been documented, *in-situ*, by Halverson and Lum [16] using video augmented differential interference contrast microscopy (VADICM), and by others using transmission optical microscopy [17].

Excessive solids loadings result in severe agglomeration of the reactants which can introduce very large defects into the uncombusted body. Consequently, it is necessary to adhere to the solids loading maximums in preparing the solvent–surfactant slips for pressure filtration casting. Since the data of Fig. 2 indicate that the highest solids loadings are obtained for Micron Ti-020 in combination with the Regal 250R carbon black or the Alfa 00641 graphite reactants, these two mixtures were selected to demonstrate the effectiveness of colloidal pressure filtration.

The pressure filtration results of the three solvent-only and three solvent–surfactant systems used to disperse the titanium and carbon or titanium and graphite slips are shown in Fig. 3. The data show that for both carbon and graphite-containing slips the highest uncombusted sample density was achieved with either the solvent–surfactant system containing a polyisobutene succinamide copolymer (Oloa 1200) in a hydrocarbon solvent (cyclohexane), or with the solvent–surfactant system containing a lubricating fluorinated polymer (L-4510) in a hydrocarbon solvent (cyclohexane). The results also indicate that slips made with carbon blacks achieve higher uncombusted sample densities than slips made using graphite powders. This can be attributed to the fact that the carbon blacks possess a higher surface area than the graphite powders, providing a greater number of surfactant adsorption sites. Improved surfactant adsorption enhances the steric repulsion of the carbon-containing reactant, thereby improving particle–particle stability in the slip and particle–particle packing and sliding during the final stages of the compaction process. Fig. 3 also shows that Ti + C slips made from solvents without a surfactant result in lower uncombusted sample densities compared to slips when a surfactant is used. The parenthetic values given in the figure indicate the weight percent surfactant used in the solvent–surfactant system before addition of the reactants.

3.2. Thermal-vacuum outgassing studies

The release of volatile gases caused from the vaporization of adsorbed species on the reactant's surface can

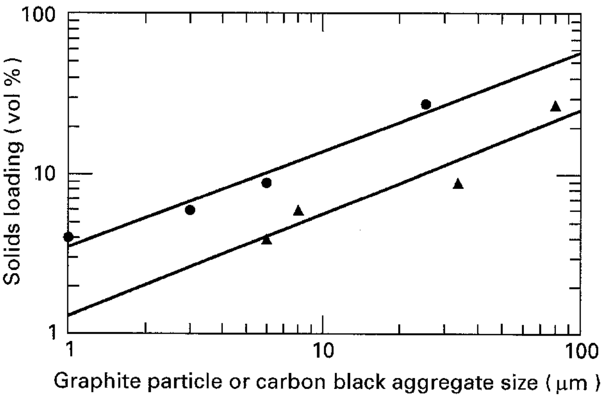


Figure 2 Solids loading as a function of aggregate or particle domain size for Ti + C mixtures according to the 50- (●) and 100-percentile (▲) of the particle size distribution.

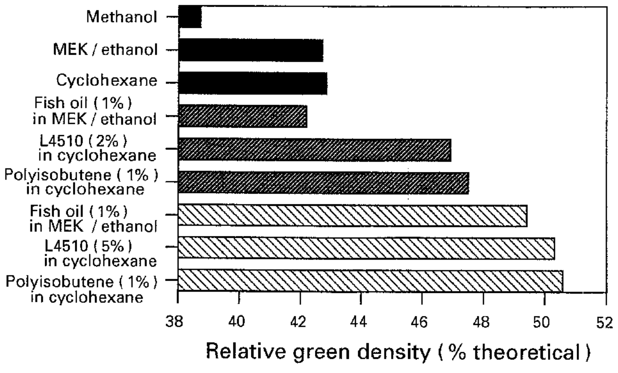


Figure 3 Colloidal pressure-filtration results for Micron Ti-020 titanium dispersed with Cabot Regal 250R carbon black (■) in solvent only, (▨) with surfactant and Alfa 00641 graphite (▧) with surfactants.

nullify the gains made by colloidal consolidation techniques used to improve uniformity in the combustion-synthesized product. Removing undesirable sources of volatility prior to synthesis requires that an appropriate thermal-vacuum outgassing treatment be applied to the uncombusted reactants after they have been consolidated. To establish the optimum preconditioning variables (temperature, time, vacuum) for the synthesis of TiC two parametric studies were performed.

The first study examined the oxidation of the titanium reactants in a vacuum where TiO_2 could form and remain stable. The second study examined the solid-state diffusion of carbon into the titanium in a vacuum where the formation of TiO_2 is not thermodynamically favoured. Emphasis in these two studies was placed on the conversion of the titanium reactant to its oxide or carbide rather than on chemical changes of the carbon reactant. This is because the uncombusted samples contained a major portion (65 vol %) of the metal reactant. Samples containing carbon black, rather than graphite, were used in these studies. This is because equal weight Ti + C compacts containing graphite would possess a substantially lower carbon-reactant surface area than those made from carbon black. It was felt that the greater surface area associated with the carbon blacks would present a larger number of adsorbed species to be volatilized as well as a greater number of contact sites for carbon diffusion.

The results of the first study are given in Fig. 4, where the oxidation of the titanium in Ti + C compacts was monitored (based on TiO_2 formation) at two outgassing temperatures (1073 K and 1173 K) and at times ranging from 0–60 min. The results indicate that under a vacuum of 27–67 Pa considerable oxidation of the titanium reactant can occur as determined from the X-ray analysis based on the intensity of the (1 1 0) peak for TiO_2. Since the removal of adsorbed species is a kinetic process, a finite amount of time will be required for complete desorption to occur. Fig. 4 shows that there are two competing phenomena; namely the desorption of volatile species and the oxidation of the titanium reactants. The data indicate longer times at lower temperature are required when the preconditioning environment contains even minor amounts of oxygen. At this vacuum level the oxygen content is in the range of 100–170 p.p.m.

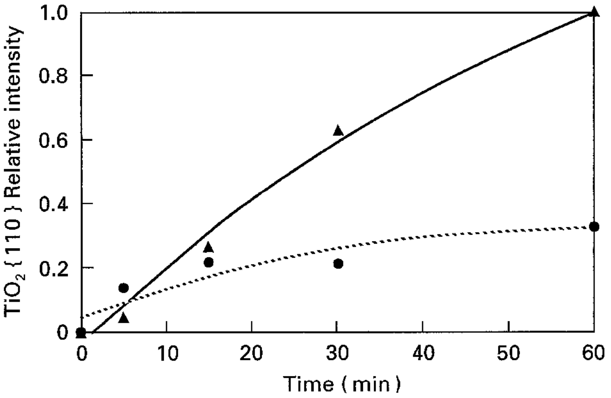


Figure 4 Oxidation of Micron Ti-020 titanium mixed with Cabot Monarch 900 carbon black resulting from outgassing in a low-vacuum environment (27–67 Pa). (▲) 1173 K; (●) 1073 K.

It is important to note that a relative TiO_2 peak height of 1.0 in Fig. 4 does not indicate complete conversion of the titanium reactant to the oxide. Rather, it indicates the relative amount of TiO_2 present compared to reactants that underwent thermal-vacuum outgassing at 1173 K for 60 min. Portions of the X-ray diffraction scans from the samples preconditioned in this study are shown in Fig. 4. The scans show that TiO_2 is forming, expectedly, at the expense of elemental titanium. The scans cannot be compared on an absolute basis because different detectors (on different diffractometers) were used to obtain the results. However, they can be compared on a relative basis and account for the results of Fig. 4 being presented as relative peak heights instead of as integrated intensities.

The curves in Fig. 4 are second-order regressions of the data points. The shape of these regressions indicates parabolic growth of the oxide layer on the reactant's surface. At 1073 and 1173 K the diffusion coefficients for oxygen in α-titanium are reported as 4.0×10^{-15} and 2.5×10^{-14} $m^2 s^{-1}$, respectively [18]. This implies that after 1 hour at these temperatures, the surface of the Micron Ti-020 particles will have formed an oxide coating with a thickness of 4 and 30 μm, respectively. The latter suggests substantial conversion of the titanium reactants to TiO_2 after 1 h at 1173 K.

The results of Figs 4 and 5 indicate that the oxidation of titanium can occur rapidly at temperatures as low as 1073 K when the outgassing environment is 27–67 Pa vacuum. Fig. 5 also indicates the presence of trace amounts (2–5 wt %) of TiC in all of the preconditioned samples. The diffusion coefficient of carbon in α-titanium at 1073 and 1173 K has been reported as 6.0×10^{-13} and 4.0×10^{-12} $m^2 s^{-1}$, respectively [19]. These imply that the diffusion of carbon in titanium should be faster than the diffusion of oxygen. Only trace amounts of TiC were detected because carbon diffusion is dependent primarily upon Ti and C particle contacts (i.e. bulk and surface diffusion), whereas the diffusion of oxygen is kinetically assisted by the gas transport of oxygen atoms to all parts of the titanium surface.

In order to reduce the amount of oxygen contamination a second study was performed by preconditioning the uncombusted samples at a vacuum level of 3–8 Pa. The results of this study are presented in Fig. 6. The curves in the figure are again second-order regressions of the data points. In this study, temperatures between 1073 and 1573 K were investigated, with the time at each temperature being maintained for 1 h. X-ray diffraction analyses of the preconditioned samples under these conditions did not reveal the presence of TiO_2 nor TiO. Instead, a less stable oxide, Ti_2O, was found to be predominant at the lower temperatures.

Fig. 6 shows the relative intensity (peak height) for Ti_2O relative to the sample with the highest Ti_2O content (1073 K after 1 h). This oxide is substantially

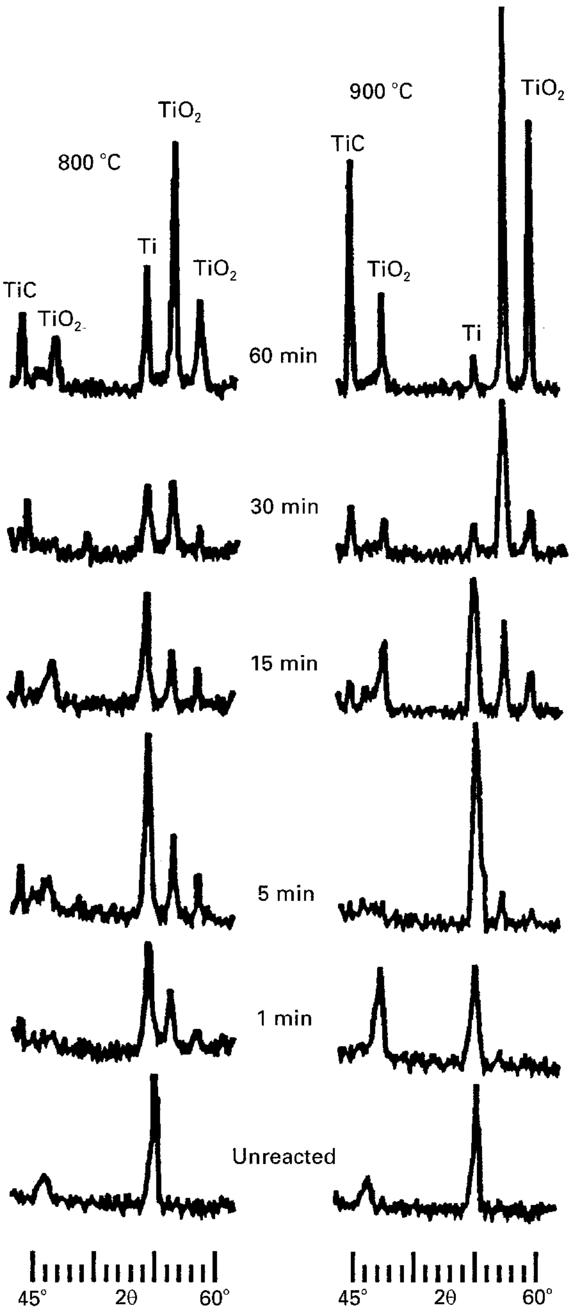


Figure 5 X-ray diffraction scans for the 1073 and 1173 K data points shown in Fig. 4.

reduced at higher preconditioning temperatures, becoming negligible after 1 h at 1573 K. The results of this study are thermodynamically supported by phase equilibria data reported in the literature [20, 21]. The lower oxygen content associated with thermal-vacuum outgassing at 3–8 Pa helps to reduce the tendency for oxidation of the titanium reactant. At this pressure, oxygen levels are at values in the range of 10–20 p.p.m., which do not favour oxygen transport, thus allowing carbon diffusion to dominate.

In Fig. 6, the intensity (peak height) for TiC is given relative to the sample with the highest TiC content (1573 K after 1 h). The diffusion of titanium in TiC and carbon in TiC at 1573 K is reported to be 4.0×10^{-25} and 2.0×10^{-17} m^2 s^{-1}, respectively [22–25]. These data indicate that after 1 h a layer thickness of only 250 nm of each titanium particles's surface is converted to TiC. The complete conversion

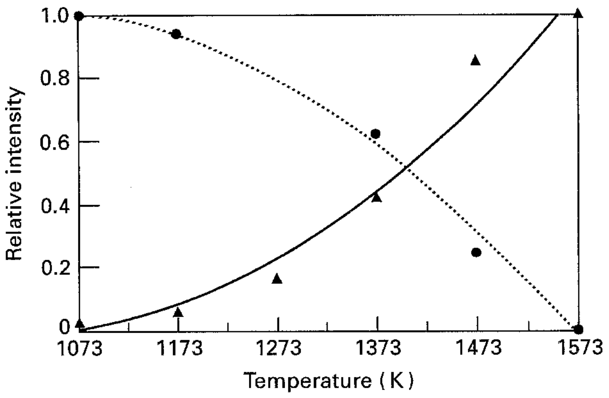


Figure 6 Effect of outgassing in a vacuum of 3–8 Pa on the formation of Ti_2O {1 0 1} (●) and TiC {1 1 1} (▲) .

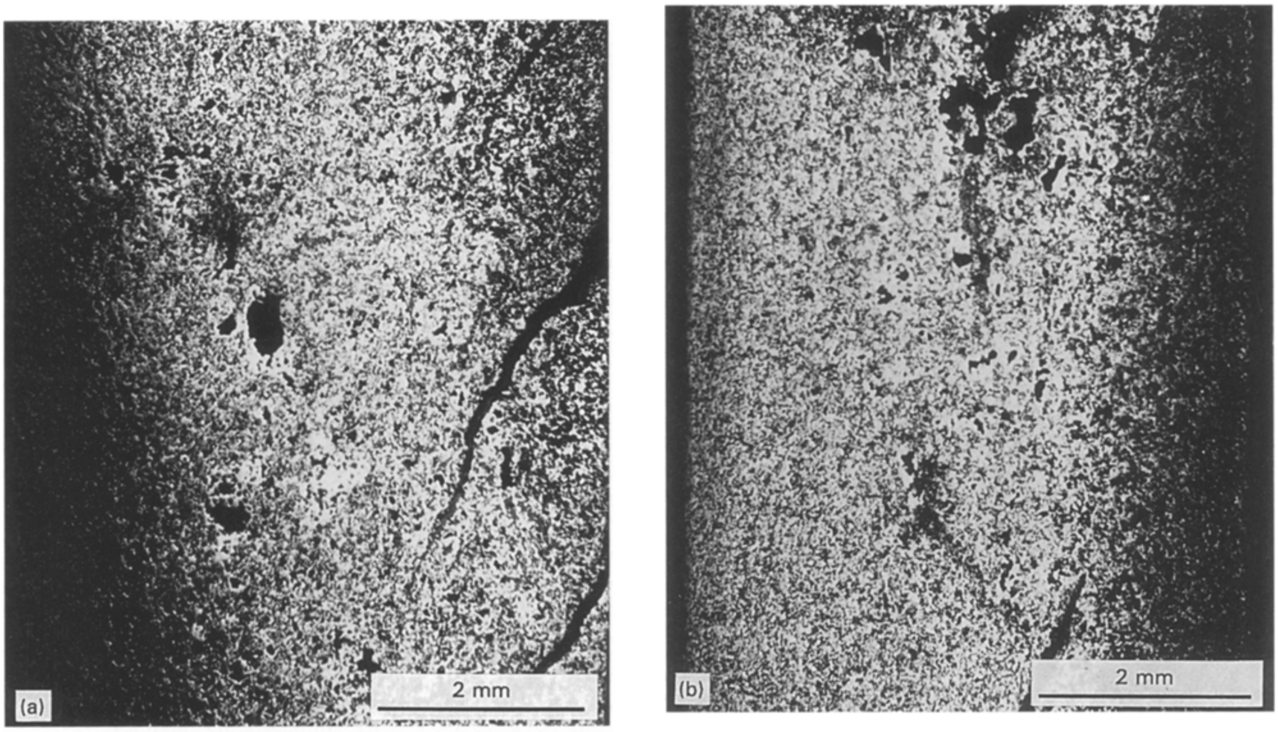
of a 40 μm diameter Micron Ti-020 particle to TiC in 1 h would require a temperature of 2273 K. Even though only a small amount of the surface is converted, diffusion also results in partial sintering of the uncombusted body. This is evidenced by the fact that thermally preconditioned samples are easier to handle (without breaking) than unconditioned samples.

The formation of TiC during outgassing reduces the driving force of the combustion reaction resulting in lower wave velocities, conversion efficiency, and the degree of sintering that occurs between TiC product gains [26–28]. For this reason, it was decided to use 1133 K and 3–8 Pa for 1 h as the optimum thermal-vacuum outgassing condition for comparing the combustion synthesis of outgassed versus non-outgassed cold-pressed and colloidal-pressure-cast Ti + C compacts.

Microstructural comparison of combustion synthesized TiC products are shown in Fig. 7(a)–(c). Fig. 7(a)–(b) show microstructures of cold-pressed Ti + C compacts (Micron Ti-020 titanium and Alfa 00641 graphite) with and without thermal-vacuum preconditioning, and Fig. 7(c) shows the microstructure of the colloidal-pressure-cast Ti + C compact which was outgassed prior to combustion. These microstructures progressively illustrate the improvements obtained first by applying thermal-vacuum treatment and second by improving particle packing, uniformity, and reactant homogeneity in the uncombusted body. Similar improvements were also realized when samples containing Regal 250R carbon black were studied. Without preconditioning, very large (millimetre size) surface cracks occur in the synthesized part. By outgassing, these cracks are substantially reduced, although considerable non-uniformity remains in the product. Microstructural uniformity is best achieved in the colloidal-pressure-cast product.

4. Summary

Colloidal processing and thermal-vacuum outgassing studies have been performed to investigate product microstructure uniformity in porous combustion-synthesized TiC bodies. Microstructural defects introduced into the uncombusted samples during consolidation can be substantially reduced through the



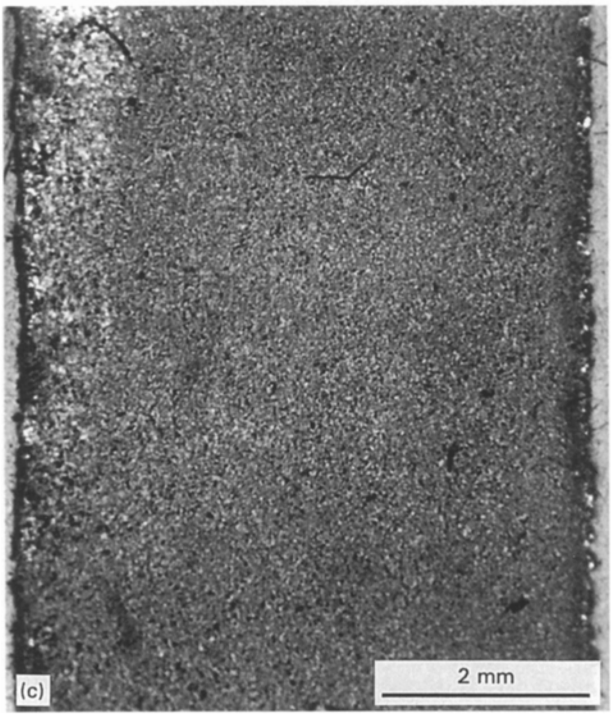


Figure 7 Low-magnification microstructural comparisons of SHS TiC preforms (Micron Ti-020/Alfa 00641) illustrating the effect of sample outgassing and colloidal processing methods on improving product uniformity: (a) ultrasonically-mixed and uniaxially-cold pressed, 34.5 MPa, not outgassed; (b) same as (a) but samples were outgassed; (c) pressure-cast and outgassed.

application of colloidal consolidation methods. Pressure filtration casting of Ti + C colloidal suspensions is strongly influenced by the degree of solids loading in the slip. The results of this study have shown that Ti + C solids loading is directly related to the particle size of the carbon reactant in a logarithmic fashion. This relationship indicates that particles greater than 10 μm are required to obtain solids loadings greater than 10 vol %. Solids loadings up to 25 vol % have been obtained when graphite powders, rather than carbon blacks, are used in the consolidation of the uncombusted body.

The violent outgassing of volatile species during gasless combustion synthesis of a Ti + C body also has been shown to be responsible for a considerable amount of non-uniformity in the combusted product. The results of this effort have shown that thermal-vacuum preconditioning of the uncombusted body, prior to its ignition, can eliminate microstructural exfoliation and sample disintegration. Low vacuum environments ($\geq$ 25 Pa) have been shown to result in excessive oxidation of titanium reactants processed between 1073 and 1173 K for 15–60 min. This results in the formation of a surface layer of TiO_2 on the titanium particles which inhibits TiC product formation during synthesis and leads to incomplete conversion of the reactants. Higher vacuum environments (3–8 Pa) were shown to be more effective in that the formation of Ti_2O is thermodynamically favoured over the formation of TiO_2. Because Ti_2O is less stable, its presence during synthesis does not inhibit TiC product formation to the extent that TiO_2 does.

Furthermore, the rapid solid-state diffusion of carbon into the titanium also requires that preconditioning temperatures be limited to some extent. The results of this study have shown that excessive amounts of TiC can also form at the surface of the titanium reactants if the preconditioning temperature is too high. Because excessive amounts of TiC in the uncombusted body will serve as a diluent to the reaction, the optimal thermal-vacuum treatment was established to be 1133 K for 60 min in a vacuum of 3–8 Pa. All TiC combustion synthesis reactions that were preconditioned in this manner exhibited negligible exfoliation without disintegrating the product produced. Combining colloidal pressure filtration techniques and thermal-vacuum outgassing treatments can produce combustion-synthesized TiC product microstructures with reduced defects and improved microstructural uniformity.

References

1. J. TRAMBUKIS and Z. A. MUNIR, *J. Amer Ceram. Soc.* **73** (1990) 1240.
2. Z. A. MUNIR and N. SATA, *Int. J. Self-Prop. High-Temp. Synth.* (1993) in press.
3. K. H. EWALD, MS Thesis, University of California, Davis, 1993.
4. Z. A. MUNIR, *J. Mater. Synth. Process.* (1993) in press.
5. J. B. HOLT and Z. A. MUNIR, *J. Mater. Sci.* **21** (1986) 251.
6. D. C. HALVERSON, K. H. EWALD and Z. A. MUNIR, *Ibid.* (1993) in press.
7. V. K. PROKUDINA, V. I. RATNIKOV, V. M. MASLOV, I. P. BOROVINSKAYA, A. G. MERZHANOV and F. I. DUBOVITSKII, in "Combustion processes in chemical technology and metallurgy," edited by A. G. Merzhanov (Chernogolovka, Russia, 1975) p. 136.
8. R. C. NELSON, R. W. HEMWALL and G. D. EDWARDS, *J. Paint Tech.*, **42** (1970) 636
9. J. RAMSBOTHAM, *Progress in Organic Coatings* **8** (1980) 113.
10. F. M. FOWKES and R. J. PUGH, in " Polymer adsorption and dispersion stability" edited by E. D. Goddard and B. Vincent (The American Chemical Society, 1984) pp. 331–56.
11. R. J. PUGH and F. M. FOWKES, *Colloids and Surfaces* **9** (1984) 33.
12. 3M Company, *Fluorad*: Well Stimulation Additive. Other fluorinated surfactants are available under the trade names *Zonyl* (Du Pont) and *Forakyl* (Autochem).
13. D. GALLAGHER, PhD Dissertation, University of Washington, Seattle, 1988.
14. P. D. CALVERT, E. S. TORMEY and R. L. POBER, *Amer. Ceram. Soc. Bull.* **65** (1986) 669.
15. J. W. BRIDGE, D. C. HALVERSON and B. Y. LUM, in Proceedings of the 89th Annual Meeting of the American Ceramic Society, Pittsburgh, PA, April 1987.
16. D. C. HALVERSON and B. Y. LUM, Poster session presented at the 88th Annual Meeting of the American Ceramic Society, Chicago, IL, May 1986.
17. D. C. AGRAWAL, R. RAJ and C. COHEN, *J. Amer. Ceram. Soc.* **72** (1989) 2148.
18. D. DAVIS, G. BERANGER and E. A. GARCIA, *J. Electrochem. Soc.* **130** (1983) 1423.
19. J. ASKILL, "Tracer diffusion data for metals, alloys, and simple oxides" (Plenum Press, New York, 1970).
20. E. M. LENIN, C. R. ROBBINS and H. F. MCMURDIE, in "Phase diagrams for ceramists," Vol. II, edited by M. K. Reser (American Ceramic Society, Columbus, OH, 1969) p. 9.
21. E. M. LENIN and H. F. MCMURDIE, in "Phase diagrams for ceramists," Supplement, edited by M. K. Reser (American Ceramic Society, Columbus, OH, 1975) p. 14.
22. S. SARIAN, *J. Appl. Phys.* **40** (1969) 3515.
23. C. J. QUINN and D. L. KOHLSTEDT, *J. Am. Ceram. Soc.* **67** (1984) 305.
24. S. SARAIN, *J. Appl. Phys.* **39** (1968) 3305.
25. *Idem, Ibid.* **39** (1968) 5036.
26. S. D. DUNMEAD, D. W. READEY, C. E. SEMLER and J. B. HOLT, *J. Amer Ceram. Soc.* **72** (1989) 2318.
27. V. M. SHKIRO and I. P. BOROVINSKAYA, in "Investigation of combustion regularities of titanium–carbon mixtures," edited by A. G. Merzhanov, Chernogolovka, 1975, p. 253, for Lawrence Livermore National Laboratory, LLNL Ref. No. 03006.
28. A.G. MERZHANOV, G. G. KARYUK, I. P. BOROVINSKAYA, S. YU. SHARIVKER, E. I. MOSHOVSKII, V. K. PROKUDINA and E. G. DYAD'KO, *Sov. Powder Metall. Met. Ceram.* **20** (1981) 709.

*Received 3 December 1993
and accepted 3 February 1995*