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The One-Step Synthesis of Dense Titanium-Carbide Tiles

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Self-propagating, high-temperature synthesis (SHS), which is an attractive process for forming alloys, cermets, ceramics, and composites, has been combined with a rapid quasi-isostatic consolidation technology called the Ceracon™ process. This one-step synthesis and densification route has been applied to the rapid fabrication of large 15 cm × 15 cm × 2.5 cm titanium carbide tiles. A cost analysis of this process based on prototype quantities shows that the cost of the process is 30–50% of that of current manufacturing processes.

INTRODUCTION

The reaction between particulate materials in a self-propagating mode is an attractive alternative to conventional materials processing techniques due to the simplicity of the process, the low-energy requirement, the higher purity of the products, and the possibility of one-step synthesis and densification. The self-propagating, high-temperature synthesis (SHS) process continues to generate interest because of the significant number of current and potential applications, including:

- Heating elements ($MoSi_2$).
- Shape memory alloys (TiNi).
- High-temperature structural alloys (NiAl).
- Armor materials (TiB_2 and TiC).
- Powders for structural ceramics (Si_3N_4, TiC, and TiN).
- Coatings for the containment of corrosive media and liquid metals (products of iron and Al_2O_3 in a thermite reaction).

U.S. materials manufacturing industries have not vigorously pursued the commercialization of the SHS products for commercial and defense applications because of two major limitations in SHS-processed materials: the high cost of the starting pure-metal ingredients and the significant amount of porosity in the resulting material.

The first problem is being addressed[1] through the use of cheaper starting materials—TiO_2 instead of pure titanium, for example. The TiO_2 is reacted with magnesium and TiC to form TiC-MgO composites. Another example is the use of CrO_3 in reaction with boron to form CrB_2.

The problem of significant intergranular voids and agglomerates in the SHS-processed material is inherent to the SHS process, which is a gasless reaction of the powder ingredients to form TiC. The known efforts to improve density include the application of hydraulic pressure[2] by scientists in the former Soviet Union with limited success. Synthesis and densification have been attempted in a single process by hot pressing, hot rolling, hot isostatic pressing (HIPing), and high-temperature shock waves while the reaction is occurring.[3,4] Lawrence Livermore National Laboratory has produced TiB_2/Fe composites to 95 percent of theoretical density.[5] The use of expensive processes such as HIPing and hot pressing is not attractive because of the extended processing times and the degradation of the material due to phase decomposition.

THE CERACON PROCESS

The Ceracon process is a low-cost powder metallurgy process for achieving full-density, near-net shape parts.[6] It is a simple consolidation technique that utilizes a conventional powder metallurgy setup. The Ceracon process is a quasi-isostatic, hot-

Table I. Effects of Cold Isostatic Pressure on the Ignition Characteristics and Density of the (Titanium + Carbon) Preform

Cold Isostatic Pressure (MPa)	Theoretical Density (%)*	Time for Initiation of Combustion Wave (s)	Time from Initiation of Wave to Flare (s)	Post-Ignition† Density (%)‡	Wave Tavel before Flare
2	71	11	7	52.85	
83	75	13	9	53.46	
241	85	62	5	54.27	
310	86	79	5	53.46	
379	87	65	4	55.73	

* Theoretical Density = 3.811 g/cm³.
† Theoretical Density = 4.92 g/cm³.
‡ Combustion synthesized not consolidated.

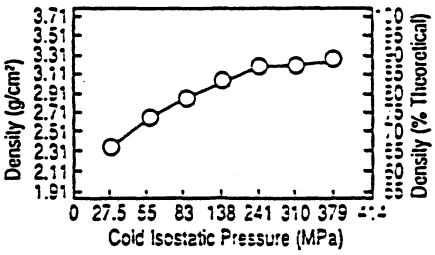

Figure 1. The effect of cold isostatic pressure on green density.

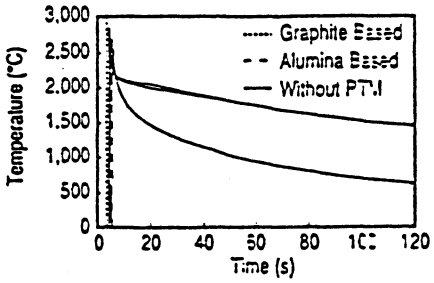

Figure 2. Time-temperature profile for the TiC part upon ignition in various pressure transmitting media.

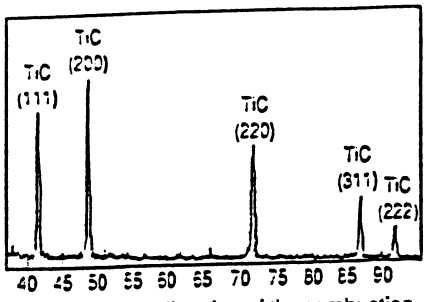

Figure 3. X-ray diffraction of the combustion-synthesized and Ceracon-forged TiC.

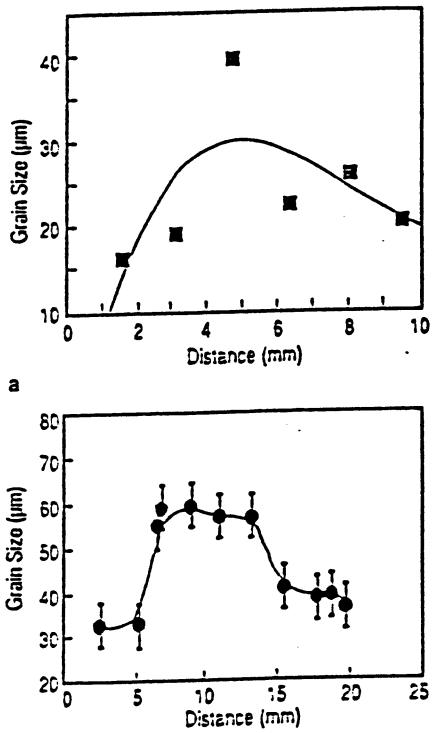

Figure 4. Grain size as a function of distance along the cross-section for (a) a 6.35 cm square cross-section TiC tile and a (b) 10.16 cm square cross-section TiC tile.

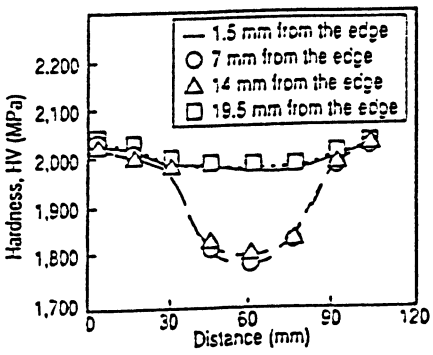

Figure 5. Hardness traverses along the cross section of a 10.16 cm TiC tile.

consolidation technique much like HIPing, except that it utilizes a ceramic particulate material as a pressure transmitting medium (PTM) instead of the gas medium used in HIPing. Pressures up to 1.24 GPa can be used, and materials can be processed at unlimited upper temperatures. The process consists of four steps: fabrication of green preform, transfer (after heating) of the part and grain to a Ceracon die, consolidation of part that is immersed in the hot PTM column, and part removal and grain recycling.

The low temperatures in conjunction with the short-time consolidation capabilities of the quasi-isostatic, hot-consolidation, high-pressure process have been used to consolidate a broad range of material systems, including steel; Al, Ti, Cu, Zr, W, Nb, and their alloys; Ni and Co superalloys; ceramics, including ITO, TiC, AlN and superconductors; intermetallics such as aluminides and silicides; glassy and amorphous materials; and composites.

By combining the combustion synthesis and Ceracon forging processes into a single-step technique (CS/CF), the hot particulate in the Ceracon forging process serves as a combustion initiator and pressure transfer medium. This technique has been successfully applied at Ceracon, with the U.S. Army Research Laboratory's support, to fabricate large 15 cm × 15 cm × 2.5 cm TiC tiles.

PROCEDURE

Selecting Precursor Powders

Ultrafine microtitanium (20 μm) from Micron Metals of Salt Lake City, Utah, was found to be suitable for fabricating small TiC specimens (i.e., <25.4 mm diameter and height) and this was validated in a separate study by the U.S. Army Research Laboratory. Larger specimens of TiC with dimensions of 5 cm × 5 cm × 2 cm or more were found to exhibit a more violent reaction with an increased speed-of-combustion wave travel, including a flare and audible explosion. Because of the higher cost of the ultrafine microtitanium, the safety issues arising from storing and handling the very fine titanium powder, and the higher rate of oxidation. Therefore, coarse titanium powder was selected and used successfully in the program. Also, literature from research in the former Soviet Union indicates that coarse titanium powder slows down the velocity of the combustion wavefront and results in parts having significantly reduced cracking.[8]

Powder Blending

Both wet ball milling and dry milling have been used to blend the titanium and carbon powders. Wet milling of larger batches becomes less desirable than dry milling due to the additional effort required in complete evaporation of the solvent (ethanol); increased cost, longer milling, and longer evaporation time; possibilities of oxidization of the titanium during drying; and increased hazard during the evaporation process.

Aluminum jars 30 cm long × 17.5 cm diameter with an approximate volume of 7.5 L were lined with silicone rubber. Zirconia cylinders 1.2 cm × 1.2 cm long were used as media and filled approximately 50 vol.% of the mill jar. Titanium and carbon powders in a 1:0.9 molar ratio (corresponding to 81.58 wt.% Ti) were weighed out in a protective atmosphere. The mill jars were rotated at 60–80% of the critical speed for four to six hours. Each mill jar produced 2 kg of blended TiC powder. The blended powders were stored in sealed containers under argon immediately after separation from the media.

Cold Isostatic Pressing

Blended powders were cold isostatically pressed at various pressures (55–380 MPa) into discs approximately 4.5 cm diameter × 1 cm. The effect of the cold isostatic pressure on the green density is shown in Figure 1. These green preforms were inserted into a furnace preheated to 1,200°C with an air environment. A videotape camera was used to record the combustion wave propagation and characteristic behavior. After insertion of the preform disc into the furnace, a wave was seen initiating from the top edge of the disc. This wave traveled through the disc, which showed a pronounced conflagration. Table I shows the time of the wave from ignition to flare-up and the amount of wave travel before the flare.

With an increase in cold isostatic pressure, the density of the preform increases and it takes longer for the preform to ignite. This is in accordance with the literature from the former Soviet Union,[10] where researchers noted increased thermal conductivities with increased green densities. This results in a channeling away of the heat, resulting in longer times for ignition. With increasing green densities, the time from ignition to conflagration is also reduced, causing increased violence during the flare-up. The violence during flare-up increases the degree and probability of cracking or breaking during combustion synthesis. At lower densities, the green preforms of blended TiC powders had poor strengths, producing problems during handling prior to ignition. They also showed a propensity towards cracking before and during the CS/CF cycle. These results corroborated the calculations that preform densities of around 65–75% produced by cold isostatic pressures of 55–67 MPa would be optimum. Cold isostatic pressures below 55 MPa produced very fragile and difficult-to-handle preforms,

limiting testing to lower density samples.

In-situ CS/CF of TiC

During the in-situ CS/CF process, the PTM is heated to 1,200°C. The medium is then poured into the Ceracon process die, which is heated to temperatures around 200°C. The green preform is inserted into the column of the hot PTM. Once the preform tile reaches the ignition temperature, a wave initiates, followed by a very distinct conflagration. After the conflagration, there is a slow burn. Shortly after the burn concludes, pressure is applied and released seconds later. Figure 2 shows a time-temperature profile for the TiC part upon ignition. Temperatures of 2,850°C are reached upon ignition. The part is quickly removed from the column of PTM and cooled to room temperature for several hours.

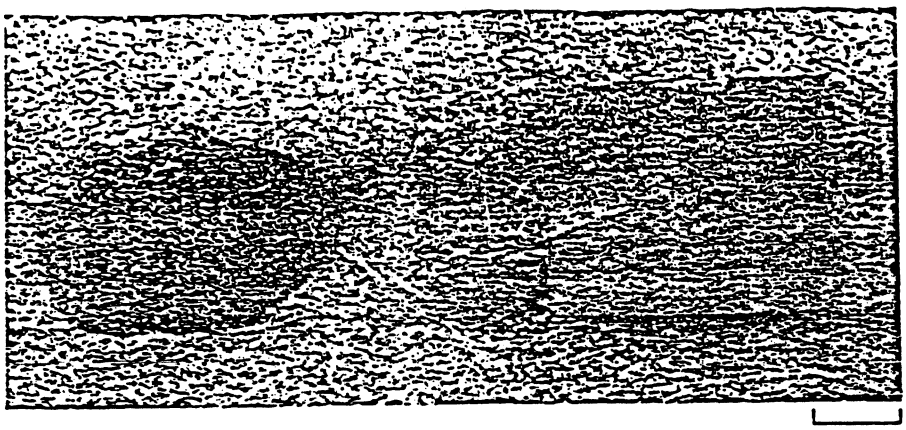

Figure 6. Starting powder and a CS/CF titanium carbide tile.

PROPERTIES

X-ray diffraction of the as-consolidated material reveals that the reaction product is phase-pure titanium carbide. The peaks are identified in Figure 3. Co-Kα radiation was used, and the lattice parameter was calculated to be equal to 0.433 ± 0.0078 mm. The lattice parameter can be correlated to the stoichiometry of the final product. Reference 11 provides a plot listing the data of numerous investigators. The C/Ti atomic ratio varies from 1 to 0.5 (there is a wide homogeneity region for TiC in the phase diagram), and the lattice parameters vary, correspondingly, from 0.433–0.430 nm. The results, displayed in Figure 3, indicate that the C/Ti ratio is 0.9. This is, in essence, the initial composition used in the experiments reported.

Optical microscopy of sample cross-sections (surface perpendicular to major dimensions of disk) revealed an equiaxed grain structure with significant differences in grain size. The maximum grain size increased with the size of the specimen. Figure 4 shows plots of grain size versus position along the cross-section of the 6.4 cm and 10.2 cm compacts; the thickness of the compacts are 2 cm and 2.4 cm, respectively. The grain size variation is clearly evident and is larger for the 10.2 cm compact, because of its slower cooling rates. The density of the CS/CF TiC tiles is around 95% of theoretical.

The microhardness was measured across and along the cross-sections of the specimens. Figure 5 shows the results for the 10.2 cm compact. The regions close to the top, bottom, and lateral surfaces display higher hardness values. The harness within the compact is correspondingly lower.

Fracture toughness measurements were made by measuring cracks emanating from the indentation produced by a microhardness tester. The indentation diagonals are equal to 0.02 mm when a Vickers indenter with a load of 500 gf was used. The average crack size was 27 mm. The fracture toughness is obtained from the following equation and is characteristic of a well-bonded ceramic:

$$K_{IC} = 0.16Ha^{1/2}c^{-3/2} = 0.16 \times 0.47\ Pc^{-3/2} = 1.7\ MPa{\cdot}m^{1/2}$$

Ceramic machining and grinding using diamond wheels and blades proved to be the most economical route with the least amount of grinding damage that could be incorporated in production. Figure 6 shows a typical 10 cm × 10 cm × 1.25 cm titanium-carbide tile fabricated through the CS/CF process.

A cost model developed for manufacturing 1,000 tiles per year using the CS/CF technology showed a significant cost reduction compared to conventionally hot pressed or HIPed material. The manufacturing cost would be reduced to 30–50% of conventionally prepared tiles.

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