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Microwave sintering of titanium diboride*

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Using a 2.45 GHz, 6 kW microwave furnace adapted for inert gas sintering, titanium diboride (TiB_2) can be rapidly microwave-sintered to >90% of theoretical density with sintering temperatures of 1900 to 2100 °C and soak times of 30 min or less. Densification behaviour with low-level additives was evaluated; 3 wt% chromium diboride (CrB_2) was an excellent sintering aid–grain growth inhibitor. A special covering system was required to produce oxide-free TiB_2. Specimen surface and interior temperatures were determined with a "hole experiment". Comparison with conventional sintering indicates that microwave sintering of TiB_2–3 wt% CrB_2 occurs at lower temperatures (i.e., 200 °C lower) and can yield material with improved hardness, grain size, and fracture toughness.

1. Introduction

Titanium diboride (TiB_2) ceramics are of considerable interest for aluminium evaporation boats, wear components–liners, cutting tools, armour, and electrodes. The attractive properties of TiB_2 include high elastic moduli, electrical conductivity, hardness, and melting temperature (~ 2980 °C). The considerable difficulties in sintering the material have been discussed in the literature [1–4]. To achieve high densities without hot-pressing, submicrometer *pyrophoric* powders [1] have been used which are very difficult to handle in even small-scale processing. Another approach has been to use liquid phase sintering or hot-pressing (with nickel additives to create the liquid phase) [4], where liquid is exuded during the process; again they are very difficult to handle. Ordinary sintering at high-temperatures with TiB_2 is said [4] to yield grain sizes over 15 μm, thereby resulting in enhanced residual stress and microcracking, with attendant decreased mechanical properties.

Since the literature indicated that over 2000 °C is necessary for densifying TiB_2, the microwave sintering method (recently overviewed by Sutton [5]) was selected in order to determine if TiB_2 could be heated to the required sintering temperatures and if improved sintering behaviour would result. An evaluation of the microwave processing of boron carbide (B_4C) was conducted simultaneously with this study of TiB_2, since both materials have similar uses and properties. Experimentation with B_4C is still in progress and the results will be reported later.

2. Experimental procedure

This work was conducted with a special microwave furnace system designed by Kimrey of Oak Ridge National Laboratory (ORNL) Fusion Energy Division. The unit is shown in Fig. 1 and consists of a 2.45 GHz microwave generator‡ with adjustable 6 kW power output. The microwaves are directed through the waveguide into the applicator cavity, which is designed to allow evacuation and backfilling with an inert gas atmosphere (argon or nitrogen) or to operate in air. Flowing argon was used for all TiB_2 testing. Fig. 2 shows the optical pyrometer directed to observe specimens during testing. The viewport is protected with a grid to prevent microwave leakage. All specimens were packed in a "casket" as shown in Fig. 3. The importance of "casketing" for high-temperature microwaving and the attendant materials interaction considerations cannot be overstated. A discussion of "casketing" issues has been presented elsewhere [6]. A view of the "casket" system on opening

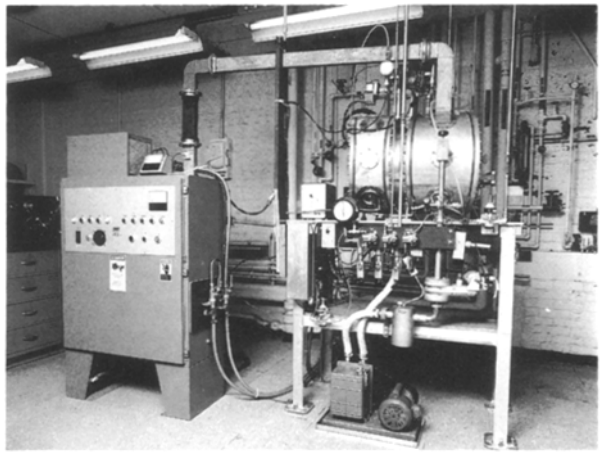

Figure 1 2.45 GHz, 6 kW microwave furnace system.

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† Operated for the U.S. Department of Energy by Martin Marietta Energy Systems, Inc., under contract DE-AC05-84OR21400.
‡ Cober Electronics, Inc., Stanford, CT, USA.

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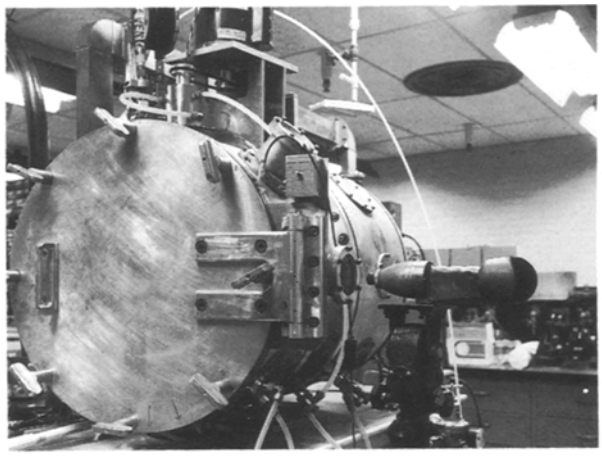

Figure 2 Optical pyrometer (right side) set to view specimen in the applicator cavity.

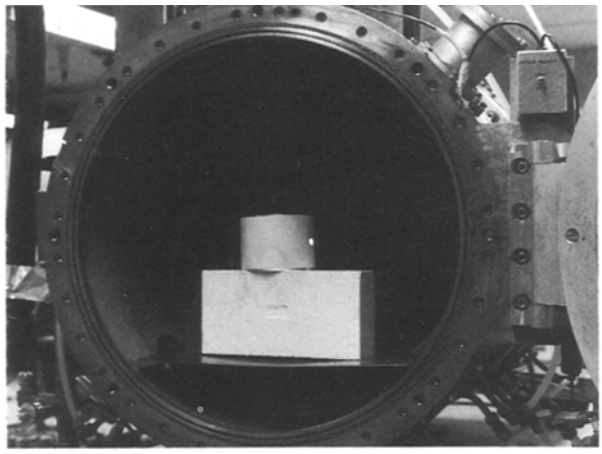

Figure 4 "Casket" system on opening the microwave unit after a sintering run.

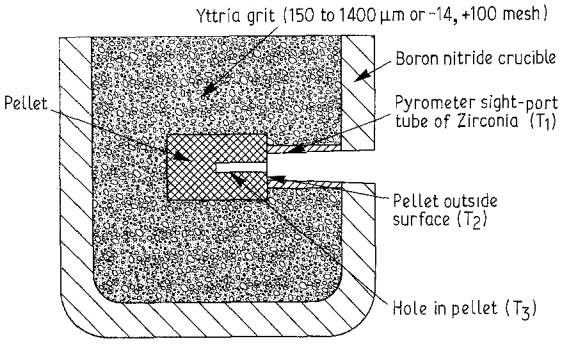

Figure 3 Typical "casket" arrangement (shown for hole experiments).

the microwave unit is shown in Fig. 4. The bright area indicates the $> 2000\,^{\circ}C$ temperature during a 20 min test.

Characterization of the titanium diboride starting powder is given in Table I and micrographs in Fig. 5. Grades U and S were tested, material from two vendors. Note that a range of average particle sizes is given; the lower number represents the average particle size derived from the surface area by using the relationship

$$d_{av} = \frac{6}{\sigma(SA)}$$

where d_{av} is the average particle diameter in μm, σ the theoretical density in g cm^{-3} and SA the surface area in $m^2\,g^{-1}$. The higher number was determined by Microtrac* (forward light scattering with laser source) analysis. From the scanning electron microscopy (SEM) photos of the starting powder shown in Table I, actual average particle sizes probably fall within the range given. The problem of accurately determining the average particle sizes for sub-sieve size particles is well known.

Surface areas were measured by nitrogen gas adsorption analysed by the Brunauer–Emmett–Teller (BET) equation [7]. Chemical analyses were used to determine the major constituents (Ti, B) as well as C, O, N which are routine contaminants. Spark source mass spectroscopy (SSMS) and emission spectroscopy (ES) were used to determine minor impurity levels. The numbers reported in Table I are the higher numbers determined by SSMS or ES.

Although Table I shows that fluorine contamination was below 50 w.p.p.m. (and thus not reported), examination of the surfaces of both grades U and S powders by electron spectroscopy for chemical analyses (ESCA) indicated fluorine species on the surfaces of the powders. A powder pre-processing treatment step was investigated: powders were contacted with boiling water for 3 h followed by drying and then blending under rapid agitation with methyl alcohol followed by filtering. The treatment reduces the surface contamination of fluoride on the powders; oxide surface levels increase slightly, either from the treatment step or from being exposed when the fluoride

TABLE I Starting material characterization titanium diboride

		Grade U	Grade S
Surface area ($m^2\,g^{-1}$)		0.8	3.5
Average particle size (μm)		2–11	0.4–3
Chemical analyses (%)			
TiB_2			
(68.9)	Ti	67.6	65.9
(31.1)	B	30.0	29.5
	C	0.42	0.17
	O	0.61	1.96
	N	0.08	0.21
Impurities over 50 w.p.p.m. (w.p.p.m.)			
	Si	75	40
	Ca	65	140
	Cr	10	140
	Fe	85	170
	Zr	60	40
	W	10	420

* Leeds and Northrup Co., St Petersburg, FL, USA.

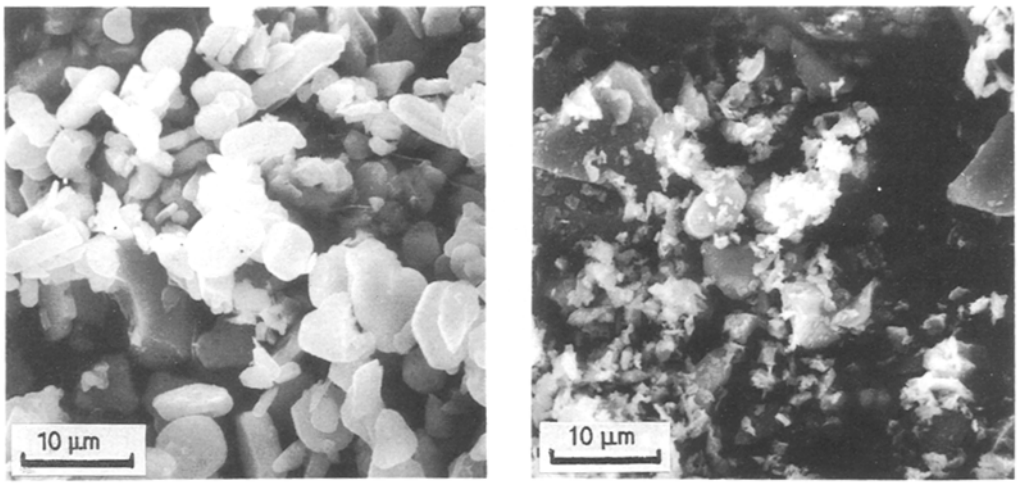

Figure 5 Micrographs of starting materials (a) grade U, (b) grade S.

layer is reduced. The treated TiB_2 was tested to determine the effects of differing surface conditions on microwave sinterability.

All pellets tested were undirectionally cold-pressed at from 69 to 220 MPa (10 000 to 32 000 psi). A polyvinyl acetate–chloride solution (9.5% PVAC in a methylethylketone {MEK} liquid carrier) was used as a pressing aid–binder which gives 1.8% binder on a dry basis. Sintering temperatures from 1700 to 2100 °C were evaluated at soak times of up to 90 min; heatup times were generally less than 40 min.

Additives such as molybdenum (Mo), chromium diboride (CrB_2), boron carbide (B_4C), and molybdenum disilicide ($MoSi_2$) were all nominally -325 mesh, over 99% purity powders. A carbon additive was also evaluated: carbon was derived from Varcum* furan resin, based on 40% conversion to carbon on heating in inert environment. An acetone slurry of the resin was added to TiB_2 powder and the coated powder was dried, pressed into pellets and cured at 200 °C in air and then slowly heated in argon to 1000 to 1100 °C to thoroughly outgas the pellets before sintering.

Density measurements on sintered pellets were determined by the Archimedes method (water medium, vacuum impregnated for wet weights). Portions of pellets were sawn with a diamond saw and mounted and polished for metallographic examination. An appropriate etchant described previously [1] utilized 3 drops of concentrated HF plus 10 cm^3 of concentrated HNO_3 plus 3 cm^3 of concentrated HCl plus 10 cm^3 of glycerine. Grain sizes were determined manually by counting techniques on selected specimens.

Microindentation hardness and fracture toughness measurements were determined on selected polished, unetched specimens, using the method described by Evans [8]. Scanning electron microscopy (SEM), microprobe, and X-ray diffraction analyses were also performed on selected specimens.

Comparison with conventional sintering necessitated the use of a rapid heating furnace. Astro Industries, Inc.† Model 1000A graphite-resistance furnace was used, with optical pyrometry for temperature monitoring.

3. Results and discussion

The screening study of additives utilizing grade S powder yielded the data given in Fig. 6. Highest densities were obtained with 3 wt % additions of carbon, Mo (treated), or CrB_2. The boiling water–methanol leach treatment of TiB_2 powder before pressing had a pronounced effect compared to using as-received TiB_2 powder. However, when additives were used, the treatment caused very little change in the observed densities, with the exception of the molybdenum additive. Since molybdenum forms volatile oxides, perhaps the treatment enables molybdenum to better affect the oxide layer on the powder surfaces.

The CrB_2 additive yielded higher density material with less grain growth compared to other additives to TiB_2. Thus, the remainder of this study concentrated on TiB_2 with the 3 wt % CrB_2 addition.

After the initial screening study with grade S powder, a test with grade U powder was undertaken comparing TiB_2 pellets pressed at 220 MPa (32 000 psi). A pellet of TiB_2 with 3% CrB_2 addition was compared to a pellet with no addition (pure TiB_2) on microwave sintering at 2100 °C for a 1 h hold, with the results shown in Fig. 7. The pressed pellet alone was 62% of theoretical density, whereas the microwaved pellets with no addition and with 3% CrB_2 addition were 70% and 98% of theoretical density, respectively. As with the grade S screening study (see Fig. 6), the effect of CrB_2 as a sintering aid with grade U powder was strongly demonstrated, since little sintering occurred without the CrB_2 addition. Grade U material was used for the remainder of the study, since grade U was more readily obtained and yielded the finer-grained sintered product.

The densification against time and temperature relationship for TiB_2–3 wt % CrB_2 (utilizing the Y_2O_3-grit-pack "casket" of Fig. 3) is shown in Fig. 8. The rapid increase in density up to a plateau-point density

* Produced by BTL Specialty Resins Corp., Niagara Falls, NY, USA.
† Now Thermal Technology, Inc., Santa Rosa, CA, USA.

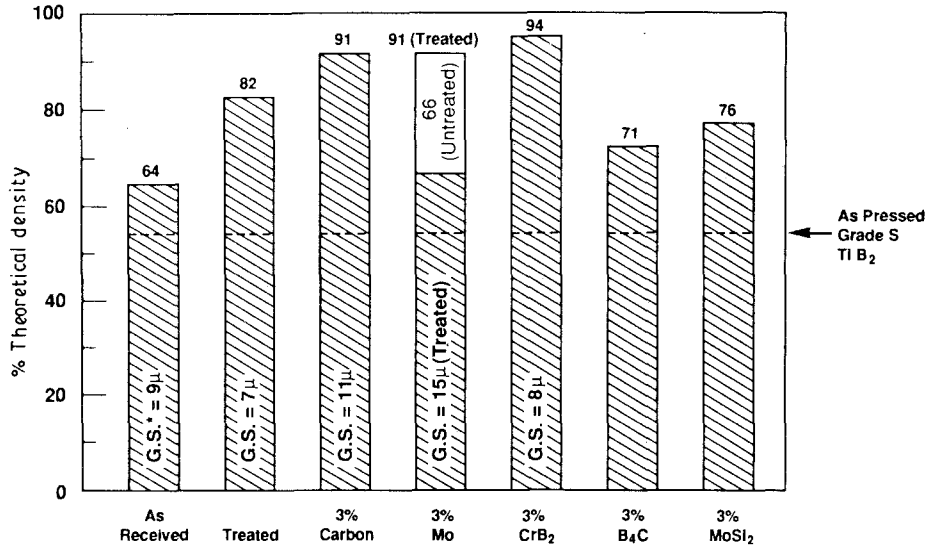

Figure 6 Effect of treatment and additives on the microwave densification of titanium diboride (Note: pellets (~ 2.5 cm diameter × 1.5 cm high) pressed unidirectionally at 68.9 MPa (10 000 psi); sintered at 2050 °C, 30 min hold) G.S = grain size.

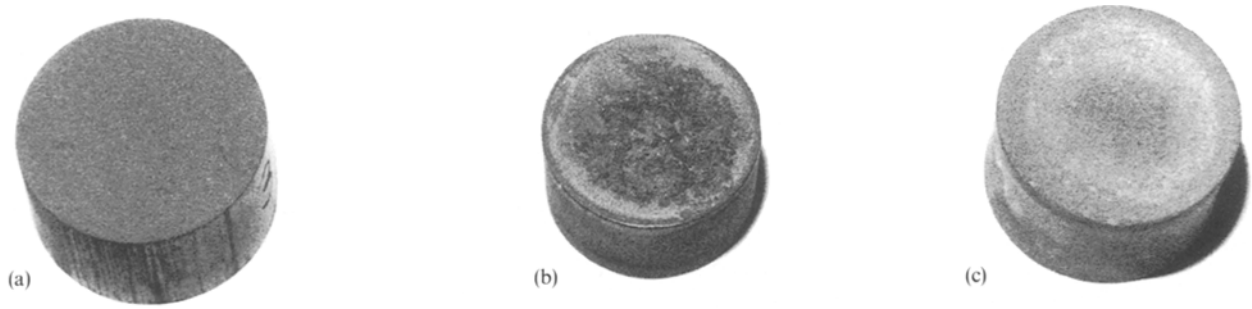

Figure 7 Grade U titanium diboride–densities after pressing and microwave sintering (a) 62% theoretical density, pressed, (b) 98% theoretical density, 3% CrB_2 added, sintered 2100 °C, 1 h, (c) 70% theoretical density, no addition, sintered 2100 °C, 1 h.

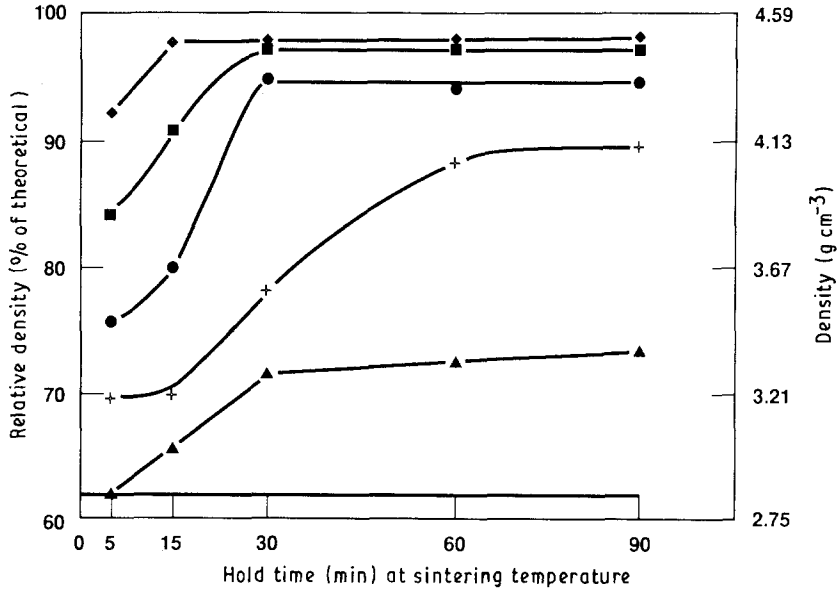

Figure 8 Densification against time for the microwave sintering of TiB_2–3% CrB_2 (◆ 2100 °C, ■ 2000 °C, ● 1900 °C, + 1800 °C, ▲ 1700 °C, — pressed density).

is indicative of liquid phase sintering. Examination by microprobe revealed a liquid phase in the grain-boundary regions: the liquid phase consisted of TiB_2, CrB_2, and very small amounts of iron, chromium and nickel as well as tungsten. These minor impurities probably result from the use of stainless steel containers and WC milling media to dry mix the CrB_2 additive into the TiB_2 powder. Further study with microprobe and SEM revealed considerable amounts (3 to 6 wt % typically) of yttrium present in discrete

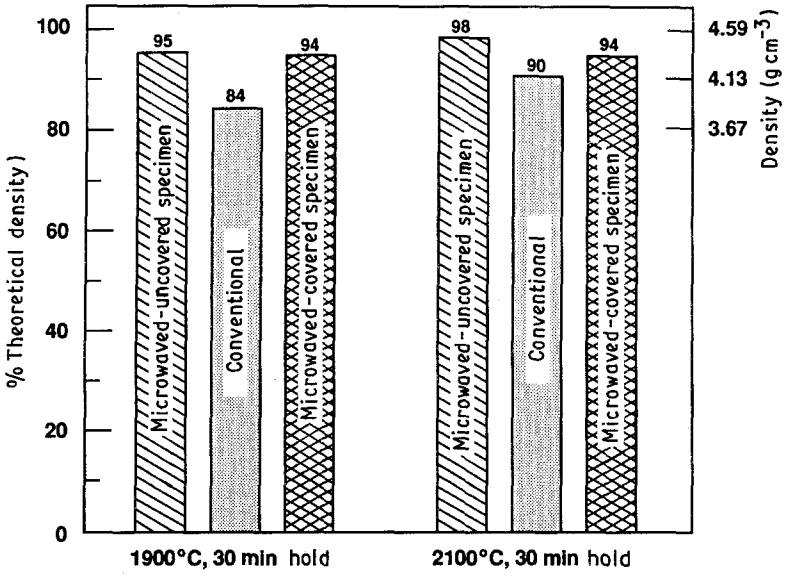

Figure 9 Comparison of microwave and conventional sintering of titanium diboride–3% chromium diboride (Note: pellets pressed unidirectionally at 220 MPa).

particles (typically $< 10\,\mu m$) dispersed uniformly throughout the matrix TiB_2. The X-ray diffraction analysis was unable to resolve the phase, but microprobe study revealed the grains to be a mixed yttrium–titanium oxide, containing no boron. Therefore, a mixed TiB_2–3 wt % CrB_2–x% Y–Ti–O (where x is estimated to be 4 to 8 wt % and the titanium level varies from zero to about the same level as the yttrium) was inadvertently produced by this microwave sintering utilizing the yttria grit "casket". Of course, this soft oxide phase added to the high-hardness TiB_2 matrix can act as a crack blunting agent and this might possibly actually produce a better product than pure TiB_2 or TiB_2–3 wt % CrB_2 alone. In order to investigate this possibility and to determine if microwave sintering has a "microwave effect" (enhanced sintering such as reported [5] for other microwaved materials), an oxide-free product was desired.

Several experiments were conducted to determine if yttria could be prevented from entering the pellets. Paintable coatings of several refractories (BN, TiB_2, HfO_2, and others) were inconsistent as barriers against yttria – as determined by microprobe analyses of microwaved pellets; however, a covering system of Grafoil* "glued" on to a pressed pellet (with the PVAC–MEK solution used for a pressing aid–binder in making the pellets) was consistently successful in stopping the yttria pickup. Two or more Grafoil layers, each 0.25 mm thick, are necessary. A tungsten coating using 100 g of tungsten powder to 25 g of PVAC–MEK solution was necessary on the outside of the Grafoil covering. The tungsten in some way "pumps" the system to prevent the Grafoil from reflecting the microwaves: perhaps tungsten carbide is formed to some extent. Without the tungsten layer, temperatures of $< 2000\,°C$ can be obtained with the Grafoil covering, and temperatures rapidly decline. With the tungsten layer, temperatures of 2100 °C can be attained and sustained for normal soak times. Microprobe analyses revealed that specimens covered with the Grafoil–tungsten system contained no yttrium or tungsten.

Since the oxide-free TiB_2 could now be produced, a comparison of microwave and conventional sintering was made. The results are shown in Fig. 9. Note that the theoretical density given in Figs 8 and 9 is 4.59 $g\,cm^{-3}$, instead of the theoretical density of 4.52 $g\,cm^{-3}$ for pure TiB_2 or 4.55 $g\,cm^{-3}$ for TiB_2–3 wt % CrB_2 (based on 5.60 $g\,cm^{-3}$ for CrB_2). The 4.59 $g\,cm^{-3}$ value assumes 8 wt % Y_2O_3 from 6.3% Y contamination (the largest amount determined) where all the oxide formed is yttria. Specimens also contain very minor amounts of stainless steel, tungsten carbide, etc., which elevate the theoretical density somewhat. In any case, the comparison of Fig. 9 indicates that microwave sintering yields improved density compared to conventional sintering utilizing similar (or close as possible) heating rates. Comparing the microwaved oxide-free TiB_2–3% CrB_2 (covered specimens) with the microwaved oxide-containing specimens (uncovered), it appears that oxide-containing specimens achieve somewhat higher density, and a plateau-point density is reached with the oxide-free material, since both 1900 and 2100 °C sintering temperatures yielded the same final densities. The fact that microwave sintering yields material $> 90\%$ dense at only 1900 °C sintering temperature is a distinct advantage over conventional sintering, which requires a 2100 °C sintering temperature to achieve material with densities over 90% of theoretical.

The microstructure of these microwave-sintered TiB_2–3% CrB_2 specimens is illustrated in Fig. 10, showing a side-by-side comparison of specimens that were polished-and-etched and specimens that were fractured and examined by SEM. Fig. 10a shows the covered specimen that was microwaved at 1900 °C for a 30 min hold, whereas Fig. 10b shows the covered specimen microwaved at 2100 °C for a 30 min hold. There appears to be little difference in appearance

* Produced by Union Carbide Corp., NY, USA.

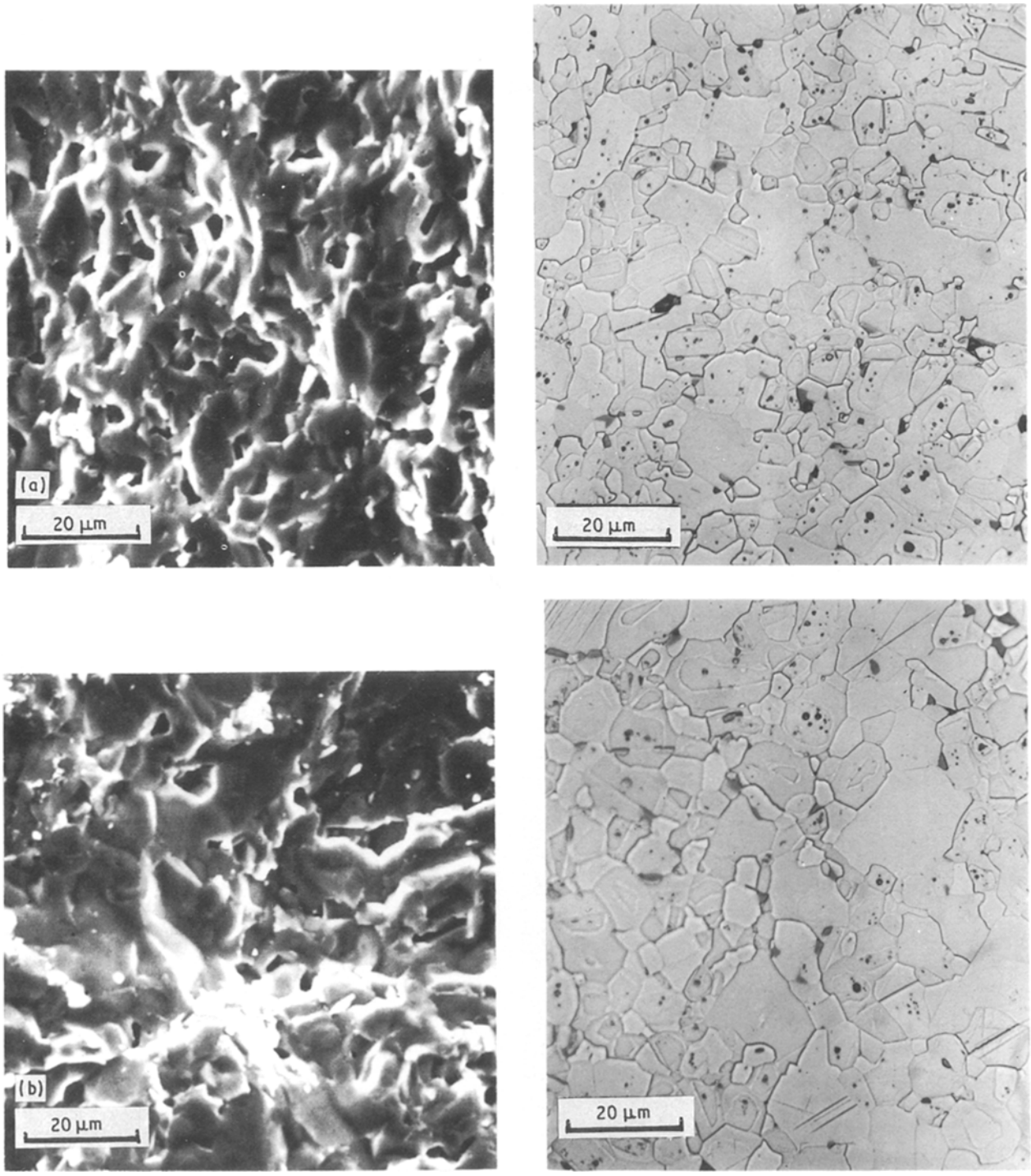

Figure 10 SEM of fracture surface and polished, etched metallographic section of microwave-processed, covered samples of TiB_2–3% CrB_2 (a) Sintering conditions: 1900 °C, 30 min hold, (b) Sintering conditions: 2100 °C, 30 min hold.

other than the grain size being slightly larger with the higher processing temperature.

Fig. 11 illustrates the microstructure of an uncovered TiB_2–3% CrB_2 specimen microwaved at 2100 °C for a 15 min hold. The dark areas represent porosity that occurred from polishing pullouts of the soft oxide phase; the dark grey areas are some oxide grains that did not pull out during polishing. The oxide grains are $< 10\,\mu m$ size and are distributed through the uncovered specimens.

The microstructure of a commercially prepared (the vendor of grade U powder) hot-pressed specimen of $> 99\%$ density (bulk density = $4.47\,g\,cm^{-3}$) TiB_2 without CrB_2 and made with grade U starting powder is shown in Fig. 12. Comparison with microwaved specimens (Figs 10 and 11) indicates much larger grain size for the hot-pressed material. The CrB_2 additive appears to reduce grain growth as well as to enhance sintering.

Hardness, fracture toughness from indentation measurements, and grain size determinations of microwaved, conventionally-sintered, and hot-pressed TiB_2 specimens are presented in Table II. The microwaved uncovered TiB_2–3% CrB_2 specimens (which have yttria or yttrium–titanium oxide levels of up to 8 wt % from the processing) have a higher hardness

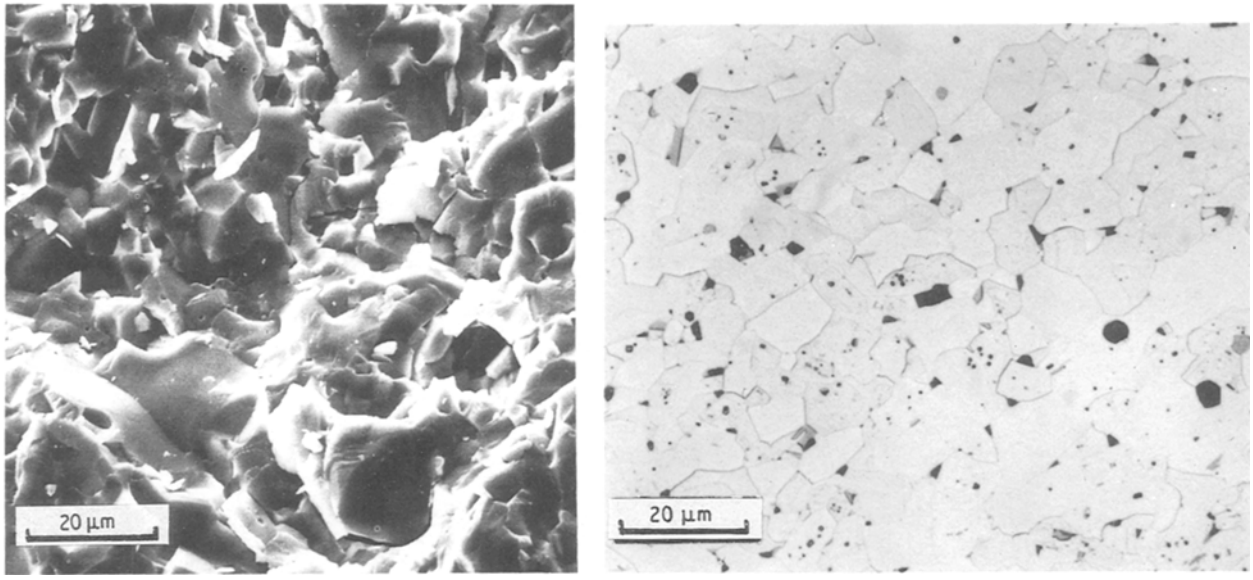

Figure 11 SEM of fracture surface and polished, etched metallographic section of microwave-processed, uncovered (*oxide contaminated*) sample of TiB_2–3% CrB_2, sintered at 2100 °C, 15 min hold.

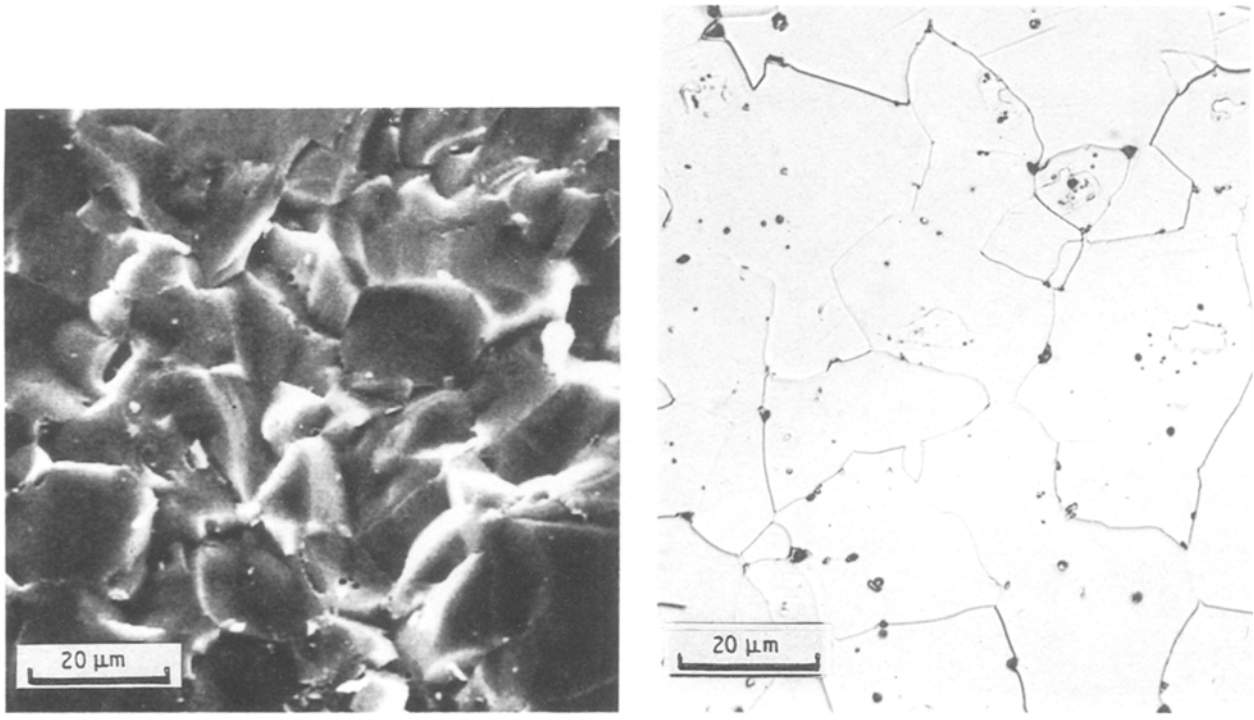

Figure 12 SEM of fracture surface and polished, etched metallographic section of a commercially hot-pressed TiB_2 (no CrB_2) specimen, pressed at 2000 °C, 13.8 GPa, 1 h hold.

than the covered specimens (oxide free) or the conventionally sintered specimens. Also, the uncovered specimens have a finer grain size and a high fracture toughness. The yttria or yttrium–titanium oxide phase is an apparent additional grain growth inhibitor along with the CrB_2 and enhances the fracture toughness somewhat.

The yttria-free (covered) microwaved TiB_2–3% CrB_2 material has a hardness closer to that of conventionally sintered TiB_2–3% CrB_2. Grain size of the yttria-free material is greater than that of the yttria-containing (uncovered) material, and fracture toughness is lower compared to other sintered specimens. All the sintered specimens had enhanced fracture toughness over the much-larger-grained, hot-pressed material. These fracture toughness measurements allow a relative comparison, yet the different densities of the specimens could affect the result. Thus, the effects of yttria (or mixed oxides of yttria and titania) and processing method (microwaving as opposed to conventional and hot-pressed) on fracture toughness and mechanical properties should be further studied. Comparison of hardness and fracture toughness values with published data [8, 9] is difficult, since different techniques and additive levels were evaluated as compared with this study.

TABLE II Physical properties of TiB_2 specimens

Specimens	Conditions	Hardness, Vickers DPH-1 kg load (GPa) [Standard deviation in parentheses]	Indentation hardness technique for fracture toughness[a]		Estimate of average grain size (μm)
			Fracture toughness (M Pa $m^{1/2}$) [Standard deviation in parentheses]	Hardness, Vickers DPH- at load shown (GPa) [Standard deviation in parentheses]	
TiB_2–3 wt % CrB_2:					
Microwaved-uncovered	1900 °C 30 min	28.9 (4.1)	6.24 (0.40)	15.8 (0.6) at 8.7 kg load	4
Conventionally sintered	„	17.8 (1.3)	5.66 (0.56) 5.66 (0.93)	8.6 (0.7) at 8.3 kg load 9.3 (0.7) at 18.6 kg load	4
Microwaved-covered	„	22.6 (1.2)	5.16 (0.27)	14.5 (1.5) at 8.3 kg load	6
TiB_2–3 wt % CrB_2:					
Microwaved-uncovered	2100 °C 30 min	27.0 (1.3)	6.10 (0.17)	17.9 (0.7) at 8.5 kg load	4
Conventionally sintered	„	17.9 (1.4)	6.10 (0.71)	11.3 (1.8) at 8.3 kg load	12
Microwaved-covered	„	21.7 (0.6)	5.25 (0.46)	13.5 (1.1) at 8.2 kg load	8
Hot-Pressed TiB_2 (no CrB_2)	2000 °C 1 h, 13.8 MPa	26.7 (0.5)	4.78 (0.57)	16.1 (1.9) at 7.7 kg load	20

[a] Method of Evans [8], using $E = 530$ GPa.

Temperature measurements in high-temperature microwave sintering experiments are subject to some question as to the uniformity of the specimen temperatures. Since the specimen is the heater with microwave sintering, the situation is quite different from conventional heating; and the necessity for appropriate "casketing" has been addressed [6]. Fig. 3 shows the setup used for temperature measurements with the "hole experiment". The temperatures, T_1, T_2, and T_3 are distinctly different during initial heating with microwaves. At high temperatures, the three temperatures converge and the pellet reaches equilibrium as illustrated in Fig. 13. Above ~1800 °C, the temperatures on the surface and within a TiB_2–3% CrB_2 pellet are the same. Since the zirconia sight tube heats up first, and since the zirconia heating might cause some variation in the specimen heatup behaviour, the experiment was repeated with a boron nitride sight-port and the specimen outside and inside temperature profiles were the same as shown in Fig. 13; however,

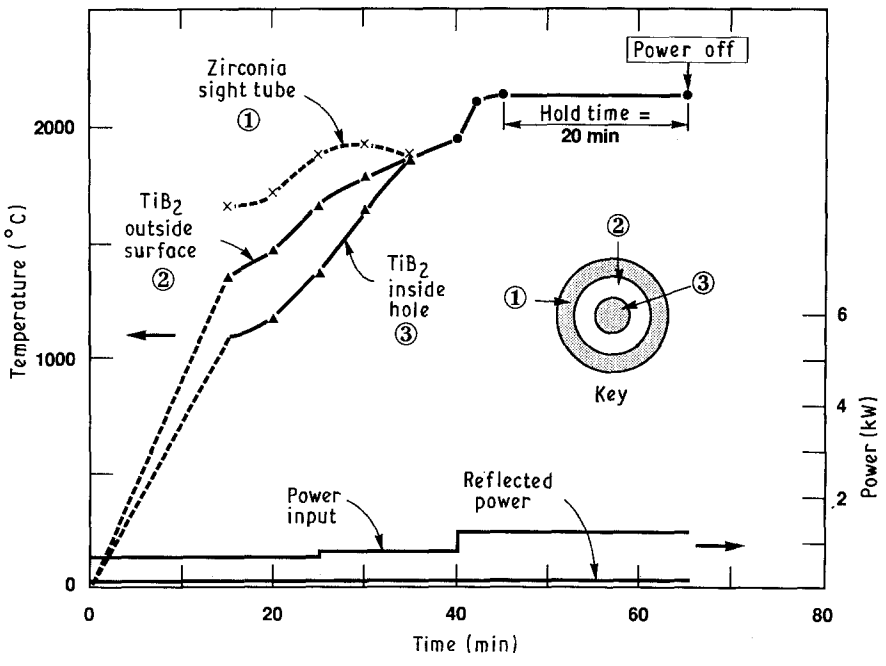

Figure 13 Temperature plotted against time profile for 'hole experiment' with TiB_2–3% CrB_2 pellet (3.17 cm diameter, 1.77 cm height initially, 39.6 g.)

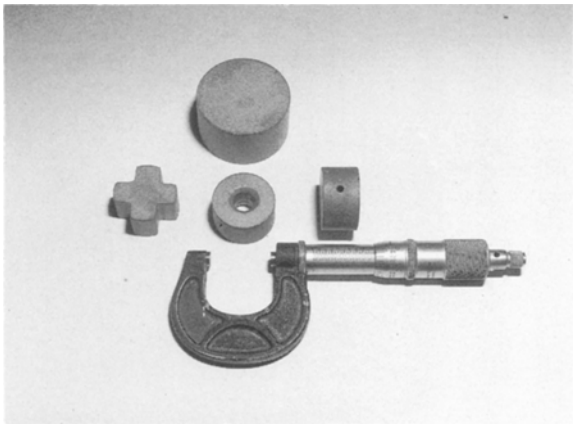

Figure 14 Variety of TiB_2–3% CrB_2 parts produced by high-temperature microwave sintering.

the BN sight tube temperature was not distinguishable, indicating the sight tube did not reach "red heat". Notice in Fig. 13 the low level of reflected power, indicating the excellent microwave absorption of TiB_2.

The variety of parts produced during this study is shown in Fig. 14. The largest part processed was 7.6 cm diameter by 2.5 cm high (3 in diameter × 1 in high). All parts in Fig. 14 were $\geqslant 95\%$ dense. The pellet used for the "hole experiment" is shown on the right; the hole extended to the middle of the pellet. The other shaped pellets were prepared by light grinding the as-pressed pellet before microwaving.

4. Conclusions

This investigation has shown that microwave sintering at temperatures of 1700 to 2100 °C is feasible. These temperatures are believed to be the highest temperatures yet attained by microwave heating and are suitable for the rapid densification of titanium diboride–3% chromium diboride. An enhanced-sintering "microwave affect" occurs with 2.45 GHz processing as compared to conventional sintering. The "casketing" interactions were found to lead to oxide contamination – adding up to 8 wt % yttria as $< 10\,\mu m$ particles that seem to reduce grain growth. With a special covering technique, oxide-free TiB_2–3% CrB_2 specimens with grain size below 15 μm can be routinely produced by microwaving. Hardness and fracture toughness data indicate that microwave processing can yield a product that is equal to or better than conventionally-sintered material and much improved over hot-pressed material.

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