

LEGIBILITY NOTICE

A major purpose of the Technical Information Center is to provide the broadest dissemination possible of information contained in DOE's Research and Development Reports to business, industry, the academic community, and federal, state and local governments.

Although a small portion of this report is not reproducible, it is being made available to expedite the availability of information on the research discussed herein.

Received by OSTI

MAR 06 1989

Los Alamos National Laboratory is operated by the University of California for the United States Department of Energy under contract W 7405 EN G 16

LA-UR--89-533

DE89 007988

TITLE MICROWAVE SINTERING OF TITANIUM DIBORIDE

AUTHOR(S) J. D. Katz, R. D. Flake, G. P. Scherer, MST-4

SUBMITTED TO Ceramic Engineering and Science,
Cocoa Beach, FL
Jan. 15, 18, 1989

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

By acceptance of this article the publisher conveys that the U.S. Government retains a nonexclusive, royalty free license to publish or reproduce the published form of this contribution or to allow others to do so for U.S. Government purposes.

The Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy.

MASTL

Los Alamos National Laboratory

Los Alamos, New Mexico 87545

MICROWAVE SINTERING OF TITANIUM DIBORIDE

J.D. Katz, R.D. Blake and C.P. Scherer

Los Alamos National Laboratory
Los Alamos, NM 87545

Presented at the 13th Annual Conference
On Composites and Advanced Ceramics
Cocoa Beach, FL
January 15-18, 1989

ABSTRACT

INTRODUCTION

Microwave processing is a suitable technique for a wide range of ceramics including oxides and non-oxides. Among the ceramics which have been successfully heated and sintered at Los Alamos using microwaves are alumina¹, boron carbide², zirconia³ and alumina-silicon carbide composites⁴. Several advantages over conventional heating techniques are realized because energy is coupled directly to the ceramic body. Additionally, processing times are much shorter and energy costs lower. The longest processing time for any of the samples reported in this paper was 12 minutes.

Microwave heating results from the energy dissipated by a ceramic placed in a microwave field. The power dissipated by a ceramic dielectric in an electric field is given by the following equation:

$$P = (2\pi f\epsilon)(E^2/2)\tan \delta \quad (1)$$

where P is the power dissipated, f is the frequency, ϵ is the dielectric permittivity, E is the electric field strength and $\tan \delta$ is the loss tangent for the dielectric. It is readily apparent from this equation, that the ceramic must have an appreciable loss tangent and dielectric permittivity in order for significant heating to occur.

For lossy materials such as titanium diboride the microwaves are absorbed before they can fully penetrate the sample. The depth of penetration into the sample is quantified by defining the skin depth which is the distance at which the electric field falls to $1/e$ (which

is equal to 37% of the field strength at the surface. The skin depth is calculated by the following formula:

$$\text{Skin Depth} = 1/(\pi f \mu \sigma)^{1/2} \quad (2)$$

where f is the frequency, μ is the permeability and σ is the dc conductivity. The skin depth has been calculated for 100% dense titanium diboride for some of the frequencies commonly used in microwave processing of ceramics in Table 1. At 2.45 GHz the skin depth is 4.47 μm . The skin depth drops to 1.32 μm at 28 and 0.90 μm at 60 GHz. These values for the skin depth were calculated for theoretically dense titanium diboride, in the green body which is only 55% of theoretical density the skin depth is somewhat larger, but should approach the calculated values as density increases. As the skin depth vanishes, the material behaves like a perfect conductor, in which case power is dissipated as heat by the induction of surface currents.

The titanium-boron phase diagram^b is shown in Fig. 1. (Fenish⁶ and Spear et al.⁷ have reported the existence of the compound Ti_3B_4 , but because of the lack of experimental data, the phase field for this compound is not represented on this diagram.) Titanium diboride is a strongly bonded covalent compound and as such has an extremely high melting point of 3225°C. Typical processing of titanium diboride consists of hot pressing in graphite dies between 2150 and 2300°C, depending on the quality of the powder. Hot pressing under these conditions are sufficient to achieve 98 to 99% of theoretical density.

Some limited work on the conventional pressureless sintering of titanium diboride has been reported by Edey¹ and Zaverukha⁸ and Baumgartner and

Steiger⁹. Kislyi and Zaverukha performed vacuum sintering on micron sized titanium diboride powders heated as high as 2000°C. These authors reported linear shrinkages of up to 14%. Baumgartner and Steiger reported on the sintering of submicron titanium diboride powders synthesized by a gas phase plasma process. These workers achieved densities of 99.4% of theoretical by vacuum sintering at 2200°C for an hour.

EXPERIMENTAL

Hermann C. Stark^{*} titanium diboride powder, lot HCST-2087, was used in this study. The average particle size was determined to be 4.4 μm and the B.E.T. surface area was measured at 1.84 m^2/gm . The principle impurities are tungsten at 4000, cobalt at 400, iron at 350 and chromium at 300 ppm. Powders were consolidated by uniaxial pressing (without binders or sintering aides) to 10,000 psi followed by isostatic pressing to 50,000 psi. This double pressing procedure resulted in 1 cm diameter X 1 cm high pellets of approximately 55% green density.

Because of the propensity of titanium diboride to oxidize, 2.45 GHz microwave processing was performed under flowing argon using the facility, shown in Fig. 2. This facility consists of a 6 kilowatt microwave power supply, a 2 ft X 2 ft X 2 ft resonant cavity equipped with a rotating specimen table and a two-color infrared pyrometer.

All specimens were heated from room temperature to the peak temperature. Upon achieving the peak temperature, power was shut off and the sample

^{*}Hermann C. Stark, Berlin, West Germany

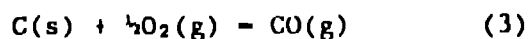
allowed to cool to room temperature. A typical time versus temperature curve is shown in Fig. 3.

RESULTS AND DISCUSSION

Figure 4 is a plot of density versus peak sintering temperature for titanium diboride samples microwave sintered under flowing argon. The apparent density is as high as 89% of theoretical for titanium diboride and temperatures as high as 2245°C were achieved. Unfortunately, there does not appear to be any rational relationship between sintering temperature and density. The reason for this becomes apparent upon further examination. Figure 5 is a scanning electron micrograph of a sample which was heated to 1872°C under flowing argon. Examination of the micrograph shows that both titanium diboride which appears as the dark phase and an unidentified light phase are present. The light phase is present in larger amounts in samples which were heated to higher temperatures and/or for longer times. X-ray analysis was performed to identify the phases present in these samples. A typical x-ray pattern is shown in Fig. 6. In addition to titanium diboride which was identified as the major phase in all of the samples, Ti_2O , TiO , Ti_2O_3 and $TiBO_3$ were identified in at least one of the samples. Table 2 lists the phases found in each sample in order of amount present. Also listed in Table 2 are the sintering time and temperature.

The presence of oxidation is not totally unexpected which is why sintering was performed under an argon flush. To understand why titanium diboride oxidizes so readily it is instructive to construct a stability diagram for the $Ti-B-O$ system. Such a diagram has been constructed for this system at 1877°C and is shown in Fig. 7. Unfortunately,

thermodynamic information is not available for $TiBO_3$ or Ti_2O , and therefore, it was not possible to represent these phases on the stability diagram. In spite of this shortcoming much information can still be gleaned from Fig. 7. Titanium forms several oxides because of its extremely high affinity for oxygen. To completely stop any oxidation from occurring at this temperature the oxygen potential would have to be approximately 10^{-18} atmospheres. Since attainment of an oxygen potential in the 10^{-18} atm range is a difficult task, especially in the present microwave cavity, a different approach was taken. Carbon was placed in the cavity to act as a gettering agent via the following reaction:



Where this reaction is to come to equilibrium in the microwave chamber at $1827^\circ C$, the oxygen potential would be about 10^{-15} atmospheres. An oxygen potential in this range will not preclude oxidation, but hopefully it should limit it to an acceptable level.

Figure 8 is a plot of density versus peak sintering temperature for titanium diboride samples microwave sintered in the presence of carbon and under flowing argon. In this plot density increases with temperature until $1860^\circ C$ after which it abruptly decreases. All of the samples sintered under these conditions were analyzed by x-ray diffraction. These results are tabulated in Table 3 along with information concerning the processing parameters.

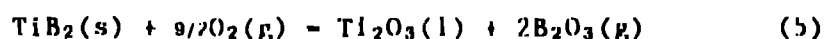
Figures 9 and 10 are micrographs of titanium diboride samples sintered below $1860^\circ C$ with both a carbon getter and flowing argon. The micrographs are devoid of the light oxide/borate phase as indicated by

x-ray analysis. Figure 11 shows that a denser rim forms along the outer surface of the sample during sintering. The thickness of this rim is 200-300 μm which is many times greater than the microwave skin thickness of 4.47 μm . It is not clear at this time if rim formation is due to a microwave skin effect or some other reason.

The reason for the abrupt fall-off in density for samples sintered at temperatures above 1860°C can be determined by examination of their microstructures. Figure 12 shows that the region adjacent to the surface for a sample heated above 1860°C. Adjacent to the surface is a band 200-300 μm thick which contains large voids 20-75 μm in diameter. The formation of these voids accounts for the observed drop-off in density. The reason the void formation starts at 1860°C is probably due to the loss of a TiO_2 protective film which melts at this temperature. Once the protective film is lost rapid oxidation with the evolution of $\text{B}_2\text{O}_3(\text{g})$ occurs which causes the observed void formation according to the following reactions:



and



CONCLUSIONS

Titanium diboride can be heated to high temperatures using microwaves. The highest temperature obtained in this study was 2245°C. Unfortunately, oxidation was a problem, especially at the higher temperatures although an argon flush and a carbon getter were used. To completely stop oxidation the oxygen potential must be below 10^{-16} atmospheres.

Using an argon flush and a carbon getter, titanium diboride was successfully densified to 82% of theoretical without measurable oxidation by heating with microwaves to 1860°C. Density actually decreased upon reaching temperatures above 1860°C due to void formation adjacent to the surface. Void formation is thought to be due to the formation of $B_2O_3(g)$ which evolves rapidly above 1860°C because of the loss of a TiO_2 protective film which melts at this temperature.

REFERENCES

- 1.) T.T. Meek, R.D. Blake and J.J. Petrovic, Ceram. Eng. Sci. Proc., Vol. 8, pp. 861-871, 1987.
- 2.) J.D. Katz, R.D. Blake, J.J. Petrovic and H. Sheinberg, Mat. Res. Soc. Symp. Proc., Vol. 124, pp. 219-226, 1988.
- 3.) T.T. Meek, H. Sheinberg and R.D. Blake, Def. Sci., April-June 1985.
- 4.) J.D. Katz, R.D. Blake and J.J. Petrovic, Cer. Eng. Sci. Proc., Vol. 9, No. 7-8, pp. 725-734, 1988.
- 5.) E. Rudy, AFML-TR-65-2, Part V: "Compendium of Phase Diagram Data"; p. 198, A. F. Materials Lab., June 1969.
- 6.) R.G. Fenish, Trans. Metall. Soc. AIME, Vol. 236, p. 804, 1966.
- 7.) K.E. Spear, P. McDowell and F. McMahon, J. Am. Ceram. Soc., Vol. 69, No. 1, pp. C-4-C-5, 1986.
- 8.) P.S. Kislyi and O.V. Zaverukha, Sov. Powder Met., Vol. 7, pp. 549-551, 1970.
- 9.) H.R. Baumgartner and R.A. Steiger, J. Am. Cer. Soc., Vol. 67, No. 3, pp. 207-212, 1984.

TABLE I

Frequency (GHz)

	2.45	28	60
Skin Depth (μm)	4.47	1.32	0.90

TABLE II

Sample	Density	Peak Temperature	Total Time	Phases
1	3.47	1872	8.5	TiO,Ti2O3
2	3.42	1887	9.5	Ti2O3
3	3.95	1770	13	unidentified
4	3.42	1902	9	none
5	3.54	1875	11	none
6	3.56	2000	4.6	none
7	3.94	1919	8	TiBO3,Ti2O
8	3.99	2089	6	Ti2B5,Ti2O
9	3.30	1985	4.5	none
10	3.61	1824	16.5	TiBO3
11	3.40	2234	14.5	Ti2O3
12	3.27	1965	14.5	unidentified
13	3.28	1961	14.5	none
14	3.39	1715	12	Ti2O3
15	3.59	1940	9.5	none
16	3.43	1807	10.5	Ti2O3,TiO
17	3.49	1890	11	none
18	3.45	1871	13	none
19	3.49	1870	11.5	none

LIST OF FIGURES

- Figure 1.) Titanium-Boron phase diagram.
- Figure 2.) Photograph of Los Alamos 2.45 GHz microwave processing facility. The power supply is on the left, the microwave cavity is on the right and the two color IR pyrometer is in the foreground.
- Figure 3.) Typical plot of time versus temperature for a sample of titanium diboride processed using 2.45 GHz microwaves.
- Figure 4.) Plot of density versus peak sintering temperature for titanium diboride sintered under flowing argon.
- Figure 5.) Scanning electron micrograph of titanium diboride sintered at 1872°C under flowing argon. Note the presence of both a light and dark phase.
- Figure 6.) Typical x-ray pattern for a titanium diboride sample sintered under flowing argon. TiB_2 and $TiBO_3$ were identified in this sample.
- Figure 7.) Stability diagram calculated for the Ti-B-O system at 2100 K (1827°C).
- Figure 8.) Plot of density versus peak sintering temperature for titanium diboride sintered under flowing argon in the presence of carbon.
- Figure 9.) Scanning electron micrograph of titanium diboride sample sintered at 1890°C, note that the white oxide phase is not present.
- Figure 10.) Scanning electron micrograph of titanium diboride sample sintered at 2000°C, note that the white oxide phase is not present.
- Figure 11.) Scanning electron micrograph of titanium diboride sample showing dense outer rim.
- Figure 12.) Scanning electron micrograph of titanium diboride sample showing region adjacent to surface containing voids thought to be caused by the rapid evolution of $B_2O_3(g)$.

B-Ti

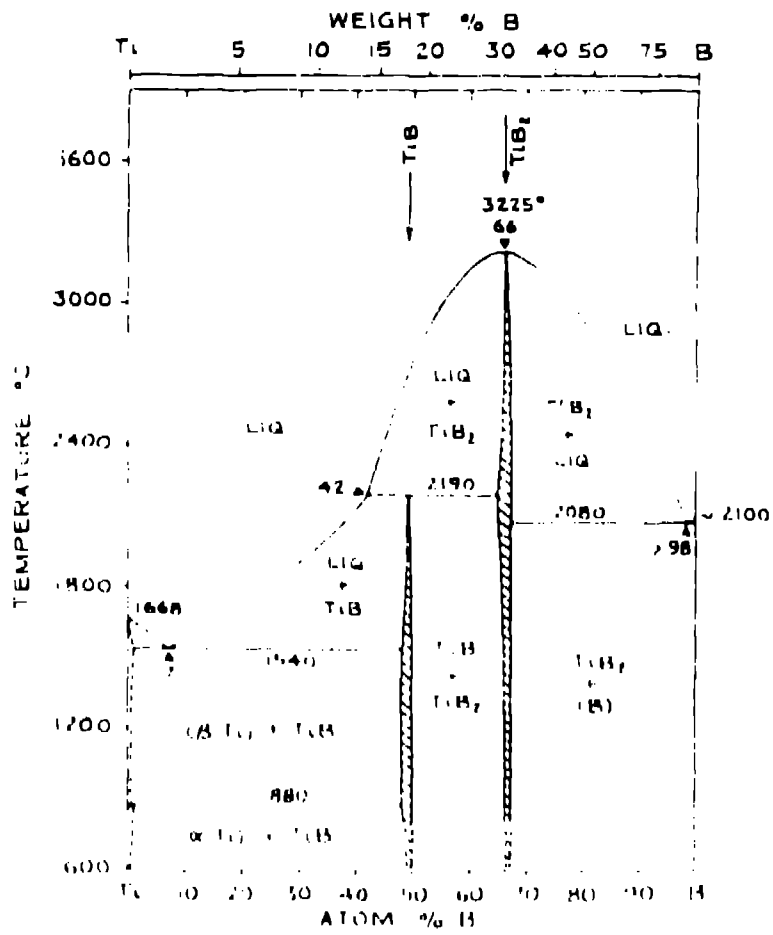


Figure 1



Figure 2

Density vs. Sintering Temperature

No Carbon

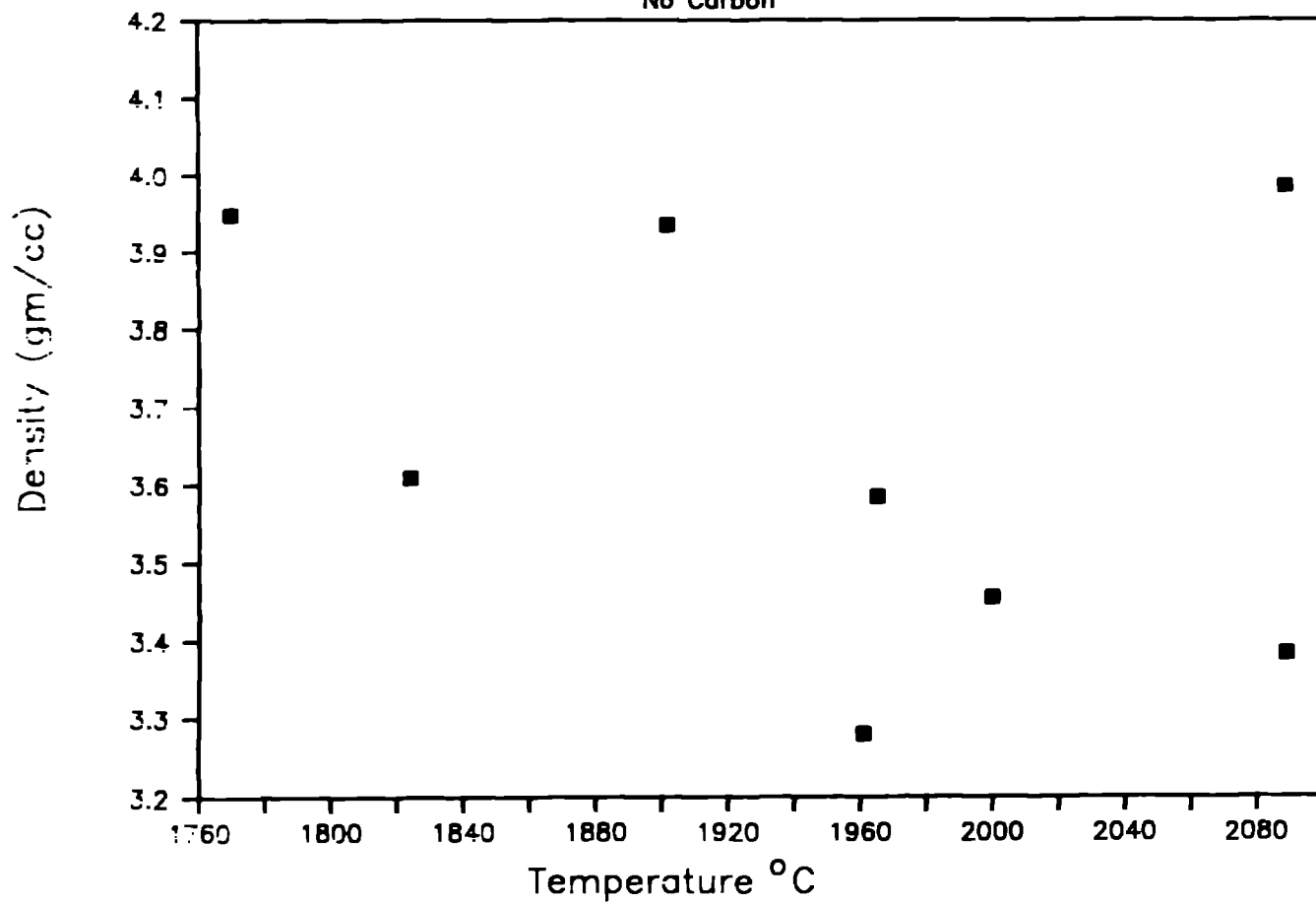
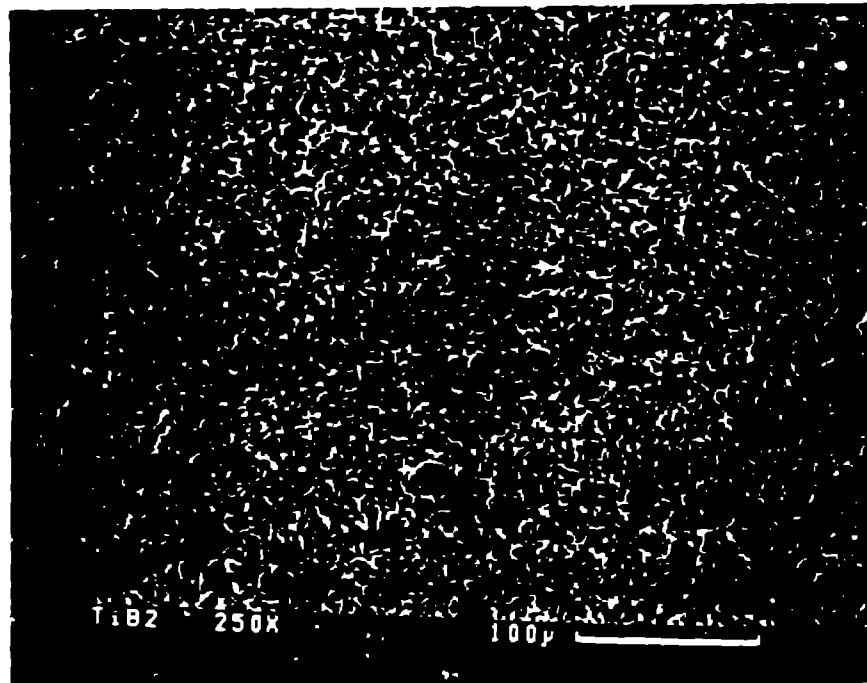


Figure 4



TiB₂

Figure 5

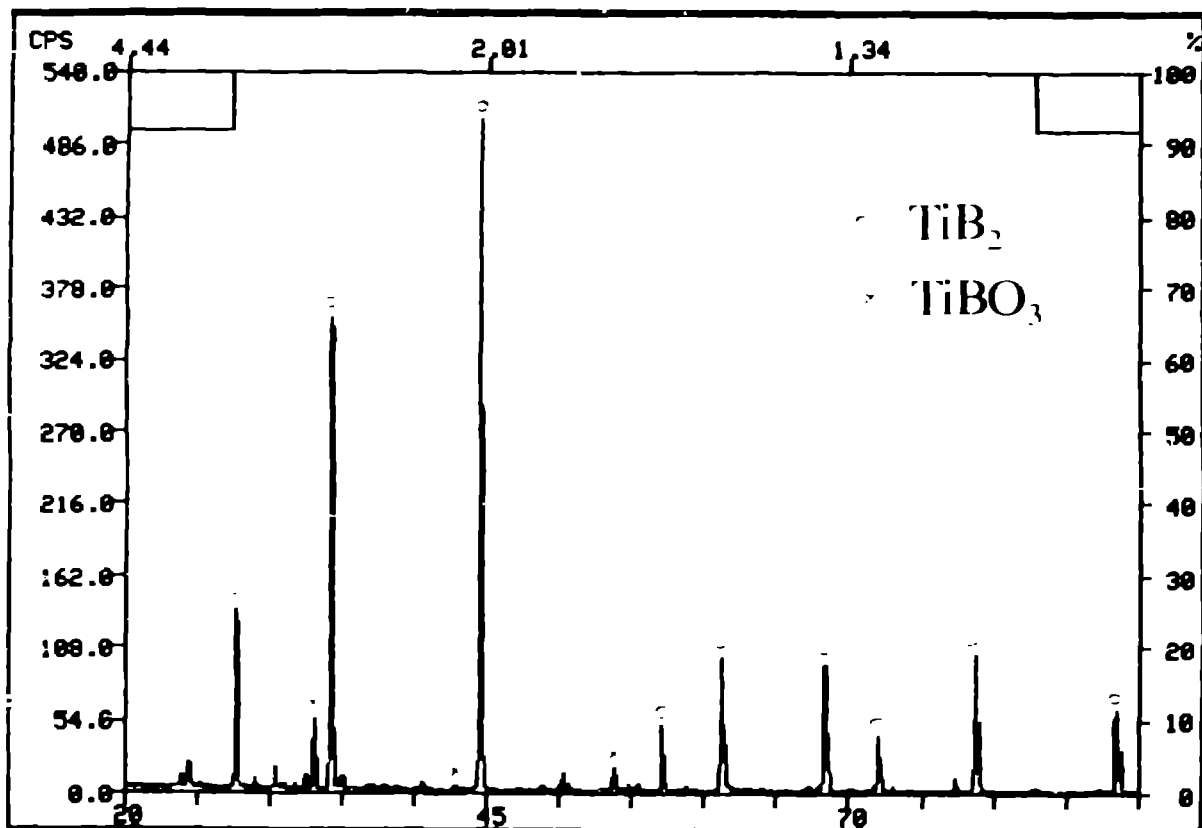


Figure 6

Ti-B-O Phase Stability Diagram

2100 K

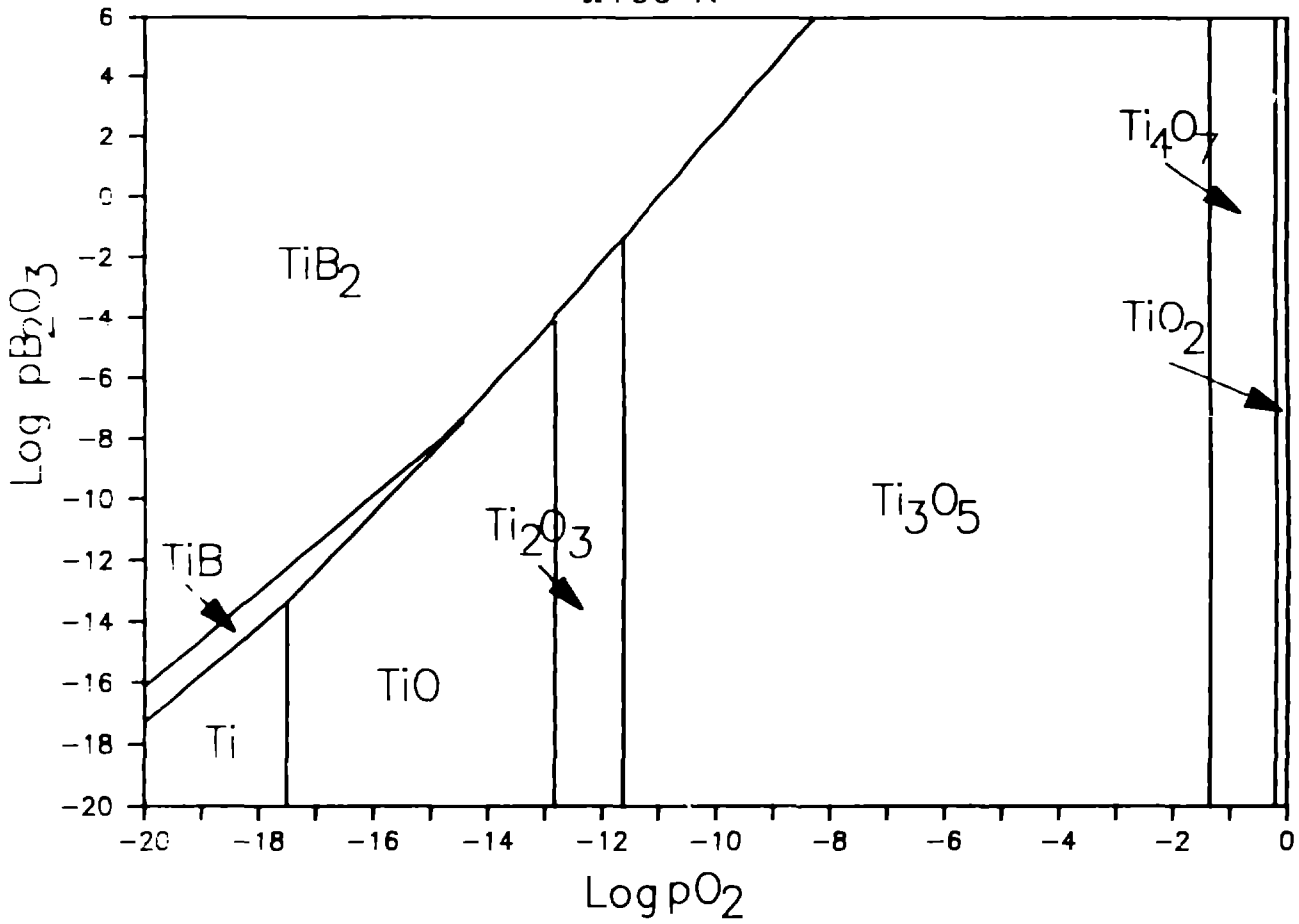


Figure 7

Density vs. Sintering Temperature

Carbon Present

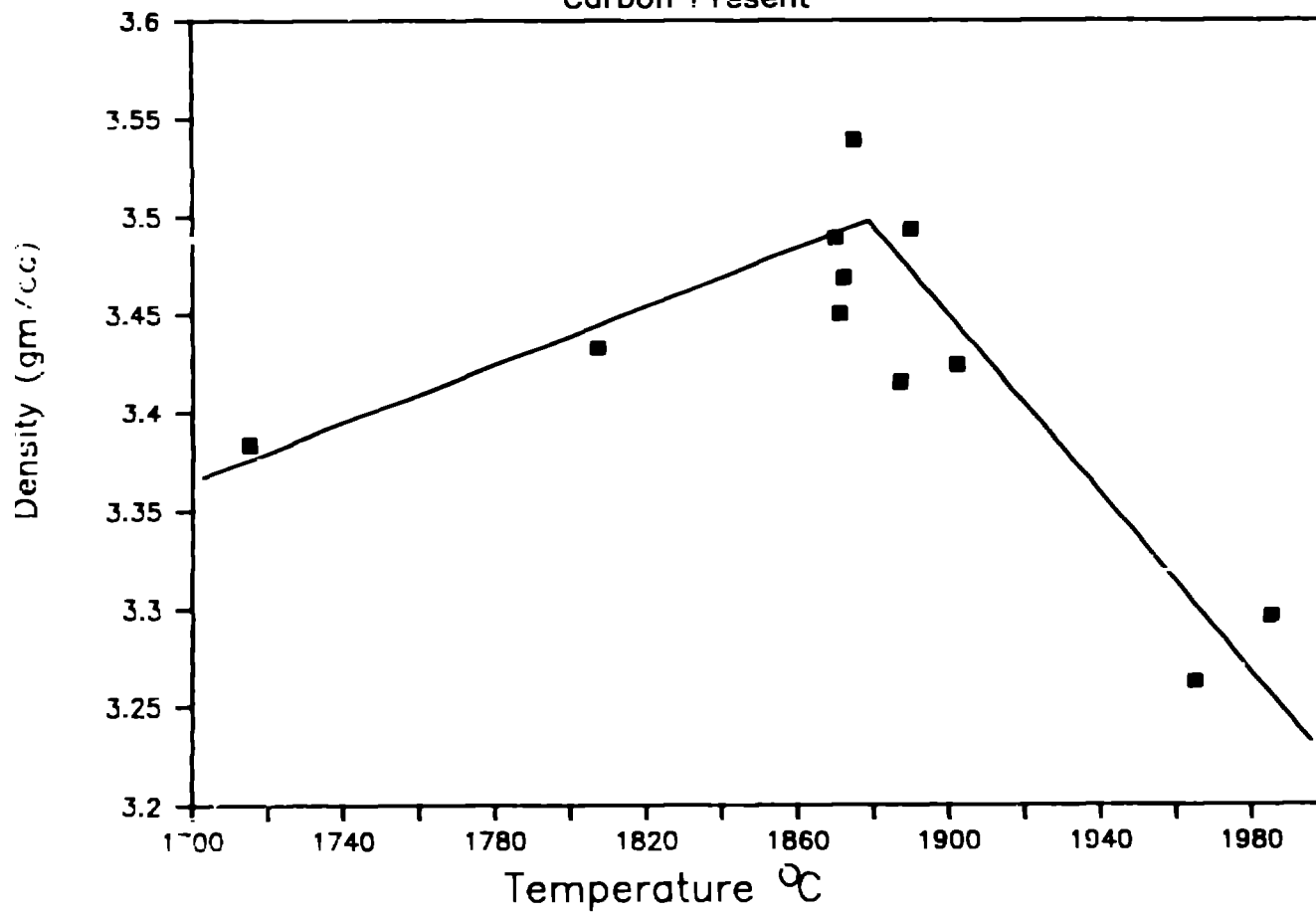
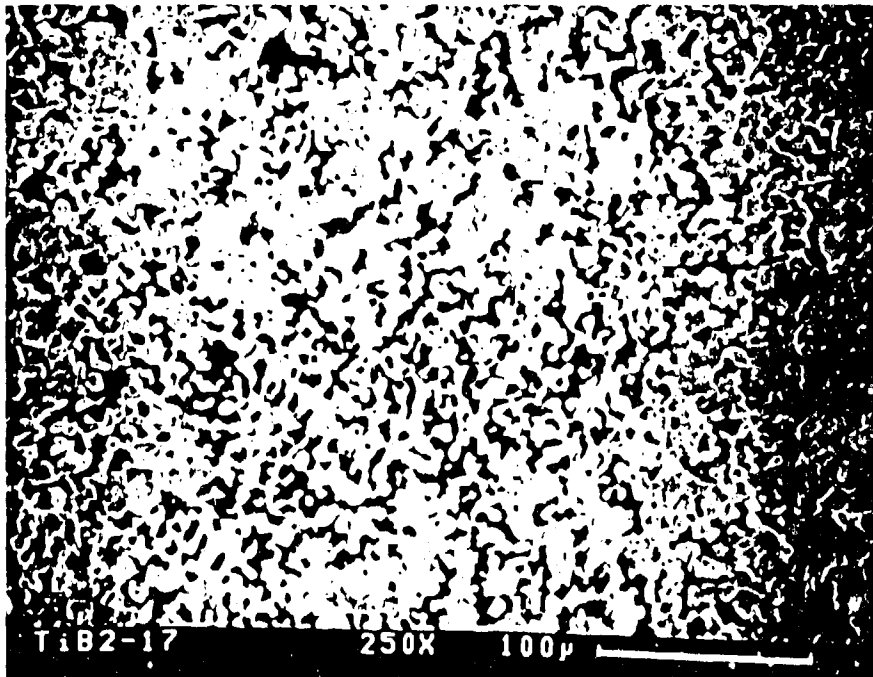


Figure 8



TiB2-17

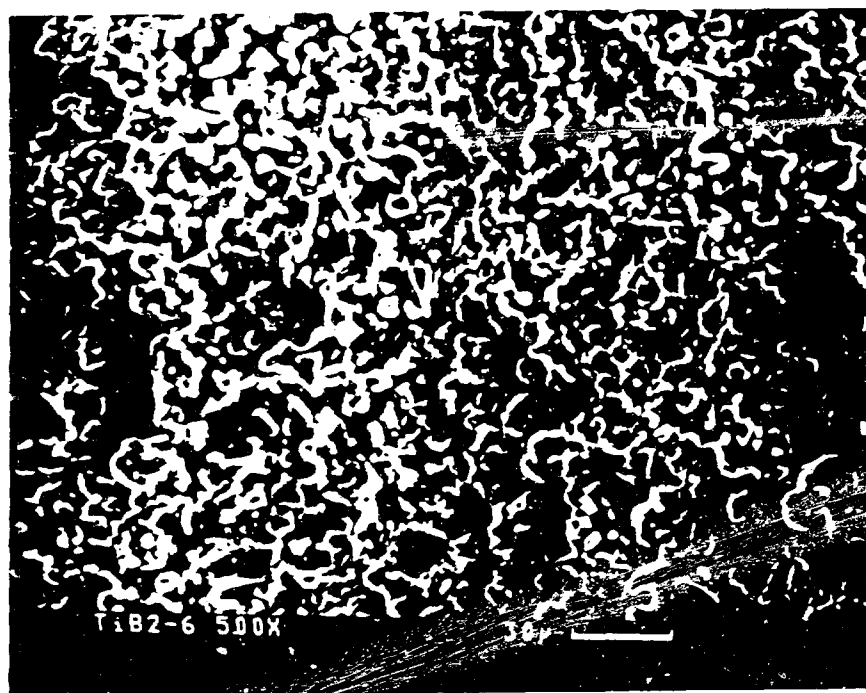


Figure 10

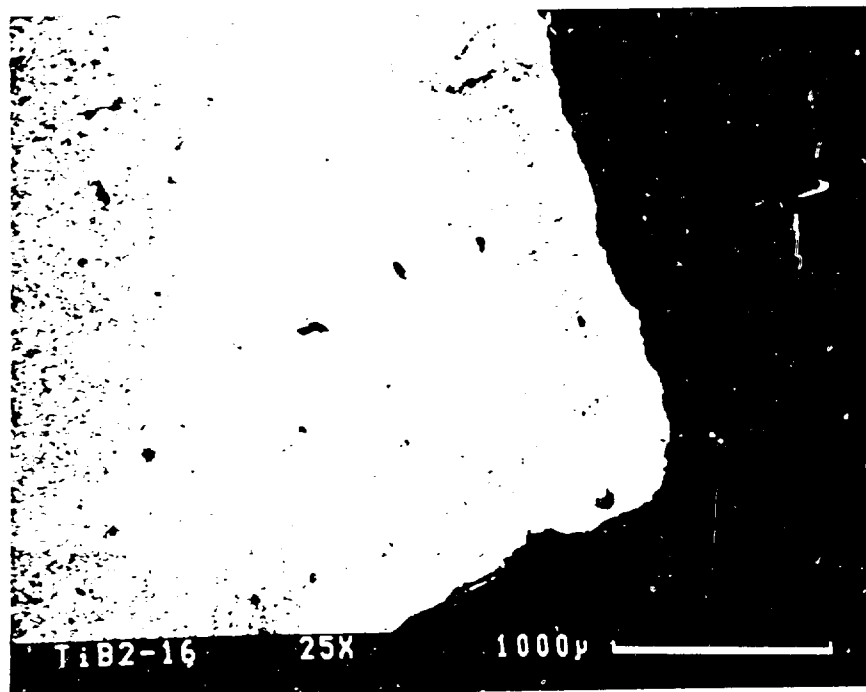


Figure 11

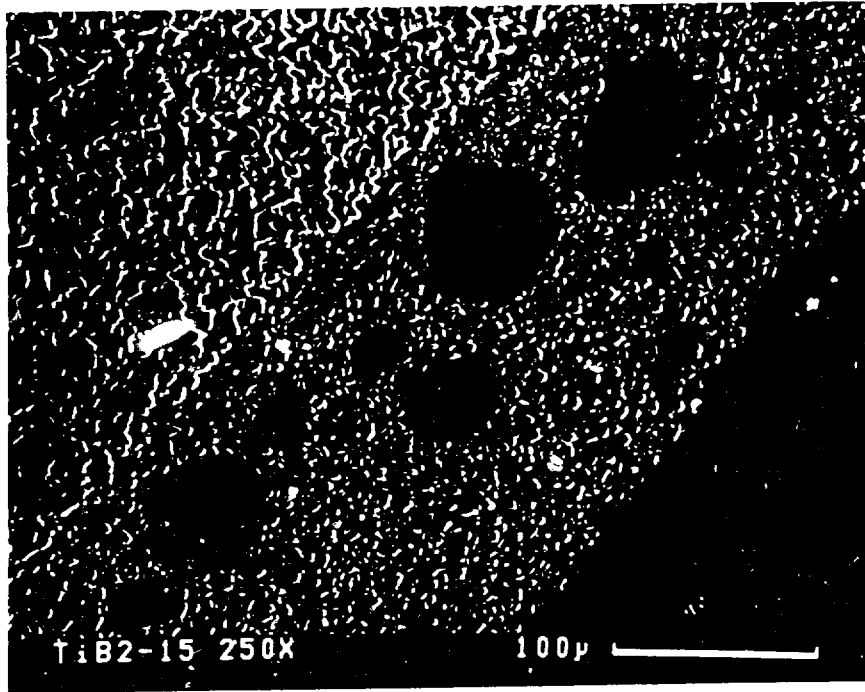


Figure 12