REACTION SYNTHESIS/DYNAMIC COMPACTION OF TITANIUM CARBIDE AND TITANIUM DIBORIDE

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A novel approach for producing dense ceramics and intermetallics is described. This approach combines reaction synthesis with a high velocity forging step (10-15 m/s impact velocity) to achieve densification and near-net shape. Compaction is necessary because reaction synthesized titanium carbide and diboride are extremely porous. By combining these two processes, titanium carbide and diboride disks with densities greater than 96% were produced.

Elemental powders of titanium and carbon or boron are dry mixed in a jar with a grinding medium. The powder is then pressed into a cylindrical green body which is placed into an insulated cavity within the forging die of the forging machine (Dynapak). Because the reaction is strongly exothermic (44.1 kcal/mol for TiC and 66.8 kcal/mol for TiB_2), the final product is raised to a temperature above its ductile-to-brittle transition. The forging step accomplishes two objectives: (1) densification, and (2) shaping. After the forging step, the titanium carbide (or boride) is removed from the forging die and placed within a furnace for slow cooling.

The major problem encountered in this study has been thermal shock. Insulating the titanium carbide during and after

the hot forging step and raising the temperature of the surroundings by use of a furnace were used to decrease cracking.

SEM observation of titanium carbide reveals the grains are equiaxed with an average size of 44 μm. This is indicative of crystallization or recrystallization after the forging step. Low strain-rate fracture surfaces are primarily intergranular, while at higher strain rates, the fracture mode is primarily transgranular. Vickers microhardness values are comparable with those obtained from a commercially hot-pressed material. Preliminary dynamic compressive strength measurements indicated a value greater than 1.7 GPa at a strain-rate of 10^2 per second for TiC.

I. INTRODUCTION

Reaction synthesis (or combustion synthesis, or SHS) is a materials processing technique by which ceramics, ceramic composites, and intermetallic compounds may be produced. The reaction synthesis process results from an exothermic, self-propagating reaction among elemental powders or solid reactants immersed in a reacting gaseous atmosphere. A review of the subject is provided by Munir and Anselmi-Tamburini [1]. Extensive research efforts in the Soviet Union by Merzhanov and co-workers [2-5] have led to the industrialization of this method and to the synthesis of hundreds of materials. In the U.S., the principal efforts in SHS are by Holt and co-workers [6,7] at Lawrence Livermore National Laboratory, Niiler and co-workers [8,9] at BRL, Munir and co-workers [10] at the University of California, Davis, and K. Logan [11] at Georgia Institute of Technology. Of particular relevance to the research described herein is the work of Niiler and co-workers [8,9] in which the reaction synthesis is followed by explosive compaction. Recent calculations by Wilkins [12] have shown that the pressures generated in titanium carbide and boride by explosive detonation process in the fixture used by Niiler and al. are very low: 0.5 GPa. This was the motivation for the substitution of dynamic compaction in a high-speed forging machine for explosive compaction.

II. EXPERIMENTAL MATERIALS AND TECHNIQUES

The powders used in this research consisted of elemental titanium, boron, and carbon. The titanium powder size is 325 mesh (maximum diameter of 44 μm); the average graphite particulate size in 2 μm; the boron particle size is ~325 mesh (<44 μm). The powders were mixed in a grinding jar for two hours in order to produce a homogeneous powder mixture.

The powders were then compacted into disks (3- and 4-in diameter) at a pressure of approximately 50 MPa, yielding a green compact with a density of approximately 60% of the theoretical. The titanium carbide was produced from the reaction Ti + 0.9 C, while titanium diboride was produced from the mixture Ti + B, to which 20 wt pct of pre-synthesized TiB_2 was added. The addition of inert TiB_2 reduced the velocity of the reaction front and the heat output, therefore ensuring the integrity of the compact after reaction. A typical microstructure after reaction synthesis is shown in Figure 1. The clear regions are TiC and the dark regions are the mounting epoxy. The body is approximately 50 pct porous.

Compaction was achieved in a suitably modified DYNAPAK unit. This is a quick release high-energy forging machine developed for metal-working applications. The hammer derives its kinetic energy from compressed nitrogen gas. The machine was modified for the specific objectives of this investigation. It is schematically shown in Figure 2. The hammer is propelled down and impacts the workpiece at velocities ranging from 10 to 15 m/s. Thus, the dynamic pressures generated are very low. The maximum energy output of the DYNAPAK in this investigation was 25 kJ. Figure 2 shows a schematic of the machine in the "ready" and "fired" position.

Special dies were designed for the forging of the compact. They contained refractory insulation to minimize heat losses from compact during and after forging. The details of the assembly are described by LaSalvia [12]. After the reaction was completed, the forging hammer was accelerated against the hot, porous ceramic. The forging hammer was then raised and the extractor activated. The specimen was then removed, by means of special tongs, and inserted in a furnace, under protective argon atmosphere, at the temperature of 1,100 ^{0}C. The specimens were allowed to cool in the furnace, over a period of 12 hours.

From the compacts, specimens for optical and scanning electron microscopy were obtained by sectioning with a diamond saw. Mechanical property measurements consisted of the determination of the Vickers microhardness and dynamic compressive failure strength. Dynamic compressive strength was determined using the split Hopkinson bar technique. Cubes with 10 mm sides were sectioned from the compacts and placed between the transmitter and incident bars. The pulse rise was shaped by means of a copper disk placed between the striker and the incident bars. This ensured a sufficiently large rise time, not necessary for metallic specimens.

III. RESULTS AND DISCUSSION

It was possible, after process development, to eliminate a great fraction of the thermal cracks, very prevalent in titanium carbide. The titanium diboride compacts did not exhibit the same propensity for cracking. Figure 3 shows titanium carbide and diboride compacts; the cracks

observed for titanium carbide are only surface features and are due to hot tearing (breaking of the thin surface layer that is rendered brittle very early in the forging process). The circumferential cracks observed for the titanium diboride specimen are due to insufficient lateral confinement.

Figure 4 shows both the bulk and center density as a function of specific energy of the DYNAPAK (energy divided by mass of compact) for titanium carbide. Because of heat losses, the surface material is cooler and less ductile than the center material. The difference between the two curves shows this. A specific energy of 70 J/g is required to produce compacts that have a density of 96% throughout. This specific energy can be used to estimate the flow stress of the ceramic at the imposed strain rate (~2 x 10^2 s^{-1}). Carroll and Holt [13,14] developed an expression for the energy required to consolidate a porous material. Equating this energy to the kinetic energy of the machine, one has:

$$E_K = \frac{2}{3} \sigma_y V_s \{\alpha_0 \ln \alpha_0 - (\alpha_0 - 1) \ln (\alpha_0 - 1)\} \quad (1)$$

where σ_y is the flow stress of the material, α_0 is the initial (before compaction) distention (ratio between specific volumes of porous and densified material). From Figure 1, one can estimate α_0 (=2). Hence,

$$E_K = 0.942 \sigma_y V_s \quad (2)$$

V_s is the specific volume of the titanium carbide. Equation 2 yields:

$$\sigma_y = 425 \text{ MPa.}$$

This is the flow stress of the titanium carbide immediately upon completion of the reaction. The temperature is estimated to be in the 2000-3000 ^{0}C. range. Further work is required to determine the dynamic mechanical response of a hot, porous, plastic ceramic.

The microstructure of titanium carbide is shown in Figure 5(a). The average grain size, as measured by the linear intercept method, is 44 μm. The grains are equiaxed, indicating that crystallization, or recrystallization occurred after plastic deformation. This supports the synchrotron radiation experiments performed by Wong and Holt [15], that showed that the final TiC structure formed only one minute after the reaction was completed. Two intermediate structures were observed. Porosity is also observed in Figure 5(a); it is more prevalent at the grain boundaries. Because of heat losses, the grain size close to the surface was smaller than in the center of the compacts. The titanium diboride microstructure is shown in Figure 5(b). The voids that can be seen are due to the particle pullout during cutting and polishing operations. The grain size is approximately 8 μm. This indicates that either bonding between

the pre-synthesized and combustion synthesized material is not very good, or that grain-boundary cohesion is poor.

Vickers microhardness measurements across the thickness are shown in Figure 6. These values are quite high: HVN 2250 for TiC; HVN 2425 for TiB_2. These values compare favorably with hot pressed TiC and TiB_2 (HVN 2235 for hot pressed TiC). The microhardness profiles across the cross-section show that the values are consistently high.

The dynamic strengths of the titanium carbide specimens was established at strain rates that fluctuated between 50 and 100 s^{-1}. The compressive strengths varied considerably, and the highest one was equal to 1.7 GPa. The variation is due to pre-existing cracks in the specimens. The fracture morphology differed considerably from the one obtained from the thermal cracks. While dynamic fracture tended to be of a mixed transgranular-intergranular mode, the slow fracture, induced by thermal stresses, was totally intergranular. These morphological differences are due to the higher energy available under dynamic crack propagation. Figure 7 shows the two morphologies. It can also be noted that the thermal fracture surface seems to be covered by a surface layer, possibly an oxide or a nitride. This layer is cracked along the grain-boundary edges.

V. CONCLUSIONS

It is demonstrated that dynamic forging is a feasible process to consolidate ceramics produced by combustion synthesis. Dynamic compaction in a rapid forging machine has considerable advantages over hot pressing (lower turn-around time) and over explosive compaction (it is readily adaptable to automated industrial production).

VI. ACKNOWLEDGEMENTS

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Fig. 1 *Porous microstructure of reaction synthesized TiC.*

Fig. 2 *High-speed forging machine (impact velocity: 10-15 m/s); (a) ready and (b) fired positions.*

Fig. 3 *Appearance of (a) titanium carbide and (b) titanium diboride compacts.*

Fig. 4 *Compact (bulk) and center density as a function of specific energy for TiC.*

Fig. 5 *Optical micrographs showing the grain structure of the reaction synthesized dynamically compacted (a) TiC and (b) TiB_2.*

Fig. 6 *Vickers microhardness profiles across the cross-section for (a) TiC and (b) TiB_2.*

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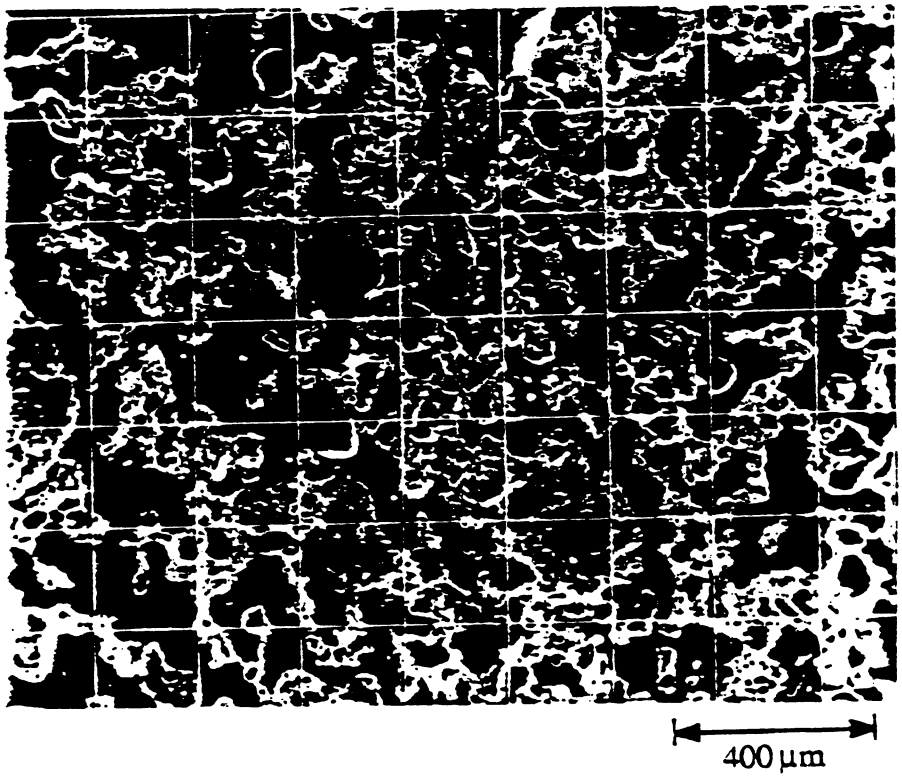

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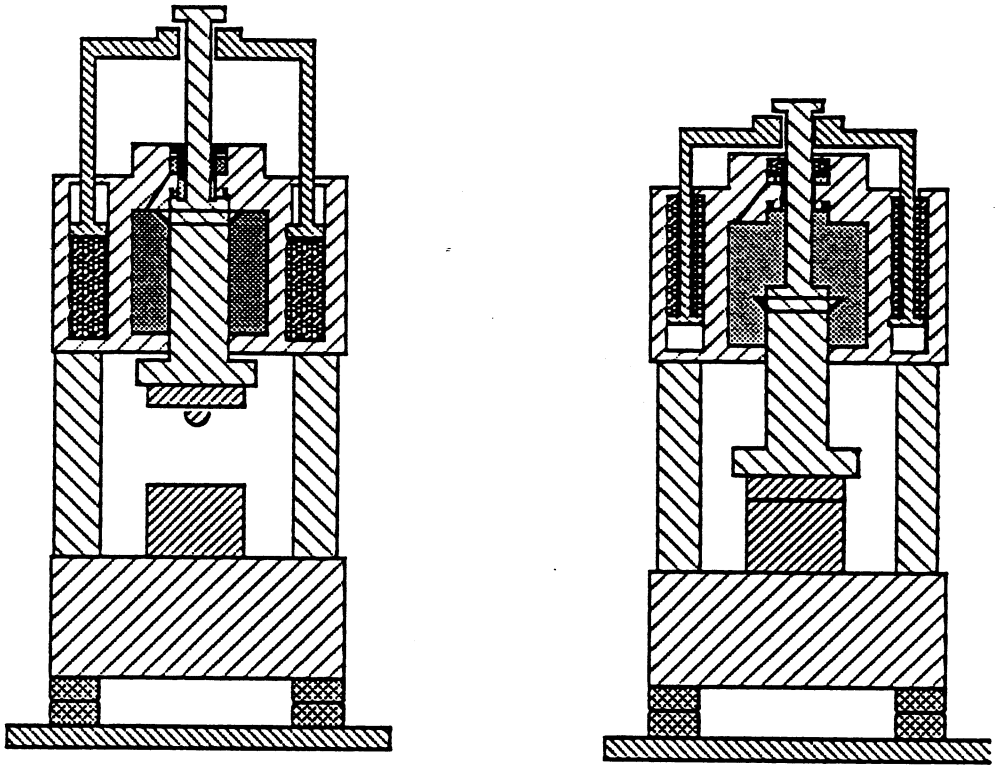

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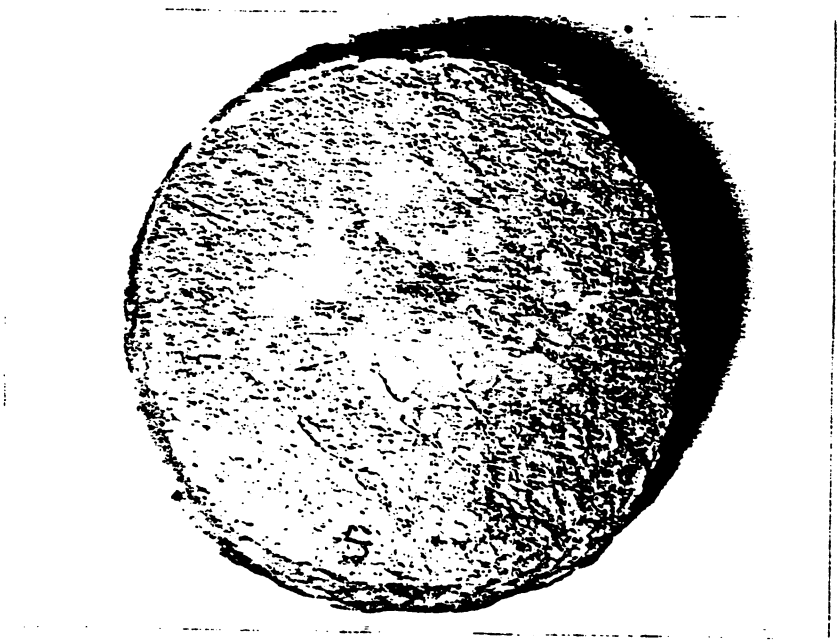

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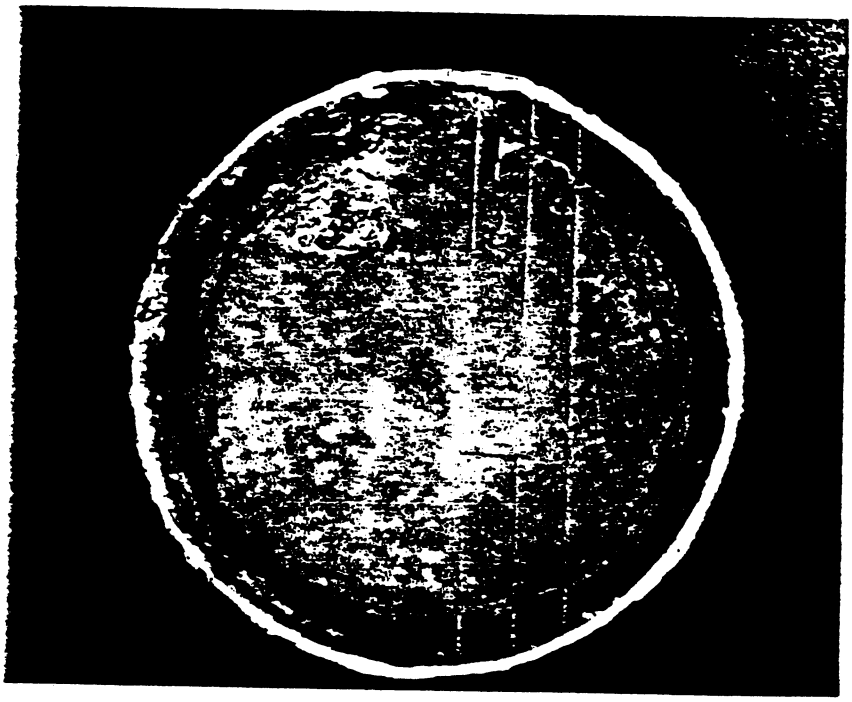

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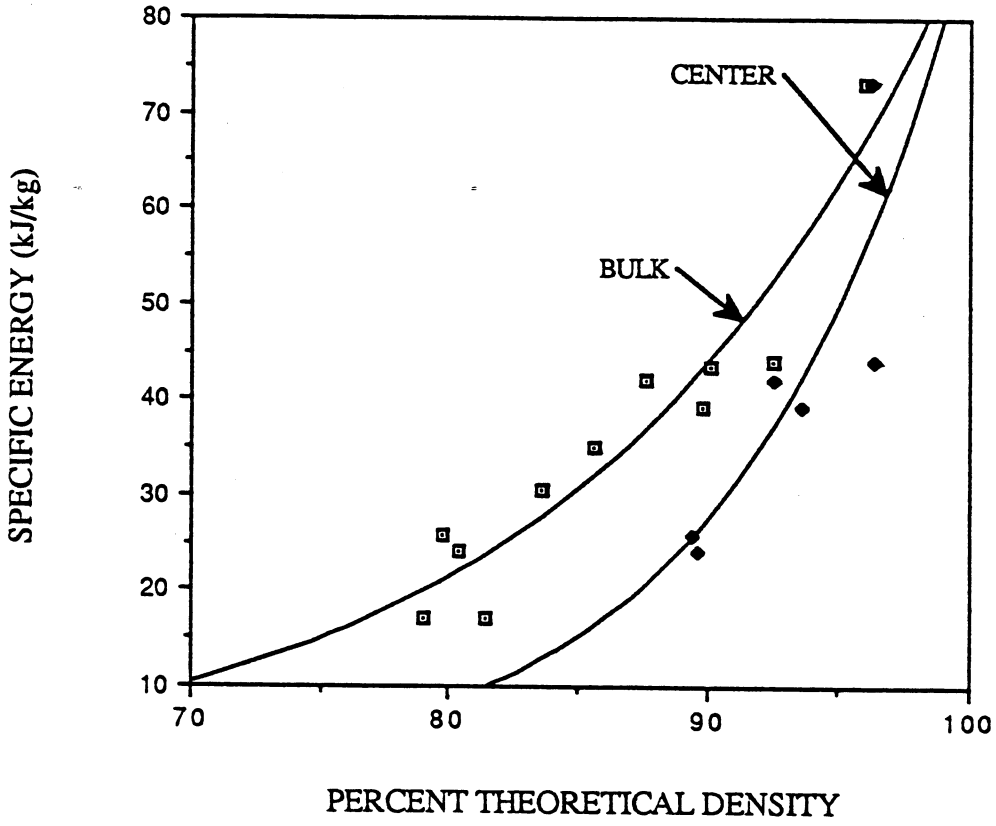
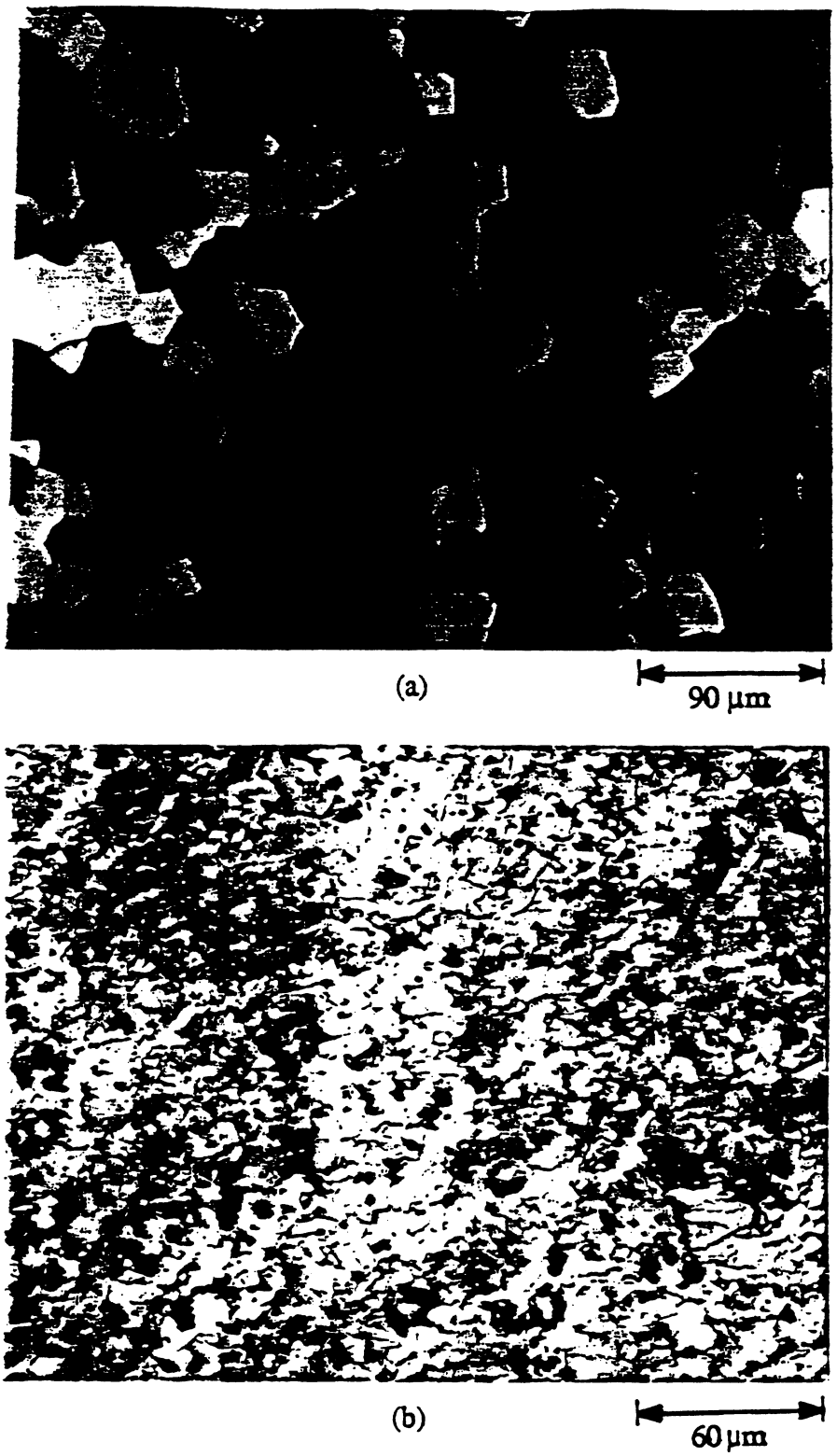


Fig. 4 *Compact (bulk) and center density as a function of specific energy for TiC.*



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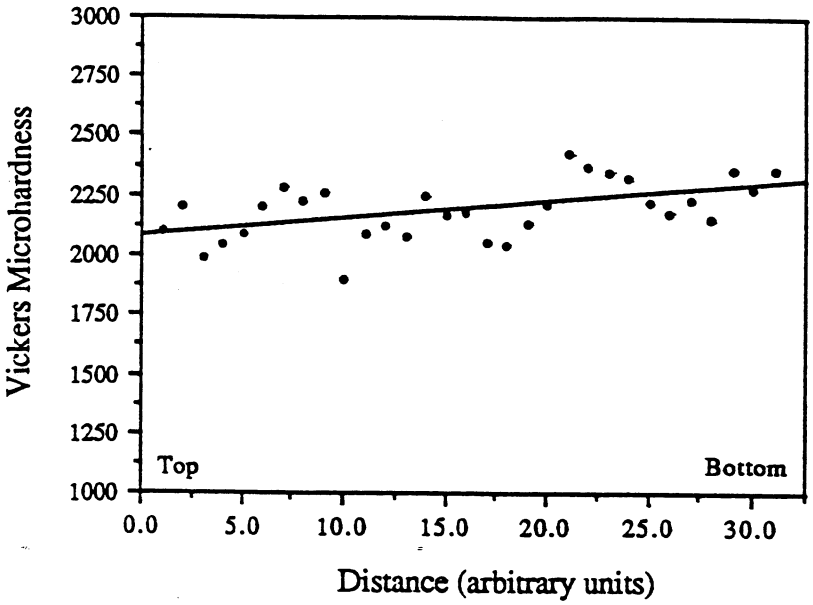

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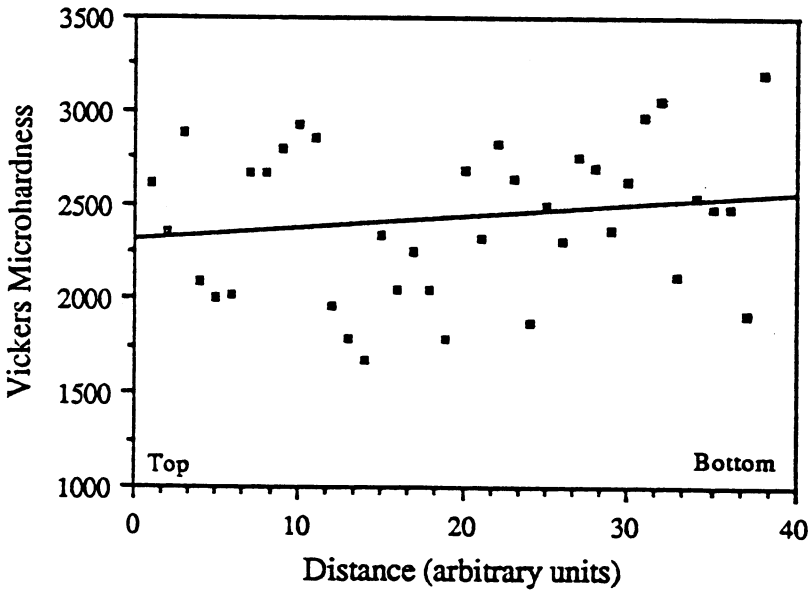
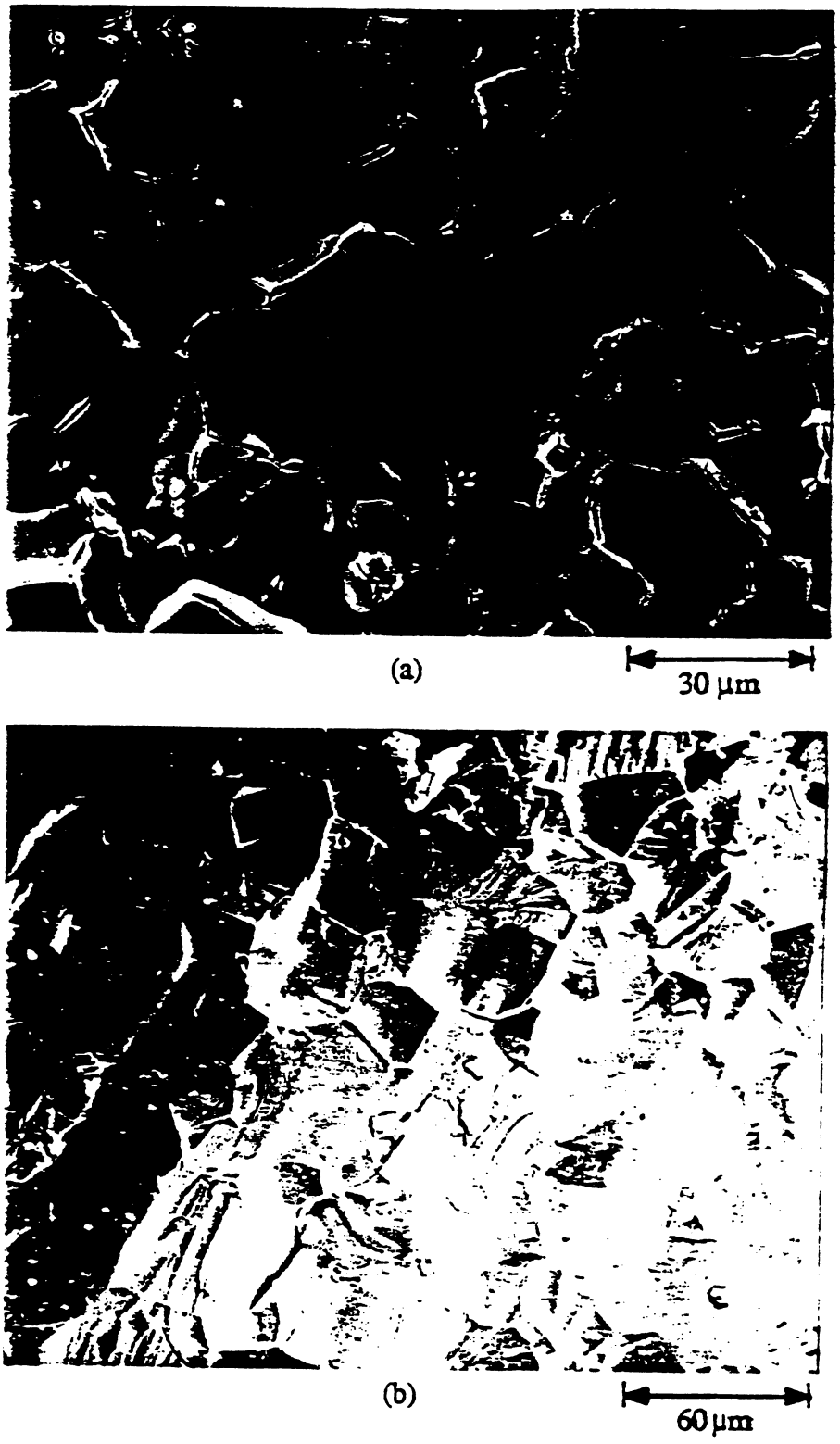


(b)

Fig. 6 *Vickers microhardness profiles across the cross-section for (a) TiC and (b) TiB_2.*



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