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X-RAY LINE BROADENING STUDIES ON ALUMINUM NITRIDE, TITANIUM CARBIDE AND TITANIUM DIBORIDE MODIFIED BY HIGH PRESSURE SHOCK LOADING†

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ABSTRACT

Powders of AlN, TiC and TiB_2 have been subjected to controlled shock loading with peak pressures in the samples between 14 to 27 GPa and preserved for post-shock study. Broadened x-ray diffraction peak profiles are analyzed by a simplified method and show increases in residual lattice strain and small decreases in crystallite size. Strain values range from 10^{-5} to 10^{-4} for TiB_2 and to values larger than 10^{-3} for TiC and AlN.

INTRODUCTION

There are numerous observations of enhanced solid state reactivity in powders which have been subjected to shock compression and preserved for post-shock examination. Early work included reports of enhanced catalytic activity [1,2], enhanced sinterability [3], and formation of compounds in powder mixtures [4,5]. Recent, more quantitative, studies include observations of enhancement in catalytic activity in shock-modified rutile approaching five orders of magnitude [6,7], greatly enhanced solubility in shock-modified silicon nitride [8], reduction in reaction start temperature for shock-modified zirconia in reaction with lead oxide [9], and reduction in the monoclinic to tetragonal transformation temperature in zirconia [10].

Such enhancements in solid state reactivity are thought to be the result of the introduction of defects due to shock-induced plastic deformation, crystallite size reduction or particle morphology changes [11]. As there is little information on defects in shock-modified materials and significant plastic deformation is rare in brittle refractory materials, we are carrying out a program to study shock-induced defects and crystallite size reduction with x-ray diffraction line broadening. Prior work includes detailed studies on rutile and aluminum oxide [12,13] and on zirconia [10,14,15]. The present work reports less detailed and more approximate analysis of x-ray diffraction line broadening in aluminum nitride, titanium carbide and titanium diboride.

EXPERIMENTAL

The powders employed in this study were obtained from H. C. Stark, Inc. as their AlN (grade E), TiC (special grade) and TiB_2 (vacuum grade) and were characterized and studied using various methods [16]. The powders were received and stored under argon.

The powders were pressed in place in copper recovery fixtures designed to provide controlled high pressure explosive loading and preserve the samples in place for post-shock study. The peak pressure experienced by the powder is controlled by the selection of the high explosive and the geometry of the high explosive as well as that of the sample recovery fixture. Shock-induced increases in mean bulk temperature are sensitive to the initial packing density and this density was varied from 44 to 62% of solid density. At the higher density the temperature varies from about 250 to 450°C depending on the peak shock pressures which varied from 14 to 27 GPa. The lower packing density results in an additional increase in temperature of about 200°C.

The shock modification experiments on the various powders are listed in Table I. The peak pressures shown and the temperatures given above are derived from an extensive series of numerical simulations with a large computer code [17]. The numerical simulations are thought to provide realistic estimates of the shock conditions since the recovery fixture design, choice of high explosives, choice of materials and the use of plane wave explosive loading are carefully coordinated to achieve conditions suitable for simulation [7]. Even though a planar loading is used, the dominant loading pulse is radial in character due to the low mechanical impedance of the powder samples. Although the pressures and temperatures cited are based on rutile powder as the sample material they are thought to well represent the present powder materials.

To minimize oxygen contamination the powders were handled in a dry box filled with argon, including loading in the recovery fixtures and removal from the fixtures. Upon removal from the fixtures the sample was homogenized and the powders were lightly ground to 100 mesh.

TABLE I. Schedule of Shock Compression Experiments

Experiment	Fixture	Explosive	Density		Peak Pressure
-	-	-	Mg/m^3 ,	%	GPa
Aluminum Nitride					
28G820	Bertha A	Comp B	1.91	59	14
20G820	Momma Bear A	Baratol	2.02	62	17
11G820	Baby Bear	"	2.02	62	20
26G820	Momma Bear A	Comp B	1.95	60	22
10G836	" "	"	1.47	45	22
16G820	Baby Bear	"	2.02	62	27
11G836	" "	"	1.47	45	27
Titanium Carbide					
27G820	Momma Bear A	Baratol	2.92	59	17
12G820	Baby Bear	"	3.05	62	20
24G820	Momma Bear A	Comp B	3.05	62	22
6G836	" "	"	2.22	45	22
15G820	Baby Bear	"	3.05	62	27
3G836	" "	"	2.22	45	27
Titanium Diboride					
25G820	Momma Bear A	Baratol	2.80	62	17
13G820	Baby Bear	"	2.77	62	20
23G820	Momma Bear A	Comp B	2.80	62	22
5G836	" "	"	2.03	45	22
14G820	Baby Bear	"	2.80	62	27
4G836	" "	"	2.03	45	27

X-ray samples were loaded in carefully presized 0.2 mm Lindemann glass capillaries in argon and sealed with a hot wire. The samples were then examined with nickel filtered CuKα radiation and a standard 114.5 mm Norelco powder camera.

The procedure of the present work of employing the less desirable film technique to determine diffraction profile widths rather than diffractometer determined line profiles as in our other studies resulted from both sample reactivity and requirements set upon our diffractometer for other uses. Initial studies showed that as-received powders would react slightly upon exposure to air and that grinding the material in air showed an accelerated reaction. Shock-loaded materials typically show defect concentrations of higher levels than ground samples; hence, on these materials the less desireable, simplified technique was felt warranted. The simplified method employed the widths of diffraction lines (β) measured for low, mid and high two-theta lines determined for both the standard (s) and shock loaded (sl) samples. The differences, $\delta = (\beta^2 - \beta^2)^{1/2}$ for such line, were obtained and fit upon curves of line breadth as a function of two-theta calculated as the sum of the squares of the size and strain contributions (Gauss squared method). The size contribution to line broadening is given by the Scherrer relationship, i.e.,

$$\delta_c = \lambda/L \sin \theta \quad ,$$

where L is the "average" crystallite size, θ the usual scattering angle and λ the wavelength employed. The strain (ε) is based on the small incremental change or spread in the average d values and is given by the relation

$$\delta_\varepsilon = -4\varepsilon \tan \theta \ .$$

More complex Fourier transform techniques using the Gauss-squared and Warren-Averbach analysis have been carried out on our other line profile studies on Al_2O_3 and TiO_2 [12,13] as well as initial studies on TiC exposed to air. Values within 50% of those obtained using the simplified procedure are typically obtained for strain values; size values differ by about 20%. These differences are not any greater than those obtained employing the Hall-Williamson rather than the Gauss-squared procedures on the same integral breadths (or β line widths) data [13].

Results and Discussion

TiC

Figure 1 shows our strain versus shock pressure results for TiC. Strain values range from 7×10^{-4} to 3×10^{-3} over the pressure interval investigated, showing substantial increases from the essentially undetectable level of 1×10^{-5} for the as-received material. The lower initial packing density and resulting higher shock temperature results in higher strain values for the same pressure loading. Evidently in this refractory, plastic deformations are aided by the higher temperature of the lattice. The strain values appear to be increasing in this pressure range in a rather linear fashion rather than reaching saturation values as has been seen for Al_2O_3 and TiO_2. Crystallite size reduction is not evident in this material, remaining at essentially the 2000Å value of the as-received powder. Previous strain values of 5×10^{-4} and 2×10^{-3} have been reported for peak pressures estimated to be near 12 GPa [18,19]. There is no evidence for new shock-induced phases in this material.

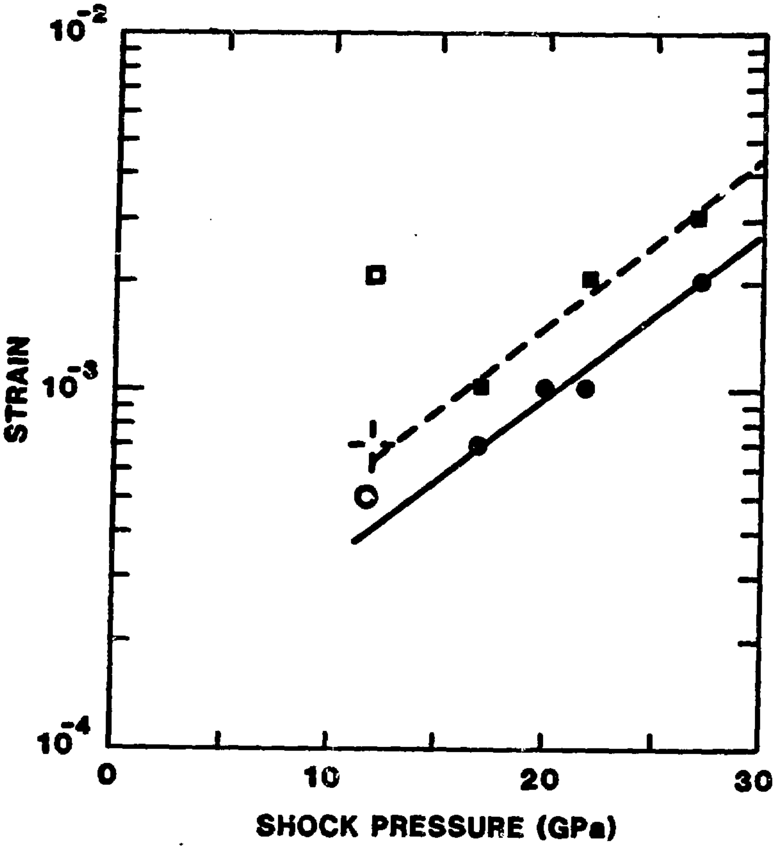

Figure 1. Strain values versus peak shock-loading pressures for TiC. Present data: solid squares, solid circles, and star for 2.22, 3.00, and 2.92 Mg/m^3 initial packing densities, respectively; open square and circle ref. 18 and 19, respectively.

TiB_2

Figure 2 shows the corresponding results on TiB_2. An apparent temperature effect is also noted here though the nature appears anomalous, perhaps due to the relative errors of the points, since lower shock-loading pressures would be expected to show a smaller rather than larger difference in strain. Values range from $1x10^{-5}$ to $3x10^{-4}$, the lower values are barely detectable in comparison with the $1x10^{-5}$ as-received value. Crystallite size reduction again is not evident in this material, nominally remaining at the 3000Å value of the as-received material. As was the case for TiC the residual strain does not reach saturation in the pressure range of the present work.

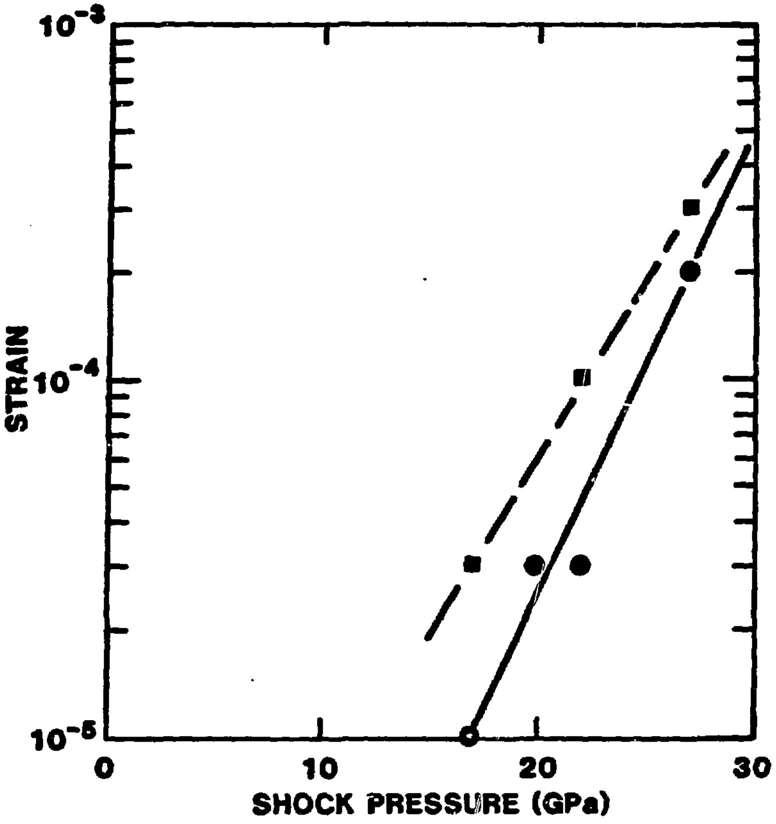

Figure 2. Strain values versus peak shock-loading pressures for TiB_2. Present data are squares and circles for ~ 2.03 and 2.80 Mg/m^3 initial packing densities, respectively.

AlN

Figure 3 shows our results on AlN. Values of strain are very near a constant value of $3x10^{-3}$ over the pressure interval of 14 to 27 GPa. This represents a two order of magnitude increase over the as-received value of $2x10^{-5}$. The initial packing density does not appear to have a significant effect on the strain value of the recovered powders from the 2000Å as-received values. Crystallite size has been reduced to near 700Å for all these powders. Previously reported strain values on AlN [20] span $1x10^{-3}$ to $2x10^{-3}$ for pressure values ranging from 10 to 32 GPa employing samples with an initial strain value of $5x10^{-4}$.

AlN can be plastically deformed more readily than the other two refractories studied [21]. Thus the temperature rise caused by the shock loading is not as important as it is for the other two refractories. This results in a near saturation at strain levels of $3x10^{-3}$.

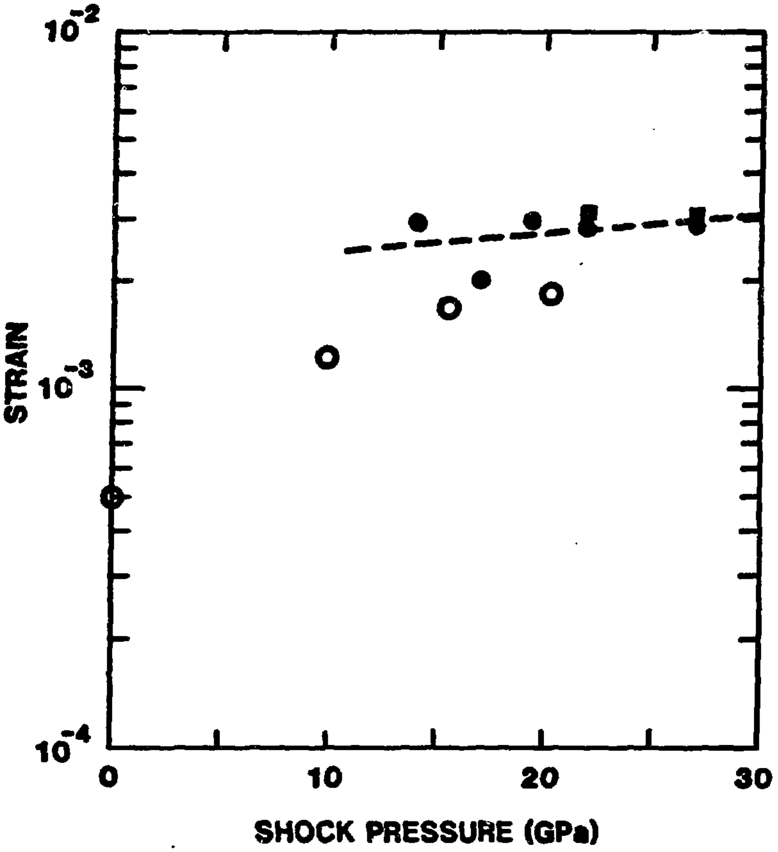

Figure 3. Strain values versus peak shock-loading pressures for AlN. Present data: solid squares and circles for ~ 1.5 and 2.0 Mg/m^3 initial packing densities, respectively; data from ref. 20 are open circles.

CONCLUSIONS

These studies on the present refractories together with our other recent studies [12,13] clearly show the strong dependence of the residual strain on pressure and on the specific materials. A peak pressure of 15 GPa results in essentially no strain in TiB_2 whereas strain values in AlN and Al_2O_3 approach 3×10^{-3} at this pressure loading. For Al_2O_3, 5×10^{-3} values are obtained near 27 GPa [12]. A similar large difference in the materials response to the shock induced temperature rise is also noted. Clearly in the case of TiC and TiB_2, the more plastic deformation results in higher recovered strain values for the lower initial packing density samples; for AlN this temperature rise appears to have little influence, either because of a saturation effect or because of annealing occurring at a level essentially matching the possible additional increase. For TiO_2 our results show a strong reduction of strain at the higher peak pressure values suggesting that annealing plays a predominant role in the final strain value.

The strain values by shock-loading are observed to exceed values obtained by more conventional methods, such as grinding or ball-milling ceramic materials. Values obtained are more typical of those found in heavily cold worked metals and further serve to emphasize that under the extreme conditions of shock compression unusual defect states are achieved.

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