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Specific surface area studies of shock-modified inorganic powders

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Modification of inorganic powders with high-pressure shock-wave loading is of interest for shock-activated sintering, material synthesis, shock-enhanced catalytic activity, dynamic compaction, and shock-enhanced solid-state reactivity. The specific surface area of shock-modified powders is a direct quantitative measure of powder morphology changes, yet few studies have been carried out on powders subjected to controlled shock-loading conditions. In the present work aluminium oxide, zinc oxide, aluminium nitride, titanium carbide and titanium diboride powder compacts were subjected to controlled shock-loading to peak pressures of from 4 to 27 GPa at various starting densities, and characterized with specific surface area measurements by the BET (gas adsorption) method. Low-temperature cyclical thermal pretreatment and outgassing pretreatment of the shock powders at 250° C were employed; the former improves the reliability of the BET measurements, and makes the surfaces of the shock-modified powders more chemically active than those of the starting powders. Each powder shows a somewhat different response to shock-loading, ranging from a decrease in specific surface by a factor of six for zinc oxide to a 200% increase for titanium diboride. Shock-induced changes in specific surface show four characteristic behaviours as shock pressure is increased. Well-understood and controllable shock-loading conditions are found to be essential to shock-modification studies. An update on earlier measurements on rutile, zirconia and silicon nitride is also reported.

1. Introduction

When specimens are placed in intimate contact with detonation waves from high explosives or impacts of high speed projectiles, intense pressure pulses with rapid increases and decreases of pressure propagate through the specimens. These pressures pulses typically persist for times of a few microseconds. The modification of inorganic powders by such high-pressure shock-compression has been of interest for many years. Highlights of early work were the synthesis of diamond from graphite in 1961 [1], the synthesis of titanium carbide [2] and zinc ferrite [3] in 1963, demonstration of shock-enhanced catalytic activity in 1965 [4], and of shock-activated sintering in 1966 [5]. Interest has recently revived in this area [6], and the very considerable work by scientists in the Soviet Union since 1965 [7] has raised fundamental questions concerning physico-chemical processes in shock-compressed condensed matter, and suggests that there may be potential for significant impact on materials technology.

As powder materials are frequently composed of particles with complex morphologies, it is important to characterize them with quantitative specific surface area determinations. The BET method involving adsorption of nitrogen (see Section 2) is the standard method for such measurements. Shock-modification is expected to change particle morphology; hence, surface

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TABLE I Properties of powders

Material	Grade	MPS[*] (μm)	Impurities[†]
ZnO[‡]	– 200 mesh	–	99.9% pure
Al_2O_3[§]	RC-HP-DBM	3.14	0.045% MgO, 0.011% SiO_2
AlN[¶]	Grade E	37.6	6.6% Al_2O_3, 300 ppm Ti, 40 ppm Si, 30 ppm Fe, others < 10 ppm
TiC[¶]	Special grade	3.93	1.16% oxygen as TiO_2, 300 ppm Al, 100 ppm Fe, 100 ppm Co, 100 ppm Cr, 30 ppm Ca, others < 10 ppm
TiB_2[¶]	Vacuum grade	14.6	Trace TiN, 0.66% oxygen as TiO_2, 300 ppm Al, 34 ppm Fe, 30 ppm 30 ppm Co, 30 ppm Cr, others < 10 ppm

[*] Mean particle size by suspension light scattering.

[†] Final Report, DARPA Dynamic Synthesis Program (Lawrence Livermore National Laboratory Report UCID 19 663–84).

[‡] Source: Cerac.

[§] Source: Reynolds.

[¶] Source: H. C. Stark.

measurements are essential to its characterization. Nevertheless, there are few data on powders subjected to controlled, quantified shock-loading conditions.

It is the object of this paper to report the results of a study of the influence of shock-modification on the specific surface areas of powders of aluminium oxide, zinc oxide, aluminium nitride, titanium carbide and titanium diboride. An update on prior measurements of rutile, zirconia and silicon nitride is also given. These powders represent inorganic materials with a broad range of physical characteristics, and the study provides an opportunity to determine their influence on changes in particle morphology resulting from comminution, interparticle bonding, surface chemical activity, and major changes in particle configuaration.

2. Experimental procedure

The powders were obtained from commercial sources as indicated in Table I, where characteristics of the powders are listed. Except for inadvertent exposure, the non-oxide powders were kept in commercial-grade argon atmospheres for the entire process of powder storage, shock experimenting and post-shock handling. Although the argon was not of high purity and did not eliminate surface contamination with oxygen or water, it did serve to minimize these effects.

The shock-modification experiments were designed to subject the powder samples to high explosive loading in such a manner that the samples were preserved intact (sealed) in their capsules for later study. The shock-modification system, consisting of four explosive loading configurations and five sample recovery capsules, provides the capability to vary the peak pressure from 4 to 27 GPa. Increases in temperature result from the rapid shock compression, and the density of the powder compact prior to the shock compression controls the magnitude of the increase in temperature. Various studies of shock-induced modification [8–13] have shown that the peak presssures calculated in the various types of apparatus provide a consistent basis on which to characterize the shock process. Less experimental evidence is available to confirm the temperature calculation (which gives a measure of mean bulk temperatures) but observed shock-induced modifications appear consistent among several different powders. Electron spin resonance measurements of point defects have been carried out on a number of powders and are quite sensitive to temperature calculations. A short description of studies of the recovery fixtures, their basic configurations and the results of the calculations are given in previous papers [14, 15].

A schedule of the shock-modification experiments on the five powders is given in Table II. As indicated in the table, aluminium nitride, titanium carbide and titanium diboride were

TABLE II Schedule of shock-compression experiments[‡]

Material	Experiment	Fixture	Explosive	Pre-shock compact density ($Mg\,m^{-3}$)*	Peak pressure (GPa)	Peak temperature (° C)
ZnO	49G836	Momma Bear	Baratol	3.01(55)	7.5	225
	50G836	Momma Bear	Comp *B*	3.01	16	425
	48G836	Momma Bear *A*	Baratol	3.01	16	300
	51G836	Momma Bear *A*	Comp *B*	3.01	22	400
Al_2O_3	21G820	Bertha	Baratol	2.34(59)	4	100
	15G836	Big Bertha *A*	Comp *B*	2.25(56)	13	350
	29G820	Momma Bear *A*	Baratol	2.31(58)	17	250
	31G820	Baby Bear	Baratol	2.36(59)	20	150
	12G836	Baby Bear	Baratol	2.35	20	150
	30G836	Momma Bear *A*	Comp *B*	2.34	22	350
	37G836	Momma Bear *A*	Comp *B*	2.32(58)	22	350
	7G836	Momma Bear *A*	Comp *B*	1.80(45)	22	550
AlN	20G820	Momma Bear *A*	Baratol	2.02(62)	17	150
	11G820	Baby Bear	Baratol	2.02	20	100
	26G820	Momma Bear *A*	Comp *B*	1.95(60)	22	300
	16G820	Baby Bear	Comp *B*	2.02	27	425
TiC	27G820	Momma Bear *A*	Baratol	2.92(59)	17	160
	24G820	Momma Bear *A*	Comp *B*	3.05(62)	22	300
	15G820	Baby Bear	Comp *B*	3.05	27	425
	12G820[†]	Baby Bear	Baratol	3.05	20	425
	6G826	Momma Bear *A*	Comp *B*	2.22(45)	22	550
TiB_2	25G820	Momma Bear *A*	Baratol	2.80(62)	17	150
	23G820	Momma Bear *A*	Comp *B*	2.80	22	300
	14G820[†]	Baby Bear	Comp *B*	2.80	27	425
	13G836	Bertha *A*	Comp *B*	2.03	17	425
	5G836	Momma Bear *A*	Comp *B*	2.03(45)	22	550

*Figures in brackets give percentage of powder compact density relative to solid density.

[†] Seal opened during shock experiment causing brief exposure to air.

[‡] For description of fixture and explosive leading to derived values for pressure and temperature see [14, 15].

shock-modified at only the highest pressures (17 to 27 GPa). Aluminium oxide was studied more extensively than the other powders. For aluminium oxide, titanium carbide and titanium diboride experiments were conducted at 22 GPa but at lower compact powder densities, in order to study the effects of the higher shock-induced increase in temperature.

After shock-modification the sample fixtures were cut open and the powder samples were lightly ground, if required, to pass through a 100-mesh screen. In most cases the entire sample was homogenized and divided into 100 mg samples for surface area analysis. In certain shock-modified samples, powders were sampled from various locations within the recovery capsule.

Surface area measurements were carried out in a standard flow apparatus using a six-point BET analysis [16]. Care was taken to examine the adsorption isotherms for each powder to ensure that the data were collected over the appropriate adsorbate coverage region.

Powder samples were preconditioned by either repetitive cooling of the sample to liquid nitrogen temperature under flowing nitrogen (*repetitive pretreatment*) or by heating the sample to 250° C in flowing helium for three hours (*thermal pretreatment*). The technique and analysis were checked against standard powders and by repeated measurements on the same samples. Each value reported is the mean of at least three consecutive determinations. The accuracy of an individual measurement is estimated to be 3%, and higher confidence is gained by combining the three independent determinations.

The effect of pretreatment was studied for one shocked TiC (Experiment 6G836) and one shocked TiB_2 (5G836). After the normal sequence (repetitive pretreatment, surface area determination, thermal pretreatment, surface area determination) the repetitive pretreatment was again given to the samples without exposing them to air. The resultant surface areas were the same as those determined after the previous thermal pretreatment. The samples were then exposed to air for three days; this air exposure caused the repetitive specific surface value to drop back to the first value determined. Subsequent thermal pretreatment resulted in the previously established value for the specific surface area.

3. Results

The widest range of shock pressures for shock-modification was achieved for alumina. The specific surface area of alumina first increased from that of unshocked powder and then decreased as the shock pressure increased, as indicated in Fig. 1. The circles represent the specific surface area measured after thermal pretreatment. These data indicate a broad maximum in the surface area in the region of 10 GPa. The variation of surface area with pressure is evident even though the absolute value only changes by 20% from an initial 8 $m^2 g^{-1}$. Repetitive pretreatment of shocked alumina, indicated by crosses, gave surface areas lower than the corresponding thermal pretreatment. The difference between the two values is more pronounced for the shocked samples than for the unshocked sample. The alumina recovered from the edge and centre of the powder disc in Experiment 12G836 has a surface area of 6.5 $m^2 g^{-1}$. Both of these values are significantly different from the 7.0 $m^2 g^{-1}$ found for the homogenized sample. Calculations indicate that the edge region experiences a significantly higher temperature during the shock loading.

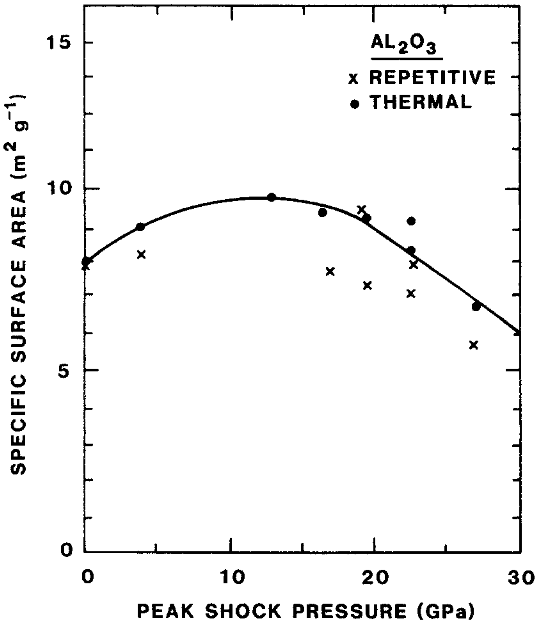

Figure 1 The influence of peak shock pressure on the BET specific surface is shown for aluminium oxide. Results for two powder pretreatments are shown. The "repetitive" pretreatment is a low-temperature cycling while the "thermal" pretreatment is at 250° C in helium. The thermal pretreatments are found to give the most representative results.

The specific surface area of zinc oxide decreases smoothly with increasing shock pressure. As can be seen in Fig. 2, the surface area decreased by a factor of three at the lowest shock pressure, and continued to decrease to give a factor of almost ten at the highest shock pressure.

The surface area data of aluminium nitride shown in Fig. 3 appear to show a pressure dependence similar to that observed for alumina. The high-pressure data are sparse because of the formation of an unidentified yellow liquid during the thermal pretreatment of the powder. The results from the repetitive pretreatment support the trend indicated by the thermal pretreatment data. The decrease in surface area of 50% from the initial value of 2 $m^2 g^{-1}$ is more pronounced than that determined for the alumina. The increased sensitivity of shock-modified aluminium nitride to surface chemical contamination is reflected in changes in the surface area of the shock-modified material with pre-treatment and in the observation of the yellow liquid.

The four shocked samples of titanium carbide had surface area increases of more than 50% from the initial, unshocked value of 2 $m^2 g^{-1}$ (Fig. 4). Another sample (not shown) came from a capsule that inadvertently opened to the atmosphere during the shock-loading. The surface area of that sample was lower than for the others. While any conclusion concerning the pressure dependence drawn from these data alone would be speculative, the observations fit the increasing and then decreasing trend with increasing shock pressure observed for alumina and aluminium nitride. Two shock treatments (24G820 and 6G836) gave essentially identical surface areas for the same shock pressure, but different values of the starting powder compact density. The lack of an influence of starting compact density and its resulting temperature change indicates that shock-modification at the

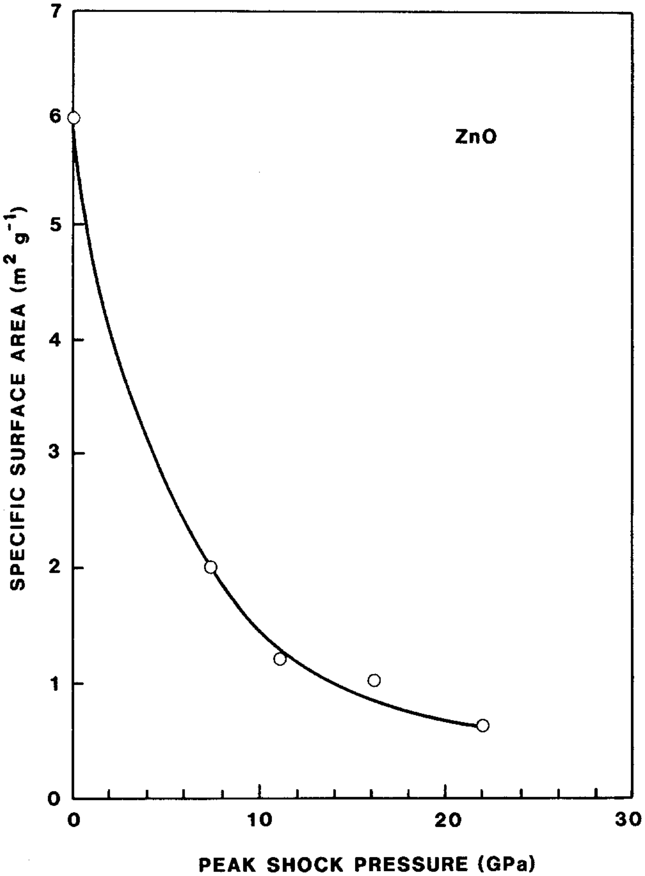

Figure 2 The specific surface of zinc oxide powders is found to decrease strongly at low shock pressures. The powders were subjected to thermal pretreatment.

different peak temperatures did not cause an observable effect on surface area for this refractory powder.

The three shocked samples of titanium diboride had surface area increases of 100 and 200% above the unshocked area of 0.6 $m^2 g^{-1}$ (Fig. 5). Two other samples were inadvertently exposed to air during shock treatment and produced a yellow liquid during the thermal pretreatment; hence, only the values for repetitive pretreatment of those samples could be obtained. Because the values for the thermal and repetitive pretreatment of sample 23G820 seem reversed compared with the other powders, this sample was re-run. Both pretreatments gave surface values identical to the previous thermal pretreatment one. Evidently the sample suffered an irreversible loss of surface area during the first thermal pretreatment. No clear trend in the specific surface area is apparent from the data.

4. Discussion

The most immediate observation from the shock-induced alteration of surface area is that even though the various powders have been subjected to extremes of pressure and rates of loading and unloading, the alterations in surface area are only an order of magnitude or less. Thus, major changes observed in solid-state reactivity of shock-modified powders are not due to changes in specific surface area.

The shapes of the plots of specific surface area against peak shock pressure indicate quite different behaviours at different shock pressures, and suggest the dominance of different phenomena in various shock pressure regions. The shock compression history in low-density powder compacts is dependent upon the particular fixtures and loadings, but typically consists of an early relatively low pressure wave (about 3 GPa) followed by a relatively slow stepwise increase (lasting several microseconds) to peak pressure. The release of pressure occurs over a period of several microseconds. During the early low-pressure phase, large increases in density occur as the particles are compressed together and the void volume decreased. The largest part of the shock-induced increase in temperature occurs in this early low

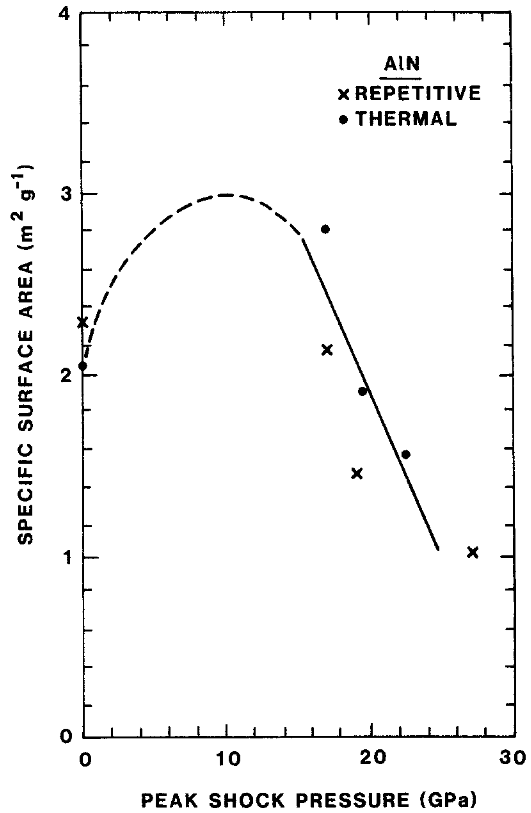

Figure 3 The specific surface of aluminium nitride powders is not greatly affected by shock-loading. The dashed line shows the low-pressure behaviour suggested but not directly described by the data.

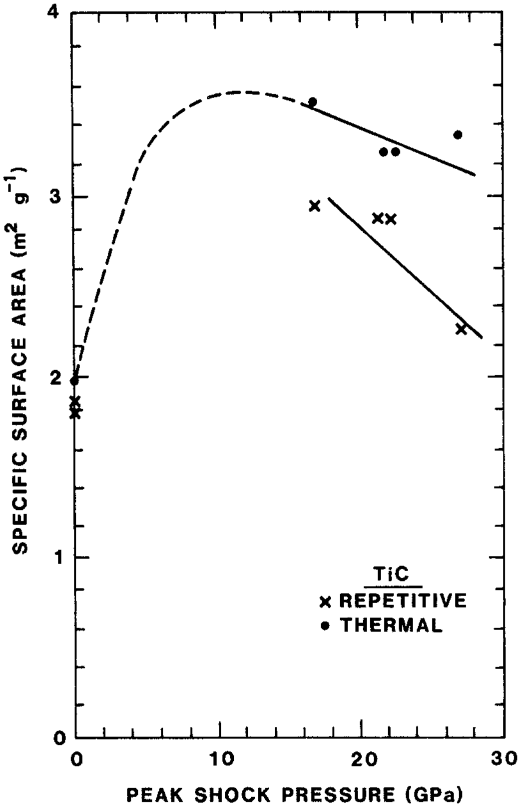

Figure 4 Shock pressure is seen to cause a significant increase in specific surface of titanium carbide powders. The dashed line shows the low-pressure behaviour suggested but not directly described by the data.

pressure phase. During the powder compaction process, waves reverberate in the particles and large stress gradients can lead to comminution and reorientation of particles. Plastic deformation of particles leads to more intimate particle configurations, while dislocations and point defects which intersect the surfaces can act to clean them. Freshly comminuted or cleaned surfaces are highly reactive and conducive to solid-state bonding at high pressure. Defects also cause greatly enhanced atomic diffusion. As pressure is released, large pressure gradients can cause localized tensile stresses which can comminute previously bonded particles. Thus, depending on the sensitivity of the material to comminution, plastic deformation under shock, and solid-state bonding, a net increase or decrease in specific surface may result.

The three typical behaviours of the present paper and those reported previously [17–20] follow general patterns indicated in Fig. 6. Curve (a) shows a monotonic increase in specific surface with pressure, which suggests that the shock process results in comminution of particles with little subsequent bonding in the high-pressure, high-temperatue state. Curve (b) shows a behaviour dominated by interparticle bonding. Curve (c) suggests a process of comminution at low pressure followed by interparticle bonding at higher pressure. The behaviour indicated by Curve (d) is likely to be the result of a high-pressure phase transition [21].

In the present work ZnO and Al_2O_3 exhibit the most distinctive behaviours. The continuous large decrease in specific area of ZnO with increasing pressure is characteristic of a shock-induced bonding process, while that of Al_2O_3 is characteristic of a comminution process at low pressure followed by bonding at higher pressure. There are fewer data for AlN, TiC and TiB_2, but they appear to show a behaviour characterized by low-pressure comminution followed by higher-pressure bonding.

Of the two methods used to condition the powders, thermal pretreatment is thought to yield the true surface area when it is not likely to alter the

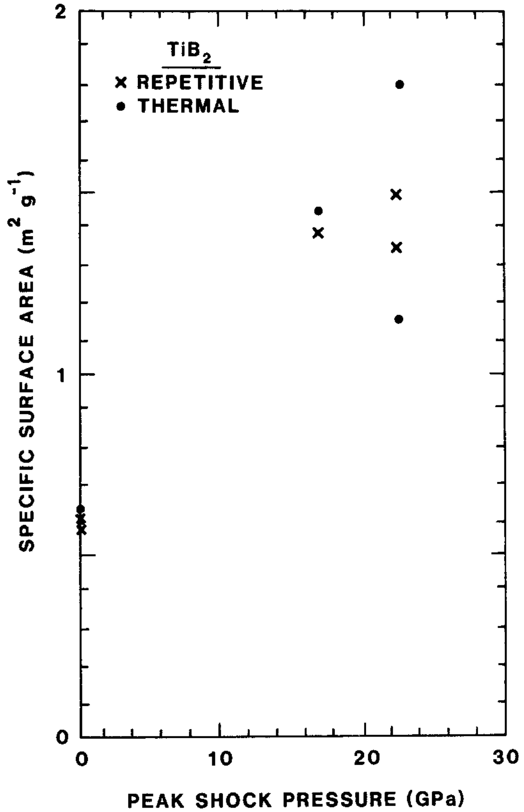

Figure 5 A large increase in specific surface is seen for titanium diboride, and more scatter is observed than for other powders.

powder surface morphology [16]. By reproducing surface-area measurements from low-temperature pretreatment after re-exposing the powder to air, we verified that the thermal pretreatment did not generally alter the powder surface.

The low-temperature repetitive pretreatment does reveal an interesting but unexplored phenomenon. The larger difference in the values of thermal and repetitive specific surface areas for shocked samples show them to be significantly more reactive to moisture in the air than the unshocked samples. When the shock compression process causes severe modification of the powder surfaces (i.e. formation of the unidentified yellow liquid), the repetitive pretreatment serves to indicate a lower bound to the newly created surface area.

The shock recovery capsule was opened to the atmosphere during two of the shock-compression experiments reported in this paper. In each case the surface area was lower than expected from the trend of the other data points. The opened-capsule results can be ascribed to interaction of the powder surfaces with oxygen and water during the post-shock annealing.

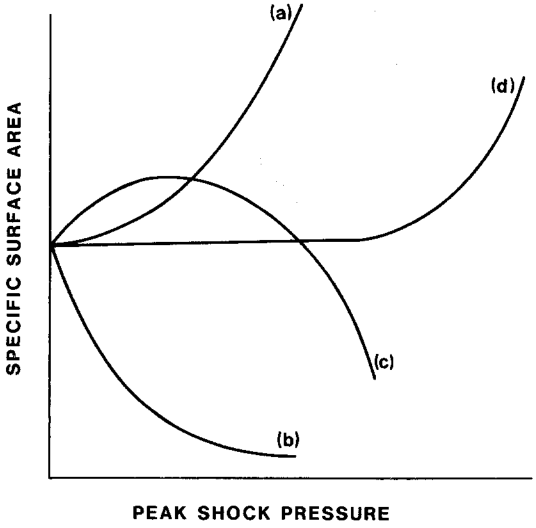

Figure 6 The observed shock pressure dependence on the specific surface of powders appear to be of four characteristic types: (a) is indicative of particle comminution, (b) is indicative of interparticle bonding, (c) shows low-pressure comminution followed by bonding at higher pressure, and (d) is typical of a high-pressure phase transition.

The trends in surface-area changes reported for AlN in this paper are in good qualitative agreement with those of Anan'in *et al.* [21]. They reported a maximum in the specific surface area, similar to ours, that increased the area by 40% from an initial value of near to 4 m^2 g^{-1}. Their values do not show as strong a maximum as ours, we see an actual loss in area at high shock pressure. Quantitative comparison is not possible, however, as the pressure estimates of these authors are based on one-dimensional determinations of pressures incident on the powders from the loading rather than the peak pressure in the powder [15]. Nevertheless, the trends in this direct comparison, and for Al_2O_3 of the present work and for ZrO_2 [20], all confirm the existence of a maximum in surface area in the shock pressure range [17].

The results of specific surface studies of shock-modified TiO_2, ZrO_2 and Si_3N_4 reported earlier and carried out in the same apparatus [22] are shown in Fig. 7. (Note that the data are re-plotted with respect to the pressure in the powder, rather than to the incident pressure in the copper capsule as reported earlier [22].) With the exception of the ZrO_2, the behaviours are characteristic of low-pressure comminution with interparticle bonding

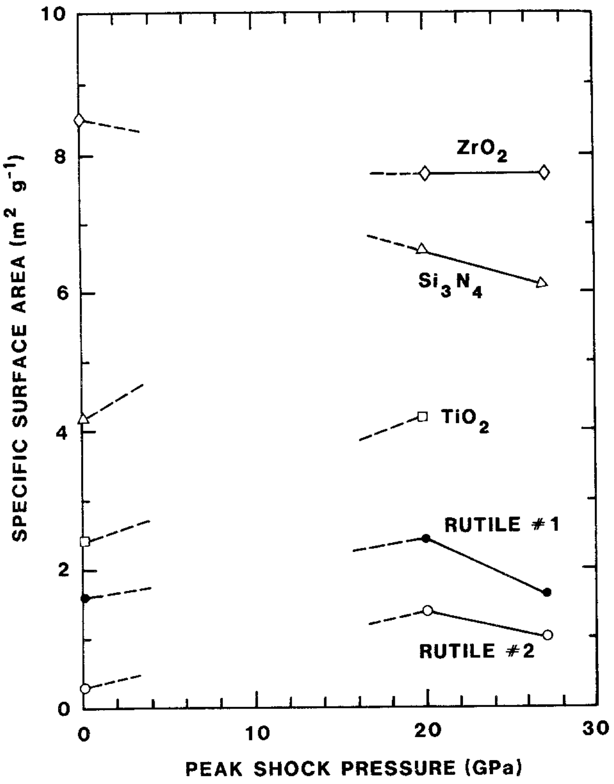

Figure 7 Data from a previous study [22] show behaviours similar to those of the present study. (Note that the pressure scale shown here is updated to show the results of two-dimensional numerical simulations.)

at higher pressure. A similar overall behaviour for the various TiO_2 powders of Fig. 7 indicates that shock-modification of specific surface is not strongly influenced by the starting specific surface values. The behaviour of ZrO_2 shown in Fig. 7 is quite different from that of the other powders, but it is known [11] that a structural transition has occurred under the loading conditions shown.

Scanning electron microscopy observations should, in principle, be useful to observe comminution or bonding. Such observations have been carried out on powders of the present study, but the powders do not have a distinctive particle morphology which can serve as a distinct marker. Only in the case of Si_3N_4 does the distinctively needle-like starting morphology provide a basis for observing shock-induced particle morphology changes. The shock-modified Si_3N_4 was found to show no needle-like material. The powder appears to have been well comminuted at some time early in the pressure pulse, and later bonded into larger particles.

The importance of the shock-modification fixture and the shock-compression history are brought out in the surface-area variation within a single shock-loaded powder. The calculable differences in pressure and temperature history at various locations within the powder during the loading/unloading process are reflected in the specific surface area. In our case, we found as much as a 10% variation in surface area with location where the average surface area was modified by 30%. In an overall sense the present work demonstrates that the resulting specific surfaces are strongly dependent on shock pressure, and without its quantitative specification the results of such shock-modification studies are of very limited value. The present work shows that study of specific surface can provide a meaningful probe of the effect of shock-modification, and the results can be used to infer the dominance of various processes experienced by powders in shock modification.

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References

1. P. S. DECARLI and J. C. JAMIESON, *Science* **133** (1961) 821.
2. Y. HORIGUCHI and Y. NOMURA, *Bull. Chem. Soc. Jpn.* **36** (1963) 486.
3. Y. KIMURA, *Jpn. J. Appl. Phys.* **2** (1963) 312.
4. Y. HORIGUCHI and Y. NOMURA, *Carbon* **2** (1965) 436.
5. O. R. BERGMANN and J. BARRINGTON, *J. Amer. Ceram. Soc.* 49 (1966) 502.
6. B. MOROSIN and R. A. GRAHAM, in "Shock Waves in Condensed Matter", Menlo Park, 1981, edited by W. J. Nellis, L. Seaman and R. A. Graham (American Institute of Physics, New York, 1982) p. 4.
7. G. A. ADADUROV and V. I. GOL'DANSKII, *Russian Chem. Rev.* **50** (1981) 948.
8. E. L. VENTURINI and R. A. GRAHAM, in "Defect Properties and Processing of High-Technology Nonmetallic Materials", edited by J. H. Crawford Jr, Y. Chen and W. A. Sibley (North-Holland, Amsterdam, 1984) p. 383.
9. M. J. CARR, R. A. GRAHAM, B. MOROSIN and E. L. VENTURINI, *ibid.*, p. 343.
10. B. MOROSIN and R. A. GRAHAM, *ibid.*, p. 335.
11. B. MOROSIN, R. A. GRAHAM and J. R. HELLMANN, in "Conference on Shock Waves in Condensed Matter", Santa Fe, July 1983, edited by J. R. Asay, R. A. Graham and G. K. Straub (North-Holland, Amsterdam, 1984) p. 383.
12. W. F. HAMMETTER, J. R. HELLMANN, R. A. GRAHAM and B. MOROSIN, Proceedings of Conference on Shock Waves in Condensed Matter, Santa Fe, July 1983, edited by J. R. Asay, R. A. Graham and G. K. Straub (North-Holland, Amsterdam, 1984) p. 391.
13. B. MOROSIN and R. A. GRAHAM, *Mater. Sci. Eng.* **66** (1984) 73.
14. L. DAVISON, D. M. WEBB and R. A. GRAHAM, in "Shock Waves in Condensed Matter", Menlo Park, 1981, edited by W. J. Nellis, L. Seaman and R. A. Graham (American Institute of Physics, New York, 1982) p. 67.
15. R. A. GRAHAM and D. M. WEBB, in "Shock Waves in Condensed Matter", Santa Fe, July 1983, edited by J. R. Asay, R. A. Graham and G. K. Straub (North-Holland, Amsterdam, 1984) p. 211.
16. S. LOWELL, "Introduction to Powder Surface Area" (Wiley, New York, 1979).
17. A. V. ANAN'IN, O. N. BREUSOV, A. N. DREMIN, V. F. TATSII and F. A. FEKHRETDINOV, Proceedings of First All-Union Symposium on Shock Pressures, October, 1973, Vol. 2, edited by S. S. Batsanov (Moscow, 1974). Translation in Sandia National Laboratories Report SAND80–6009 (1980).
18. A. V. ANAN'IN, O. N. BREUSOV, A. N. DREMIN, V. B. IVANOVA, S. V. PERSHIN, V. F. TATSII and F. A. FEKHRETDINOV, *Sov. Powder Metall. Metal Ceram.* No. 10 (1979) 858.
19. *Idem, ibid.* No. 8 (1974) 662.
20. *Idem, Fiz. Khim. Obrabotki Mater.* No. 6 (1976) 31 (in Russian).
21. *Idem, Sov. Powder Metall. Metal Ceram.* No. 9 (1976) 714.
22. R. A. GRAHAM, B. MOROSON, E. L. VENTURINI, E. K. BEAUCHAMP and W. F. HAMMETTER, "Emergent Process Methods for High Technology Ceramics", edited by R. F. Davis, H. Palmour III and R. L. Porter (Plenum Press, New York, 1984) p. 719.

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