

Thermoanalytical Measurements of Shocked Alumina Powder

Chong-Hee, Kim

KAIS

(Received Aug. 11, 1977)

폭발 충격을 받은 Alumina 분말의 열분석

김 중 희

한국과학원 재료공학과

(1977년 8월 11일 접수)

초 록

급격하게 충격을 받은 Linde A alumina 분말에 대해서 동적시차열량 제법 (dynamic differential calorimetry)으로 잔류응력 energy를 측정 조사하고 투과전자현미경으로 결함구조를 조사하였다.

충격을 받지않은 alumina 분말과 비교해 보면 충격을 받은 분말을 대개 800°C 내지 1200°C 범위에서 energy 방출을 보여 주었으며, 충격을 받은 데다수의 α -alumina 결정들은 변형으로 인한 결함구조를 보여 주었다.

INTRODUCTION

Abnormally high fracture surface energies commonly measured for alumina ceramics and the existence of residual strain energy as evidenced by X-ray microbeam study in shocked alumina powder¹ have suggested that plastic processes involving generation and movement of dislocations are associated with fracture and impact damage events in α -Al₂O₃. Other investigators^{2,3,4} have described many evidences of plastic work in alumina ceramics and have associated the observed defect structures with fracture behavior. The present work is aimed at substantiating such findings by means of thermoanalytical measurements of thermally activated releases of shock-induced internal strain energy by dynamic differential calorimetry.

Residual strain energy (existing in the form of dislocations and/or other structural defects) may be considered as non-thermodynamic excess energy, i. e. the excess is only metastable and should not exist under conditions of true thermodynamic equilibrium. Such strains can,

in fact, be reduced or removed by thermal (annealing) treatment.

The energy released during annealing can be detected experimentally by various thermoanalytical methods. The basic method is known as differential thermal analysis (DTA), in which sensitive differential thermocouples are employed to measure slight temperature differences between the sample material and an appropriate (and usually inert) reference material while both are being heated (or cooled at a uniform rate within a uniform (usually massive) thermal environment. Apparatus for dynamic differential calorimetry (DDC) is based upon a rather different specimen holder geometry featuring a less massive thermal environment. It facilitate quantitative estimates of the total energy involved in the causative process (proportional to the integrated area under the peak for a given energy release or absorption).

MATERIALS AND PROCEDURE

Explosively shocked alumina particulates* were obtained for thermoanalytical and electron microscopic exam-

ination, together with a control specimen of the original usiginal unshocked alumina (Linde A)**.

Dynamic Differential Calorimetry (DDC) was employed to detect and measure the energy stored as annealable defects in explosively shocked alumina. A differential analysis apparatus*** was modified for these measurements by the addition of an appropriate sample holder and differential thermocouple****. The modification of the DTA method has been described by David⁵ and by Campbell⁶. The ring-type differential thermocouple employed allows the detection of differential signals as small as 0.05 microvolts. Approximately 150 mg of shocked alumina powder were encapsulated in platinum foil by means of a Encapsulator****. The encapsulated sample was placed on one of the two ring thermocouples and an equivalent weight of similarly encapsulated reference material was on the other. Both were heated to 1,200 °C at a rate of 10 °C/min in Ar gas atmosphere.

For transmission electron microscopy, the particulates were deposited on carbon support film from an ultrasonically agitated suspension in acetone. A JEOLCO JEM-120 transmission electron microscope operating at 120 kv was employed for the observation of defect structures

RESULTS AND DISCUSSION

The control material contained two phases, (Fig. 1). The dominant α -Al₂O₃ final product has irregular, rounded, often protuberant shapes, while the intermediate, metastable γ -Al₂O₃ minor phase is extremely fine grained

and flocky*.

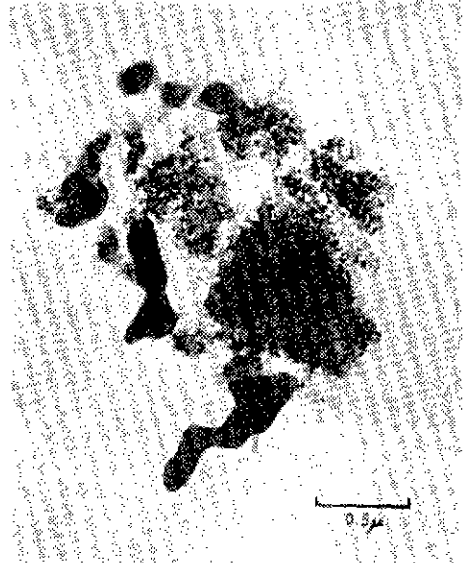


Fig. 1

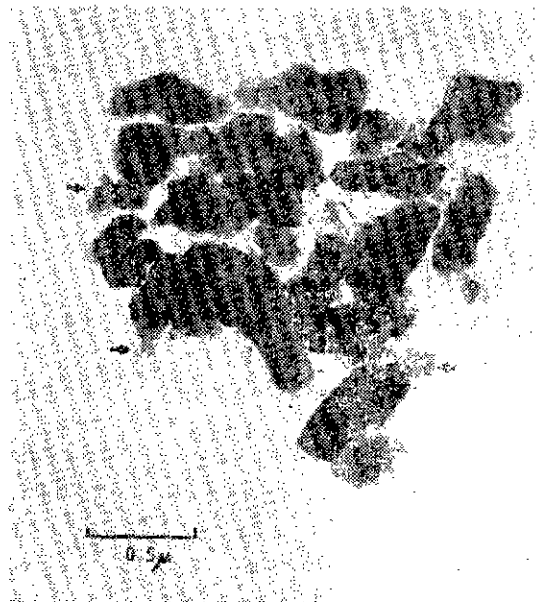


Fig. 2

After explosive shocking at particle velocities in the 300-1,000 in/sec range,⁷ the material was found to be significantly altered, (Fig. 2). The γ -Al₂O₃ particles

*These independently obtained findings are in good agreement with the manufacturer's published descriptions of this material.

*Specimen provided by Dr. Oswald R. Bergmann, Eastern Laboratory, Explosives Department, E. I. du Pont de Nemours & Company, Inc., Gibbstown, New Jersey.

**Alumina Powder, Linde A grade, a product of Linde Division, Union Carbide Corp., East Chicago, Indiana.

***Model DTA-12A Differential Thermal Analysis Apparatus, a product of Robert L. Stone Company (now a Division of Tracor, Inc.) Austin, Texas.

****Type SH-11BB2-PDZ Sample Holder with Pt-Pt 10 % Rh ring-type differential thermocouple. Each ring of the thermocouple supports a very small platinum vessel containing specimen or reference, respectively.

*****Sample Dish Former and Encapsulator, a product of Tracor, Inc., Austin, Texas

were deflocculated and dispersed, and some of the α - Al_2O_3 particles had been fractured in neck regions. In direct transmission,* many of the α - Al_2O_3 grains showed evidences of defect structure resulting from deformation including dislocation contrast effects and/or regions of twinning.

Characterization of Excess Energy by Dynamic Differential Calorimetry

Figure 3 is a plot of dynamic differential calorimetry traces over the range $700^\circ\text{--}1,200^\circ\text{C}$ for an unshocked alumina control specimen (compared with sapphire) and for three different experiments with shocked alumina (compared with three different reference specimens: (1) sapphire, (2) unshocked control material, and (3) triply annealed shocked alumina).

The sapphire reference is considered to have no latent heat effects over the $20^\circ\text{--}1,200^\circ\text{C}$ heating range, but both the unshocked control and the triply annealed material are likely to undergo phase transformations and/or sintering within this temperature span, and cannot be considered to be truly inert.

In these plots, the solid curves represent the measured differential EMF's obtained as small pressed pellets of sample and reference materials (closely matched in weight, 150mg) were being heated—for the first time—at a rate of $\sim 10^\circ\text{C}/\text{min}$ in shallow platinum vessels in the special ring-type differential thermocouple. The lower edge of the shaded region beneath each curve for shocked alumina represents the trace of the base line. The baseline is temperature dependent, and was determined by repeating the heating cycle a second time without disturbing the specimen holder. Baseline curves have been adjusted vertically—slightly—to provide a normalizing coincidence with the upper curve; normalizing has been based upon establishing an arbitrary zero difference in EMF between test and baseline runs at a small inflection point (characteristic of all runs with this specimen holder) just below 800°C .

The area of the shaded region is amenable to direct

*These sounded grains are too opaque and variable in thickness for very effective dislocation studies by transmission microscopy. To obtain acceptable contrast and depth of focus, these plates were exposed at relatively low magnifications, then enlarged photographically.

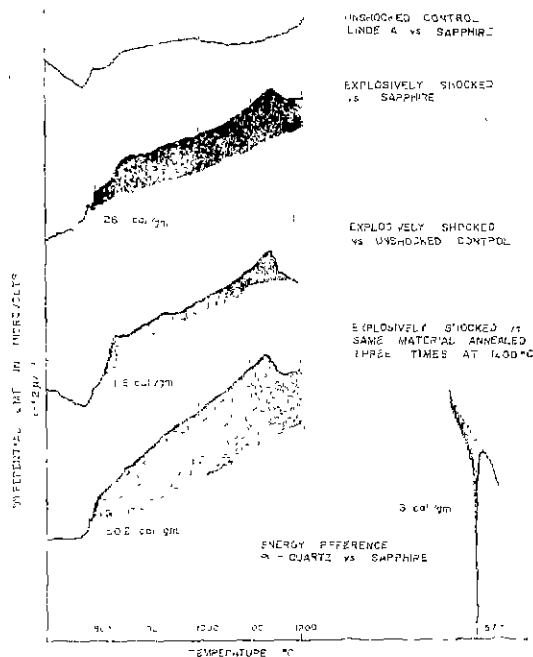


Fig. 3

measurement by planimeter methods, and may be considered to be proportional to the total exothermic release of energy during the first heating to $1,200^\circ\text{C}$. To provide a (tentative) reference standard for scaling the energy quantities involved, a plot of the endothermic α -to- β quartz inversion peak has been included. The energy required for this transformation has been variously reported as 2-4cal/g.⁸ For the purposes of this report, the value arbitrarily has been considered to be 3 cal/g.

Plots for shocked alumina—regardless of the reference material selected—consistently indicate a broad exotherm over most of the range above 800°C , with two or more characteristic peaks, of which the one at $\sim 1130^\circ\text{C}$ is the most prominent. These peaks do not occur in the control specimen, nor do they recur during second heating runs for shocked material. It seems clear that these exotherms represent—in part—significant releases of energy associated with the annealing of shock-induced strains in α - Al_2O_3 . However, they are not unambiguous, because other reactions, also exothermic, are considered

to be highly likely within this temperature range. They include (a) annealing of strains in the γ -Al₂O₃ second phase (b) transformations of γ -to α -Al₂O₃ and (c) sintering [resulting in a reduction of total surface energy] of α -Al₂O₃. Unambiguous characterization of specific energy profiles associated with annealable excess energy per se will require deformed monophase particulate material free of the confounding effects noted here. These effects, particularly the sintering, are considered to account for significant fractions of the substantial energy differences denoted by the shaded areas.

These results demonstrate the effectiveness of the DDC method and electron microscopic techniques in sensing stored energy effects in shock-modified alumina particulates. The estimated quantities of energy released, even in the most conservative case (shocked vs unshocked), are very substantial (-14.6 cal/g). These results are considered to be in excellent qualitative, though not necessarily quantitative, agreement with the earlier findings of Bergman and Barrington⁷ and Heckel and Youngblood¹ about enhanced sinterability attributable to strain effects in shocked alumina. They also appear to substantiate the role of contributions to sintering kinetics attributable to annealable excess energy (denoted by the "little q" term in a temperature dependent factor, $e^{-\frac{(Q-q)}{RT}}$) contained in a model for densification proposed elsewhere.⁹

LIST OF REFERENCES

1. R. W. Heckel and J. L. Youngblood, "X-ray line broadening study of explosively shocked MgO and α -Al₂O₃ powders", *J. Amer. Ceram. Soc.* **51** (7) 398-401 (1968).
2. J. Congleton and M. J. Petch, "Dislocation movement in the brittle fracture of alumina", *Acta Met.* **14** (10) : 1179-1182 (1966).
3. J. Congleton, N. J. Petch and S. A. Shields, "The brittle fracture of alumina below 1000 °C", *Phil.*

Mag. **19**: 795-809 (1969).

4. B. J. Hockey, "Observation of plastic deformation in alumina due to mechanical abrasion", *Am. Ceram. Soc. Bull.* **49** (4): 498(1970).
5. D. J. David, "Introduction to theory and application of DTA and considerations of Stone Instrumentation features", Laboratory Equipment Digest, April, June, 1968.
6. W. B. Campbell; pp. 121-131 in kinetics of Reactions in Ionic Systems, Edited by T. J. Gray and V. D. Frechette, Materials Science Research, Vol. 4, Plenum Press, New York, 1969.
7. D. R. Bergmann and J. Barrington, "Effect of explosive shock waves on ceramic powders", *J. Amer. Ceram. Soc.* **49** (9) 502-507(1966)
8. W. J. Smothers and Y. Chaing, "Handbook of Differential Thermal Analysis, Chemical publishing Co., Inc., New York, 1966.
9. H. Palmour III, R. A. Bradley, and D. R. Johnson; pp. 392-407 in kinetics of Reactions in Ionic Systems, Edited by T. J. Gray and V. D. Frechette, Materials Science Research, Vol. 4. plenum Press, New York, 1969.

LIST OF FIGURES

1. Linde A alumina powder as received. This is the unshocked control material. Compare with explosively shocked Linde A in Fig. 2.
2. Explosively shocked Linde A alumina powder. Large γ -Al₂O₃ flocks have been broken and dispersed. Some neck-growth regions in α -Al₂O₃ grains (indicated by arrows) have been broken. Asterisks locate contrast effects considered to be sites of shock-induced imperfections in several different α -Al₂O₃ grains.
3. Dynamic differential calorimetry of explosively shocked Linde A alumina powder. These curves, and their tentative interpretations, are described in text.