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Kinetics of property change associated with atmospheric humidity changes in alumina powder granules with PVA binder

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Abstract

A microcompression testing machine was used on single Al_2O_3 powder granules to study their stress–strain behavior as a function of relative humidity. The test granules were prepared by spray-drying slurries containing 3 mass% poly(vinyl alcohol) and Al_2O_3 powder. The stress–strain curves and granule strength were determined at regular time intervals, after step changes in atmospheric humidity. When stress was applied, deformation increased rapidly with the stress. This stress corresponded to the fracture strength of the granule. In a dry atmosphere, the granules deformed linearly with increasing stress, and a rapid change in strain was noted above a certain critical value of increased stress. In a wet atmosphere, the granules deformed continuously at lower stress. The mechanical properties of the granules changed rapidly with time when the atmospheric relative humidity was changed. Within 3 min of exposure to a new atmosphere, the mechanical properties of the granules reached equilibrium values. The change in properties with humidity was controlled by moisture diffusion in the granules and was reversible. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Al_2O_3; Granules; Humidity; Powders; Powders-mechanical properties

1. Introduction

Moisture strongly affects the properties of ceramics made by the powder-compaction process.[1–3] A simple explanation of this effect is that moisture governs the mechanical properties of the binder and, thus, of the granules, controlling the compaction behavior and the resultant structures of the green bodies, as well as of the sintered bodies.[4–9] A dry atmosphere makes the granules hard and elastic and tends to cause large flaws in both the green compacts and the sintered ceramics. A wet atmosphere softens the granules and contributes to the formation of uniform structures in both the green and sintered bodies.

In all past studies, experiments were performed under equilibrium conditions: the moisture contents of the samples were equilibrated for a long period of time before measurements were taken, to ensure a constant moisture content in the granules. However, these conditions may not be met in the commercial production of

ceramics, or even in the research laboratory. Atmospheric humidity varies continuously with time and, thus, so does the equilibrium moisture content.[10,11] The compaction behavior of the granules changes with time after the granules have been exposed to an atmosphere with a humidity different from that in which they were originally equilibrated. In addition, a permanent change in properties may occur in the granules during the wet period, as was noted for a powder compact. Past study shows that compacts become significantly stronger after a process of wetting and subsequent drying.[1,2] Control of the compaction process requires an understanding of the kinetics of property change associated with changes in atmospheric humidity.

Stress–strain measurements for individual granules[12–15] can be applied conveniently to evaluating the effects of various processing factors on granule characteristics—for instance, the effects of humidity and of time on the deformation behavior of the granules. Commercial equipment is available for determining this relationship under a constant rate of deformation. However, traditional evaluation, which involves die compaction, is not convenient for the present purpose, although

it is well suited to examining compaction behavior under equilibrium conditions, as has been done in many past studies. Under dynamic conditions, the results deduced by traditional evaluation are strongly affected by contact conditions between the sample and the atmosphere, such as the mass of the granules, the geometry of the die, and the method by which the granules are charged into the die.

The present paper reports on changes in the stress–strain behavior after humidity changes for individual Al_2O_3 granules containing various amounts of poly(vinyl alcohol; PVA). The characteristics of the powder and of the granules are examined first, because those characteristics significantly affect the results and require documentation. A new characterization tool, called the immersion liquid microscopy,[16–18] also is applied in the present study, to examine the binder distribution and the internal structure of the granules. The deformation characteristics of the granules also are reported. The kinetics of change for the stress–strain behavior are discussed quantitatively, in terms of moisture diffusion in the granules.

2. Experimental procedure

The starting materials used in the present experiments were industrial-grade commercial Al_2O_3 (Al160SG-1, Showa Denko Co., Ltd., Tokyo, Japan) and poly vinyl alcohol (PVA205, Kurare Corp., Tokyo, Japan) as a binder. According to the supplier, the average particle size of the Al_2O_3 powder was 0.6 μm. The degree of polymerization and the degree of hydrolysis of the binder were 500 and 88%, respectively. The starting materials were mixed with distilled water (solids:water = 1:1) in a ball mill for 16 h to prepare slurries with binder contents of 3 mass%. No dispersant was used in this slurry.

A spray dryer (Model No. SD-13, Mitsui Kozan, Tokyo, Japan) was used to prepare granules at inlet and outlet air temperatures of 200 and 100 °C, respectively. The granules were equilibrated with the moisture in the atmosphere by placing them on a flat sheet for at least 3 h, after which they were stored in an airtight container. The relative humidity (RH) of the atmosphere was controlled to within a few percent of specified values. Commercial microcompression equipment (Model No. MCTE-500, Shimadzu Corp., Kyoto, Japan) was used to examine the compaction behavior of individual granules. The cap of the airtight container was opened, and the granules were placed on the sliding stage of the equipment. One granule with a diameter of ~50 μm then was selected under a microscope for examination. After its diameter had been measured in two directions, the granule was moved to a loading device by sliding the stage slowly. The stress–strain curve was obtained at a loading rate of 90 mN/s at 25 °C. The tensile strength of the granule, S_t, was determined using the equation proposed by Hiramatsu et al.,[19]

$$S_t = 2.8P_f/\pi D^2 \tag{1}$$

where P_f is the applied load at fracture and D the average diameter of the granule. The values obtained with Eq. (1) are rough measures of strength, because the equation is valid only for the elastic deformation of a small strain.

Optical microscopy was used to observe the compaction process. Scanning electron microscopy (SEM; Model No. JSM-5310L, JEOL, Tokyo, Japan) was used to examine the morphology and structure of the granules. The liquid-immersion technique also was applied to examine the internal structure of the granules. For that examination, the granules were immersed in methylene iodide to make them transparent, and their internal structure was observed by optical microscopy in the transmission mode (Model No. OPTIPHOT, Nikon, Inc., Tokyo, Japan).

3. Results

Fig. 1 shows an SEM micrograph of the powder particles in the present study. The particle size, distribution, and slightly elongated shape are typical for this type of industrial-grade low-soda Al_2O_3.

Fig. 2 shows an SEM micrograph of the granules used in the study. All of the granules appear to have spherical shapes. The granule sizes are distributed within a wide range, with a mean size of ~50 μm. The surface of the granules appears to be smooth. Similar micrographs were taken for all of the granules used in this study, and they all showed excellent flowing characteristics; the tap densities of the granules were 1.0–1.1 g/cm³.

Fig. 3 shows a liquid-immersion photomicrograph of the granules. Essentially, all of the granules are spherical. Their internal structure is very uniform and solid.
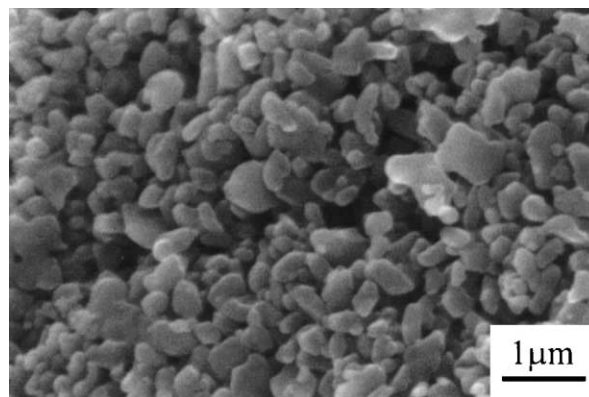

Fig. 1. SEM micrograph of aluimina particle.

No pores are found in most of the granules. The rim of the granules appears darker than the other regions; this dark layer at the circumferential region of the granules corresponds to the segregated binder. The binder scatters light more readily than does Al_2O_3, because of large mismatching of the refractive index. The dark region disappeared in the present study after the samples were heated at high temperature for binder removal. Similar structures were noted for all of the granules.

Fig. 4 shows typical stress–strain behavior of granules in humid (25 °C, 80% RH) and dry (25 °C, 40% RH) atmospheres. In the dry atmosphere, the granules deformed almost linearly with applied stress, up to a strain of ~7%, and then deformed rapidly thereafter. This behavior corresponds to brittle fracture. The stress required for initiating the rapid deformation, 2.1 MPa, corresponds to the fracture strength of the granule. The granules deformed more easily in the humid atmosphere, showing plastic deformation. The strain increased gradually, but slowly, with increasing stress, up to a larger strain. At a stress of >1 MPa, the strain increased rapidly. This increased stress is tentatively assigned to the fracture strength of the granule, because no abrupt change was noted in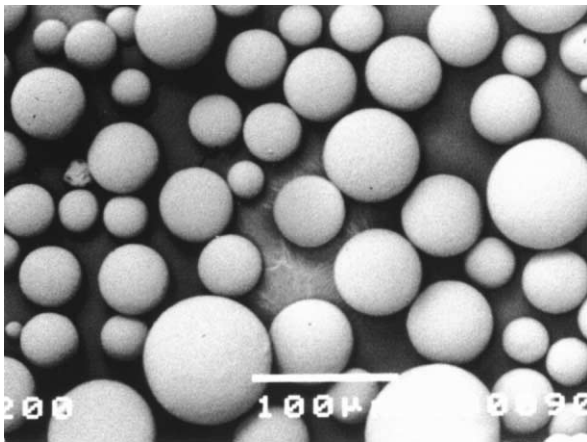 the stress–strain curve. In situ optical microscopic observation showed that the granules developed cracks in the dry atmosphere just before the rapid deformation. No cracks were noted in the humid atmosphere; the granules just deformed continuously with increasing load. Unfortunately, no clear micrograph was taken, because of very poor optical conditions in the stressing device.

Figs. 5 and 6 show long-term and short-term changes, respectively, in the fracture strength of the granules after exposure to an atmosphere with a different humidity from that in which the granules were initially equilibrated. In Fig. 5, each datum point represents the

Fig. 2. SEM micrograph of granules (PVA 3wt.%).
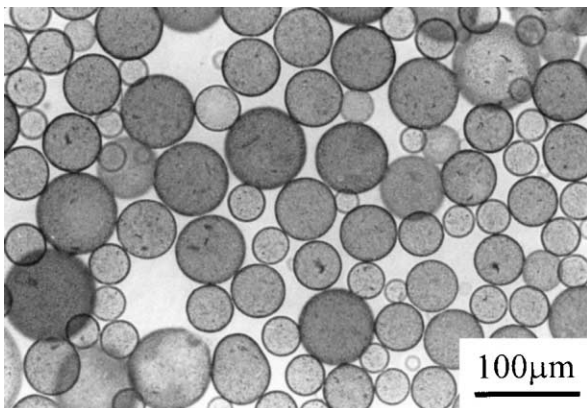
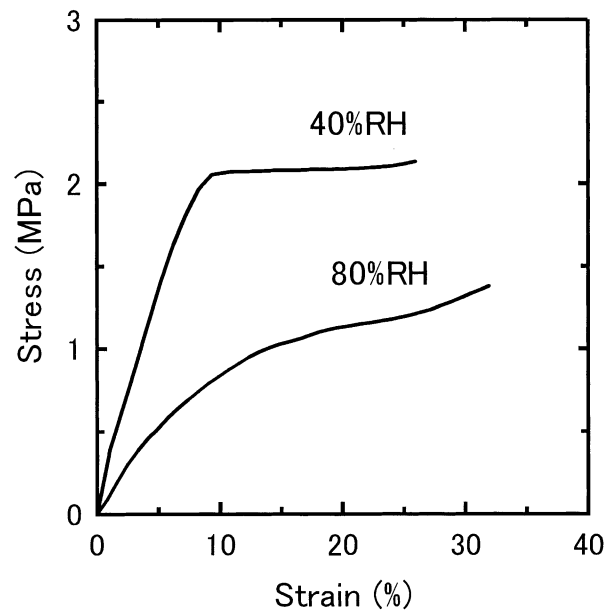Fig. 3. Liquid immersion photograph of granules (PVA 3wt.%).

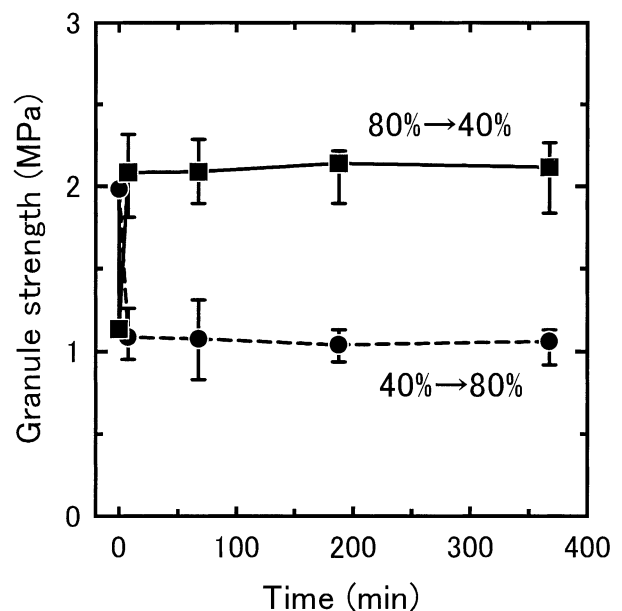Fig. 4. Stress–strain behaviors of granules (25 °C).

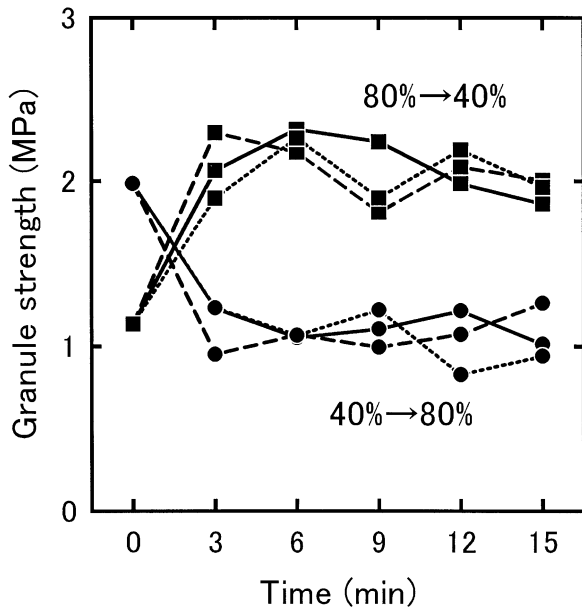Fig. 5. Long term change of fracture strength of granules (25 °C).

Fig. 6. Short term change of fracture strength of granules (25 °C).

strength measurements taken on 5–10 granules. The strength varied slightly, but the mean strength values reached equilibrium within ~15 min after the granules were exposed to a new atmosphere, under all conditions. The equilibrium values were determined solely by the temperature and the humidity, rather than by the history of the granules. Virgin properties were recovered even after the granules had undergone extensive changes in temperature and humidity.

In Fig. 6, each datum point corresponds to a single strength measurement. Three independent runs of the experiment agreed in showing that granule strength reached equilibrium values within 3 min after the granules were exposed to a new atmosphere. In Fig. 6, the time intervals for the data are sparse, because it took at least 3 min to make one measurement. Repeated trials failed to shorten the time required for the first measurement.

4. Discussion

Atmospheric exposure caused a very rapid property change in the granules. For granules with a typical size of 50 μm, the property change was complete within 3 min at 25 °C after exposure of the samples to a new atmosphere.

Under equilibrium conditions, the present results were consistent with those reported for die compaction, and the humidity governed the stress–strain behavior.[1–4,9] The granules deformed gradually with increasing stress in the humid atmosphere, and their fracture strength was low. In the dry atmosphere, the strain increased linearly with increasing stress, and the samples failed in

a brittle manner. This phenomenon clearly resulted from the marked effect of moisture on the glass transition temperature of PVA.[5–8] The glass transition temperature of PVA is near room temperature under the experimental conditions of the present study, and elastic–plastic behavior depends markedly on the specific moisture content.

When the humidity in the atmosphere was varied, the stress–strain behavior of the Al_2O_3 granules changed very rapidly. The change was complete within 3 min, under all conditions examined, and was reversible in both directions. Granule strength returned quickly to its virgin value when the temperature and humidity were returned to their original values. This very rapid change of strength after the granules were exposed to a new atmosphere has interesting implications. If diffusion controls the average moisture content in the granules and, thus, their strength, it should be possible to estimate the saturation time using a simple relation for moisture diffusion into a granule,

$$t = x^2/D \tag{2}$$

where x is the radius of the granule.

In a separate paper, we estimated the apparent moisture diffusion coefficient, D, in a compact, an analogue of a granule, from the weight-change experiment, after step changes in RH.[20] The diffusion coefficient was on the order of 10^{-5} cm^2/s in a spherical Al_2O_3 compact containing 3 mass% PVA at 30 °C and 50% RH. These values gave a saturation time of <1 s for a granule with a 50 μm diameter, a result consistent with that of the present study and much shorter than needed to complete the first strength measurement. The strength of the granules attained equilibrium in 3 min.

The assumption that the average moisture content governs granule strength may require discussion, because the binder is enriched in the surface region of the granule as seen in Fig. 3. The mechanical properties of this surface region should play an important role in the deformation behavior of the granules. In dry condition, the surface binder region forms a hard shell. On the other hand, the surface region become soft when binder absorbs moisture in wet condition because of a lowering of the glass transition temperature of the binder. If so, the kinetics of property change would be even more rapid, because the moisture would not have to diffuse into the granules. Eq. (2) gives the upper the limit of time needed for the completion of deformation behavior under a diffusion-controlled kinetic. A similar surface segregation of the PVA binder was commonly found on the granule surface in our study, and its origin is ascribed to the flow of water containing PVA during the spray-drying process.[21–23]

The diffusion-controlled kinetics also should be discussed here. Other mechanisms may be operative in

such a small system as these granules. In past studies, diffusion was found to govern the kinetics for changes of moisture content in a powder compact with a diameter >1 cm. In a smaller body, the rate of moisture absorption at the surface may limit the kinetics. No information is available for the kinetics of absorption, and that problem remains for future study.

The reversibility of granule strength after an extensive thermal and humidity history has not been guaranteed a priori and is in marked contrast to results for a powder compact containing PVA as a binder.[1,2] In the powder compact, the strength increased significantly when the powder was made wet and then dried after compaction. This difference can be explained by the formation of new bridges between granules and the recovery of broken binder bridges in the compact. Bonding between granules strongly affects compacts strength. Under dry conditions, the granules cannot adhere, even under an applied pressure of compaction. Only after the compact has been subsequently made wet the binder is able to soften and adhere. This new bonding then contributes to the strengthening of the compact after the humidity has returned to the original value. Additional structural change also may occur within the granules. The granules are significantly deformed, and some of the binder bridge may be broken during compaction, especially under dry conditions. A subsequent increase in moisture content softens the binder and contributes to the recovery of broken bridges. Neither of these phenomena is expected to occur in free granules. The binder remains a fairly firm solid and does not flow extensively, even at maximum humidity, under the present experimental conditions.

The present results do not necessarily suggest that compaction behavior during die pressing can be controlled by the humidity of the surrounding atmosphere under all circumstances, especially in industry, where a large mass of granules is used. When the mass of granules poured into a die cavity is large, most of the granules may fail to make good contact with the atmosphere. A thick layer of granules covers the granules deep within the die cavity, behaving as a barrier for moisture diffusion. In addition, moisture may not be supplied rapidly enough, even when the granules are well exposed to the atmosphere. The change in moisture content is on the order of 0.5 mass%. The total amount of moisture needed for equilibration is 0.5 g for 100 g of granules. To supply that amount of moisture, the volume of humid air (80% RH) would have to be >0.02 m^3, a volume much higher than that in the dead space of a normal compacting machine.

5. Conclusions

The relationship between relative humidity and the characteristics of single granules was studied with a microcompression testing machine. The test granules were prepared by spray-drying slurries containing 3 mass% PVA and Al_2O_3 powder. The stress–strain curve and granule strength were measured, and the following results were obtained.

1. The surface of the granules without organic additives was rough. The surface of granules containing PVA binders was covered uniformly with primary particles. The binder was distributed nonuniformly in the granules.
2. Granules showed a nonlinear increase in strain with increasing stress, under all conditions. A decrease in the initial slope of the curve was noted as RH increased, showing that the granules had been softened by moisture.
3. The mechanical properties of the granules reached an equilibrated value rapidly and reversibly with the changing relative humidity of the atmosphere. Moisture diffusion controlled this property change, which was complete within 3 min after exposure of the granules to a new atmosphere.

Acknowledgements

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