balanced against the necessity of multiple staging to obtain greater total transfer than one equilibrium stage in concurrent flow.

The assumption of an equilibrium composition at the interface is apparently not justifiable for a phase which approaches the equilibrium composition closely, while the rate of transfer into the other phase is still high.

ACKNOWLEDGMENT

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NOTATION

c = concentration, lb. mole/cu. ft.
c^* = equilibrium concentration, lb. mole/cu. ft.
k = local individual-phase coefficient for mass transfer based on packed volume, $(hr.)^{-1}$
$\bar{k}$ = mean individual-phase coefficient for mass transfer based on packed volume, $(hr.)^{-1}$
L = flow rate of continuous (water-rich) phase, lb. mole/(hr.)(sq. ft. of column cross section)
V = flow rate of dispersed (isobutanol-rich) phase, lb. mole/(hr.)(sq. ft. of column cross section)
x = mole fraction of component in continuous (water-rich) phase
y = mole fraction of component in dispersed (isobutanol-rich) phase
Z = packed distance from inlet, ft.

Subscripts

A = isobutanol
L = continuous (water-rich) phase
o = at inlet to packing
V = dispersed (isobutanol-rich) phase
W = water
α = any component

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Slow Compression Crushing of Single Particles of Glass

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Glass cylinders and spheres were crushed by slow compression in a hydraulic press. In all experiments the elastic energy stored in the specimen prior to fracture was measured. In some experiments the surface area of the resultant powder was measured by gas adsorption; in others the heat generation upon fracture was measured. The latter experiments show that considerable additional energy is fed into the fracturing specimen from the press. Local stress concentrations, and hence energy level at fracture, varied widely with particle shape. Calorimetric experiments suggest that real differences in crushing effectiveness, that is new surface per unit actual work done on the specimen, do occur. These differences are not due directly to the magnitude of the energy fed in from the press but rather to the effectiveness with which the stored or feed-in energy is used.

Single particles of glass spheres or cylinders, lying either on their flat or round side, were slowly compressed between the flat jaws of a hydraulic press until crushing occurred. Slow compression is defined here to be any form of compressive loading of a specimen at rates sufficiently slow to permit a static rather than dynamic analysis of the forces applied. The elastic energy stored in the specimen prior to fracture was calculated, and the surface area of the resultant powder was determined by gas adsorption, or the heat generation in the sample was calorimetrically determined (*1*).

Axelson's (*2*, *3*) slow compression crushing experiments on quartz prisms showed that when a specimen happened to fail at low elastic energy concentration the surface area produced per unit stored elastic energy was as much as 17.6 times higher than when the specimen failed at high elastic energy concentration. Thus it appears that it might be possible to obtain more surface area production from a given effort if crushing could somehow be induced at low-energy levels.

Particle shape and orientation were varied in the present work in order to attain a wide range in the stored elastic energy of the specimen at fracture.

GLASS SPECIMENS

Glass is isotropic, very nearly elastic to the point of fracture (*7*), has well-known properties, and furthermore flaws or strains can be observed either by ordinary or polarized light. Also the surface area of even small samples of glass can be measured by gas adsorption. Pyrex glass fabricated into small cylinders and spheres was used. Two sizes of cylinders and one size of spheres were used. The large glass cylinders were 0.5 in. high by 0.5 in. in diameter, and the small glass cylin-

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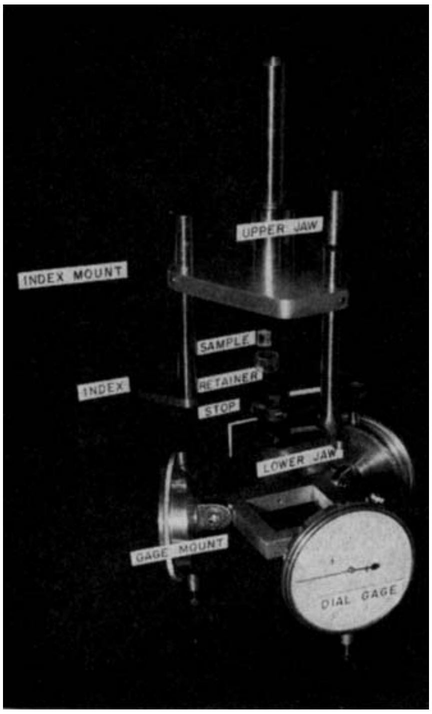

Fig. 1. Press detail.

ders were 0.355 in. high by 0.365 in. in diameter; the spheres were 0.5 in. in diameter. The spheres and the flat faces of the cyinders had finely ground surfaces, and the round surfaces of the cylinders were fire polished.

All the glass specimens were annealed by heating to above 560°C. for at least 3 hr. and cooled at less than 33°C./min. The annealed specimens showed no strains when examined under polarized light.

GAS ADSORPTION

The gas-adsorption apparatus was designed to measure surface areas of 30 to 10,000 sq. cm. by the method of Brunauer, Emmett, and Teller (*4*), and was similar to that used by Johnson (*6*), Axelson (*2*), and Heney (*5*), with the exception that modifications were made to allow area determinations on four separate samples simultaneously. Ethane gas was adsorbed at −183°C., the temperature of liquid oxygen. The precision of the method is usually about ±10%.

DESCRIPTION OF PRESS

The press was constructed of two 12 in. x 12 in. x 1 in. steel plates fastened about 16 in. apart by three 1-in. diameter steel rods and equipped with a 10 ton hydraulic jack. In four experiments a 120,000 lb. capacity testing machine was used. The jaws were of tool steel hardened to maximum hardness and finally ground smooth.

The pressure gages, 0 to 6,000 and 0 to 20,000 lb./sq. in., were calibrated in place with a proving ring.

Three dial gauges were fixed to the lower jaw by a mounting bracket and the indices fastened to the upper jaw by another bracket as shown in Figure 1.

Since the dial gauges measured the total displacement between the points of attachment to the press, it was necessary to calibrate for the deformation of the included press parts. Hardened steel cylinders of various lengths and diameters were compressed on their flat faces in the press and the deflection and load recorded. The deflection of the press parts was determined as a function of load and specimen diameter by subtracting the calculated displacements of the cylinders from the measured displacements. When spheres or cylinders on the round were crushed the press, deformations were calculated from elastic theory. The use of the average of the readings of three-dial gauges was shown to effectively eliminate error even when the specimens were placed eccentrically on the jaws.

A short section of flexible plastic tubing slightly taller than the specimen itself was placed around the specimen to act as a sample retainer (Figure 1). This retainer formed a good seal against the jaws as the load was applied and effectively prevented loss of the crushed material. An appropriate C-shaped steel stop, equipped with a handle to allow rapid removal of the sample, surrounded the sample and retainer and served to restrict the travel of the jaws to less than 0.044 in. upon crushing.

GENERAL CRUSHING PROCEDURE

The glass specimen was placed inside the sample retainer and steel stop, a load of about 100 lb. was applied to seat the sample, and the dial gauges were set to read zero. Simultaneous readings were made of the dial and pressure gauges as the pressure was applied. Usually 2 to 5 min. elapsed from the start of loading until fracture occurred.

CALCULATION OF ELASTIC ENERGY STORED IN THE SPECIMEN

A typical load-displacement plot is shown in Figure 2. The area under the line represents the total elastic energy stored in the specimen and press components between the gauge and index mountings. The stored elastic energy in the specimen alone (E_s) was obtained by subtracting the energy in the press parts (almost 0.3 of E_s) from the total energy measured. Whenever sudden partial failure of the specimen occurred, it was assumed that the displacement was at constant load. The total possible error due to this assumption and to errors in the jaw deformation and gauge caibrations are believed to be less than ±5% of the stored elastic energy in the specimen (E_s).

In four experiments the specimens were crushed without the use of dial

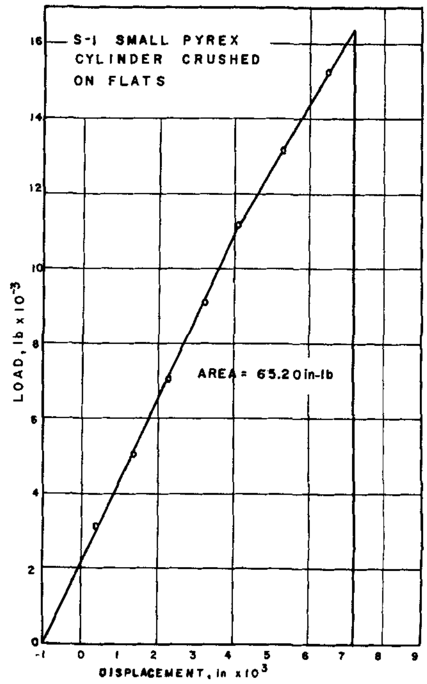

Fig. 2. Typical load plot.

gauges. In this case the stored elastic energy to the specimen (E_s) was computed from the load and the elastic properties of the specimen and is expected to be within ±15% of the true value of E_s.

SPECIMEN SHAPE AND ORIENTATION

In order to control the energy level at which crushing occurred the stress distribution in the specimen was altered by changing the geometry of the glass specimen to include two sizes of cylinders and one size of spheres and also by changing the nature of the specimen-jaw contact, for example by compressing the cylinders on their flat faces or on their rounded surface. Loading glass cylinders on their flat faces yielded a comparatively uniform stress distribution in the specimen and allowed high average levels of elastic strain energy to be attained before crushing occurred. Crushing spheres and cylinders on the round, on the other hand, provided experiments wherein high stress concentrations were attained in the regions of contact of the glass with the steel jaws. In the cases of spheres and cylinders crushed on the round, fracture was thus forced to occur at relatively low values of stored elastic energy; hence experimental work with these should help to clarify the possible relationships of energy concentration, local stresses, and crushing efficiency.

In this series of experiments five sets of slow compression crushing experiments were performed: large (0.500- by 0.500-in. diameter) cylinders crushed on their flat faces

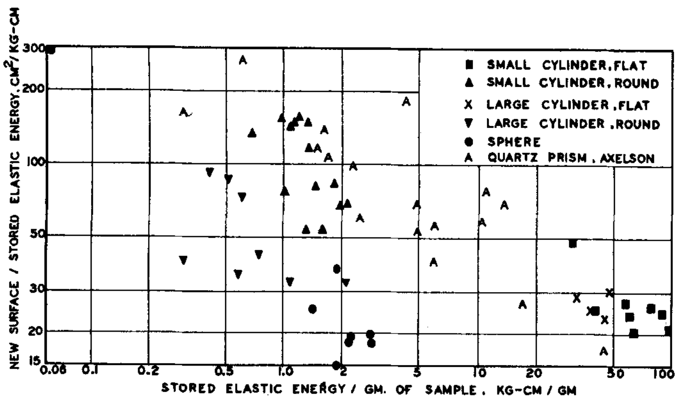

Fig. 3. Slow compression of Pyrex glass loaded for uniform or high local stress distribution.

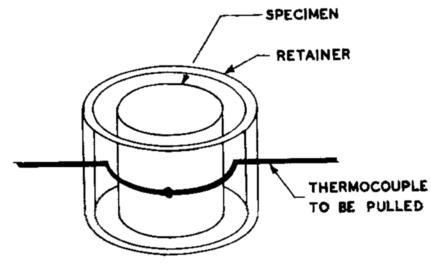

Fig. 4. Thermocouple assembly.

(this set is referred to as LCF), large cylinders on the round surface (LCR), small (0.355- by 0.365-in. diameter) cylinders crushed on flat faces (SCF), small cylinders crushed on the round (SCR), and 0.500-in. diameter spheres (S). All experiments except the LCF set were performed in the press assembly described in the crushing apparatus section and shown in Figure 1. The LCF experiments required a force beyond the maximum available with the press described, and for these experiments the Baldwin machine was used.

CRUSHING RESULTS

A change in the specimen shape and its orientation on the jaws effectively caused crushing to occur over a wide range of elastic energy levels, from 0.062 kg.-cm./g. for a sphere (S) to 96.8 kg.-cm./g. for a small cylinder crushed on the flat faces (SCF). Both the large and small cylinders loaded on the flats (LCF and SCF, respectively) invariably crushed at high energy levels to fine powders.

Crushing experiments carried out at low energy levels (LCR, SCR, and S) yielded products ranging from several large fragments to powder. The large fragments were always from portions of the specimen outside the region having the highest strain energy content prior to fracture, that is outside the regions of jaw contact. The large fracture surfaces of these fragments were initially oriented parallel to the applied load. Because a crack cannot transect an existing crack the fracture surfaces of these large particles must have formed before any other cracks had invaded the region. Specimens loaded on the flats almost to the point of disintegration also show this preliminary splitting. Thus the vertical splitting of the sample can be considered the first event leading to complete specimen breakdown in slow compression crushing and might well be an important factor contributing to the feed-in of energy to the specimen from the press structure after fracture initiation. This is expected because vertical splitting allows energy to be consumed in forming new surface without causing the specimen to disengage from the press jaws, as randomly directed cracks would.

While the experimental data obtained fall in groups according to the type of loading and specimen, the experimental points are highly scattered (Figure 3). However general trends can be readily noted. New surface per unit stored elastic energy (A/E_s) is plotted as ordinate and is a measure of the effectiveness of the crushing operation. The average energy concentration at fracture [stored elastic energy per weight of specimen, E_s/w] is plotted as the abscissa.*

It is at once apparent that a wide range of A/E_s was obtained, even at given average energy concentration. Values of A/E_s for Pyrex glass varied from 15 sq. cm./kg.-cm. to 295 sq. cm./kg.-cm., a 19 to 1 change in the crushing effectiveness. The standard deviations of the data are several times greater than would be expected from the experimental errors of surface area measurement (A) and stored elastic energy (E_s).

Even when shape and orientation effects are neglected, a statistical rank correlation of all the data of Figure 3 shows that there is a 90% probability that crushing at low energy levels (E_s/w) yields more new surface per unit stored elastic energy (A/E_s) than crushing at high energy levels. The trend and location of data of Axelson, also shown on Figure 3, are in general agreement with the present data.

For cylinders on the round (SCR or LCR) rank correlation at the 95% level indicates that a larger value of A/E_s is obtained when the cylinders happen to break at low rather than high energy levels. No similar trends are statistically significant for the crushing of cylinders on the flats or spheres.

From Figure 3 the data for the various sets of experiments are seen to lie in different regions of the plot. Both the small and large cylinders crushed on the round, with an average value A/E_s of 102 ± 24 sq. cm./kg.-cm. and 57 ± 18 sq. cm./kg.-cm. respectively, show a high crushing effectiveness.* The small and large cylinders crushed on flats both show low crushing effectiveness, with values of average A/E_s of 27 ± 7 sq. cm./kg.-cm. and 27 ± 5 sq. cm./kg.-cm. respectively. With one exception the effectiveness of the crushing of spheres (average A/E_s of 22 ± 6 sq. cm./kg.-cm.) was also low.

The variations in new surface per unit stored elastic energy may be related to the differences in shape and orientation of the specimens, or to the possible feed-in of energy to the specimen from the press after the fracture initiates. The elastic energy of the press, especially the jaws, and their possible effects on the crushing process will be considered in some detail.

POSSIBILITY OF ENERGY FEED-IN

If the glass fractured extremely rapidly so that it almost immediately disengaged from the jaws, the total energy available for crushing would be the stored elastic energy. Poncelet (8) estimates that a slow compression crushing process is completed within 20 μsec. from its initiation. Disengagement may occur because the inertia of the jaw material prevents sufficient acceleration to maintain contact. If however the specimen failed sufficiently slowly or in a step-by-step manner so as to allow the jaw surfaces to follow the specimen and continue to exert a force on it, additional energy will be fed into the failing specimen. This energy feed-in is given by $E_f = W - E_s$, W = work done on specimen,

* Tabular material has been deposited as document 6623 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $1.25 for photoprints or for 35-mm. microfilm.

* Throughout the text the quantities following the plus or minus signs denote the 95% confidence limits of the associated data.

E_s = stored elastic energy, and E_f = feed-in energy. A combination of calculations based on elastic theory and experimental measurements of force and press deformation showed that the total energy stored in the press and specimen prior to fracture ranged from about 4 times (for the S set) to 30 times (for the SCF set) the stored elastic energy. Thus much energy is available for possible feed-in. In order to establish the importance of energy feed-in from the press during a crushing process a calorimetric technique was devised to measure the total energy content of the fractured specimen.

HEAT GENERATION UPON CRUSHING

An estimate of the heat generation for small cylinders crushed on flats was obtained by the use of a thermocouple placed around the sample (Figure 4). Immediately after crushing occurred, the thermocouple leads were manually pulled taut to center the junction in the loosely packed powder. The temperature rise was recorded after being suitably preamplified. The heat generation was calculated simply by multiplying the temperature rise by the sample heat capacity. The true maximum temperature of the specimen will always tend to be higher than the recorded temperature because of heat losses to surroundings and imperfect thermal contact between thermocouple and powder. The heat generation (Q_m) obtained by this procedure ranged from 94 to 168% of the stored elastic energy E_s with an average value of 121%. Temperature rises of from 7.0° to 13.7°C. were measured upon crushing of the specimen.

Supporting experiments were performed on small cylinders on the flats and on the rounds in which the specimen was dumped into a small liquid-filled calorimeter as quickly as possible after crushing. Both blank experiments and theoretical calculations were used, with good agreement, to determine that about 52% of the initial heat of the sample was lost in the transfer operation. The over-all error for individual experiments is estimated to be less than ±25% for SCF and ±50% for SCR. The calorimeter experiments for SCF yielded estimates of heat generation (Q) from 96 to 205% of the stored elastic energy (E_s) with an average value for 100 Q/E_s of 143 ± 20.4%. For corresponding calorimeter experiments on SCR the range of 100 Q/E_s was 44 to 380% with an average value of 156 ± 48.8%.

The results of both the pulled thermocouple and the calorimeter experiments show that the heat generated upon crushing was often greater than 100% of the stored elastic energy (E_s) and demonstrate that energy feed-in from the press is important and cannot be neglected.

The calorimeter experiments also indicate that the energy feed-in varies widely from one experiment to another within a group. This follows since the observed differences in percent heat generation (100 Q/E_s) are larger than the estimated experimental errors.

On the average several times as much new surface is produced for a given production of heat by crushing small cylinders on rounds as is obtained by crushing small cylinders on the flats. This suggests that the efficiency of SCR experiments is greater than that of SCF experiments if one considers that new surface represents useful energy consumption and the heat production represents wasted energy. This is shown by a comparison of Equations (2) and (3).

The average values of A/E_s used in Equations (2) and (3) are obtained from the data of Figure 3, which contains the results of experiments in which area and stored elastic energy (E_s) were measured. The average values of Q/E_s used in Equations (2) and (3) are obtained from the results of experiments in which heat generation Q and stored elastic energy (E_s) were measured.

For small cylinders crushed on the round:

$$\frac{(A/E_s)\text{ avg, SCR}}{(100Q/E_s)\text{ avg, SCR}} = \frac{102.4 \pm 24.0}{156 \pm 48.8} = 0.66 \pm 0.26 \quad (2)$$

and for small cylinders crushed on the flat sides:

$$\frac{(A/E_s)\text{ avg, SCF}}{(100Q/E_s)\text{ avg, SCF}} = \frac{27.1 \pm 7.2}{143 \pm 20.4} = 0.19 \pm 0.06 \quad (3)$$

The approximately three to one ratio of the terms of Equations (2) to (3) indicated that the enhanced efficiency of SCR experiments does not appear to be due to relatively more energy feed-in but rather to the more effective use of the feed-in to produce surface.

The ratio of surface production to heat generation is a convenient measure of crushing effectiveness, since knowledge of the actual work input to the specimen or the surface energy of the material is not required for its evaluation.

SUMMARY AND CONCLUSIONS

Calorimetric measurements show that considerable heat is generated in the specimen in single particle crushing. The quantity of heat generated is often greater than the stored elastic energy in the specimen. Thus the strain energy in the press is fed into the fracturing specimen after the crushing process initiates. The observed initial splitting of the specimen parallel to the applied load may be an important contributing factor in the mechanism of energy feed-in, since the splitting allows energy consumption without causing the specimen to disengage from the press. An analysis of the press assembly and specimen as a system of springs shows that the total energy available for crushing can be many times the elastic energy stored in the specimen immediately prior to fracture.

The average energy concentration in the specimen at fracture by slow compression has been effectively varied by altering the distribution of stresses in the particle through the use of specimens of various shapes and orientations. Specimens crushed at low average energy level, corresponding to a high stress concentration, tended to yield more new surface per unit stored elastic energy input (prior to fracture) than specimens crushed at high average energy level, corresponding to evenly distributed stresses. Calorimetric experiments suggest that real differences in crushing effectiveness, that is new surface per unit actual work done on the specimen, do occur. Furthermore these differences in efficiency are not directly due to the magnitude of the energy feed-in from the press but rather to the effectiveness with which the stored or feed-in energy is used.

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