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SPONTANEOUS FRAGMENTATION OF AN ALPHA-ACTIVE CERAMIC --

A MECHANISM FOR DISPERSION OF SOLID WASTE?*

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INTRODUCTION

$^{238}\text{PuO}_2$ is a short half-life (89 y) alpha-active ceramic often added to simulated solid nuclear waste to induce accelerated irradiation damage. Radiation effects in PuO_2 itself are also of interest, since this ceramic structurally resembles certain forms of nuclear waste. Some fabricated bodies of $^{238}\text{PuO}_2$ have been found to undergo spontaneous fragmentation,^{1,2} resulting in a loss of material to the surrounding area. On the other hand $^{239}\text{PuO}_2$, with a half-life of 2.4×10^4 y, has not been observed to exhibit such behavior. If the mechanism responsible for fragmentation is operative in nuclear waste, the results could be dispersion of finely-divided waste. Even if the phenomenon is restricted to materials with greater rates of alpha decay than are characteristic of nuclear waste, fragmentation may cause misleading results from leach tests of waste forms doped with short half-life actinides. This paper reports on studies under way to characterize spontaneous fragmentation in $^{238}\text{PuO}_2$ and to determine the mechanism(s) responsible.

PROCEDURE AND RESULTS

Two forms of $^{238}\text{PuO}_2$ were available for this study. Fabrication methods for each were similar, involving hot-pressing in a graphite die at 1530°C and subsequent firing in an oxidizing atmosphere at 1440°C to restore full stoichiometry. The average density of each was 86% of theoretical. Nevertheless, the end product differed considerably: Material I was characterized by a

*Work performed under the auspices of the U. S. Department of Energy.

network of large cracks throughout the as-fired body, while Material II was essentially free of such cracks. All samples tested were fragments of larger bodies broken up earlier by impact testing as part of another study. Material I is also characterized by density gradients in the original body; thus random small pieces may differ in density from piece to piece.

All tests were carried out at room temperature; however, sample temperatures were slightly higher due to the considerable self-heat of $^{238}\text{PuO}_2$ (4 W/cm³, for the 80% isotopic purity material studied here). Displacement damage and helium content build up in this ceramic with low-temperature storage after fabrication. In all but one case the history of samples studied here is such that the materials are considered "old", i.e., contain a high concentration of damage and helium. The exception is the material used for the weight change experiment, which was annealed just prior to initiation of the test.

Studies of Material I were carried out in ambient (glove box) air, while Material II was tested in a variety of controlled environments. Results are described in the following sections.

Material I -- Ambient Air

This form of $^{238}\text{PuO}_2$ undergoes spontaneous fragmentation readily during storage, as shown in Fig. 1. Particle sizes shown range from a few mm to the limit of detection with the unaided eye. An aqueous suspension technique and extraction replica electron microscopy were used to determine particle size distribution below 10 μm ; the distribution was heavily weighted toward the finer fragments, with more than 90% being between 1 and 0.1 μm (the limit of detection at the magnifications used). In one instance a 10 μm particle was found to have broken up further during storage (Fig. 2), showing that fragmentation continues even in microscopic particles.

An experiment was carried out to determine roughly the magnitude of the rate of spallation. A collection of 70 small, irregular samples* of typical size 3 mm was annealed in flowing air for 6 h at 1600°C to remove accumulated displacement damage and helium.^{3,4} A day later, periodic weighing of fines released by spontaneous fragmentation was begun. Fines were collected by dry-sieving through a 420 mesh sieve, using slight agitation. Figure 3 shows the cumulative weight of fines collected this way over a period of 266 days. A roughly linear increase of cumulative weight with time was observed, although a slight decrease in slope may have occurred at 20 days.

*Major non-actinide impurities in this material (in wt ppm) were: Ta 500; Mg 300; Si 230; Fe 140; Ca 100; and Ni 55.

Fig. 1. (Left) Fragmentation product resulting from 4 months' storage of 23 chunks of $^{238}\text{PuO}_2$ (2 shown).

Fig. 2. (Right) Spontaneous breakup of a 10-micron fragment observed after several weeks' storage.

Surfaces of other samples from this batch (not annealed) were periodically replicated during the 266-day test to remove any loosely-adherent particles. Fines were extracted continually during this period, confirming that regular release with time does occur.

The possibility was considered that the significant self-heating power of $^{238}\text{PuO}_2$ might induce thermal stresses sufficient to cause spontaneous fragmentation. Finite element computer codes were used to evaluate thermal and stress fields in a cylinder 3 mm dia by 3 mm in height (roughly the size of the samples used in the weight change experiment).⁵ Calculated stresses were low, with worst-case conditions* resulting in a maximum tensile stress of 6.4 MPa and a maximum compressive stress of 3.5 MPa. These stresses alone are not sufficient to cause fragmentation.

Material 11 -- Various Environments

In this study, five similar-sized pieces of Material 11** (160 mg each) were stored in test tubes containing toluene, dry air, wet

*Vacuum environment, steel-on-steel thermal conductance at one end, and thermal conductivity of the ceramic reduced to 10% of its original value as a result of lattice damage.

**Major non-actinide impurities in this material (in wt. ppm) were: Ca 250; Si 230; Fe 200; Mg 150; Na 80; and Ni 65.

Fig. 3. Weight of fine particles ($<34 \mu\text{m}$) released by spontaneous fragmentation as a function of time.

air, distilled water, or brine for 71 days. Toluene is commonly used to achieve a moisture-free environment for static fatigue studies of ceramics and glasses. Dry air was obtained by the use of molecular sieve activated in vacuo at 250°C , while 100% relative humidity air was attained through use of a closed water bath. Salt content of the brine was 40 g per liter of distilled water. The amount of residue from each sample was determined by periodically removing the piece from its test tube to temporary storage area with the same environment, and then measuring the quantity of $^{238}\text{PuO}_2$ remaining in the tube by gamma counting the entire tube.

Results of this study to date are shown in Fig. 4. A strong environment-dependence is observed, with most samples exhibiting an approach to saturation. Relatively high rates of residue generation were observed for $^{238}\text{PuO}_2$ stored in an aqueous environment. This is apparently not due to thermal shock accompanying immersion of the samples, since exposure to toluene resulted in low release rates. As a comparison, if data from Fig. 3 (normalized either for weight or surface area of starting sample) were plotted on Fig. 4, the weight change curve would roughly superimpose on the distilled water curve, reaching a maximum value of 10^{-4} g. Some of the residue collected in the test tubes is visible to the naked eye, with $\sim 70\%$ of the count in the distilled water being attributable to the presence of fragments. Particle size analysis of this residue will be carried out at the conclusion of the test.

Fig. 4. Weight of residue accumulated during storage in various environments.

DISCUSSION

It seems likely, based on the fact that spontaneous fragmentation has been reported only in short half-life $^{238}\text{PuO}_2$, that a high rate of alpha decay is responsible. Given that assumption, the question remains whether the phenomenon results from radiation-induced alterations to the ceramic itself or to its environment. With respect to the former possibility, structural degradation might result from thermal stresses, damage induced lattice strain, or the effects of helium deposition. Calculations indicate that thermal stresses could not alone be responsible for fragmentation of mm sized particles. Further, since such stresses decrease with sample size, they could not account for breakup of the

*Fragmentation studies of $^{239}\text{PuO}_2$ have been initiated to test this hypothesis.

10 μm particle shown in Fig. 2. Thermal stresses may, however, play a major role in fracture of large samples.

Lattice damage in $^{238}\text{PuO}_2$ is produced both by the 5.49 MeV alpha particle and the 93 keV ^{234}U recoil nucleus. The range of the latter can be estimated from calculations by Fleischer⁴ to be 200 $\text{\AA}$, while alpha particle range is expected to be ~ 10 microns. Turcotte and Chikalla³ have shown that lattice dilation builds up rapidly with time at room temperature, reaching 50% of saturation in ~ 3 days and 90% at ~ 10 days. Thus virtually all data reported here were obtained with the ceramic in the near-saturation condition.

Since PuO_2 has a cubic crystal structure, lattice dilation should be isotropic. Thus significant fracture-inducing stresses from this source are expected only near the surface, where damage gradients and therefore strain gradients exist. The thickness of this strained layer would be ~ 10 microns at most. Since many fragmentation particles are larger than this, it may be concluded that damage-induced lattice strain is not directly responsible for the phenomenon in question. However, microcracks induced in this layer could lead to fragmentation of larger particles, if sufficient stresses were present from other sources to propagate the cracks.

Helium deposition does not saturate, but continues at a rate of 0.2 at.%/y. At elevated temperatures gas atoms can migrate to grain boundaries and form bubbles, thus compromising the structural integrity of the ceramic.⁴ However, this is not expected at the low storage temperatures utilized here. In principle, accumulation of atomic helium will induce lattice strains as does displacement damage. In reality, the contribution of helium (and of ^{234}U atoms) is insignificant.⁵

We must also consider the possibility that alpha particle-induced radiolysis of the surrounding medium causes spontaneous fragmentation. By this argument, radiolysis would result in the formation of corrosive (that is, chemically active) products which attack the surface of the ceramic in such a way as to free small particles. The dependence of residue generation rate on environment (Fig. 4) supports this view.* Possible radiolysis products from the environments studied include: H_2 , OH , and H_2O_2 from water, NO_2 from air, and HNO_3 from air-water systems. Several of these products

*In another study of environment-dependence, Fleischer and Raabel,^{7,8} investigated the release of clusters of atoms from PuO_2 powder during storage in simulated lung fluid, water, and vacuum. A strong dependence on the surrounding medium was found, with no release observed in vacuum. It was postulated that recoil nuclei-damaged microvolumes were released by exposure to water, but radiolysis was not considered in this work.

could prove corrosive to PuO_2 . In studies of UO_2 , Wang and Katayama⁹ reported that the addition of H_2O_2 to water significantly increases the rate of attack of this ceramic, and could result in disintegration into fragments. It is noteworthy that neither water nor air is present in significant amounts in toluene, and that exposure to this medium in the present work resulted in the lowest observed accumulation of residue.

Fragmentation during storage may be enhanced by the presence of pre-existing microcracks (e.g., from earlier impact testing), which could propagate under the combined influence of a corrosive environment and internal stresses as in static fatigue. Possible sources of such stresses include thermal or compositional gradients, or strain gradients resulting from radiolysis-enhanced formation of a surface compound such as a hydrous oxide. The observation that Material I generated roughly two orders of magnitude more residue than did Material II under similar conditions (averaging wet air and dry air results for the latter) may correlate with the tendency of Material I to undergo cracking in fabrication. The trends toward saturation in amount of PuO_2 lost from Material II could then be attributed to the presence of microcracks on the surface of an otherwise relatively crack-free material.

SUMMARY

Results reported here show that:

- spontaneous fragmentation of $^{238}\text{PuO}_2$ generates a wide range of particle sizes, from a few nm to 1000 Å or less
- the phenomenon may continue with time or may saturate, depending on starting material
- the magnitude of the effect is dependent on storage environment.

Neither thermal stresses nor lattice damage appear to be solely responsible for fragmentation, but radiolysis of the environment could play an important role. Work is continuing in an effort to identify the controlling factors in this phenomenon.

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