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CONF--821107--9

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TITLE:

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SUBMITTED TO:

Materials Research Society Proceedings, Boston,MA Nov. 1-4, 1982

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Los Alamos, New Mexico 87545

FORM NO 836 R4
ST NO 2329 5/81

EFFECT OF STORAGE TEMPERATURE ON SELF-IRRADIATION DAMAGE OF ^{238}PU-SUBSTITUTED ZIRCONOLITE*

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ABSTRACT

^{238}Pu-substituted cubic zirconolite ($CaPuTi_2O_7$) was stored at ambient temperature, 575 K, and 875 K until alpha decay doses of 2.4 to 3.6 x 10^{25}/m^3 had been accumulated. The ambient temperature material swelled to a saturation value of 5.5 vol%, and the originally crystalline structure was transformed to one with an amorphous matrix and small domains that had retained their crystallinity. At 575 K lesser amounts of swelling (4.1 vol%) and transformation were observed, reflecting concurrent partial recovery. The material held at 875 K remained crystalline, swelled only 0.4 vol%, and exhibited formation of isolated defect clusters.

INTRODUCTION

Zirconolite is a major phase of ceramic nuclear waste forms such as SYNROC [1] and Sandia titanate waste [2]. This phase, which has the nominal composition $CaZrTi_2O_7$ and a monoclinic crystal structure, serves as a host for actinide isotopes which induce self-irradiation damage by alpha decay. Such damage could have deleterious effects on waste stability by inducing swelling (with consequent microcracking of multiphase waste forms), metamictization, and reduction of thermal conductivity [3,4]. It is therefore advisable to evaluate the irradiation response of zirconolite.

Alpha decay of actinides involves emission of an ~5 MeV alpha particle and recoil of the decaying nucleus. The latter particle, of lesser energy (~100 keV) but more massive, is responsible for ~94% of the displacement energy in a typical radiolysis-insensitive [5] waste phase [6]. Self-damage in synthetic zirconolite has been studied at ambient temperature by doping with short half-life ^{238}Pu [3,4] or ^{244}Cm [7], or by Pb-ion implantation [8]; under these conditions damage levels characteristic of 10^6 y of storage time for SYNROC containing 10% high-level waste can be duplicated in the laboratory in times of one year or less. Natural mineral analogues with sufficient U or Th content to have induced significant self-damage have also been investigated [8-10]. Here irradiation times are of order 10^8-10^9 y, and storage temperatures are those dictated by geologic conditions.

It is important to characterize the effect of elevated temperature on the damage response of zirconolite, in an engineering sense because temperature is an important variable in the storage environment and at a more fundamental level to obtain a better understanding of the nature of the damage process itself. In the work reported here, we have evaluated temperature-dependence of self-damage effects in a fully ^{238}Pu-substituted composi-

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

tion ($CaPuTi_2O_7$) with cubic symmetry by measuring swelling, changes in x-ray and electron diffraction parameters, and microstructural alterations. Results are compared with those from other studies of damage in synthetic and natural zirconolite.

EXPERIMENTAL PROCEDURE AND RESULTS

Powders of PuO_2, CaO, and TiO_2 in the molar ratio 1:1:2 were dry ball-milled together for 24 h and cold-pressed into cylinders at 12 MPa using an organic binder. The TiO_2 was in the form of rutile, while the CaO was freshly made by air-firing of $CaCO_3$. Isotopic purity of the plutonium was ~80% $^{238}PuO_2$ (half-life = 88 y), with the remainder being made up of isotopes of longer half-life.

The cylinders were calcined in air at 1275 K for 24 h, then crushed and ball-milled again. The resulting powder was cold-pressed at 59 MPa into cylinders of ~10 mm diameter and height; these were air-fired at 1675 K for 16 h and furnace-cooled. Spectrochemical analysis of the fabricated material identified major cation impurities to be (in wt ppm): 600 Zr, 300 Fe, and 150 each of Ni and Mg. X-ray, microprobe, and metallographic analyses showed that the material consisted of a cubic* matrix phase of nominal composition $CaPuTi_2O_7$ and average grain size ~20 μm, along with 2-3 vol% PuO_2, a lesser amount of an unidentified phase, and ~7 vol% porosity. The as-fabricated structure (Fig. 1) was crack-free except for a few cracks associated with widely-dispersed sintering flaws. Microcracking behavior during storage was similar to that observed in an earlier study [3]; some pre-existing cracks extended, but cracking never became generalized or severe as was the case for multiphase material [4].

Cylinders of Pu-substituted zirconolite were placed in dilatometers the day after fabrication, and changes in length monitored in air at ambient temperature,** 575 K, and 875 K for 270 days. The accumulated dose of 3.6×10^{25} α/m^3 corresponds to ~4×10^5 y of SYNROC storage time for the commercial reactor waste form [10]. Length changes were converted to volume swelling assuming expansion to be isotropic. Bulk swelling results are shown in Fig. 2.

A small quantity of material was crushed and packed into a capillary tube for periodic Debye-Scherrer x-ray examination during room-temperature storage. Measurements were begun 11 days after fabrication, so that the starting value of lattice parameter (0.5066 nm) was obtained by extrapolation to the first day of storage. Other capillaries were placed in 575 K and 875 K furnaces 11 days after fabrication. In this case the starting value of lattice parameter was taken to be that measured after 11 days at ambient temperature (0.5077 nm). Capillaries were removed from the furnaces at ~21-day intervals for 16 h x-ray exposures at room temperature. No attempt was made to take into account these brief periods out of furnace.

X-ray dilational swelling was determined by analysis of (initially) 12 reflections, using procedures described earlier [3]. For samples stored at ambient temperature and 575 K, line intensities weakened as alpha decay doses accumulated until the x-ray amorphous condition was reached at ~1.8 and 2.2×10^{25} α/m^3 respectively. Debye-Scherrer patterns from the 875 K sample showed

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*The fluorite cubic structure is closely related to the monoclinic form [3,11], and is the initial crystalline product obtained by heating amorphous zirconolite [9-11].

**Self-heat of ^{238}Pu resulted in a temperature elevation of ~50 K above room temperature [3].

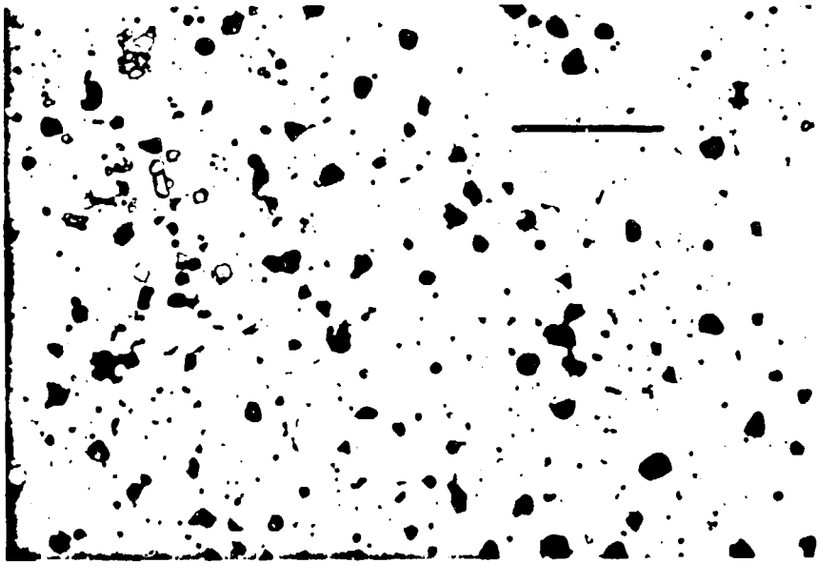

Fig. 1. Photomicrograph of as-sintered ^{238}Pu-substituted zirconolite (lightly etched). Minor phases are PuO_2 (widely dispersed), an unidentified phase (clustered), and porosity (black). Bar = 50 μm.

only slight loss of line intensity during the experiment. X-ray results are shown in Fig. 2, along with those for bulk swelling.

Transmission electron microscopic (TEM) examination of material stored at ambient temperature was carried out at 4, 50, 100, 154, and 182 days. Samples were prepared by extracting thin shards with electron-transparent edges from freshly-fractured surfaces using replication techniques [3]. Examination of the shards, which were supported by carbon substrates, was carried out at 100 kV. After 4 days' storage, the material exhibited a strongly-crystalline electron diffraction pattern and a dense array of damage clusters (Fig. 3). At 50 days the damage clusters were more prominent but the structure remained crystalline. Evaluation at 100 days showed that most diffraction spots had disappeared, and the microstructure consisted of an amorphous matrix with small crystalline domains. Dark-field images taken for two specimen tilts chosen to strongly excite different Bragg diffracted beams revealed that most domains shared a common orientation (Fig. 4). The interface between crystalline and amorphous material could not be well defined; smaller values of deviation parameter s led to a smaller apparent domain size,

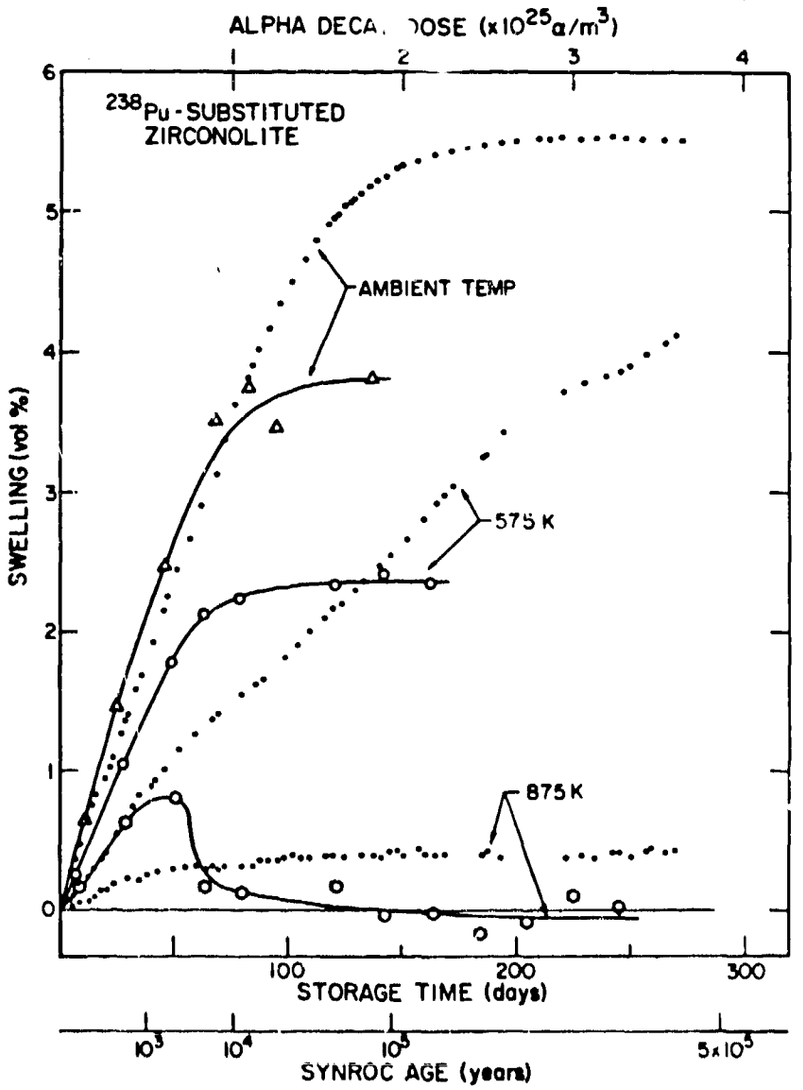

Fig. 2. Bulk swelling (solid symbols) and lattice dilational swelling (open symbols) as a function of storage time and alpha decay dose at three temperatures. Equivalent SYNROC age is also shown.

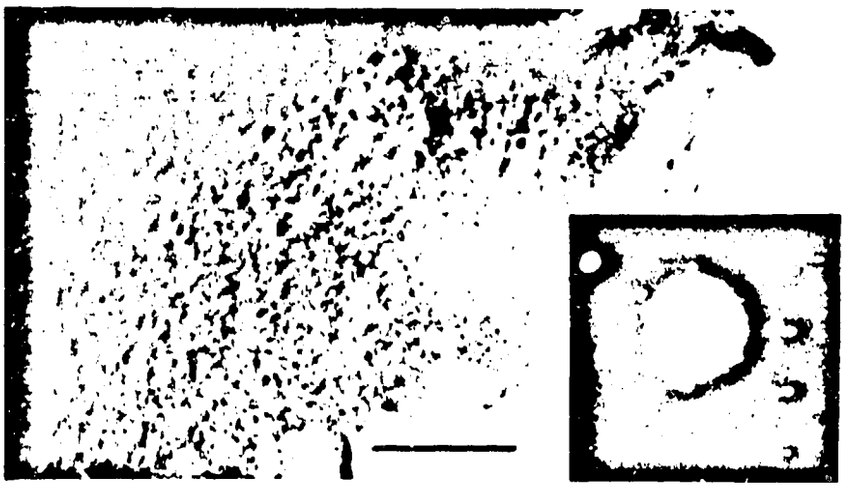

Fig. 3. Bright-field image and corresponding diffraction pattern from Pu-substituted zirconolite after 4 days' storage at ambient temperature. The diffuse rings in the diffraction pattern are from the carbon substrate. Bar = 0.3 μm.

indicating considerable internal strain and perhaps gradient of order. Examination at 154 and 182 days showed continued weakening of Bragg diffracted intensities with increasing dose to the point where meaningful dark field studies were not possible. However, faint diffraction maxima and a heterogeneous microstructure were still observed, indicating that conversion to the fully-amorphous state had not occurred at a dose of 2.4×10^{25} α/m^3.

The x-ray capillary that had been stored at 575 K was cooled to room temperature after 180 days, and the powder particles examined a day later by TEM. The electron diffraction pattern and dark-field imaging showed partial amorphization (Fig. 5), but considerably more crystallinity than was observed after 182 days of ambient-temperature storage. Diffraction patterns were characteristic of single-crystal material rather than of polycrystalline domains such as have been seen after beam-heating the fully-amorphous form [9]. TEM examination of an 875 K sample after 224 days was carried out in a similar manner, and showed a well-ordered crystalline matrix (with single-crystal patterns) containing fine-scale mottled damage.

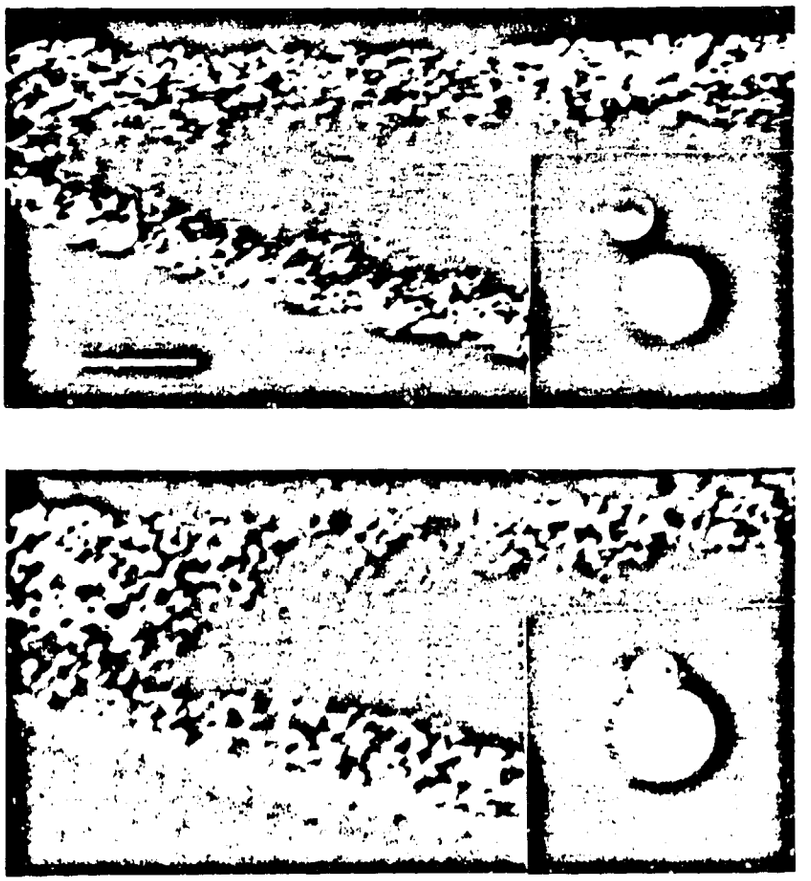

Fig. 4. Dark-field images and corresponding diffraction patterns after 100 days' storage at ambient temperature. Bar = 0.1 μm.

DISCUSSION

X-ray results

X-ray measurements were carried out to determine the dose at which Pu-substituted zirconolite becomes x-ray amorphous, and to compare x-ray dilational swelling with bulk swelling. The x-ray amorphous condition arises from a combination of small size of crystalline particles (apparent size averaging 10-15 nm in both Figs. 4 and 5) and their noncoherenc' resulting

Fig. 5. Dark-field image and corresponding diffraction pattern after 180 days at 575 K. Bar = 0.4 μm.

from the change in density of the transformed material between particles. The doses at which this condition was reached were 1.8×10^{25} α/m^3 at ambient temperature and 2.2×10^{25} α/m^3 at 575 K. Since accompanying swelling values were quite different (5.2 and 2.9 vol%, respectively), it appears that concurrent recovery at the higher temperature reduced the fraction of amorphous material present at the point where the x-ray amorphous state was attained. (Alternatively, the disordered states could have different densities.) Retention of full crystallinity at 875 K shows that a significant concentration of damage-induced amorphous regions cannot be sustained at this temperature.

In the present work as well as in earlier studies of cubic [3] and monoclinic [4] Pu-doped zirconolite, it was found that bulk and x-ray dilational swelling values disagreed. Such a discrepancy has been attributed [12] to the irradiation-induced replacement of Bragg peaks with diffuse peaks whose locations bear no precise relationship to sample volume. It is apparent from the results shown in Fig. 2 that in zirconolite, lattice parameter measurements are an unreliable indicator of macroscopic swelling at all three test temperatures.

TEM observations and the nature of the crystalline-to-amorphous transformation

TEM results show that transformation to the highly-disordered state achieved here proceeded by the following stages:

I) formation of isolated damage zones in a crystalline matrix (Fig. 3)
II) gradual conversion of crystalline regions to an amorphous state until only isolated crystalline domains remain (Fig. 4).

This sequence was also observed by Headley et al. in natural and Pb-ion bombarded zirconolite [8], and it was suggested that amorphization is attributable to gradual consumption of the material by highly-disordered damage tracks. In their work the dose at which tracks began to overlap (i.e., the onset of Stage II) was found to be $\sim 5 \times 10^{24}$ α/m^3 (equivalent), in reasonable

agreement with the observations here. Headley et al. found that the fully-amorphous state was reached at ~5 x 10^{25} α/m^3; the present studies are being continued to allow further comparison at higher doses. The observation that most crystallites share a common orientation (Fig. 4) implies that they represent residual untransformed material rather than a recrystallized product.

The question of whether zirconolite transforms to the metamict state by gradual disordering (leading to an intermediate cubic form if originally monoclinic) or by accumulation of amorphous microvolumes seems for the most part to have been settled in favor of the latter mechanism. This conclusion is supported by results of a separate experiment [4,13] in which x-ray crystallographic changes in monoclinic zirconolite were monitored by the Debye-Scherrer method as alpha decay damage proceeded. It was found that the structure remained noncubic until the x-ray-amorphous condition was reached at ~1 x 10^{25} α/m^3. However, x-ray precession photographs from natural zirconolites by Sinclair and Ringwood [10] showed that near the fully-amorphous condition the remaining crystalline material exhibited a single-crystal fluorite cubic rather than monoclinic pattern. This behavior may be attributed to disordering within each sublattice by alpha particle damage of the crystallites, leading to an average fluorite cubic symmetry, or to recrystallization in single-crystal form during storage over geologic time.

The considerable crystallinity found after storage at 575 K for 180 days indicates either that concurrent recrystallization (formation of new crystallites) occurred or that track annealing restricted the encroachment of amorphous material. Since single-crystal diffraction patterns were obtained, it can be concluded that the latter mechanism prevailed or that any recrystallized particles assumed their original orientation as has been observed in some natural zirconolites [10].

TEM observations of material held at 875 K for 224 days confirm the x-ray data, showing good crystalline order at 3.0 x 10^{25} α/m^3. It is apparent that Pu-substituted zirconolite held at this temperature exhibits behavior characteristic of a metamictization-resistant ceramic, i.e., displacements result in the formation of localized defects or clusters rather than generalized disorder. The amount of swelling observed to result from such defects is not unexpected for this damage level (270 days' storage time is equivalent to ~0.5 displacements per atom [6]); under similar conditions β-SiC has been found to exhibit swelling of ~1 vol% [14]. Saturation of swelling (and therefore of concentration of the defects responsible) was observed in SiC, and saturation also appears to have occurred in the present material.

CONCLUSIONS

Pu-substituted zirconolite exhibits saturation swelling of 5.5 vol% when self-irradiated to 2.4 to 3.6 x 10^{25} alpha decays/m^3 at ambient temperature. The accompanying transformation from a crystalline state to one characterized by an amorphous matrix with remanent crystalline domains is consistent with a model involving accumulation of disordered alpha recoil tracks. The conversion process is inhibited by aging at 575 K; at this temperature amorphization is reduced by concurrent recovery. Storage at 875 K results in only 0.4 vol% swelling resulting from formation of localized disorder in a fully-crystalline structure. These results show that damage effects such as swelling, microcracking of multiphase waste forms, reduction of thermal conductivity, and metamictization-induced increase of leach rate which can result from self-irradiation are strongly dependent on waste storage temperature.

ACKNOWLEDGMENTS

The authors wish to thank J. S. Starzynski, C. C. Land, and M. Gibbs for their valuable assistance in the conduct of this study.

REFERENCES

1. A. E. Ringwood, S. E. Kesson, N. G. Ware, W. O. Hibberson and A. Major, Geochem. J. 13, 141 (1979).

2. R. G. Dosch, A. W. Lynch, T. J. Headley and P. F. Hlava in: Scientific Basis for Nuclear Waste Management Vol. 3, J. G. Moore, ed. (Plenum Press, New York 1981) pp. 123-130.

3. F. W. Clinard, Jr., L. W. Hobbs, C. C. Land, D. E. Peterson, D. L. Rohr and R. B. Roof, J. Nucl. Mater. 105, 248 (1982).

4. F. W. Clinard, Jr., C. C. Land, D. E. Peterson, D. L. Rohr, and R. B. Roof, in: Scientific Basis for Nuclear Waste Management, Vol. 6, S. V. Topp, ed. (North-Holland, New York 1982) pp. 405-412.

5. L. W. Hobbs in: Analytical Microscopy, J. J. Hren, J. I. Goldstein and D. C. Joy, eds. (Plenum, New York 1980) pp. 437-480.

6. K. D. Reeve and J. L. Woolfrey, J. Aust. Ceram. Soc., 16, 10 (1980).

7. W. J. Gray, J. W. Wald, and R. P. Turcotte, "Radiation Damage Studies Related to Nuclear Waste Forms", Report PNL-4145 (1981).

8. T. J. Headley, G. W. Arnold, and C. J. M. Northrup in: Scientific Basis for Nuclear Waste Management Vol. 5, W. Lutze, ed. (North-Holland, New York) in press.

9. R. C. Ewing, R. F. Haaker, T. J. Headley, and P. F. Hlava, op. cit. ref. 4, pp. 249-256.

10. W. Sinclair and A. E. Ringwood, Geochem. J. 15, 229 (1981).

11. Z. V. Pudovkina and Yu. A. Pyatenko, Akad. Nauk SSSR Mineral. Muzei Tr. 17, 124 (1966).

12. C. J. Howard and T. M. Sabine, J. Phys. C: Solid State Phys. 7, 3453 (1974).

13. This work, an interim report of which was given in ref. 4, has been carried to completion (to be published).

14. R. J. Price, J. Nucl Mater. 33, 17 (1969).