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# STRUCTURAL DAMAGE IN A SELF-IRRADIATED ZIRCONOLITE-BASED CERAMIC*

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## ABSTRACT

The zirconolite phase of SYNROC nuclear waste was fabricated with 5 mol% $^{238}PuO_2$ substituted for a like amount of $ZrO_2$, in order to induce self-irradiation damage. The resulting product exhibited a matrix of monoclinic zirconolite containing ~3.8 mol% $PuO_2$ along with roughly 20 vol% of the cubic polymorph with approximately twice the $PuO_2$ content of the matrix. After a dose of $2.1 \times 10^{25}$ $\alpha$ decays/$m^3$ at room temperature (800 days' storage) swelling reached 5.5 vol% and neared saturation. The monoclinic phase became x-ray metamict at $\sim 1.0 \times 10^{25}$ $\alpha/m^3$ after slight atomic rearrangement within the crystalline material. Periodic TEM examination revealed a gradual evolution from the crystalline state to an amorphous condition with residual crystallites, consistent with a model involving conversion by alpha recoil tracks. Optical metallography showed extensive microcracking, attributed to differences in swelling rates of the two zirconolite polymorphs.

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## 1. INTRODUCTION

The individual phases of ceramic nuclear waste forms will be subjected to significant levels of self-irradiation. Most structural damage will result from alpha decay of actinide ions, which yields an alpha particle (helium ion) of energy ~5 MeV and an ~100 keV recoil nucleus. The resulting damage could have deleterious effects on waste stability by inducing swelling, disordering of the initially-crystalline structure, and reduction of thermal conductivity. Swelling is in itself not necessarily deleterious, but anisotropic growth of a non-cubic material or differential swelling in a multiphase waste form could cause microcracking with consequent increase in surface area exposed to leachants.

Zirconolite is a major actinide host phase of the SYNROC [1] and Sandia titanate [2] waste forms. Studies of self-irradiation damage in this material have been conducted by doping with $^{238}PuO_2$ [3-6] or $^{244}Cm$ [7], by Pb ion bombardment [8], and by examination of natural mineral analogues damaged over geologic times by their U and Th content [8-11]. Irradiation damage has also been investigated using neutron bombardment [12]. These studies have shown the damage response to be gradual conversion to a highly-disordered structure accompanied by significant swelling.

Self-irradiation damage in a multiphase waste form can be simulated by fabricating a zirconolite ceramic containing both the monoclinic and cubic polymorphs of this material. The usual form of zirconolite (nominal composition $CaZrTi_2O_7$) has a monoclinic superlattice structure [13]; however, substitution of Pu for Zr can result in partial or complete

conversion to the closely-related fluorite cubic form [3-5].* The cubic polymorph may be thought of as derived from the monoclinic superlattice structure by randomization of the cations and of the one oxygen vacancy per fluorite cubic cell [3]. When both polymorphs are present, Pu atoms are concentrated preferentially in the cubic phase. Such a ceramic can serve as a test material to determine the consequences of differential swelling, since the two phases swell at approximately equal rates per alpha decay event [cf.3-5,7]. In earlier work [4], we fabricated a zirconolite ceramic of composition Ca(0.8 Zr, 0.2 Pu)$Ti_2O_7$ incorporating $^{238}Pu$ (half-life=88 y) to induce self-damage, and followed the damage response up to $6 \times 10^{24}$ alpha decays/$m^3$ (equivalent to $\sim 10^3$y of storage time for SYNROC containing 10 wt% commercial waste calcine [9]). Here we report further damage effects in this material up to $2.1 \times 10^{25}$ $\alpha/m^3$, corresponding to $\sim 10^5$y of SYNROC storage time.

## 2. EXPERIMENTAL PROCEDURE AND RESULTS

Powders of $^{238}PuO_2$, $ZrO_2$, CaO, and $TiO_2$ in the molar proportions 0.2:0.8:1:2 were dry ball-milled together for 24h, then cold-pressed with an organic binder at 125 MPa into cylinders of ~10 mm diameter and height. The $TiO_2$ used was in the form of anatase, and CaO was freshly made by air firing of $CaCO_3$. Isotopic purity of the plutonium was ~80%, with the remainder being made up of isotopes of longer half-life.

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*Kesson and Ringwood [14] carried out studies involving the partial substitution of U for Zr and found that at higher concentrations of U a pyrochlore (cubic superlattice) structure was preferentially stabilized.

Samples were fired for 24 h at 1625 K in flowing air, and furnace cooled. Spectrochemical analysis of the fabricated material showed the major cation impurities present to be (in wt ppm): 2200 Si, 1100 Al, 460 Fe, 410 Cr, and 300 Mg. X-ray, microprobe, and metallographic analyses revealed that the resulting product was characterized by a monoclinic matrix, but contained roughly 20 vol% cubic phase. Also present were ∿7 vol% $TiO_2$ (rutile), a lesser amount of an unidentified plutonium-bearing, low-calcium phase, and ∿9 vol% porosity. Average size of the grains and minor phases was on the order of 10 μm. The as-fabricated structure, which was essentially crack-free, is shown in Fig. 1.

Plutonium was primarily partitioned between the monoclinic and cubic phases, but in unequal proportions. On the basis of four cations per molecule, the Pu content of the monoclinic phase was ∿0.15 instead of the nominal value for the material as a whole of 0.20. This corresponds to a $PuO_2$ content of ∿3.8 mol%, in reasonable agreement with the saturation limit of 4.1 mol% observed by Kesson and Ringwood [14] using $UO_2$ substitution. The Pu content of the cubic phase was approximately twice that of the monoclinic phase.

A cylinder of zirconolite was placed in a dilatometer the day after fabrication and macroscopic dimensional change as a function of time measured for 800 days at room temperature. The accumulated alpha decay dose of $2.1 \times 10^{25} \alpha/m^3$ (average for the two phases) corresponds to $\sim 10^5$y of SYNROC storage age [9]. Readings were converted to volume swelling assuming expansion to be isotropic. Bulk swelling as a function of number of alpha decay events is shown in Fig. 2, along with results for cubic $CaPuTi_2O_7$ [5] and monoclinic $CaZrTi_2O_7$ to which 3 wt% $^{244}Cm$ had been added [7].

A small quantity of material was crushed and packed into a capillary tube for periodic Debye-Scherrer x-ray examination, and data obtained initially for 13-15 reflections between 2θ values of $26^{o}$ and $64^{o}$. Results were analyzed by a least-squares technique. As-fabricated monoclinic unit cell dimensions were: a=1.24321 nm, b=0.72693 nm, c=1.14042 nm, and $\beta=100.53^{o}$. After ~200 days' storage it was found that a hexagonal or rhombohedral representation gave a better fit to the data (i.e., a lower standard deviation) than did a monoclinic configuration. Unit cell dimensions changed slightly as damage progressed, allowing calculation of x-ray swelling as a function of storage time (Fig. 3). Scatter of experimental data was such that only x-ray volumetric changes could be quantitatively presented. However, as was reported earlier [4], all linear dimensions increased with c showing the greatest dilation, while β was unchanged. Similar damage response was observed by Wald and Offermann [7]. After ~500 days' storage, reflections had weakened until the x-ray amorphous (metamict) condition was achieved.

Transmission electron microscopic (TEM) examination of the monoclinic matrix phase was carried out at 7, 490, and 700 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 on carbon substrates, was carried out at 100 keV. Images and diffraction patterns for the three damage levels investigated are shown in Figs. 4, 5, and 6.

A cylinder of zirconolite was sliced lengthwise, mounted and polished, and the surface examined by optical microscopy after 1, 128, 202, 364, 528, and 704 days' storage. Slight microcracking was noted at 128 days, and had become generalized by 202 days [4]. Cracking continued to increase up to

364 days, but from that point little further change was noted. Although opening of cracks was occasionally observed at the higher doses, this effect was not widespread and so we conclude that microcracking did not contribute significantly to bulk swelling. The extent of cracking at 704 days is shown in Fig. 7.

## 3. DISCUSSION

In this section we first discuss the nature of the alpha decay-induced structural damage as determined from TEM and x-ray observations, and then consider the swelling and microcracking that resulted from this damage.

### Transmission Electron Microscopy

The material examined seven days after fabrication had sustained a radiation dose to the matrix phase of only $1.4 \times 10^{23}$ $\alpha$ decays/$m^3$. At this point no significant structural damage was observed by TEM, and the electron diffraction pattern was that for the monoclinic superlattice structure (Fig. 4).

After 490 days' storage the microstructure was characterized by crystallites in a highly-disordered matrix (Fig. 5), similar to that observed in earlier studies of the monoclinic [8-11] and cubic [5] polymorphs. The crystallites were of apparent size ~10-15 nm, although the particular diffraction conditions made actual dimensions difficult to obtain [5]. The weakened diffraction patterns were those for single crystals, indicating that the crystallites comprised untransformed material rather than a recrystallized product.

Headley et al. [8] have proposed that this characteristic damage microstructure results from heterogeneous conversion of the originally crystalline structure to a highly-disordered state by accumulation of alpha recoil tracks. These tracks represent ~94% of the deposited damage energy, with the remainder

resulting from the stopping of the alpha particles themselves [12]. The dose accumulated in 490 days ($1.0 \times 10^{25} \alpha/m^3$) is expected from earlier work [5,8] to result in a mixed crystalline/amorphous structure, as was observed here.

After 700 days ($1.4 \times 10^{25} \alpha/m^3$) TEM showed further weakening of diffraction patterns, but remanent crystallites were still present (Fig. 6). At somewhat higher doses ($3\text{-}4 \times 10^{25} \alpha/m^3$) Ewing and Headley [11] and Sinclair and Ringwood [9] observed that the crystallites exhibited a face-centered cubic fluorite rather than monoclinic structure. This apparent radiation-induced conversion is considered further in the discussion of x-ray results. With respect to the present work, the electron diffraction results obtained after 700 days do not allow us to conclude unambiguously whether a monoclinic-to-cubic transformation had taken place in the remaining crystalline material, but such a possibility cannot be discounted.

X-ray

The observed unit cell dimensions for the matrix phase of as-fabricated material are very close to those reported by Rossell [13] for $CaZrTi_2O_7$ ($a=1.24458$ nm, $b=0.72734$ nm, $c=1.13942$ nm, and $\beta=100.533^\circ$). Thus the effect of substituting 3.8 mol% of $PuO_2$ for $ZrO_2$ appears to have a minimal effect on the lattice structure. A similar observation has been made [15] for the system $CaZr_xTi_{3-x}O_7$, where variations in x from 0.85 to 1.30 cause little change in structure. Such behavior on the part of a nuclear waste host is desirable, since a wide variety of cations from waste calcine must be accommodated.

As shown by TEM examination, self-damage in zirconolite evolves principally by accumulation of alpha recoil tracks. The consequence is not only a

reduction of volume of crystalline material remaining, but also a reduction of particle size and of coherent scattering from the remanent crystallites as the intervening regions become disordered and dilated. These structural changes ultimately lead to attainment of the x-ray amorphous condition, as was observed here after ~500 days ($1.0 \times 10^{25} \alpha/m^3$). It was found that after ~200 days' storage the experimental results could be better accommodated by fitting to a hexagonal (rhombohedral) representation than to a monoclinic configuration (Fig. 3). However, no conversion to the disordered cubic form was observed before the x-ray amorphous condition was reached. Representation of the structure as hexagonal or rhombohedral was suggested by the observation by Pudovkina and Pyatenko [16] that the monoclinic form of zirconolite can be closely approximated by these configurations, which can in turn be derived from a pseudo-cubic structure with $\alpha=92^{\circ}$. The crystallographic change observed here at $\sim 4 \times 10^{24} \alpha/m^3$ may be taken to indicate a slight rearrangement of atoms, possibly in the direction of the cubic polymorph, but not to the extent required for conversion to the cubic form at $3\text{-}4 \times 10^{25} \alpha/m^3$ [9,11].

According to the alpha recoil damage model, the remanent crystallites (which are the source of the sharp diffraction maxima) should be essentially undamaged until converted to the amorphous condition. However, this neglects the contribution of the alpha particles, which deposit ~6% of the damage energy from a decay event. The damage level involved is small: Reeve and Woolfrey [12] have calculated a value per decay event of ~1 displacement/atom (dpa) per $7 \times 10^{25} \alpha/m^3$, so that the total damage to the monoclinic phase at 500 days was ~0.14 dpa and that resulting from the alpha particles only ~0.01 dpa. In order to explain the structural changes in the crystallites

observed here and by others [9, 11], it may be necessary to invoke more effective damage processes such as ionization-assisted displacements (Dell and Goland [17]) or to assume that a significant amount of damage energy is deposited in the crystallites from nearby passage of recoil nuclei.

Fig. 3 shows apparent lattice dilational (x-ray) swelling calculated from changes in unit cell volume with time. Comparison with Fig. 2 reveals a large discrepancy between bulk and x-ray swelling, an observation also made in earlier work on cubic $CaPuTi_2O_7$ [3,5]. A somewhat smaller discrepancy than that seen here was reported by Wald and Offermann [7]. The failure of x-ray swelling measurements to duplicate bulk swelling behavior in materials resistant to metamictization can be attributed to the presence of certain defects or their aggregates (e.g., interstitial dislocation loops accompanied by vacancies or voids) which represent an increase in number of lattice sites, or to the irradiation-induced replacement of Bragg peaks with diffuse peaks whose locations bear no precise relationship to sample volume [18]. For a material such as zirconolite in which microvolumes are transformed to a highly-disordered state with a consequent increase in specific volume, x-ray swelling data from the remaining crystallites should typically differ from swelling results obtained by bulk measurements.

## Swelling and Microcracking

Bulk swelling up to 800 days' storage ($2.1 \times 10^{25}$ $\alpha$ decays/$m^3$) is shown in Fig. 2, along with data for cubic $CaPuTi_2O_7$ [5] and an approximate swelling curve for monoclinic Cm-doped zirconolite [7]. The results for these three materials are in good agreement. If damage proceeds as expected by gradual

conversion of discrete regions to the disordered condition, swelling should be nearly linear until a significant fraction of the material has been transformed; such behavior was seen for the single-phase cubic form. A more gradual curvature would be expected when two phases with different swelling rates are present, and this was observed for the Pu-doped monoclinic zirconolite.

The observed microcracking could in principle be attributable either to differential or anisotropic swelling. However, Wald and Offermann [7] reported no such damage in their study of the monoclinic form, from which we conclude that in the present work differential swelling between the monoclinic matrix and the ∿20 vol% cubic polymorph is responsible. Cracking was first observed at 128 days, at which time unconstrained swelling for these two phases is estimated to be roughly 0.9 vol% (monoclinic) and 1.8 vol% (cubic).* The resulting linear misfit strain of 0.3% is close to the value reported by Matthews [19] to have accompanied internal crack formation in irradiated SiC containing free Si.

Further swelling increased the extent of microcracking up to ∿364 days' storage, but higher irradiation doses did not result in further damage. Such behavior would be expected if the monoclinic and cubic forms reach saturation in swelling at about the same volume change. In that case the linear misfit strain should decrease beyond an intermediate point in the composite swelling curve. By contrast, microcracking in a multiphase nuclear waste form might

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*These values were calculated assuming for each polymorph an initial swelling rate of 3.6 vol%/1 x $10^{25}$ $\alpha/m^3$, as was observed for the cubic form [5].

continue to worsen with time as the volumetric mismatch between phases increases with accumulated dose, unless deformation and stress relaxation occur over the longer irradiation times characteristic of this application.

## 4. CONCLUSIONS

5 mol% $^{238}PuO_2$-doped zirconolite contains both monoclinic and cubic forms of this material, with the former predominating. The cubic phase contains roughly twice the $PuO_2$ content of the monoclinic phase, and so suffers self-irradiation damage at a proportionally higher rate. Both polymorphs undergo conversion to a highly-disordered state with remanent crystallites as a result of accumulation of alpha recoil tracks. Monoclinic crystallites receive sufficient damage prior to amorphization to undergo slight atomic rearrangement.

Disordering of the lattice results in bulk swelling of 5.5 vol% at $2.1 \times 10^{25} \alpha/m^3$, with differential swelling between the monoclinic and cubic phases resulting in extensive microcracking. Such behavior is expected in multiphase ceramic waste forms unless stress relaxation occurs during storage.

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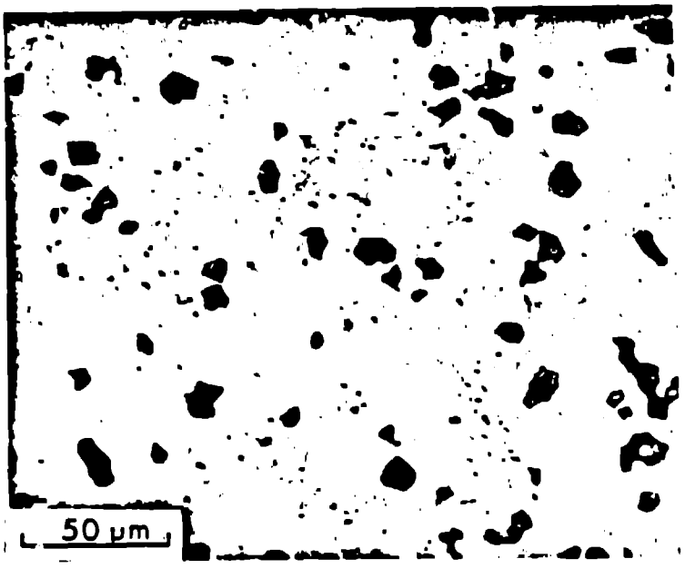



Fig. 1

Optical photomicrograph of as-sintered $^{238}PuO_2$-doped zirconolite (unetched). Prominent minor phases are $TiO_2$ (white) and porosity (black).

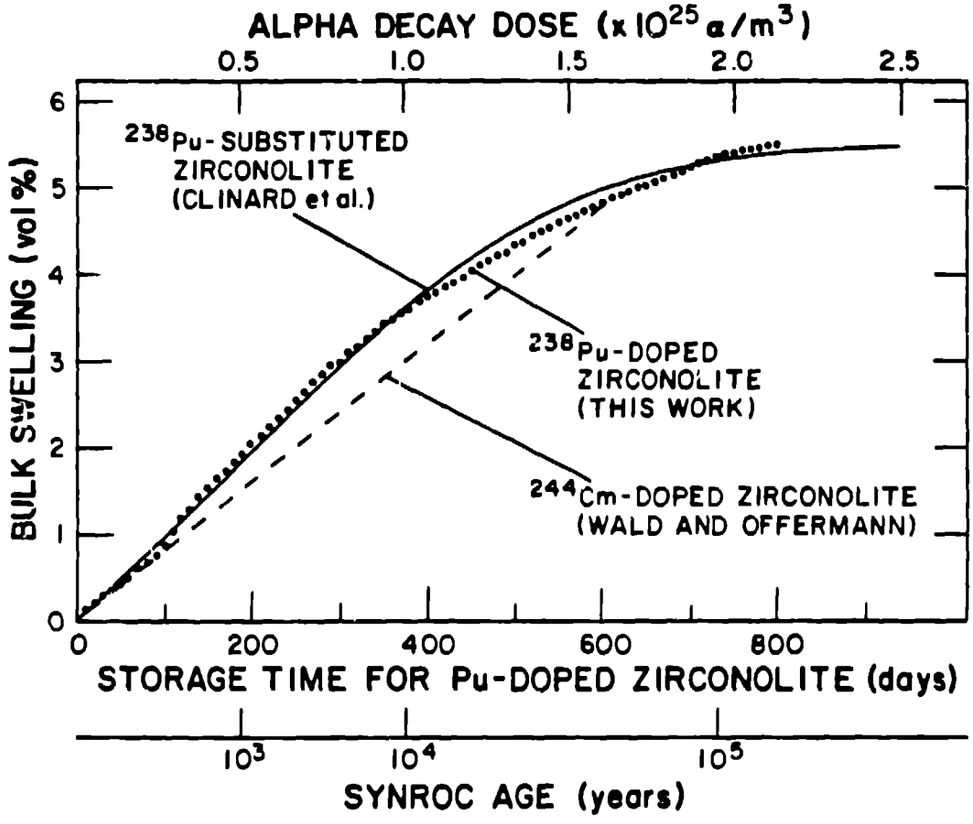



Fig. 2.

Bulk swelling of 5 mol% $^{238}PuO_2$-doped zirconolite (dotted curve) as a function of storage time, average alpha decay dose, and equivalent SYNROC age. Also shown are swelling curves as a function of alpha decay dose for $^{238}Pu$-substituted cubic zirconolite [5] and for $^{244}Cm$-doped monoclinic material [7].

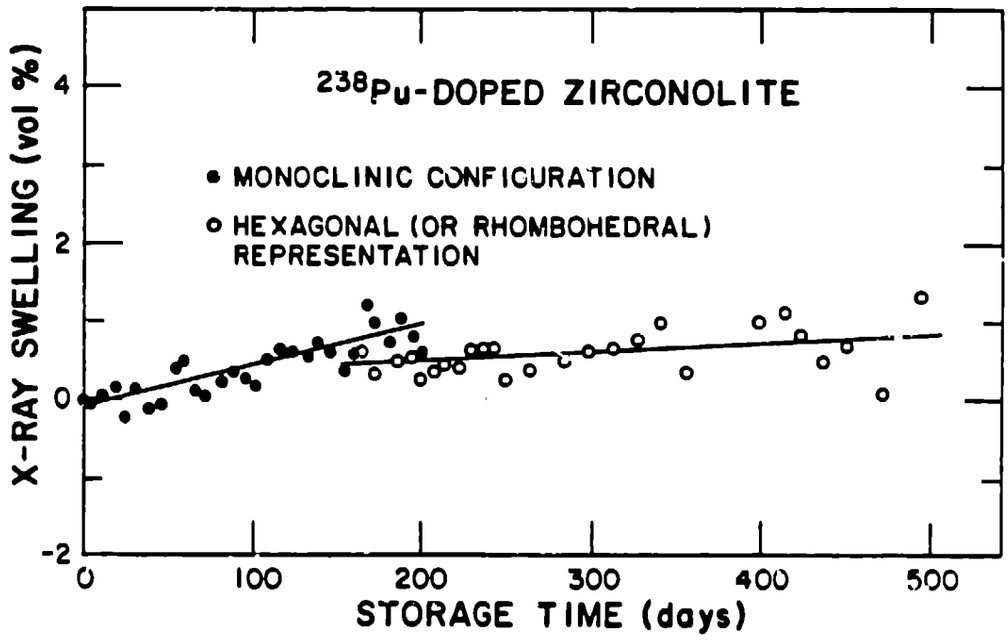
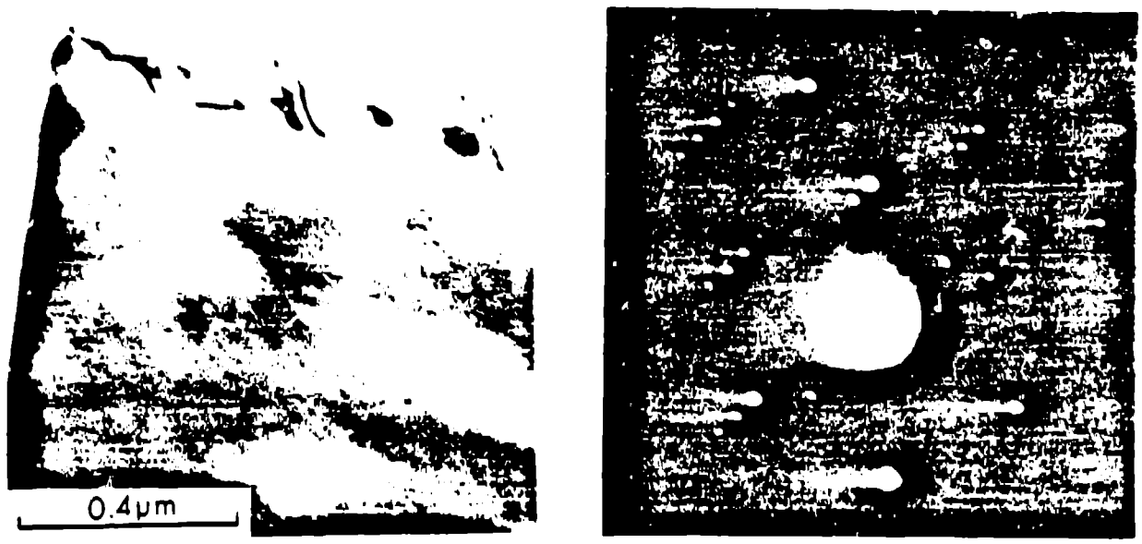



Fig. 3.

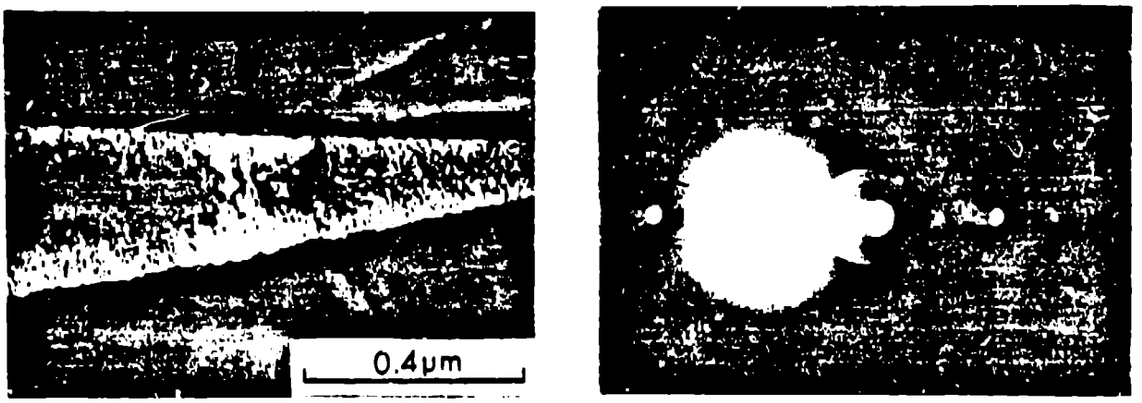
Lattice dilational (x-ray) swelling for the matrix phase as a function of storage time. At a $^{238}PuO_2$ concentration of 3.8 mol%, 500 days' storage is equivalent to an irradiation dose of $1.0 \times 10^{25} \alpha/m^3$.




(a) (b)

Fig. 4.

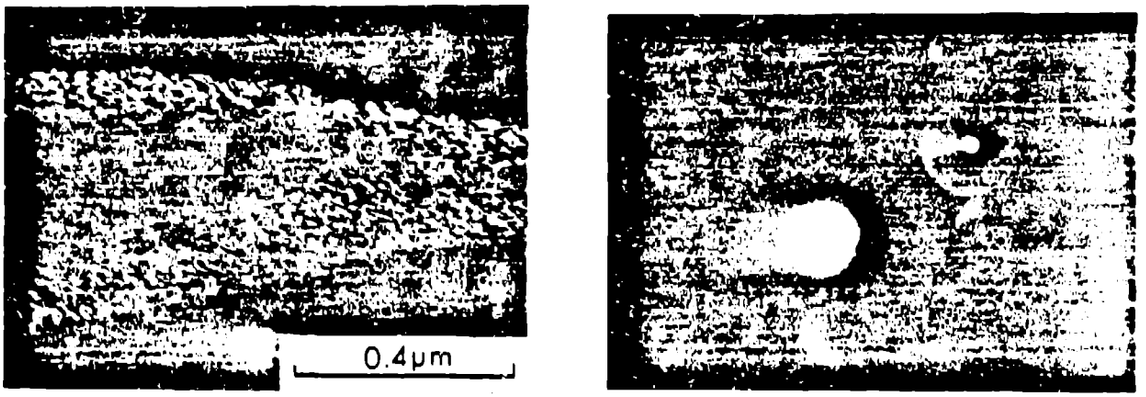
Bright-field image (a) and diffraction pattern (b) from the matrix phase of Pu-doped zirconolite after 7 days' storage.




(a) (b)

Fig. 5.

Dark-field image (a) and corresponding diffraction pattern (b) after 490 days' storage. The diffuse ring is from the carbon substrate.




(a) (b)

Fig. 6.

Dark-field image (a) and corresponding diffraction pattern (b) after 700 days' storage.

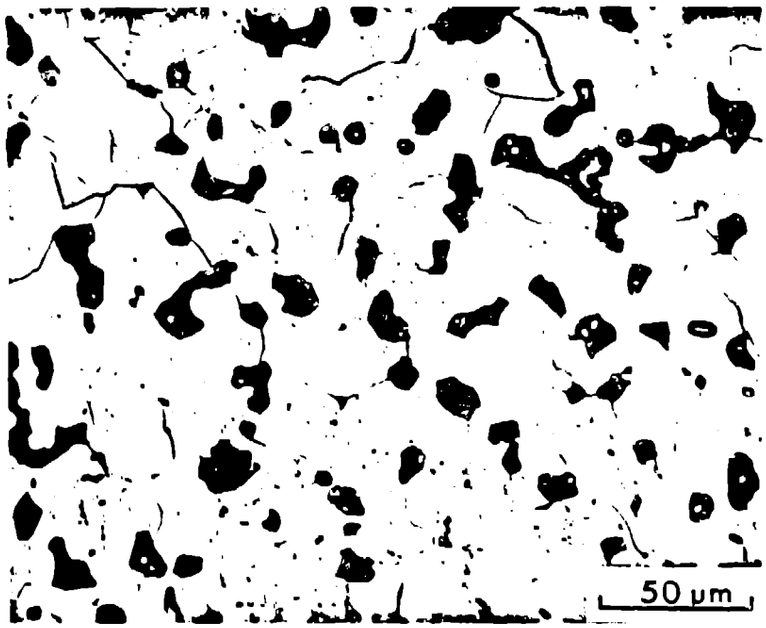



Fig. 7.

Microcracks resulting from 704 days' storage at room temperature.