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IRRADIATION-INDUCED REDUCTION OF MICROCRACKING IN ZIRCONOLITE*

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ABSTRACT

^{238}Pu-substituted zirconolite ($CaPuTi_2O_7$) was stored near ambient temperature for 231 days, equivalent to an alpha decay dose of 3.1×10^{25} α/m^3 or 3×10^5 years of storage time for SYNROC ceramic nuclear waste. Periodic indentation testing showed that hardness was decreased by alpha decay-induced conversion to the metamict state, while fracture toughness and resistance to cracking were increased, apparently as a consequence of the formation of a heterogeneous microstructure. These results imply improved stability of this nuclear waste phase as a result of self-irradiation damage.

INTRODUCTION

The zirconolite phase of the SYNROC [1] ceramic nuclear waste form will be a host for various actinide isotopes. As a result this material, which has the nominal composition $CaZrTi_2O_7$, will suffer self-irradiation damage from alpha decay events during storage. Transmission electron microscopic studies of Pu-doped [2] and Pu-substituted [3] forms of zirconolite have shown that damage proceeds primarily by accumulation of alpha recoil tracks, which gradually convert the structure from crystalline to metamict. As a consequence this ceramic undergoes extensive swelling, up to 5.4 vol % at room temperature [3].

Differential swelling among the component phases of a multiphase waste form such as SYNROC could lead to microcracking, as has been demonstrated in a simulated two-phase material [2]. Microcracking is of concern because the resulting increase in surface area could lead to increased leach rates. Therefore the ability of a waste form to resist cracking is an important factor to consider in selection of an optimal waste form.

Fracture strength of ceramics is given by the relationship

$$\sigma_f = A \sqrt{E\gamma} / \sqrt{c}, \qquad (1)$$

where E = elastic modulus, γ = fracture energy, c = critical flaw size to cause fracture, and A is a geometrical factor. It may be seen that strength is proportional to $\sqrt{E\gamma}$, the fracture toughness, at constant flaw size. In the work reported here, fracture toughness and hardness of Pu-substituted zirconolite were monitored for 231 days, equivalent to a storage time of 3×10^5 y for SYNROC-C containing 10 wt % commercial waste calcine. Results are discussed in terms of the evolving damage state, and implications for waste stability are considered.

EXPERIMENTAL PROCEDURE AND RESULTS

Samples of Pu-doped zirconolite ($CaPuTi_2O_7$) were fabricated by a technique similar to that described elsewhere [3]. Briefly, powders of PuO_2, CaO, and TiO_2 were ball-milled together, calcined, cold pressed, and sintered for 24 h at 1675 K in air. Isotopic purity of the plutonium was ~80 % ^{238}Pu (half-life = 88 y), with the remainder being made up of isotopes of longer half-life. The resulting product contained ~10 % porosity, along with minor phases [3].

The test cylinders were metallographically mounted and a series of 25 indentations made each week with a Vickers diamond indenter. Test temperature was ~350 K, the increase above ambient being attributable to the significant self-heat of the plutonium [3]. Initially both 0.050 and 0.100 kg loads were employed, but it was found that the heavier load resulted in crack patterns extensive enough to interact with pores and minor phase inclusions, so that subsequent tests were restricted to 0.050 kg loads. Typically, 15 to 20 of the 25 indentations were usable when the lower load was employed. Because of concern that cracks might extend with time before measurements could be made, initial indentations were re-examined after storage under ambient glovebox conditions for 84 days; however, no changes in crack dimensions were observed.

Hardness values were determined each week from average dimensions of the indentations, while fracture toughness was calculated from average crack sizes using the relationship

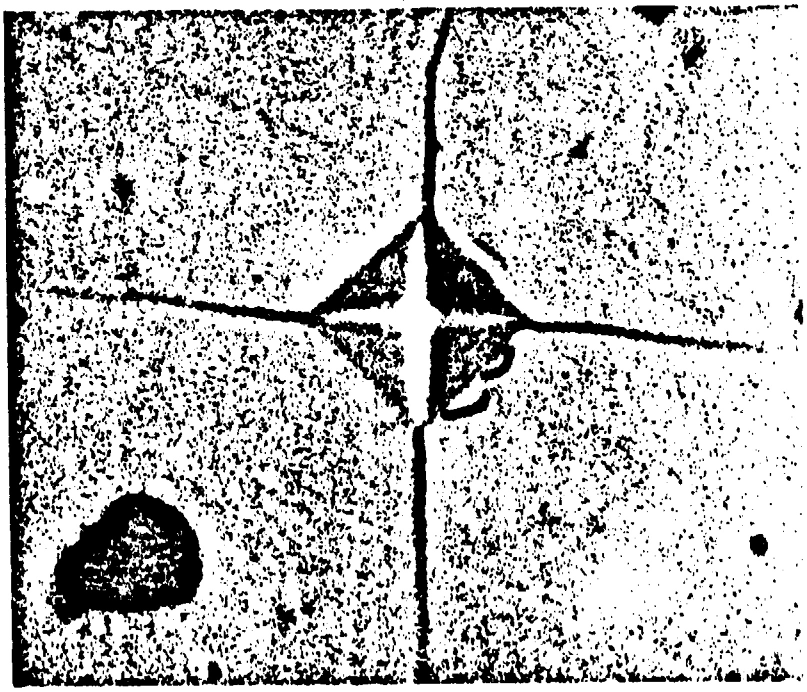
$$K_{Ic} = H\, a^{1/2}\, (E/H)^{2/5}\, [0.057\, (c/a)^{-3/2}], \qquad (2)$$

where H = hardness, a = half-diagonal of the indentation, c = distance from the center of the indentation to the tip of the crack,, and E = Young's modulus. This equation, used by Weber et al. in a study of nuclear waste glasses [4], was originally derived for use when the c/a ratio is large. However, a slightly-modified relationship is also applicable even with c/a <2 [5]. At any rate the exact formulation chosen is not of primary importance, since interest is not so much in the absolute value of fracture toughness as in its change with accumulation of radiation damage.

Since Young's modulus for zirconolite in either the crystalline or metamict form is not known, it was necessary to estimate these parameters. A value for the unirradiated material of 200 GPa was chosen as appropriate for a ceramic with a melting point of ~1800 K [3], and the reduction of modulus upon metamictization was taken to be 10 %. This estimate was based on the fact that the modulus of metamict quartz is ~30 % less than that of its crystalline counterpart [6]. Since swelling of quartz as a result of metamictization is roughly three times that for zirconolite [7] and since both silicates and titanates disorder as a result of misorientation of cation-oxygen structural units [8,9], a simple proportional correlation seems reasonable.

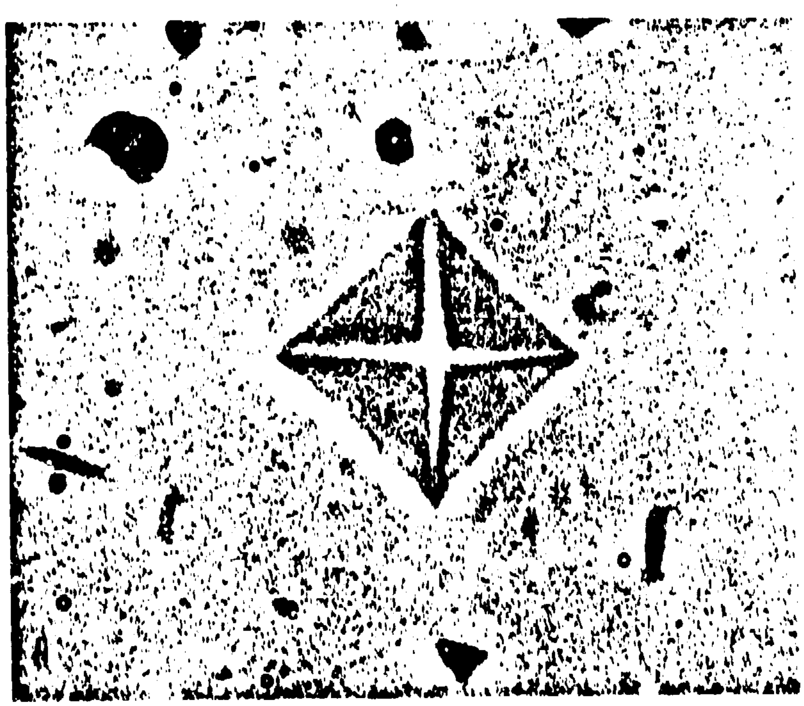
Optical photomicrographs of indentations and crack patterns made 28 days and 189 days after fabrication of the test material are shown in Fig. 1. Two irradiation-induced changes are immediately apparent: the higher-dose indentations are larger, indicating a softening of the material, and the extent of cracking is greatly reduced. Actually, as in the example shown in Fig. 1(b), indentations in high-dose material caused no discernable cracking in two-thirds of the tests.

Microhardness and crack length as a function of storage time, corresponding alpha decay dose, and equivalent SYNROC age with 10 wt % waste loading are presented in Fig. 2. Crack length here refers to the average length of one crack emanating from one corner of the indentation, and does not include the diagonal dimension of the indentation itself; this parameter is included to illustrate the extent to which microcracking was suppressed by



(a)

10μm



(b)

There are six more lines of [illegible]

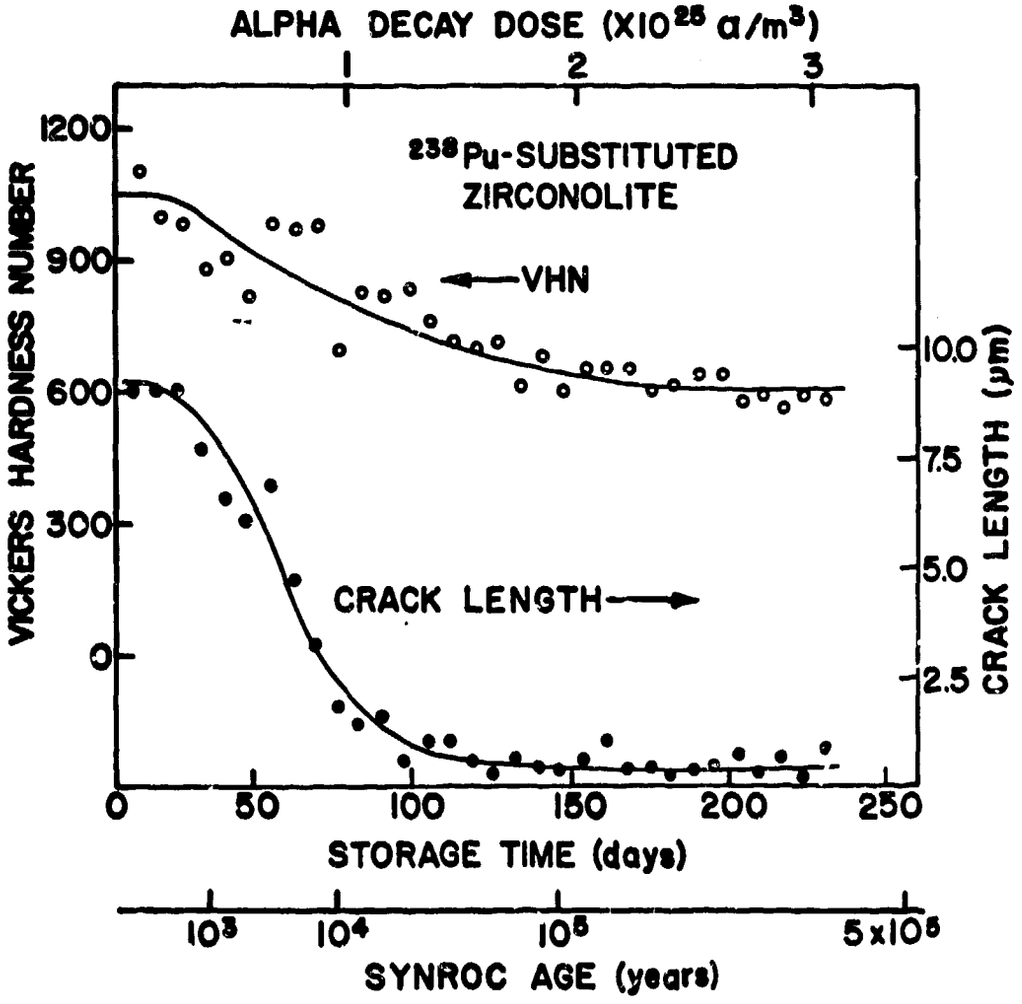
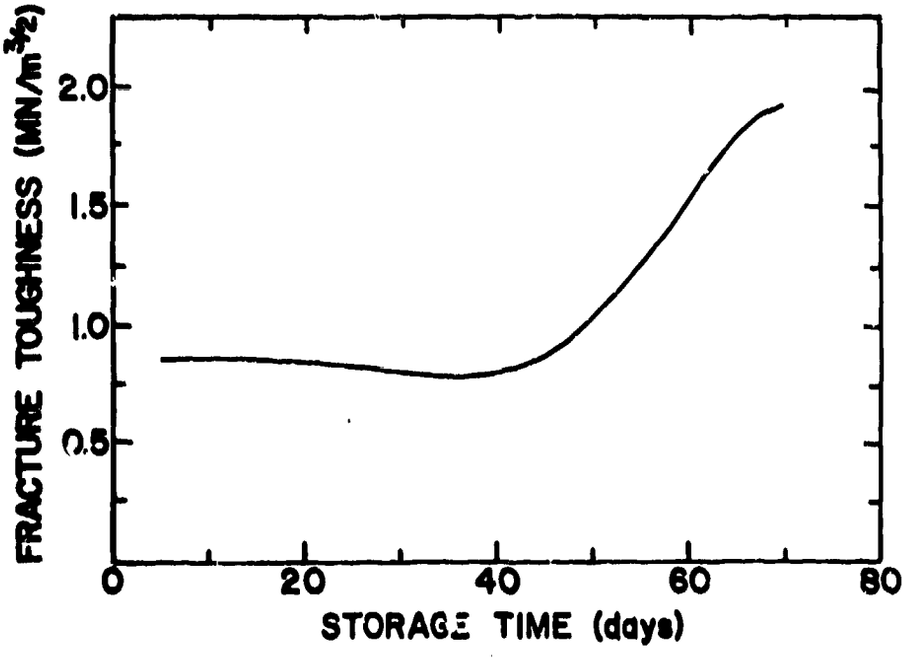


Fig. 2. Vickers hardness number and length of induced cracks as a function of storage time, alpha decay dose, and equivalent SYNROC age.



shown in Fig. 3. Initial value of c/a was 2.9, dropping to 1.6 at 70 days. Results at higher doses were not calculated because of the low values of c/a beyond that point.

DISCUSSION

The extent of softening of zirconolite as a function of self-damage is similar to that observed by Ewing [10] in a comparison of crystalline and metamict euxenite. Apparently the lattice disorder, dilation, and decrease in elastic modulus that accompany metamictization combine to bring about a characteristic reduction in hardness.

The observed increase in fracture toughness appears to be related to the formation of a composite damage microstructure. It has been established in earlier work [3,11] that accumulation of damage tracks resulting from the stopping of the ~100 KeV alpha recoil particles (^{234}U in the present experiment) gradually converts zirconolite from a crystalline to a metamict structure. Stages of damage and approximate alpha decay doses are:

Stage I -- Isolated tracks in a crystalline matrix (0.5 to 5×10^{24} α/m^3)
Stage II -- Significant track overlap (5 to 10×10^{24} α/m^3)
Stage III -- Isolated remanent crystallites in a metamict matrix (1 to 5 $\times10^{25}$ α/m^3)
Stage IV -- Completely metamict (>5×10^{25} α/m^3).

The damage level achieved to date in this study, 3.1×10^{25} α/m^3, corresponds to the middle of Stage III.

The amount of damage per decay event is obviously a function of the size of the recoil tracks. Swelling studies [3] have established that half of the total growth of this material (2.7 vol %) is achieved at a dose of 7.5×10^{24} α/m^3. If it is assumed that half of the volume has been converted at this dose and that the tracks have a spherical configuration, then each damage event results in metamictization of a microvolume of diameter of 5.4 nm. This result was used as the basis for generation of computer images of the damage microstructure as a function of alpha decay dose, with the results shown in Fig. 4. These images represent opaque sections, where white areas correspond to undamaged material, gray spots to damage tracks (some smaller than full size because of sectioning), and black areas to multiply-damaged zones.

A number of mechanisms have been proposed to explain toughening of ceramics with heterogeneous microstructures. These include crack bowing [12-14]; crack deflection [15,16]; and internal stresses associated with coherency of second-phase particles, mismatches in thermal expansion coefficient, or differences in elastic properties of these phases [17-19]. Recently, observations of increases in fracture toughness of neutron-irradiated ceramics have been attributed to interaction of cracks with strain fields around dislocation loops and to impedance of crack propagation by interaction with voids [20].

The toughening reported here may be attributable to more than one mechanism. It seems likely that some crack bowing and deflection would occur in the heterogeneous microstructure; however, the extent of conversion at 28 days (Fig. 4a) was apparently insufficient to cause significant toughening. Stage II damage is characterized by track overlap (Fig. 4b), and is accompanied by significant strengthening. Swelling at 60 days is ~3 vol % [3], indicative of a high level of internal strain, so that a major contribution to toughening from this source is likely. In support of this hypothesis, it can be pointed out that evidence of considerable internal strain was observed in earlier TEM

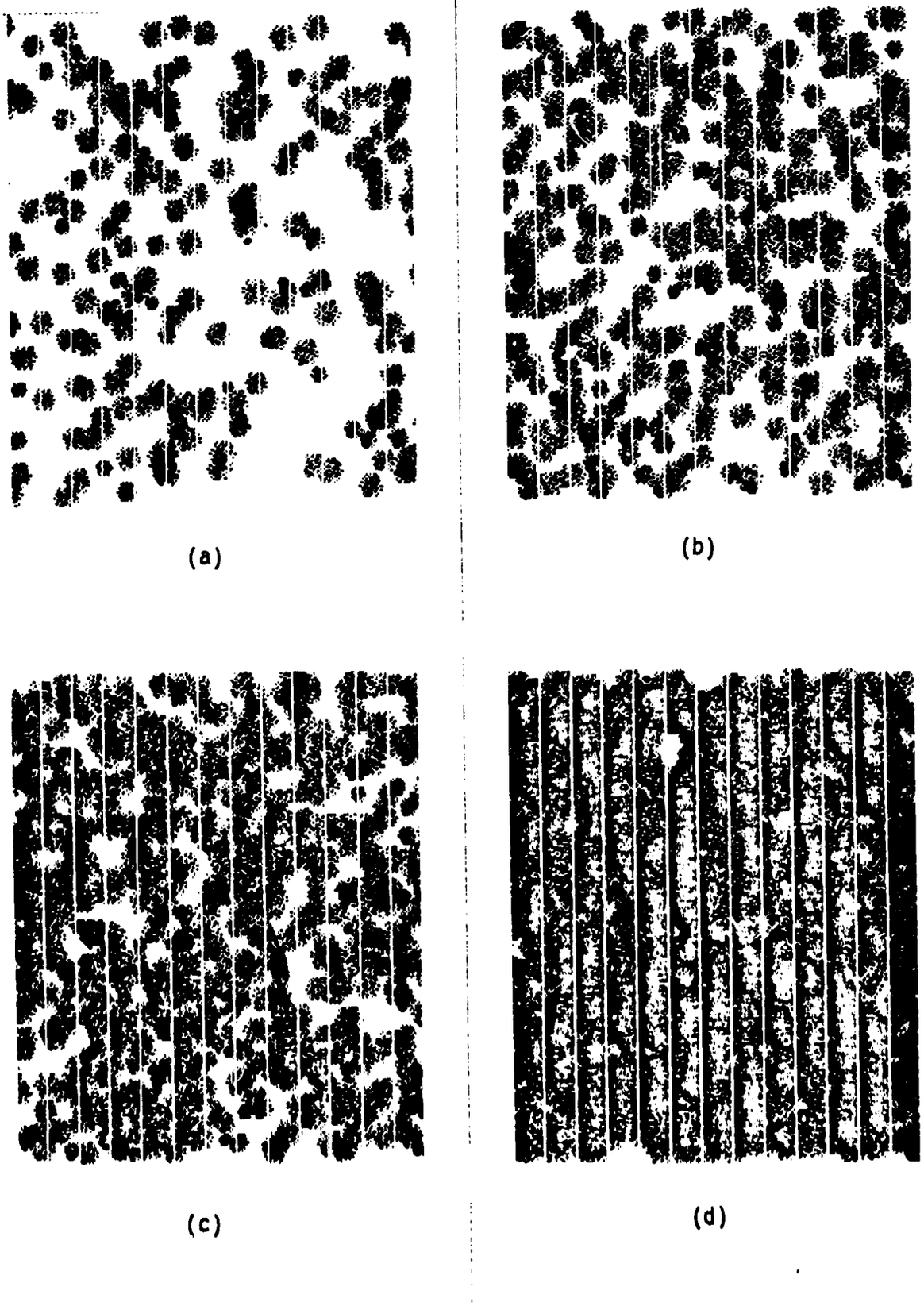


Fig. 4. Computer-generated images of damage evolution as a function of alpha decay dose: (a) 3.7×10^{24} α/m^3 (28 days); (b) 8×10^{24} α/m^3 (60 days); (c) 1.3×10^{25} α/m^3 (100 days); (d) 3.1×10^{25} α/m^3 (231 days).

phase.

As accumulation of damage tracks proceeds, introduction of these dilated regions would initially increase the level of internal strain, some of which would be accommodated by expansion of the matrix. As a result the increment of strain per decay event should decrease. Further damage would eventually result in a metamict matrix; at that point the presence of remanent crystallites of relatively high density would lead to tensile rather than compressive stresses. Nadeau and Dickson [19] showed that strengthening can result from either condition. It is apparent from these considerations that accumulation of damage is accompanied by evolution of a complex and ever-changing internal stress condition, as well as a change in the quantity, morphology, and nature of the dispersed phase.

Qualitative observations as to change of fracture toughness with self-damage can be made beyond the point where toughness can be calculated (Fig. 3). The continued rapid decrease in crack length (Fig. 2) initially more than compensates for the decrease in hardness, so that toughening would continue to occur. Eventually, however (at $\sim 1.6 \times 10^{25}$ α/m^3), crack length becomes constant while softening continues, with the result that fracture toughness would begin to show a slight decrease. Thus beyond an equivalent SYNROC age of $\sim 5 \times 10^4$ y the benefits of self-damage will begin to be reduced by a small amount. However, since the relative toxicity of the waste will have decreased to 0.1 % of that of the starting material (i.e., to about that of uranium ore) at $\sim 10^4$ y, the biological hazard will be greatly reduced by that time. At any rate, extent of microcracking may be a more important parameter than fracture toughness for this application, and cracking remained near zero to the highest dose attained here (3.1×10^{25} α/m^3, or 3×10^3 y for SYNROC waste).

At very high damage levels conversion to the metamict state is complete [3]. The contribution to toughening from the presence of a heterogeneous microstructure should disappear, but internal strain may still be great enough have a toughening effect. Eventually, however, the redamaging process, already prevalent at the 231-day level attained to date in this study (Fig. 4d), could lead to relaxation of these strains and loss of radiation-induced toughening. At the much greater times corresponding to nuclear waste storage, it is possible that thermal annealing could also bring about such relaxation; however, the similarity of damage in Pu-substituted and natural zirconolite with respective ages of 0.4 and 1.3×10^8 y [3,11] argues that no major changes will occur at ambient temperature.

CONCLUSIONS

Alpha decay damage in ^{238}Pu-substituted zirconolite causes a significant decrease in hardness and increase in fracture toughness. The former results from conversion to the metamict state, and the latter from the heterogeneous microstructure and internal strains that accompany metamictization. Thus the microcracking that is likely to accompany differential swelling of multiphase ceramic waste forms such as SYNROC should be reduced by self-irradiation damage, with the result that the probability of increased leaching will be lessened.

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