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TEMPERATURE DEPENDENCE OF ION IRRADIATION INDUCED AMORPHISATION OF ZIRCONOLITE

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INTRODUCTION

Zirconolite is one of the major host phases for actinides in various wasteforms [1] for immobilising high level radioactive waste (HLW). Over time, zirconolite's crystalline matrix is damaged by α-particles and energetic recoil nuclei recoil resulting from α-decay events. The cumulative damage caused by these particles results in amorphisation. Data from natural zirconolites suggest that radiation damage anneals over geologic time and is dependant on the thermal history of the material [2]. Proposed HLW containment strategies rely on both a suitable wasteform and geologic isolation. Depending on the waste loading, depth of burial, and the repository-specific geothermal gradient, burial could result in a wasteform being exposed to temperatures of between 100-450°C. Consequently, it is important to assess the effect of temperature on radiation damage in synthetic zirconolite.

Zirconolite containing wasteforms are likely to be be hot pressed at or below 1473 K (1200°C) and/or sintered at or below 1623 K (1350°C) [3]. Zirconolite fabricated at temperatures below 1523 K (1250°C) contains many stacking faults [4]. As there have been various attempts to link radiation resistance to structure [5, 6, 7], we decided it was also pertinent to assess the role of stacking faults in radiation resistance.

In this study, we simulate α-decay damage in two zirconolite samples by irradiating them with 1.5 MeV Kr^+ ions using the High Voltage Electron Microscope-Tandem User Facility (HTUF) at Argonne National Laboratory (ANL) and measure the critical dose for amorphisation (D_C) at several temperatures between 20 and 773 K. One of the samples has a high degree of crystallographic perfection, the other contains many stacking faults on the unit cell scale. Previous authors proposed a model for estimating the activation energy of self annealing in zirconolite and for predicting the critical dose for amorphisation at any temperature [8]. We will discuss our results and earlier published data in relation to that model.

EXPERIMENTAL PROCEDURE

Two zirconolite samples were prepared via the alkoxide route [9]. One was hot-pressed at 1473 K (1200°C) for 2 hours (1200 sample) and the other was sintered at 1723 K (1450°C) for 1 week (1450 sample). TEM specimens were prepared by crushing material under ethanol then passing holey carbon grids through the suspension and collecting fine particles on the carbon film. All girds were cleaned in an Ar plasma for 5 min. using a South Bay PC 150 plasma cleaner. Zirconolite is not the sole phase present in the fabricated material. Therefore the positions of zirconolite grains on grids were mapped on secondary electron images (SEIs). In situ ion irradiation of the TEM specimens was performed using a 1.2 MeV modified Kratos/AEI EM7 electron microscope (operated at 300kV) interfaced with a NEC ion accelerator in the HVEM-Tandem User Facility at Argonne National Laboratory. At all temperatures apart from room temperature, temperature variation was no more than 3 K. At room temperature, the temperature was 302 K during HVEM examination and rose to 328 K during ion irradiation. Grains selected for ion irradiation showed many maxima in their selected area electron diffraction (SAD) patterns. Specimens were irradiated with 1.5 MeV Kr^+ ions using the procedure described by Smith et al. [10]. For each monitored grain, between 8 and 20 negatives were taken at incremental doses. The average of the dose at which all Bragg reflections had disappeared and the dose immediately prior to that dose was taken to be the critical dose for amorphisation, D_c.

RESULTS

The 1450 sample basically has the zirconolite-2M polytype structure with a high level of crystallographic perfection. The 1200 sample also predominantly has the zirconolite-2M polytype structure but contains many stacking faults and twins on the scale of the unit cell. In spite of this difference in microstructure, the temperature dependence of the critical dose for amorphisation is similar for both samples shows (see figures 1 and 2). D_c is almost constant up to temperatures near the critical temperature for amorphisation T_c (above which recrystallisation is complete over the entire cascade volume), then it rises rapidly.

According to current theory [8], the temperature dependence of the amorphisation dose D_c can be expressed by the following equation

$$D_c = \frac{D_o}{1-\exp\left[\frac{E_a}{k}\left(\frac{1}{T_c}-\frac{1}{T}\right)\right]} \qquad \text{.............................. (1)}$$

where D_c is the critical dose for amorphisation, D_o is the amorphisation dose extrapolated to 0 K, E_a is the activation energy for self annealing, T_c is the critical temperature above which recrystallisation is complete over the entire cascade volume, k is Boltzmann's constant and T is temperature (T and T_c are in degrees Kelvin). A least squares analysis of our experimental data according to this equation yields the broken curves shown in figures 1 and 2, E_a values 0.14 ± 0.04 and 0.15 ± 0.06 eV and T_c values 637 ± 22 and 680 ± 27 K for the 1200 and 1450 samples respectively. The E_a and T_c values of the 1200 and 1450 samples are the same within experimental error.

DISCUSSION

S.X. Wang et al. [11] measured the critical dose of 1 MeV Kr^+ ions for amorphisation of six zirconolites of various compositions and state that their data for end-member zirconolite ($CaZrTi_2O_7$) indicate a two stage dependence. However, their contention hinges on the reliability of only one data point, the datum at 375 K. Unfortunately S.X. Wang et al. [11] do not show error bars or give an estimation of the reliability of their data points. Our data may or may not support a two step dependence of D_c on temperature. We will collect addtional data points and provide a full analysis in the extended paper.

White et al. [12] measured the critical dose of 1 MeV Kr+ ions for amorphisation of zirconolite at 20, 300 and 475 K and found it to be 7.1, 10 and 340, in units of 10^{14} ions/cm^2 respectively and from these data, they calculated an E_a value of 0.129 eV. At any temperature, the D_c values White et al. [12] measured are much greater than both ours and those of S.X. Wang [6]. The reasons why White et al. [12] measured such large critical dose values are not clear and are exacerbated by the fact that White et al. [12] did not estimate their errors.

Clinard [13] found that radiation damage induced swelling in Pu-substituted zirconolite and that the final volume depended on the temperature at which samples were stored (not on total storage time). At room temperature and 575 K, Pu-substituted zirconolite specimens swelled by to 5 and 4 percent respectively , while at 875 K specimens showed <0.5 percent swelling even after 600 days. In agreement with the findings of Clinard [13], the T_c values calculated both in this study and by S.X. Wang et al. suggest that self annealing will occur at temperatures at approximately 650 K.

Fabrication temperature and/or stacking fault disorder does not significantly affect the response of end-member zirconolite to radiation damage. This result is significant, if it holds for bulk samples, because it is anticipated that titanate wasteforms will be hot pressed at or below 1473 K (1200°C) and/or sintered at or below 1623 K (1350°C). Consequently the constituent zirconolite in wasteforms will contain many stacking faults.

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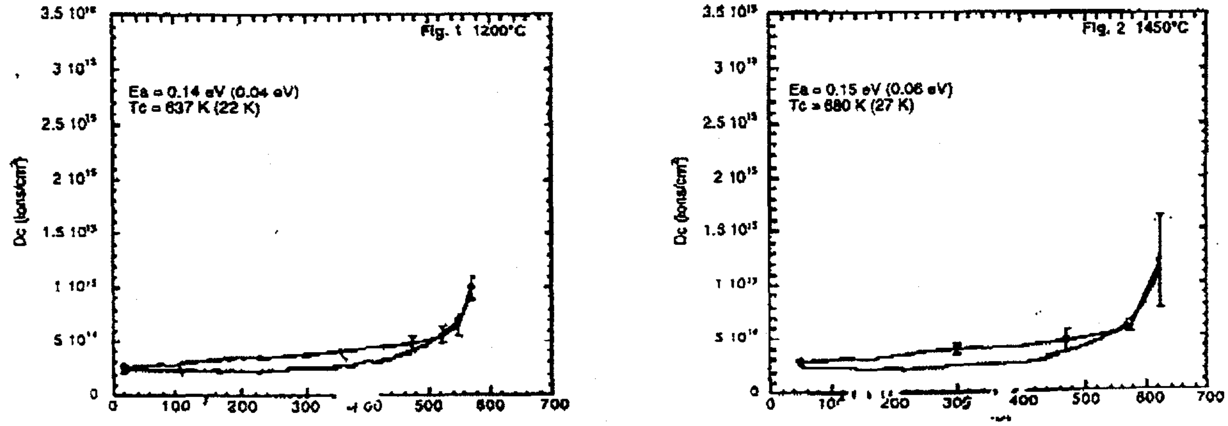

Figures 1 and 2 show Dc versus temperature data for 1200 and 1450 samples respectively. Dashed curves show least squares fits of data.