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Radiation damage in nuclear fuel materials: the "rim" effect in UO_2 and damage in inert matrices for transmutation of actinides

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Abstract

Polygonization or grain subdivision at high damage levels (often referred to as "rim effect") is gaining increasing importance for UO_2 which is the fuel of nuclear electricity producing power stations. Also, recently, the concept of replacing U-238, and hence replacing natural UO_2, by "inert matrices" for fissile U-235 or Pu-239, or also for transmutation of higher actinides (Np, Am, Cm) is being studied. High energy ion implantation was used to simulate fission damage in both UO_2 and in such matrices (e.g. Al_2O_3, $MgAl_2O_4$ etc.). The energy of implanted ions was varied between 40 keV and 2.6 GeV. Emphasis is given to the search for possible dose rate effects. Results on damage formation in UO_2 exist now for dose rate variations by more than a factor of 10^{10}. The implications for the technological application of inert matrix materials are briefly discussed.

1. Introduction

In recent years, electricity producing nuclear power stations aim at increasing the lifetime of the nuclear fuel (uranium dioxide, UO_2) for economic reasons and in order to reduce the amount of spent fuel to be stored. Also, new concepts are developed to incorporate actinides in "inert matrices", hence materials not producing new actinides as they are produced by natural uranium. These fuels are thus developed for "transmutation" of long lived actinides (Np, Am, Cm) by fission or neutron capture while producing electricity. The candidate materials are ceramics with a high melting point and with low neutron absorption cross sections such as Al_2O_3, MgO, spinel $MgAl_2O_4$, zircon $ZrSiO_4$ etc.

For the nuclear fuel UO_2, a physically very interesting phenomenon is getting increased attention since it is also of large technological importance. At extended lifetime (burnup), the cold outer part of the UO_2 pellets used as fuel in the reactor experiences more radiation damage and contains more fission damage than the bulk of the pellet due to neutron resonance capture by U-238 in this "rim" region to form fissile Pu-239. The consequence is a polygonization or grain subdivision process converting the original grains of the sintered UO_2 of some 10 μm size into about 10^4 to 10^5 new small grains of about 0.2 μm size, with obvious consequences for thermal conductivity, fission gas release, mechanical properties etc. [1–3]. At the same time, porosity is formed and the fission gas Xe becomes depleted in the new grains. In the present investigation, implantation with high energy fission product ions (mainly Xe and I) of fission energy (70 to 90 MeV) was used to study this phenomenon in order to better understand the mechanism. Parallel work is done with both lower (order of 50 to 500 keV) and higher energies (up to 2 GeV) to get a better picture of the physics involved. Typical results obtained are discussed.

For the candidate materials to be used as "inert matrices", some knowledge exists on radiation damage produced by neutrons and in conventional ($\sim 10^2$ keV energy) ion implantation. These matrices will, however, experience not only damage due to neutrons and α-decay (typically a 100 keV heavy recoil ion and a 5 MeV He ion), but also due to fission. The above type of experiments is therefore increasingly applied to the inert matrices with emphasis on consequences for phase changes and swelling.

An important problem in damage studies is that of possible dose rate effects. Considerable experimental work in this field has also been done, e.g. by comparing results on damage effects in natural UO_2 minerals of some 10^8 years age (very low dose rates), in α-decay damaged material (intermediate rates) and in ion implanted specimens (high rates). These results are also discussed.

2. Materials and experimental techniques

The materials used in the present radiation damage work are UO_2 (sinters, s, and single crystals, sc), and the

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following candidates for inert matrices: spinel $MgAl_2O_4$ (s + sc), zircon $ZrSiO_4$(s), CeO_2 (s), MgO (sc) and Al_2O_3 (s + sc) [4].

Damage was produced by controlled ion implantation, the energy range being very wide (40 keV to 1.5 MeV; 10^2 MeV region; and energies up to 2.6 GeV). The ions used were from elements occurring as fission products (e.g. Mo, Kr, Xe, Cs, I, etc.) or U. Most implantations in the 10^2 keV energy range were performed at INFP, FZK Karlsruhe, (Drs. O. Meyer and G. Linker), at CRNS Orsay (Dr. J.C. Dran), or at the Univ. of Leuven (Dr. H. Pattyn); the implantations in the 10^2 MeV range were performed at both ISL, HMI Berlin (Dr. S. Klaumünzer) and AECL Chalk River (Drs. P. Lucuta and R. Verrall); and the very high energy implants were done at GSI Darmstadt (Drs. C. Trautmann and J. Vetter). The techniques used to study damage formation and recovery were: X-ray diffraction including special techniques like the so-called omega scans [2] (Dr. G. Linker, INFP, FZK Karlsruhe), scanning and transmission electron microscopy, performed at TUI or, for TEM, also at the University of New Mexico, Albuquerque (Drs. L. Wang and R. Ewing) and the Rutherford backscattering (RBS)/channeling technique. These latter experiments were also performed at different laboratories: the Dynamitron Tandem Laboratory at the Ruhr University Bochum (Dr. M. Wielunski); INFP, FZK Karlsruhe (Drs. O. Meyer, G. Linker and A. Turos); CRNS Orsay (Dr. J.C. Dran); INFM, Univ. Padova and Laboratori Nazionali di Legnaro (Drs. A. Drigo, A. Sambo and A. Turos).

Conventional RBS with 2 MeV He^+ ions gives information only on the U-sublattice of UO_2, since the yield for oxygen in classical RBS is less than 1% of that for uranium. To achieve a separate analysis of each sublattice, the resonant $^{16}O(^4He, ^4He)^{16}O$ scattering was used, applying a He-beam of 7.53 MeV energy [5]. In this way, the signal from O-atoms in UO_2 becomes as large as that from U-ions. Resonance scattering (in combination with RBS and with the channeling technique) was also used to obtain separate information about damage in the different sublattices of inert matrices.

3. Results and discussion

For space reasons, only a limited number of typical results are shown here from the large body of data obtained in this work.

3.1. Radiation damage in UO_2

The grain subdivision process and the polygonization of UO_2 during ion implantation at low energy (range 50 to 500 keV) have been presented before [1–3,5]. Fig. 1 shows a transmission electron micrograph of the structure formed at the rim of pellets of the nuclear fuel UO_2 following a long irradiation leading to a local burnup exceeding about

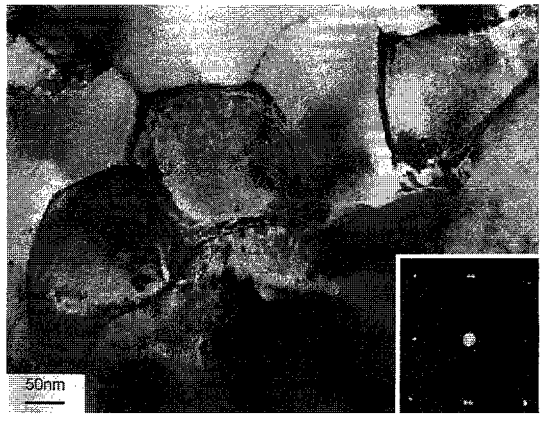

Fig. 1. Transmission electron micrograph showing the fine scale subgrain structure at the rim of a high burnup UO_2 fuel. The inset diffraction pattern shows that the misalignment between subgrains is small (< 5°).

70 GW d/tM [6]. (Note, that 10 GW d/tM correspond to about 1.1% of the U-atoms in UO_2 being fissioned, or 2.6×10^{20} fissions/cm^3, or – for the present purpose – an implantation of 1.8×10^{17} ions/cm^2 of fission products with fission energy, e.g. 72 MeV iodine ions.) The average size of the new subgrains is about 0.2 μm. The original grain size of the as-sintered starting material was 10 to 15 μm such that $\sim 10^5$ new grains originated from each original grain. The inset diffraction pattern shows a small misalignment only between the subgrains, though other investigators have also seen large misalignment in other fuels [7]. The mechanisms and the driving force for this polygonization process are still not well known. Some of the proposals made are simply unfounded, others cannot explain all observed phenomena. Sometimes, the term recrystallization is used based on certain similarities with processes occurring in the recovery of cold-worked metals. However, such a phenomenon occurs only in (deformable) metals and not in brittle ceramics, it usually needs a thermal anneal to occur and it may or may not be related to sweeping of incorporated rare gases. Also, in such metals (e.g. Ag, Cu), ion implantation does not produce any similar polygonization, and it does not affect the behavior of the cold-worked metal [8,9]. In contrast, ion implantation has previously successfully been used to produce polygonization and a structure similar to that in high burnup UO_2 fuel before, as reported at the last conference on radiation effects in insulators [2]. Xe ions were used since Xe is one of the most abundant fission products and Xe bubbles were formed as in real fuel. The mechanism suggested for polygonization in these ion-implanted specimens – which was also suggested to contribute to grain subdivision in operating fuel – was microfracture and cleavage caused by the high pressure of athermally formed small overpressurized (possibly even solid) Xe-bubbles and Xe-precipitates [2]. More recent work using prethinned

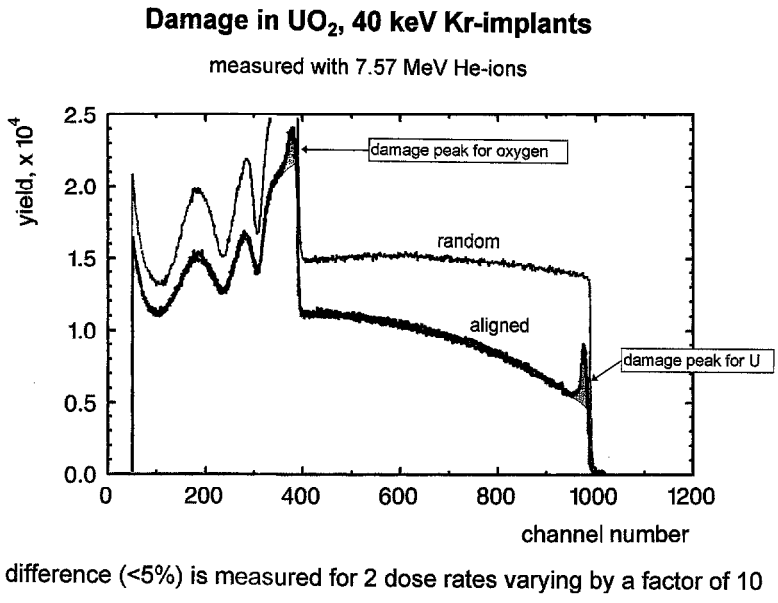

Fig. 2. Rutherford backscattering and resonance scattering spectra of 7.57 MeV He ions from a UO_2 single crystal implanted at room temperature with 300 keV Xe ions at two different dose rates varying by a factor of 10 but using the same ion fluence.

UO_2 TEM foils and higher energies of the Xe ions (1.5 MeV) has shown that polygonization occurs also during predominantly electronic energy deposition, by formation of dislocations and precipitation of knock-on atoms to form subgrain boundaries indicating that a high enough point defect concentration can cause polygonization in UO_2 as well [10], though it does not cause the porosity formation typical for the rim-structure.

A possible criticism of simulating damage effects occurring over periods of years in technological applications by ion implantation experiments performed in laboratory investigations of short duration is that dose rate effects may exist. The existing evidence is not indicating such effects. Fig. 2 gives an example for ion implantation with Xe. The damage peak formed for a given fluence is found to be independent of the dose rate if this is varied by a factor of 10 [11]. Fig. 3 shows another example [11] for implantation with He ions. Using a larger He ion energy (9 MeV) for analysis than for implantation in the backscattering investigation (1 MeV) allows the detection of the damage produced by He (simulating α-particle damage) separately in the oxygen and in the uranium sublattices. As expected, the damage is seen to occur at the end of the range of the He ions. Again, a variation in dose rate did not cause any observable change.

Damage ingrowth data in UO_2 due to α-decay can also be found in the literature, both for intermediate [12] and very low dose rates [13]. The low dose rates, lower by more than a factor of 10^{10} than in accelerated ion implantation, were found in natural UO_2 minerals where damage was formed by α-decay of U and its decay-chain. A comparison of all the data does not show any significant dose rate effects.

More work is needed for a satisfactory definition of the mechanisms causing polygonization and grain subdivision in UO_2. Such work is ongoing. In addition, reactor irradiation experiments to determine the important parameters have been started.

3.2. Radiation damage in inert matrices

As mentioned above, inert matrices are planned to replace U-238 (and thus UO_2) in nuclear fuels in order to reduce the amount of actinides formed. Such inert matrix

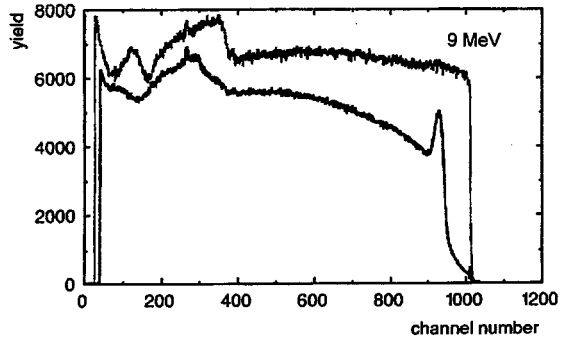

Fig. 3. Rutherford backscattering and resonance scattering spectra of 9 MeV He ions from a UO_2 single crystal implanted at room temperature with 1 MeV He ions to a total fluence of 1.1×10^{17} ions/cm^2.

materials can also be used for nuclear transmutation of actinides. They will experience α-decay damage during storage (~5 MeV α-particles and ~100 keV recoil daughter atoms at ambient temperature), and damage due to neutrons, α-decay and fission during reactor irradiation (elevated temperatures). A large body of data exists for neutron damage in one of the candidate materials, e.g. spinel $MgAl_2O_4$. Spinel is very resistant against neutron irradiation. For instance it does not swell for neutron doses of 2×10^{26} n/m^2 at 925 to 1100 K [14]. There are also results for ion implantation in the 10^2 keV energy range, and similar results exist also for another candidate material, i.e. zircon, $ZrSiO_4$. Zircon has, for instance, also been suggested as matrix to burn ex-military plutonium [15]. Nothing is known, however, for fission damage in these two materials and very little information is available for other candidate inert matrix materials such as CeO_2. We have therefore started a program to fill this gap [16–18]. The aim is to provide data for the following damage sources

- fission,
- alpha-decay (alpha-particle and recoil atoms),
- neutrons,

in order to exclude unsuitable and to select suitable matrices. In this damage consideration, the type of incorporation of the decaying and fissioning actinide is of interest. If the actinide is in solid solution, all of the matrix will be homogeneously damaged. If the actinide is present as precipitates, then, depending on their size, most damage (alpha-decay and fission) may be confined to the precipitate and only a shell around the precipitate will be damaged [4].

Two examples of this research are given in Figs. 4 and 5. Fig. 4 shows that with increasing ion dose, well distinguished damage peaks become clearly visible in all three sublattices (see arrows labelled DP) of spinel following implantation of 300 keV Xe ions. The peak appearing around channel no. 175 is due to the implanted Xe. These and other results show that spinel is not equally stable against ion impact (simulating the recoil atoms of alpha-decay), than it is against neutrons [18]. At doses above 1×10^{16} ions/cm^2, the Al atoms are in random positions, whereas the Mg sublattice is much more stable. The doses needed to create this structural damage correspond to those accumulated by α-decay in a storage time of 20 years in a spinel with 25 mol% of AmO_2. The damage level causing 50% amorphization of the Al sublattice would be reached after about 5 years of storage at room temperature.

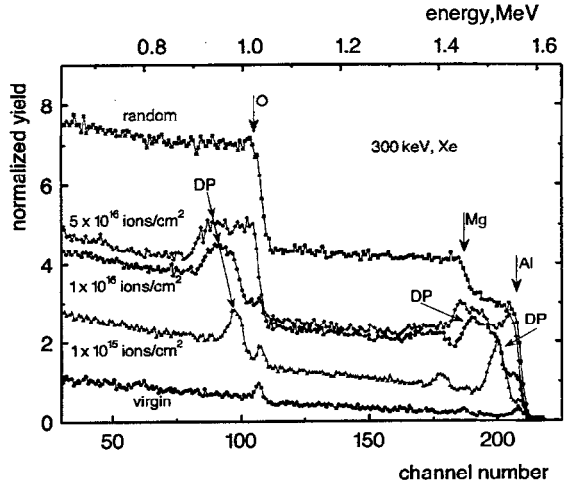

Fig. 4. Random and aligned spectra for a ⟨100⟩ $MgAl_2O_4$ spinel single crystal implanted at room temperature to 1, 10 and 50×10^{15} Xe ions/cm^2 at 300 keV energy.

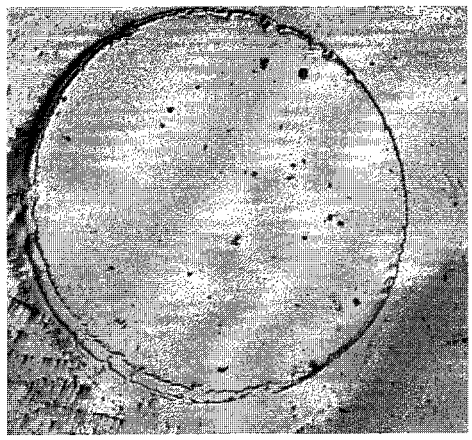

Fig. 5. "Pop-out" of the implanted area of Al_2O_3 (72 MeV iodine, 1×10^{17} ions/cm^2). The implantation temperature was about 150°C due to beam heating.

Fig. 5 finally shows results of ion implantation at fission energy [16]. The target is Al_2O_3, known for long [19] to be susceptible against ion impact and to become amorphous. The implanted area "pops out" of the specimen indicating very significant swelling.

The linear swelling measured in this way is in average 1.5 μm independent of the doses used (range 10^{15} to 10^{17} ions/cm^2). The range of the ions of 72 MeV energy is ~7.5 μm. The linear swelling is therefore ~20%. The damaged material can only swell in one direction since it is restrained by the solid undamaged Al_2O_3 in the other directions. It is not possible to quantitatively deduce the total free swelling rate. There are two extreme possibilities:

i) Swelling is only free in one direction and completely restrained in the other two directions. Since $\Delta V \sim 3\ \Delta L$, free swelling would be three times the linear swelling.
ii) The material swells in the free direction at three times the normal linear rate, since the restraint of the solid pushes all defects etc. into this one free direction.

Most probably, the real behaviour is intermediate. We thus estimate the free swelling to be ~ 30%. This corresponds to very early results of Al_2O_3 containing UO_2 irradiated in a nuclear reactor [20], however, obtained at higher dpa levels.

The important point is the dose-independence of the effect. It is also observed for rather low doses (10^{15} ions/cm^2). Also, the implanted areas of all of the Al_2O_3 specimens showed no indication of crystallinity anymore, neither in channeling nor in the specific X-ray technique (so-called omega or Ω-scans, see Ref. [2] for details) developed for such measurements. Those experiments have shown that Al_2O_3 becomes soon amorphous under the impact of fission fragments and that it shows a very large swelling.

The inert matrices are subjected to α-decay damage at ambient temperature any time following their fabrication. Neutron and fission damage will only occur at elevated temperature when damage recovery may be possible, and when critical doses for e.g. amorphization are likely to be higher than at ambient temperature. A broad data base is therefore needed for different damage sources and for different temperatures in order to select suitable stable matrices. The results presented here are a step in this direction.

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