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In situ Resonant Ultrasound Spectroscopy during irradiation of solids with relativistic heavy ions

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Abstract—Samples of steel, fused silica, CaF_2, NaCl, and a (La,Eu)PO_4 monazite ceramic were irradiated with ^{209}Bi (130 GeV) and ^{238}U (60 GeV) ions up to total fluences of 6×10^{11} cm^{-2}. During beam exposure, resonant ultrasound spectra were recorded. No radiation-induced changes in the density and elastic stiffness coefficients were observed when comparing samples before and after irradiation. The irradiation caused fully reversible shifts of the resonance frequencies in all samples except NaCl, silica and monazite irradiated with U ions. These reversible shifts are due to a temperature increase during irradiation. The heating process was modelled quantitatively by an energy balance model. The average thickness traversed by the ions was estimated from geometrical considerations and the energy deposition was calculated with the SRIM software. The results from the model and these calculations are in good agreement. For NaCl, silica and monazite, a degradation of the samples was observed. Hence, in situ Resonant Ultrasound Spectroscopy can be used to monitor sample integrity and temperatures in harsh radiation environments.

Keywords: Radiation effets in solids; Resonant Ultrasound Spectroscopy; Swift ion damage; Elasticity

1. Introduction

The study of radiation effects in solids is an important field of research addressing the need to better understand radiation damage processes and to design radiation hard materials suitable for applications in intense radiation fields, such as those present in new fission and fusion reactors [1] or repositories for nuclear waste [2,3]. In the past, radiation-induced modifications of materials were mainly investigated by using ion beams with energies in the range between keV and MeV. The penetration depth of such ions is limited to surface layers in the order of several 100 nm up to few μm and does not allow macroscopic tests of bulk materials. Irradiation experiments in which thick layers or bulk samples are completely penetrated require either neutrons or energetic ion beams (energies beyond GeV). Neutrons are available within reactor cores [4,5], but materials science experiments in a reactor core are extremely demanding. Alternatively, beams of relativistic, high-energy heavy ions can be produced by heavy ion synchrotrons, such as the SIS at the GSI Helmholtz Center for heavy ion research (Darmstadt, Germany) [6,7]. Such facilities provide the opportunity to develop experimental set-ups for in situ investigations during irradiation.

In this work, we present the results of in situ Resonant Ultrasound Spectroscopy (RUS) experiments performed during the irradiation of different solids (steel, fused silica, CaF_2 and NaCl crystals, and monazite ceramic) at the SIS. We demonstrate that RUS is a sensitive in situ technique to determine the increase of bulk sample temperatures induced by the beam and to monitor sample failure during irradiation. The materials were chosen due to their relevance in radiation materials science, which we briefly summarize in the following.

Stainless steels are suggested as structural materials for fusion and Generation IV fission reactors, as well as for spallation neutron sources. Particularly ferritic-martensitic steels are candidates for first wall, fuel assembly, core support and core internals [8]. In these applications the materials are subjected to large neutron doses and high temperatures. An investigation of steel cylindrical tubes at temperatures ranging between 673 and 873 K, hoop stresses between 0 and 200 MPa, and total doses up to 208 displacements per atom (dpa) in a Fast Flux Test Facility, shows that the diametral (or transverse) strain and the volume swelling are negligible up to 50 dpa [9]. Fused silica (amorphous silica, a-SiO_2)

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is a widely used material. Recently, its application as windows for high-power lasers had been studied [10]. Upon ion irradiation a-SiO_2 usually densifies, which is explained by a rearrangement of the ring network into smaller, compacter rings [11]. This densification reaches up to 3.5% and saturates at deposited energy densities of $\sim 10^{23}$ eV cm^{-3} [12]. For higher doses, plastic deformation is observed, i.e. the dimension parallel to the beam decreases whereas the dimensions perpendicular to it increase [13,14]. So far this effect has only been observed in amorphous materials irradiated with swift heavy ions. CaF_2 and NaCl are ionic crystals with large band gaps ($\sim$10 eV) and hence transparent in the visible spectrum. Upon irradiation, the ionic crystals become coloured due to the creation of colour centres (electrons and holes trapped at vacancy and interstitial sites) [15]. Swelling has been observed for swift heavy ion irradiations with a threshold energy deposition of $\sim$5 keV nm^{-1} [16,17]. Monazite, (REE)PO_4 where REE denotes rare earth elements from La to Gd, ceramics are considered as a nuclear waste form candidate. The immobilization of high-level nuclear waste is a pressing topic in the context of deep geological waste repositories. An optimal waste form must be able to withstand the cumulative radiation damage produced by the decay of the radioactive nuclei and the environmental conditions in the repository without mechanical disintegration. Natural samples of monazite often contain uranium and thorium (up to 27 wt.% of $UO_2 + ThO_2$), but are not found in the metamict state and posses low dissolution rates [18]. Studies of irradiation effects with ions in the elastic collision regime show a transition into an amorphous state [19]. The critical temperatures of amorphization are between 333 and 450 K [20].

To measure the elasticity of solids during ion irradiation, we employed ultrasonic techniques which are based on the excitation of vibrations in a broad frequency range and detection of resonance states of the solid under study [21,22]. Parallel-plate/plane-wave techniques typically allow a model-free derivation of elastic stiffness coefficients from the experimental data, but require the use of different transducers for longitudinal and shear waves and a coupling medium. As the coupling media (paraffin oil, resin) usually have low boiling or decomposition temperatures, these techniques are not suitable for high temperature measurements. In contrast, RUS can be employed to determine elastic stiffness coefficients at temperatures up to 1400 K [22,23]. The method is based on the determination of the eigenfrequencies of a freely vibrating body [24–27]. In practice, a sample with a well defined shape (e.g. sphere, cylinder, or rectangular-parallelepiped) is gently clamped between two piezoelectric transducers, one of which serves to excite the solid, while the other acts as a receiver. The excitation frequency is typically varied from a few kHz to a few MHz. The resonance frequencies in centrosymmetric specimens depend on the density, shape, dimensions and elastic coefficients of the sample, and temperature. To deduce the elasticity tensor, resonance frequencies are calculated from the elastic stiffness coefficients of a model and compared to the experimentally determined values. The model parameters are varied so that the sum of the squares of the differences between the calculated and observed frequencies is minimized.

Here, we studied the potential application of in situ RUS as a non-destructive real-time technique to monitor sample properties during irradiation. The development of such methods to evaluate radiation effects in solids is essential for a reliable characterization of sample degradation in harsh radiation environments, such as the monitoring of embrittlement in reactors [28].

2. Experimental

2.1. Material preparation and characterization

Five different, synthetic solids were employed in this study: HT9 martensitic steel, fused silica (a-SiO_2), CaF_2, NaCl, and a $(La_{0.5}Eu_{0.5})PO_4$ monazite ceramic. All samples were cut and polished into rectangular parallelepipeds. Polishing was performed with corundum powder (down to 5 μm) suspensions in paraffin oil. Except for the monazite ceramic, at least two samples with similar dimensions were prepared from each material. One of these samples was employed for the in situ RUS experiment, while the other was used to determine the temperature dependence of the resonance frequencies. Table 1 gives some material properties.

The steel was machined and then heat treated to achieve an increased hardness (220–230 HV30, 217–222 HB and 17.6 HRC for Vickers, Brinell and Rockwell hardnesses, respectively). For the first thermal treatment, samples were heated in argon from ambient temperature to 1323 K within one hour and then kept at this temperature for 30 min. After the annealing period the samples were quenched in air to ambient temperature. Two hours later, a second thermal treatment commenced by placing the samples into a pre-heated (850 K) furnace, where the temperature was increased to 1023 K in 30 min. Finally, after an annealing time of 60 min, the samples were again quenched in air. The tensile strength after the treatments was between 750 and 800 MPa within the expected range.

The silica sample is Heraeus Optical Quality (HOQ 310) fused quartz. It possesses a higher temperature resistance and chemical purity, and lower coefficient of thermal expansion compared to other optical glasses.

The $(La_{0.5}Eu_{0.5})PO_4$ monazite ceramic was synthesized hydrothermally from lanthanum nitrate hexahydrate, europium nitrate hexahydrate, sodium hydroxide and ammonium hydrogen phosphate at the Forschungszentrum Jülich (Germany). A full description of its synthesis has been published elsewhere [29].

Single crystals of CaF_2 and NaCl were cut with a low speed diamond wire saw. The samples were ground and polished. The parallelepiped faces were parallel to within 0.5° to the {100} planes.

Densities of pristine and irradiated samples were determined at 293.2 ± 0.2 K with the buoyancy method using water or paraffin oil. The densities of the fluids were calibrated using a synthetic quartz sample.

The parallel-plate/plane-wave technique was employed to measure the propagation of longitudinal and shear waves in order to determine the elastic stiffness coefficients c_{11} and c_{44} in the samples before and after irradiation. The measurements were performed with a network analyser (Agilent 4395A). X- and Y-cut α-quartz transducers were