Nanocrystalline Zirconia Can Be Amorphized by Ion Irradiation

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Nanocrystalline composites are finding applications in high-radiation environments due to their excellent mechanical and electronic properties. We show, however, that at the smallest particle sizes, radiation damage effects can be so strongly enhanced that under the right conditions, materials that have never been made amorphous can become highly susceptible to irradiation-induced amorphization. Because light-weight, high-strength nanocomposites are potential materials for spacecraft shielding and sensor systems, these fundamental results have significant implications for the design and selection of materials to be used in environments where a large ion flux will be encountered.

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Recent investigations have established that the thermodynamic properties of nanocrystalline solids are particlesize dependent. Size-related effects such as melting-point depressions and thermodynamic stability-field shifts have been reported [1-5]. The irradiation-induced crystallineto-amorphous transition is also an important type of structural transformation [6], but despite the 50 years of ion-irradiation data now accumulated on a wide variety of bulk materials, the crystalline-to-amorphous transition in nanocrystalline solids has not been systematically studied.

We investigated the effects of ion irradiation on embedded nanometer-scale precipitates of ZrO₂. Zirconia is employed in superplastic structural ceramics that demonstrate superb strength and fracture toughness [7], and is also used as an oxygen sensor and a fast ion conductor [8]. ZrO_2 has been the subject of numerous irradiation experiments to determine its stability in high-radiation environments [9–12] due to its applications as an inert matrix nuclear fuel and for the immobilization [13] and "burnup" [14] of plutonium from dismantled nuclear weapons. Bulk ZrO₂ exhibits no evidence of irradiation-induced amorphization at doses as high as 110 displacements per atom (dpa) [15,16]. In no case has the material demonstrated a tendency toward amorphization, even in the most extreme irradiation conditions. Only by implanting large quantities of impurity atoms, and thereby dramatically modifying its composition, can zirconia be amorphized [17]. Zirconia is, therefore, one of the most radiation-resistant ceramics currently known.

 ZrO_2 has three closely related crystalline structures: Cubic zirconia, which is stable from 2450 °C to the melting temperature (2675 °C), consists of a simple-cubic packing arrangement of oxygen anions with the Zr cations in the center of every other cube (i.e., the fluorite structure). Below 2450 °C, a displacive transition occurs in which alternate pairs of oxygen anions are slightly offset, forming a tetragonal structure. At 1173 °C, tetragonal ZrO₂ undergoes a martensitic transformation to a monoclinic polymorph in which the Zr cations are coordinated to only 7 oxygens. The cubic and tetragonal phases cannot normally be quenched, but they can be stabilized at low temperatures by the replacement of Zr with up to 15 mol % of large aliovalent cations such as the lanthanides and yttrium.

The ZrO₂ nanoparticles investigated were synthesized by the decomposition of amorphous zones formed in highpurity synthetic single crystals of ZrSiO₄ (see Ref. [18]). This produces a mixture of nearly monodisperse, randomly oriented ~3-nm-diameter ZrO₂ nanocrystals embedded in a surrounding matrix of amorphous SiO₂ (Fig. 1). By employing digital intensity scans, we confirmed the presence of electron-diffraction maxima that are characteristic of tetragonal zirconia. The sample was then irradiated at ambient temperature with 1.0 MeV Xe^{2+} ions. This ion species and energy were selected to maximize the collisional damage while avoiding a significant implantation of a chemically active impurity. The sample was tilted so that the Xe ions were incident perpendicular to the specimen surface (Fig. 2). A low ion flux $[6.25 \times 10^{11} \text{ ions/cm}^2/\text{s}]$ avoided ion-beam-induced specimen heating. During irradiation, the temperature was monitored with a thermocouple placed $\sim 1 \text{ mm}$ from the specimen, and it did not rise by more than 1 °C. Electron irradiation effects were avoided by positioning the electron beam off of the sample except while taking the TEM images. This was especially important because the electron beam was found to slow the amorphization process. The measured ion fluence was converted to a displacement dose using a displacement energy of 40 eV for both Zr and O.

After a dose of 0.3 dpa, bright areas corresponding to crystalline regions in the TEM dark-field images began to disappear. Concurrently, an electron-diffraction halo characteristic of amorphous material grew more intense (Fig. 3), the rings specific to the tetragonal ZrO_2 phase disappeared entirely, and the polycrystalline rings corresponding to the cubic phase gradually grew fainter. At a dose of 0.8 dpa, only a faint trace of the



FIG. 1. High-resolution electron micrograph showing randomly oriented precipitates of ZrO_2 embedded in amorphous SiO₂. The rings in the electron diffraction pattern (inset) are labeled: *A*, (111) plane; *B*, (002) and (200) planes; *C*, (112) plane; *D*, (202) and (220) planes; *E*, (113) and (311) planes.

crystalline nanoparticles was in evidence; and finally, at a dose of 0.9 dpa, the ZrO_2 nanocomposite was completely amorphous. These results are to be contrasted with those obtained in prior work on bulk ZrO_2 that was irradiated to doses as high as 110 dpa, with no evidence of amorphization [15].

The data can be explained by the basis of the thermodynamic stability of the zirconia polymorphs relative to their surface free energies and defects introduced during the irradiation. Studies of binary alloy systems show that ion irradiation produces transitions to metastable states (e.g., Ref. [19]). As irradiation proceeds, point defects, defect complexes, and lattice strain can accumulate in the structure and increase the free energy of the initial compound to form a high-energy metastable phase. Bulk ZrO₂ exhibits precisely this behavior. At 300 K, the monoclinic



FIG. 2. Geometry of the experimental arrangement: A layer of nanocrystals (dark circles) is irradiated with 1.0 MeV Xe ions (solid arrows) incident normal to the specimen surface. The electron beam (dotted arrow) penetrates the specimen at an angle to form images and diffraction patterns on the TEM screen.

polymorph is the equilibrium phase. Room-temperature irradiation of monoclinic zirconia induces the transition to the tetragonal and cubic structures [12], probably as a result of the effects of accumulated oxygen vacancies [20]. From the thermodynamic point of view, these defects increase the free energy of monoclinic ZrO_2 until the stability field for tetragonal zirconia is reached. Eventually, a steady state is obtained at which the defect production and defect recombination rates are equal. Continuing the irradiation of bulk zirconia produces the cubic phase, but the amorphous state cannot be obtained.

In the nanocrystalline case, the situation is radically different. Although monoclinic zirconia has a lower molar free energy at room temperature, its surface energy (γ) is higher than that of the tetragonal phase. Therefore, a critical size should exist at which the total free energy of the



FIG. 3. Sequence of dark-field images and associated electron-diffraction patterns showing the effects of room-temperature Xe-ion irradiation on nanocrystalline ZrO_2 . The number in the bottom right corner of each diffraction pattern is the ion dose in dpa. The dark-field images were taken with the objective aperture centered over the bright (111) diffraction ring. The ZrO_2 nanocrystals diffracting through this aperture appear bright in the image. The larger-scale "patchy" appearance indicates local texturing. With increasing ion dose, the bright regions and the initially sharp diffraction rings due to the crystalline ZrO_2 phase gradually disappear, indicating the transformation to the amorphous state.

two polymorphs is equal. In a classic work, Garvie [21] derived a simple equation to calculate the critical radius for the stabilization of tetragonal zirconia nanocrystals:

$$r_c = \frac{-3\Delta\gamma}{\Delta\psi + \Delta\varepsilon}.$$
 (1)

Here $\Delta \gamma$ is the surface energy difference between the tetragonal and monoclinic phases, $\Delta \psi$ is the free energy difference for an infinite crystal, and $\Delta \varepsilon$ is the change in internal strain energy for embedded particles. The interfacial energies for an incoherent boundary (the case here) are 1.46 J/m^2 for monoclinic polymorph [21] and 1.10 J/m² for tetragonal structure [22]. $\Delta \psi$ is equal to $q(1 - T/T_b)$ where q is the heat of transformation per unit volume $(-2.82 \times 10^8 \text{ J/m}^3)$ and T_b is bulk transformation temperature (1446 K). The strain energy term for this system is not known; however, for tetragonal zirconia crystals embedded in monoclinic zirconia, the strain energy is $\sim 0.46 \times 10^8 \text{ J/m}^2$. For T = 300 K, Eq. (1) gives $r_c = 6.1$ nm. Below this diameter, the tetragonal structure is the thermodynamically stable form of ZrO_2 , as supported by recent experimental evidence [23]. If strain is completely relieved by volume expansion of the thin TEM foil, then the critical radius is 4.8 nm. Either way, our particles are much smaller than the critical size for the formation of tetragonal zirconia.

The formation of amorphous zirconia should depend on a delicate balance between bulk free energy and surface free energy of zirconia polymorphs and the defect free energy introduced in a high-radiation environment. Irradiation of bulk zirconia cannot produce the amorphous state because the free energy of the system cannot be raised sufficiently high. By forming the zirconia as tetragonal nanocrystals, however, the free energy of the system is at least 1.10 J/m² higher at the outset. This corresponds to over 70 kJ/mol for particles with r = 1.5 nm. By starting off higher on the free energy "ladder," ion irradiation can increase the total free energy significantly above the level that it could reach for bulk zirconia—sufficiently far that amorphous zirconia may be formed. Adding to this effect, both defect recovery and recrystallization are known to be less efficient when the recrystallizing phase is outside of its normal stability field [24]. At this point, it is not straightforward to quantify the various defect energies, however, since the free energy of amorphous zirconia is also not known.

Other mechanisms may contribute to the striking difference in the radiation resistance of bulk versus nanocrystalline zirconia. First, ion-beam-mixing effects may dilute the chemistry of the ZrO_2 nanocrystals. Figure 4a shows the microstructure of ion-beam-amorphized $ZrSiO_4$ prior to nanocrystal formation. The material has a mottled contrast on a scale of 1 nm—typical of an amorphous material. Figure 4b shows the same specimen after the thermal precipitation of ZrO_2 nanoclusters. The nanoclusters appear as dark regions averaging ~ 3 nm in diameter.



FIG. 4. (a) Microstructure of amorphous $ZrSiO_4$. The specimen was subsequently heated to 925 °C to induce phase separation and precipitation of ZrO_2 nanoparticles (b). The sample was cooled to room temperature and then irradiated with 1.0 MeV Xe^{2+} ions to a dose of 1.5 dpa (c). Finally, the specimen was heated to 800 °C to reprecipitate the ZrO_2 nanoclusters.

After irradiation to a dose of 1.5 dpa at room temperature, the ZrO₂ nanocrystals have been amorphized; however, in this specimen, there are regions of dark contrast that are not present in the original amorphous ZrSiO₄ (Fig. 4c). These dark-contrast areas have the same dimensions as the original ZrO_2 precipitates. The specimen was reheated in the electron microscope, and at 800 °C, the ZrO₂ precipitates recrystallized (Fig. 4d). Since this temperature is considerably lower than that at which the particles originally precipitated, this provides additional evidence that the materials in Figs. 4a and 4c are different. Care was taken in obtaining the results shown in Fig. 4 to ensure that the images were acquired at the same area of the specimen under identical defocus conditions. Finally, energy-dispersive x-ray analysis was used to obtain the chemical composition of the four microstructures shown in Fig. 4. Broad-beam microanalysis showed that some large regions of the irradiated specimen were more than 80% ZrO₂ by weight, implying silica loss during high-temperature irradiation.

The ZrO₂ nanoparticles were also irradiated with 280 keV Ne⁺, which results in smaller, less dense atomic displacement cascades. The particles were readily amorphized by Ne⁺ irradiation, consistent with the defect-driven thermodynamic approach. This also implies that changes in the structure and size of collision cascades may not affect the amorphization mechanism. Finally, specimens containing 3-nm-diameter precipitates of Au embedded in amorphous SiO₂ were irradiated with 1.0 MeV Xe ions. These metal particles did not amorphize, in direct contrast to the case for ZrO₂. The thermodynamic properties of Au are very different from those of ZrO₂, as evidenced by the lack of high-temperature metastable phases and its relatively low surface free energy, and defects can readily recombine due to lattice site equivalence.

The present experiments suggest considerable future For example, the thermodynamic hypothesis work. predicts that it should become more difficult to amorphize larger particles due to the decreased surface contribution to the total free energy. Our thermal decomposition technique is not suitable for producing larger ZrO₂ nanocrystals; however, in a preliminary experiment, a monoclinic ZrO₂ crystal several hundred nm in diameter was irradiated with 1.0 MeV Xe^{2+} . This crystal did transform to either the tetragonal or cubic phase, but it did not become amorphous. In addition, the electron beam was observed to slow the rate of amorphization in some specimens, probably as a result of specimen heating or enhanced defect mobility due to radiolytic processes. Finally, the effects of embedding the nanocrystals in different hosts or using "freestanding" ZrO₂ nanoparticles would shed considerable further light on the amorphization mechanism.

To conclude, in nanocrystalline zirconia the thermodynamic stability under irradiation is a delicate balance between the bulk free energy and surface free energy of its various polymorphs and the defect free energy introduced by energetic ions. The excess surface free energy in nanocrystalline zirconia tips the balance in favor of radiation-induced amorphization. The present results show that a structural ceramic material such as zirconia that is extremely resistant to the effects of ion irradiation in bulk form may become susceptible to radiation damage when formed as embedded nanoscale precipitates. Clearly, the behavior of bulk phases under irradiation cannot be used to directly predict the response of nanocrystalline composites. There are a number of implications associated with these findings: Nanocrystalline composites have many attractive structural properties (e.g., light weight, high hardness, and durability) for future spacecraft applications [25], and they may become integral components of detectors and sensors subject to exposure to a wide spectrum of energetic ions. Solar heavy ions, in particular, are of sufficient abundance and energy to pose a significant hazard for spacecraft systems [26,27], especially for lightweight, minimally shielded vehicles or spacecraft traversing high-flux regions such as the Martian plasma sheet [28]. If significant displacive radiation damage occurs (either in isolated regions or of the entire nanocomposite), the electronic and mechanical properties of these composites may be degraded-potentially to the point of failure. Single-event upsets [29] and other types of adverse "single-ion" effects may also become more pronounced as microelectronics devices and circuitry shrink into the nano regime. The formation of nanocrystalline precipitates in proposed nuclear waste and containment materials (e.g., zircon [18]) could lead to enhanced amorphization and thermodynamic destabilization. Future work on the effects of both light- and heavy-ion irradiation on the properties of nanoscale materials will be crucial to the development of new materials that are appropriate for applications in high-flux radiation environments.

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