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Dimensional isotropy of 6H and 3C SiC under neutron irradiation

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A B S T R A C T

This investigation experimentally determines the as-irradiated crystal axes dimensional change of the common polytypes of SiC considered for nuclear application. Single crystal α-SiC (6H), β-SiC (3C), CVD β-SiC, and single crystal Si have been neutron irradiated near 60 °C from 2×10^{23} to 2×10^{26} n/m^2 (E > 0.1 MeV), or about 0.02–20 dpa, in order to study the effect of irradiation on bulk swelling and strain along independent crystalline axes. Single crystal, powder diffractometry and density measurement have been carried out. For all neutron doses where the samples remained crystalline all SiC materials demonstrated equivalent swelling behavior. Moreover the 6H–SiC expanded isotropically. The magnitude of the swelling followed a ~0.77 power law against dose consistent with a microstructure evolution driven by single interstitial (carbon) mobility. Extraordinarily large ~7.8% volume expansion in SiC was observed prior to amorphization. Above ~0.9×10^{25} n/m^2 (E > 0.1 MeV) all SiC materials became amorphous with an identical swelling: a 11.7% volume expansion, lowering the density to 2.84 g/cm^3. The as-amorphized density was the same at the 2×10^{25} and 2×10^{26} n/m^2 (E > 0.1 MeV) dose levels.

1. Introduction

Irradiation-induced anisotropic swelling of the hexagonal close packed crystal of α- SiC-based ceramics has been postulated historically [1–3], and recently implicated in, the irradiation-induced degradation of SiC ceramics. The root of this speculation has been the observed difference in the irradiation-induced properties (including strength) of irradiation-stable pyrolytic SiC (a faulted form of cubic β SiC) and certain SiC ceramics processed with hexagonal α-SiC. Such anisotropy and resulting degradation in properties does occur in many ceramics possessing trigonal crystal structures such as alumina (sapphire) [4,5] and hexagonal structures such as silicon nitride [6], aluminum nitride [7], and beryllium oxide [8]. It is therefore reasonable that α-SiC and other ceramics with a hexagonal crystal structure may display irradiation-induced differential expansion on the <a> and <c > axes leading to microcracking and loss of ceramic physical integrity.

For the case of single crystal alumina a modest ~0.1% dilation in the <a> axis occurs upon irradiation at ~400 °C, negatively trending as irradiation temperature is increased. A more exaggerated dilation in the <c > axis occurs as a function of dose occurs for the same 400 °C irradiation, resulting in just under 0.2% dilation, substantially increasing with irradiation temperature. This anisotropic expansion in the <a> and <c > direction has been implicated in the decreased mechanical strength that occurs by 1×10^{26} n/m^2 (E > 0.1 MeV) for alumina [1]. Similar, modest reductions in strength for polycrystalline alumina have been reported elsewhere in the literature [4,5]. For lower temperature irradiation (near 80 °C) [9], swelling along the <a> and <c > axes of alumina are essentially identical until about 2.5×10^{25} n/m^2 (E > 0.1 MeV) at which point the <c > axis exhibits slightly greater swelling. The anisotropic swelling of BeO at similar irradiation temperatures occurs in a more exaggerated fashion beginning at a lower irradiation dose. While the <a> axis monotonically expands to approximately 0.1% by 1×10^{25} n/m^2 (E > 1 MeV) the <c > axis expands to approximately 3.5% over the same dose range. The result of this large anisotropic expansion for BeO is the near complete loss of mechanical strength by 1×10^{24} n/m^2 (E > 1 MeV) [8].

The literature on the irradiation effects of SiC includes a wide array of SiC ceramics including those fabricated from hexagonal (α) or cubic (β) phases. A detailed discussion of the effects of irradiation on SiC properties can be found elsewhere [10]. Generally, the irradiation-stability of the β-phase SiC is founded on a relatively solid body of work on chemically vapor deposited (CVD) SiC, a highly-faulted form of pure β-SiC which can be of high purity. The

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stability of CVD SiC is generally contrasted with the instability of α and β SiC ceramics formed through conventional processing methods, which demonstrate rapid irradiation-induced degradation of engineering properties. For example, the initial 1972 work of Matthews and Hutchings [11] discusses the behavior of reaction-bonded α and β-SiC-derived ceramics irradiated to a few tenths of a dpa at 400 and 700 °C, observing significant strength loss. In that paper the ceramic degradation was attributed to differential swelling of the α-SiC and β-SiC as well as the Si phase present at the grain boundaries. In follow-on work Matthews [12] studied irradiated α-SiC powder, β-SiC powder, Si powders and their respective sintered ceramics finding little difference between the lattice-dilation of the two SiC polytypes at irradiation temperature above 400 °C and up to a few dpa. Neutron irradiation studies carried out by Matheney [2], Iseki [13], Price [14], Dienst [15] and Correli [16] all report significant strength decrease in conventionally processed α-SiC ceramics and with the general consensus of internal strain and lack of grain boundary cohesion as the driving force behind degradation. Li and coworkers [17] have carried out Si ion irradiation at 1000 °C of cubic 3-C SiC, reporting anisotropic crystal swelling, though attributed this anisotropy to a Si-substrate effect.

In one study on very low dose H implantation into β-SiC films an initial contraction along the <a> axis was observed by Jiang et al. [18] Constantini [19] and Kerbirioui [20] provide a comparison of the accumulation of lattice disorder and resulting mechanical properties in Cree single crystal α-6H–SiC and β-3C–SiC epitaxial layers indicating similar layer expansion. Pramono et al. [21] studied the effect of implanted helium on the swelling behavior of irradiated α-6H–SiC ceramics, providing data on the dilation of the <a> and <c > axes, showing them to be essentially equivalent for irradiation at 300 °C to 0.28×10^{25} (E > 0.1 MeV)

By comparing the available ion irradiation data with neutron irradiation data such as that of Matthews [12] and Price [22] it could be reasonably argued that no differential swelling exists between the most common α–6H and β–3C SiC polytypes. Moreover, it could be similarly put forward that no large difference exists in irradiation-dilation between the major axes of the 6H alpha polytype of SiC. This lack of an anisotropic swelling response to irradiation, in contrast to the hexagonal crystals above, could have a number of explanations including the lack of mobility for both Si and C vacancies as well as the Si interstitial at these irradiation temperature. Regardless, the absolute comparison of the relative swelling difference under neutron irradiation, if any, between cubic and hexagonal forms of SiC has not been directly demonstrated. As this question is of current practical interest to the community this work has been carried out to provide such a direct comparison.

2. Experimental

Materials selected for this comparative study were single crystal Hoya β-3C SiC, single crystal Cree Systems α-6H SiC, polycrystalline Rohm-Haas CVD SiC (a highly faulted β–SiC), and single crystal Si. All materials were highly pure, electronic-grade materials. Irradiation was carried out in the hydraulic tube or peripheral target tube position of the High Flux Isotope Reactor (HFIR) within a perforated “rabbit” capsule. The rabbit capsule consists of an aluminum tube (the rabbit) which has large holes drilled through the wall to allow HFIR coolant water to flow through and contact its contents. The HFIR coolant water enters the core at 49 °C and exits at 69 °C. Samples were located mid-core such that the exterior of the samples should be just above 60 °C. Samples were irradiated in a fast neutron dose range from 2×10^{23} to 2×10^{26} n/m^2 (E > 0.1 MeV) at a fast neutron flux of approximately 1×10^{19} n/m^2s corresponding to approximately 10^{-6} dpa/s. For this paper an equivalence of 1×10^{25} n/m^2 (E > 0.1 MeV) = 1 displacement per atom (dpa) is assumed. Square samples of approximately 6 mm on edge were used. The CVD SiC materials were nominally 2.8 mm thick while the α-SiC, β-SiC and Si samples were cut from wafers of 0.2 mm, 0.1 mm, and 0.5 mm thickness, respectively.

Following neutron irradiation the samples were removed from the rabbit container and ultrasonically cleaned first with ethyl alcohol and then immersed in hydrofluoric acid for approximately 30 min to remove any glassy surface layer that may have been present. Prior to x-ray examination samples were wrapped in kapton for radioactive contamination control. Lattice parameters of single crystals were measured using x-ray diffraction. X rays were generated using a Rigaku R200 generator with a Cu target operating at 45 kV and 100 mA. A Ge (220) crystal monochromator with slits selected for Cu $K_{\alpha 1}$ incident beam. The sample was mounted in reflection geometry on a 4-circle diffractometer; the angle of diffracted x-rays was determined using a Ge (220) crystal analyzer. X rays were counted using a NaI(Tl) scintillation detector. Instrumental resolution is 0.005° in 2θ. 2θ scans were taken for a series of Bragg reflections: (111), (002), (202), (113), (311), and (004) for SiC(3C) and Si; (0 0 0 6), (0 0 0 12), (1 0 -1 2), (1 0 -1 5), (1 0 -1 7), (1 0 -1 10), (1 1 -2 6), and (2 0 -2 4) for SiC(6H). The center of each Bragg reflection was found by least-squares fitting to a Gaussian profile. The lattice parameters were determined using a least-squares refinement of angles calculated using Bragg's law to measured Bragg angles. Swelling magnitude, determined based on X ray data, was quantified using the changes in these lattice parameters (5 reflections for the cubic materials and 7–9 reflections for the hexagonal materials) as a function of dose.

The microstructure of certain specimens were observed using transmission electron microscopy (field emission type JEM2100F at 200 kV). TEM foils were prepared using a focused ion beam system (FEI Versa 3D Dual Beam) operated at 30 kV for initial milling and at 2–5 kV for final thinning.

Physical dimensions were measured before and after irradiation using calibrated micrometers. However, a density gradient column (DGC) was utilized to determine (and report) immersion bulk density with calibrated floats and mixtures of methylene iodide and tetrabromomethane with much greater accuracy. It is noted that density calculated from physical dimensions and dry weight were in agreement. A representative column section is provided in Fig. 1. The denser, non-irradiated SiC samples are provided in the

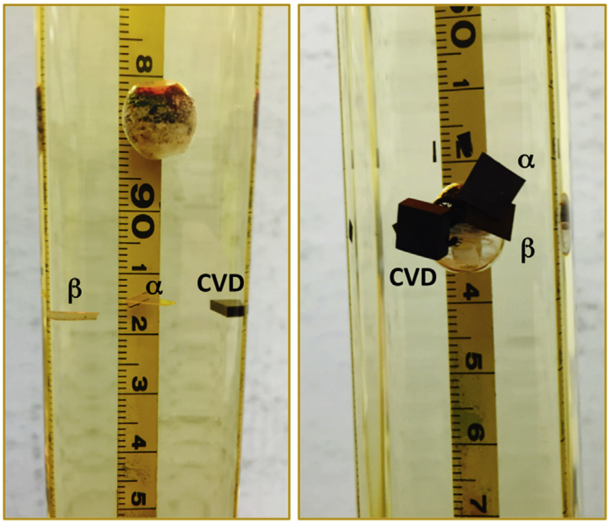

Fig. 1. Density gradient column with calibrated floats and groupings of non-irradiated and 0.5 dpa irradiated SiC samples.