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Neutron irradiation of sapphire for compressive strengthening. I. Processing conditions and compressive strength

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Abstract

Sapphire suffers a dramatic loss of *c*-axis compression strength at elevated temperatures. Irradiation of sapphire with fission-spectrum neutrons to an exposure of $\sim 10^{22}$ neutrons/m^2 in the core of a 1 MW fission reactor increased the *c*-axis compression strength by a factor of ~3 at 600 °C. Strength was similarly improved when 99% of slow neutrons ($\leqslant 0.1$ eV) were removed by ^{10}B and Cd shields during irradiation. Annealing at 600 °C for 10 min changed the yellow–brown color of irradiated sapphire to pale yellow, but had no effect on compressive strength. Annealing irradiated sapphire at 1200 °C for 24 h reduced the compressive strength to its baseline value. Transmission electron microscopy suggests that fast-neutron-induced displacement damage inhibits the propagation of *r*-plane twins which are responsible for the low compressive strength. When irradiated with ^{10}B and Cd shielding, sapphire that was not grown in iridium crucibles is safe for unrestricted handling after 1 month. Published by Elsevier Science B.V.

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1. Introduction

Sapphire is a single-crystal form of aluminum oxide (α-Al_2O_3) used as an optical window with exceptional mechanical strength and erosion resistance [1]. Its superior thermal shock resistance is degraded by loss of mechanical strength at elevated temperature. This strength loss is attributed to crack nucleation at intersecting twins on the crystal *r*-planes under *c*-axis compression (Fig. 1) [2–4]. Previous studies of BeO [5] and spinel [6,7] found a ~20–90% improvement in strength from neutron irradiation. For BeO, it was suggested that radiation-induced defects inhibited the dislocation movement necessary for crack nucleation [8]. Our work was motivated by the hypothesis that radiation-induced defects might retard twin propagation in sapphire and thereby increase its high-temperature strength. Sapphire is an ideal candidate for neutron irradiation because aluminum and oxygen are not readily transmuted into long lived radioactive species.

Neutron irradiation of sapphire has previously been studied for the application of sapphire as a window for fusion reactor systems. In most investigations, irradiation-induced defects reduced the strength of the material or had little beneficial influence [9,10]. However, neutron

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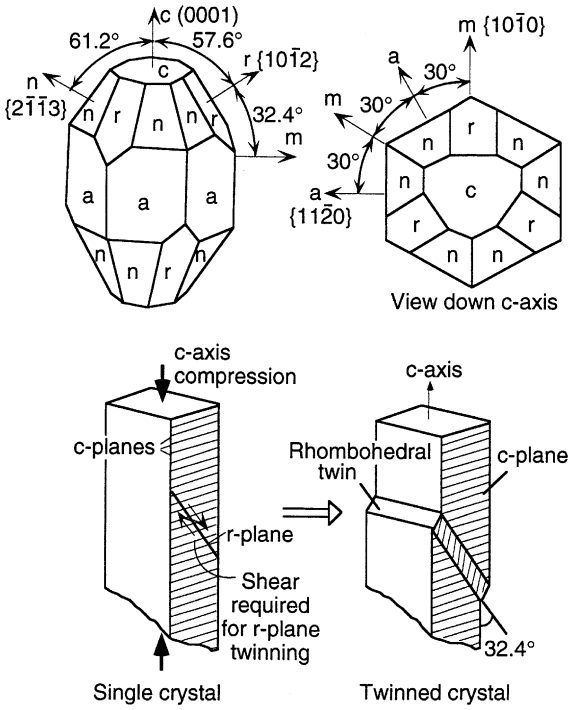

Fig. 1. Upper: Sapphire crystal showing mineralogical and Miller index notation. The *c*-axis is a three-fold symmetry axis, but sapphire is conventionally indexed on the basis of a hexagonal unit cell with the dimensional ratio $c/a = 2.730$. Lower: Schematic representation of *r*-plane twin formed by compression along the *c*-axis at elevated temperatures such as 600 °C.

fluences in these studies were typically 10^3–10^5 times greater than the fluences of 0.5–2.5 × 10^{22} n/m^2 (neutrons, n) in the present work. This paper describes processing conditions and their effect on compressive strength of sapphire at elevated temperature. The companion paper reports physical properties of irradiated sapphire [11].

2. Experimental

Irradiation of polished, Hemlite® grade sapphire [1] from Crystal Systems (Salem, MA) was performed at the 1-MW, steady-state, pool-type reactor at the University of Massachusetts, Lowell. The irradiation position used for this experiment was surrounded on two sides by the uranium fuel of the core, and located within the core's graphite reflector. This location provided a high flux of fast neutrons and, as a byproduct, the associated core gamma flux. Specimens were individually wrapped in Al foil and placed in a dry, air-filled radiation basket adjacent to the submerged reactor core for periods of ~15–200 h. (Polymer materials do not survive in the reactor, so Al foil was used to isolate the coupons from one another.) When neutron shielding was used, it was wrapped around the collection of individually wrapped specimens. Sample temperature did not exceed 100 °C during irradiation. Following irradiation, samples were washed with 8 M HNO_3, 48% HF, and water to remove surface contamination derived from the Al foil.

Mechanical testing was done at the University of Dayton Research Institute (Dayton, OH) with Instron testing machines at a crosshead speed of 0.508 mm/min. Specimens were heated at 10 °C/min and equilibrated at the final temperature for 10 min before testing. Tests were performed with or without 0.13-mm-thick Garlock 900 Grafoil® (UCAR Carbon Co., Cleveland, OH) between the sapphire and the fine ground silicon carbide test fixture [12,13]. Compression test cylinders (3.17 mm diameter × 6.35 mm long) were optically polished to a nominal scratch/dig specification [2] of 60/40 on all surfaces. The cylinder axis was parallel to the *c*-axis within 1° and ends were parallel to within 12′. Edges were typically not chamfered, but in a few cases they were chamfered.

Bright and dark field transmission electron microscope images of twin planes in sapphire were obtained on a Philips CM-30 300 keV instrument. Compression prisms and cylinders for these studies were prepared with the long axis tilted 20° off the *c*-axis toward an *r*-pole. Compression on the long axis at Sienna Technologies (Woodinville, WA, USA) preferentially activated twinning on one of the three sets of *r* planes [14]. For transmission electron microscopy, some unirradiated and irradiated (1 × 10^{22} n/m^2 [>1 MeV]) specimens were compressed until twinning, but not mechanical failure, occurred. Thin sections were then prepared by hand grinding and ion milling. Ion milling is undesirable because residual ion beam damage at the sample surface could be confused with neutron-induced damage. Attempts to thin samples by chemical milling (concen-

[1] Representative chemical analysis (μg/g) of sapphire from glow discharge mass spectrometry: Na, 0.6; Mg, 0.2; Si, 9; P, 0.1; S, 1; Cl, 3; K, 0.4; Ca, 1; Ti, 0.2; V, 0.1; Cr, 1; Mn; 0.06; Fe, 2; Co, 0.02; Ni, 0.1; Cu, 0.2; Zr, 0.1; Nb, 0.04; Mo, 0.2; W, 0.2; Li, <0.05; Be, <0.05; Ba, <0.05; La, <0.05; Ce, <0.05; Pb, <0.05; Bi, <0.05; F, <1; Zn, <1; Ga, <0.1; As, <0.1; Sb, <0.1; Cd, <0.2; Sn, <0.3.

[2] The first number of the scratch/dig specification is the scratch number, which is the width of the maximum allowable scratch in 0.1-μm units. The second number is the dig number, which is the maximum allowable diameter of a pit, bubble, pinhole or inclusion in 10-μm units. A scratch/dig specification of 60/40 permits no scratch wider than 6 μm and no dig wider than 400 μm. A more complete description is found in Military Specification MIL-0-13830A; American National Standard PH3-617, American National Standards Institute, New York (1980).

trated H_3PO_4 at 350 °C) or selective chemical etching of ion-damaged areas were unsuccessful. By comparing twinned specimens of irradiated and unirradiated sapphire, the neutron-induced defect structure could be unambiguously identified despite ion milling.

3. Results

3.1. Neutron irradiation

The predicted neutron flux at the sample position is shown in Fig. 2. The flux of fast neutrons (0.8–10 MeV energy) monitored by ^{32}S dosimetry [15] was typically 4×10^{16} n/m^2 s, subjecting a sample to 1×10^{22} n/m^2 in 70 h. Most neutrons pass through sapphire without being absorbed, so the absorption process is uniform through the sample volume. Nevertheless, for larger samples, a 180° rotation was performed after half of the irradiation to equalize the exposure from front to back.

For a fast neutron fluence of 10^{22} n/m^2, <0.1% of the atoms in sapphire are displaced from lattice sites. Of these displaced atoms, ~90% return to lattice sites and ~10% remain in interstitial sites [10]. The calculation of 0.1% displaced atoms comes from considering that the fraction of atoms displaced by neutron collisions with a 'thin' target is (total neutron fluence, n/m^2) × (displacement cross-section, m^2). For neutrons with energies of 1–10 MeV, Fig. 3 of Ref. [10] gives displacement cross sections for Al and O of $<10^3$ barns $= <10^{-25}$ m^2. For a fluence of 10^{22} n/m^2, the fraction of displaced atoms is $(10^{22}\text{n/m}^2)(<10^{-25}\ \text{m}^2) = <10^{-3}$. Each fast neutron collision displaces ~10^3 atoms [10]. Therefore the fraction of atoms suffering neutron collisions at a fluence of 10^{22} n/m^2 is $<10^{-6}$ (<1 ppm).

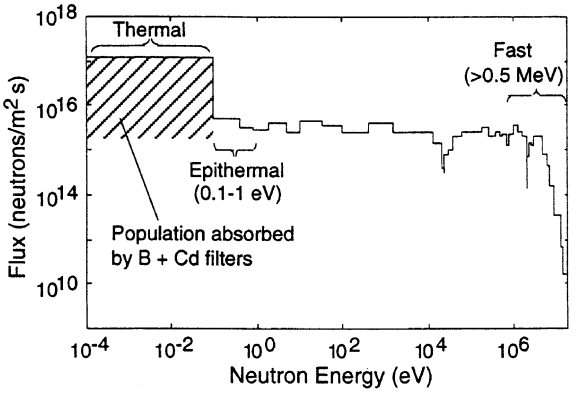

Fig. 2. Predicted neutron flux spectrum at the irradiation basket. Thermal neutrons have energies ⩽0.1 eV. Epithermal neutron energies are 0.1–1 eV. Fast neutron energies are ⩾0.5 MeV. A combination of boron and cadmium filters reduced the thermal neutrons by ~99%.

Absorption of a thermal (low energy) neutron by ^{27}Al causes transmutation to ^{28}Si:

$$(\text{n},\gamma)\ \text{reaction}: \quad {}^{27}\text{Al} \xrightarrow[\gamma\ \text{emission}]{\text{Neutron absorption}} {}^{28}\text{Al} \xrightarrow[t_{1/2}=2.2\ \text{min}]{\beta\ \text{emission}} {}^{28}\text{Si}. \tag{1}$$

Reaction (1) is abbreviated (n, γ) because it involves absorption of a neutron and emission of a γ-ray. Thermal neutron absorption by ^{16}O converts it to ^{17}O. ^{27}Al also absorbs fast neutrons (⩾2 MeV) in the (n, p) reaction, which requires a neutron and emits a proton:

$$(\text{n},\text{p})\ \text{reaction}: \quad {}^{27}\text{Al} \xrightarrow[\text{Proton emission}]{\text{Neutron absorption}} {}^{1}\text{H} + {}^{27}\text{Mg} \xrightarrow[t_{1/2}=9.4\ \text{min}]{\beta\ \text{emission}} {}^{27}\text{Al}. \tag{2}$$

^{27}Al can absorb fast neutrons (⩾5 MeV) in the (n, α) reaction, which requires a neutron and emits an alpha particle (a ^4He nucleus):

$$(\text{n},\alpha)\ \text{reaction}: \quad {}^{27}\text{Al} \xrightarrow[\text{Alpha emission}]{\text{Neutron absorption}} {}^{4}\text{He} + {}^{24}\text{Na} \xrightarrow[t_{1/2}=15\ \text{h}]{\beta\ \text{emission}} {}^{24}\text{Mg}. \tag{3}$$

^{16}O is converted to $^{16}N + {}^1H$ by the (n, p) reaction (⩾10 MeV) and the ^{16}N decays back to ^{16}O by β emission. ^{16}O is converted to $^{13}C + {}^4He$ by the (n, α) reaction (⩾2.5 MeV). It is shown below that all of these transmutation reactions proceed to an insignificant extent at the fluence of 10^{22} n/m^2 used in the present work.

Neutrons can transmute impurities in sapphire into radioactive isotopes that can pose a hazard to people. Therefore, sapphire from several sources was irradiated with the full fission spectrum of neutrons (containing a fast neutron fluence of 1×10^{22} n/m^2 plus the accompanying slow neutrons listed in the footnote of Table 1) to look for activated products. After 1 month of decay, radioactive products were measured by gamma ray spectroscopy with a Canberra High Purity Ge:Li detector. Table 1 shows that material grown by the Czochralski method (Union Carbide and Crystar Research) contains a high level of iridium impurity, making it unsuitable for this treatment. Iridium comes from the crucible used in Czochralski growth. Molybdenum crucibles used at Crystal Systems [16–18], Saphikon [19,20], and Rotem [21] do not introduce impurities that are incompatible with neutron irradiation.

To decrease residual radioactivity in irradiated sapphire, two shields were employed to absorb thermal neutrons. A 'borated aluminum' shield (Eagle-Picher Tech, Quapaw, OK, USA) contained the strongly absorbing isotope ^{10}B (4.2 mg/cm^2) dispersed in 1-mm-thick 6061 aluminum. Another effective shield was 1-mm-thick Cd metal. Most specimens were irradiated behind a combination of both shields, which reduced the population of thermal neutrons by ~99% (Fig. 2).

Table 1
Major activated impurities (pCi/g) in sapphire measured 1 month after a fast neutron exposure 1×10^{22} n/m^2[a]

Isotope (half life)	Crystal systems			Saphikon	Union Carbide	Crystar Research	Rotem Industries
	Ultra	White	Standard				
^{46}Sc (83.4 d)	480	492	145	2120	1370	40.9	262
^{51}Cr (27.7 d)	2120	3040	53.5	8040	59 100	2230	492
^{60}Co (5.27 y)	–	–	–	436	–	–	–
^{65}Zn (244 d)	–	–	128	–	–	41.7	34
^{95}Zr (64.0 d)	398	34.0	–	–	–	–	–
^{192}Ir (74.2 d)	–	–	–	–	426 000	40 200	57

[a] Sapphire suppliers: Crystal Systems, Inc., Salem, MA, USA; Saphikon, Milford, NH, USA; Union Carbide is now ICD Crystal Products, Washougal WA, USA; Crystar Research, Victoria, BC, Canada; Rotem Industries (Beer-Sheva, Israel). 'Ultra', 'white', and 'standard' are the three grades of material from Crystal Systems. Sapphire was exposed to the full spectrum (unfiltered) of neutrons from the reactor. The fast neutron fluence refers to neutrons in the energy range 0.8–10 MeV measured by ^{32}S dosimetry. Calculated neutron flux for full spectrum exposure is: >1 MeV, 2.0×10^{16} n/m^2 s; 0.1–1 MeV, 4.0×10^{16} n/m^2 s; >0.4 eV–0.1 MeV, 4.9×10^{16} n/m^2 s; <0.4 eV, 1.3×10^{17} n/m^2 s. Gamma ray flux = 4.4×10^{17} n/m^2 s.

Borated aluminum alone reduces thermal neutrons by ~95%, and reduces activation that occurs in the keV resonance absorption regions where Cd is not effective. Cd becomes highly radioactive during irradiation and tends to contaminate specimens and equipment. In contrast, borated materials with a relatively short half-life can be easily handled after a brief decay period. We recommend for future work that only the borated aluminum shield be used. Additional shielding from the Cd is not worth the hazard and expense of dealing with its radioactive waste. Sapphire irradiated behind thermal neutron shields was safe to handle and could be treated as nonradioactive one month after irradiation.

Calculated reaction rates for sapphire shielded with both borated aluminum and cadmium are shown in Table 2. The dominant reaction of fast neutrons converts 10 ppb of ^{16}O to ^{13}C + ^{4}He in 100 h. Thermal neutrons convert 9 ppb of ^{27}Al to ^{28}Si in 100 h.

The primary damage from neutron irradiation is not from the nuclear reactions in Table 2, but from collisions of fast neutrons with atoms in the lattice. The first atom struck by a fast neutron, called the 'primary knock-on atom', is energetic enough to create significant lattice disorder when it strikes its neighbors and they strike their neighbors. An average fast neutron collision in alumina results in ~1000 displaced atoms [10].

Table 2
Calculated reaction rates (reactions/m^3 s) at UML reactor position C-2[a]

Process	^{27}Al	^{16}O	Total
(n, α)	7.7×10^{13}	1.9×10^{15}	1.9×10^{15}
(n, p)	4.1×10^{14}	4.0×10^{10}	4.1×10^{14}
Thermal absorption (n, γ)	1.1×10^{15}	1.4×10^{10}	1.1×10^{15}
Non-thermal absorption	2.6×10^{15}	1.9×10^{15}	4.5×10^{15}
Total absorption	3.7×10^{15}	1.9×10^{15}	5.6×10^{15}

[a] Based on 1 MW reactor power with borated aluminum plus Cd shields. Calculated neutron flux with both shields is: >1 MeV, 2.0×10^{16} n/m^2 s; 0.1–1 MeV, 4.1×10^{16} n/m^2 s; >0.4 eV–0.1 MeV, 4.4×10^{16} n/m^2 s; <0.4 eV, 1.7×10^{15} n/m^2 s. Gamma rays, 2.6×10^{17}/m^2 s.

3.2. Effect of neutron irradiation on compressive strength

The goal of this work was to improve the compressive strength of sapphire for a proposed application at 600 °C. Therefore, the effect of neutron irradiation was evaluated by measuring the compressive strength of *c*-axis sapphire cylinders at 600 °C. Fig. 3 shows that the compressive strength of sapphire increased with increasing neutron dose.

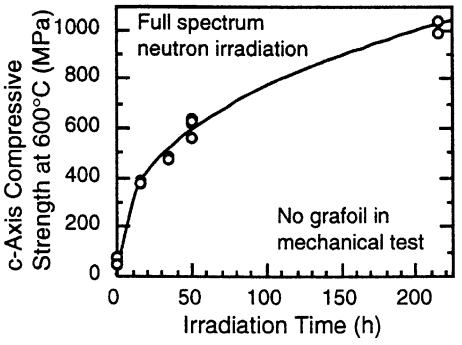

Fig. 3. *c*-Axis compressive strength of sapphire at 600 °C as a function of irradiation time with fission-spectrum neutrons (i.e. no shielding). The spectrum of neutrons is described in the footnote of Table 1. An irradiation time of 70 h corresponds to a fast neutron flux of ~1×10^{22} n/m^2. Specimens were not decolorized at 600 °C prior to testing and no Grafoil was used in the mechanical tests.

3.3. Decolorization

Neutron irradiation changes sapphire from colorless to dark yellow brown. The color intensifies with increasing irradiation. After heating to 600 °C for compression testing, the color lightened to pale yellow. It has been observed previously that alumina irradiated with 1.5×10^{24} n/m^2 had a dark yellow color that changed to white after heating at 1000 °C. At 600–800 °C, the material remained light yellow [22].

In this paper we distinguish the terms 'decolorization' and 'annealing'. Decolorization is a heat treatment at 600 °C intended to remove most of the color caused by neutron irradiation without significantly affecting strength. Annealing is a higher temperature treatment intended to reverse the strengthening effect of neutron irradiation.

The dark color of irradiated sapphire is undesirable for cosmetic reasons for some applications. Therefore we decolorized sapphire to pale yellow after irradiation by heating it in alumina boats to 600 °C at 10 °C/min, holding for 10 min, and ramping down at 10 °C/min. (After decolorization, samples continued to fluoresce under long wave UV exposure.) In one experiment, four specimens that had been irradiated with fission spectrum neutrons (no shielding) for 43 h were decolorized at 600 °C and then mechanically tested. The mean *c*-axis compressive strength was ~10% lower than that expected from Fig. 3, which we interpret as indicating that decolorization has little effect on mechanical strength.

3.4. Effect of filtering out slow neutrons and effect of gamma radiation

Cadmium and/or ^{10}B shielding was used during irradiation to reduce the flux of thermal neutrons by 95–99%. Shielding prevented the activation of impurities that would render the sapphire radioactive for many months after irradiation. Table 3 shows that there were no significant differences in the strength of sapphire irradiated with or without shielding. Because removal of 99% of thermal neutrons had little effect on the strength, we conclude that fast neutrons were primarily responsible for the observed strengthening, either by displacement damage or fast neutron transmutation.

Table 3
Effect of radiation shielding in *c*-axis compressive strength of sapphire at 600 °C[a]

Shielding	Strength ± standard deviation (MPa)	Number of specimens
None	653 ± 96	6
Cd	645 ± 67	10
Cd + ^{10}B	622 ± 57	10

[a] Measured with Grafoil after 60 h of irradiation. Incident neutron energies are described in the footnote to Table 1. Shielding removes much of the low energy neutrons.

Gamma radiation, which can also produce displacement damage in sapphire, could contribute to strength enhancement. However, defect production rates for high-energy core gamma photons are several orders of magnitude below that of a fast neutron [23]. The gamma photon flux from the reactor is 3.3×10^7 Rad/h. A fast neutron fluence of 1×10^{22}/m^2 exposed the specimen to 1.6 GRad of gamma radiation. To assess the effect of gamma radiation on strength, *c*-axis compressive coupons were exposed to a ^{60}Co gamma source for 504 h, which provided the equivalent of the gamma radiation received in ~30 h of neutron irradiation. (However, the spectral distributions of radiation from the reactor and the ^{60}Co source are different, with the reactor photon distribution shifted to higher energies.)

Fig. 4 compares the effect of ^{60}Co gamma radiation to the effects of neutron irradiation with Cd and/or B shielding. Gamma radiation does not account for very much of the strengthening observed after 30 h of neutron irradiation.

3.5. High-temperature annealing

If displacement-induced damage is the mechanism by which neutron irradiation increases compressive strength, we expected that at sufficiently high temperature, recombination or aggregation of point defects would return the strength to normal values. Table 4 shows the effects of high temperature annealing on strength. A 30 min anneal at 1000 °C had little effect on

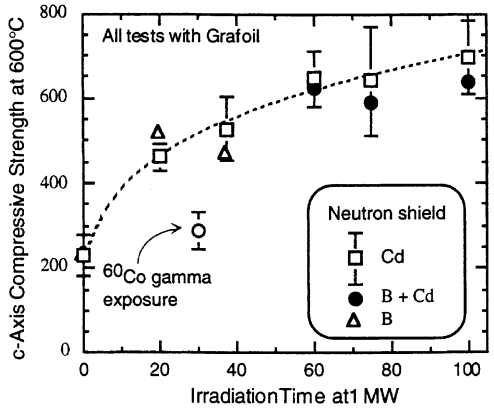

Fig. 4. *c*-Axis compressive strength of sapphire at 600 °C as a function of irradiation time with different neutron shields. Error bars show the standard deviation for data sets obtained with Cd shielding. Error bars are not shown for data from ^{10}B or ^{10}B + Cd shields. Specimens were decolorized at 600 °C prior to testing. The dotted line is only a guide for the eye. One data point shows ^{60}Co gamma irradiation equivalent to the gamma dose received in 30 h of neutron irradiation.

Table 4
Effect of annealing on *c*-axis compressive strength of neutron-irradiated sapphire at 600 °C[a]

Shielding used during irradiation	Annealing condition after irradiation	Strength ± standard deviation (MPa)		
		Before annealing	After annealing	Baseline strength (unirradiated)
Cd	1000 °C/30 min	697 ± 87[b,c]	619 ± 85[b]	~200[d]
Cd + ^{10}B	900 °C/20 h	638 ± 57[b,c]	465 ± 57[b]	~200[d]
^{10}B[e]	1200 °C/24 h		293 ± 123[e]	255 ± 56[e,f]

[a] *c*-Axis cylinders were irradiated with a fast neutron fluence of 1.4×10^{22} n/m^2. Strength was measured with Grafoil between the cylinder and the load blocks. Annealing was done in air with heating and cooling rates of 10 °C/min. There were five samples in each set.
[b] Crystal systems sapphire.
[c] Coupons decolorized with 600 °C/10 min anneal after irradiation.
[d] Taken from Table 1 of Ref. [11].
[e] Saphikon *c*-axis rods with polished ends with as-grown cylindrical surfaces.
[f] Saphikon material annealed at 1200 °C/24 h.

strength, whereas annealing at 900 °C for 20 h decreased the strength significantly, and a 1200 °C anneal for 24 h removed most of the strength derived from neutron irradiation.

As stated before, we distinguish decolorization at 600 °C from annealing at higher temperature. Decolorization removes most of the neutron-induced color without affecting mechanical strength.

3.6. Transmission electron microscopy of twin boundaries

For this experiment, *c*-axis sapphire cylinders and prisms with and without radiation treatment were compressed to their yield point, leaving intact *r*-plane-twinned specimens. Differences between irradiated and unirradiated material were observed at the twin boundary by dark field transmission electron microscopy. Fig. 5(a) shows that the step edges of the twin boundary in unirradiated sapphire are linear and evenly spaced at intervals of ~0.7 μm. In general, twin propagation in crystals occurs by motion of twin-boundary step edges, as illustrated schematically in Fig. 5(b). In the irradiated sample (Fig. 5(c)), the twin-boundary steps are irregular and unevenly spaced due to pinning at defect clusters, which appear as dark dots with diameters of 5–25 nm.

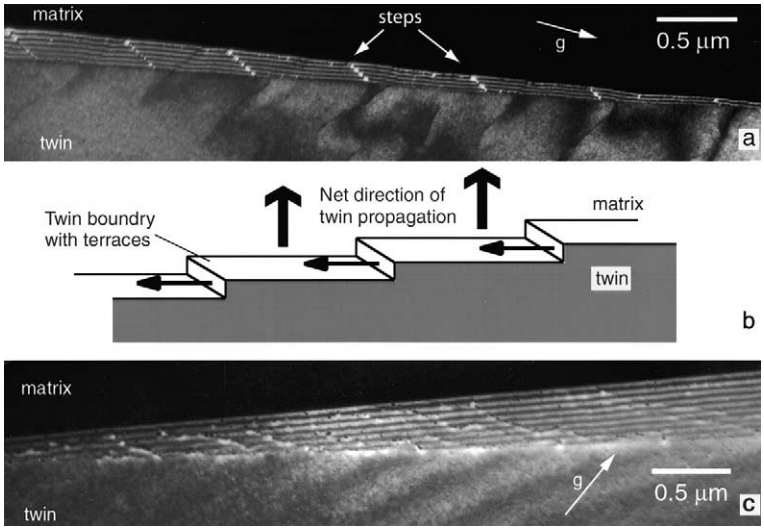

Fig. 5. Dark field transmission electron micrographs of twin boundaries in (a) sapphire and (c) irradiated sapphire. The **g** vectors, which indicate the orientation of the diffracted beam used to create the images, are $(11\bar{2}6)$ $(1\bar{1}04)$, for (a) and (c) respectively. The schematic (b) shows the evenly spaced step edges of a twin boundary propagating through the unirradiated sapphire crystal. In irradiated sapphire, defect clusters (dark spots in (c)) pin the motion of the step edges, leading to irregularly spaced, rough edges.

Table 5
Strength of $^{10}B_2O_3$-doped sapphire at 600 °C[a]

Mechanical test	Strength ± standard deviation (number of specimens)				
	Undoped unirradiated	$^{10}B_2O_3$-doped unirradiated	Undoped irradiated 1.0×10^{22} n/m^2	$^{10}B_2O_3$-doped irradiated 0.5×10^{22} n/m^2	$^{10}B_2O_3$-doped irradiated 1.0×10^{22} n/m^2
c-Axis compression	274 ± 85 [55]	512 ± 109 [5]	712 ± 85 [30]	692 ± 59 [5]	841 ± 71 [5]
c-Plane disk flexure	536 ± 119 [11]	586 ± 11 [2]	1285 ± 244 [13]	–	1040 ± 179 [5]
a-Plane disk flexure	760 ± 146 [10]	–	683 ± 262 [25]	–	734 ± 80 [5]

[a] All sapphire specimens were annealed at 1200 °C for 24 h in air prior to the experiments in this table. Neutron fluences refer to fast neutrons only. Specimens were exposed to the full spectrum of neutrons described in the footnote of Table 1. There was no Cd or ^{10}B shielding. Irradiated material was decolorized at 600 °C for 10 min prior to mechanical testing. $^{10}B_2O_3$-doped material was made at Crystal Systems by the Heat Exchanger Method [15,16] by adding 0.1 wt.% $^{10}B_2O_3$ to the Al_2O_3 charge. Tests were conducted with Grafoil between the sapphire and the test fixture. Data for undoped, unirradiated material and undoped, irradiated material are from Tables 1 and 2 in Ref. [11]. Ring-on-ring biaxial flexure tests of disks (38 mm diameter × 2 mm thick) are described in Ref. [11].

3.7. Effect of ^{10}B doping

For this experiment, sapphire was grown with 0.1 wt% $^{10}B_2O_3$ (99.59% ^{10}B from Eagle Picher, Quapaw, OK, USA) in the Al_2O_3 charge. ^{10}B has a large cross-section for neutron capture, so it decreases neutron activation of impurities in the sapphire. Absorption of a thermal neutron by ^{10}B leads to fission of the nucleus:

$$(n,\alpha)\ \text{reaction}: {}^{10}\mathrm{B} \xrightarrow[\gamma\ \text{emission}]{\text{Neutron absorption}} {}^{11}\mathrm{B} \xrightarrow[t_{1/2}=0.1\ \text{ns}]{\alpha\ \text{emission}} {}^{7}\mathrm{Li} + {}^{4}\mathrm{He}. \quad (4)$$

The kinetic energy of ^7Li (0.84 MeV) and ^4He (1.47 MeV) is rapidly transferred into the sapphire, producing significant displacement damage along relatively short pathlengths.

Mechanical effects of ^{10}B doping are shown for *c*-axis compression and two flexure orientations at 600 °C in Table 5. Without any irradiation, boron doping increased the *c*-axis compressive strength of sapphire from 274 to 512 MPa. The compressive strength of doped sapphire after 0.5×10^{22} n/m^2 irradiation (fast:thermal neutrons ≈1:2) was comparable to that of undoped sapphire after 1×10^{22} n/m^2 irradiation (692 vs. 712 MPa). Thus, ^{10}B doping had little effect on the flexure strength of unirradiated or irradiated sapphire.

4. Discussion

Weakness in *c*-axis compression of sapphire at elevated temperature was not identified until the 1980s [2]. Most research involving neutron irradiation of sapphire was performed in the 1960s, and was focused on low-temperature characterization. We find that neutron irradiation increases the *c*-axis compression strength of sapphire at 600 °C. Table 3 shows that the compressive strength of neutron-irradiated sapphire was approximately the same whether or not Cd or ^{10}B shielding was used to filter out 99% of the thermal neutrons. Therefore we conclude that fast neutrons (0.8–10 MeV energy) are responsible for the strengthening. Fig. 4 shows that exposure to gamma radiation equal to about half of that incurred during neutron irradiation had little effect on the compressive strength of sapphire.

Transmission electron micrographs in Fig. 5 suggest that the mechanism of compressive strength enhancement by low level (10^{22} n/m^2) fast neutron irradiation is slip pinning – retardation of twin propagation by defect clusters and, perhaps, isolated defects. These defects are metastable and can be thermally annealed at 1200 °C for 24 h, returning the material to its pre-irradiated state. If strengthening were due to transmutational doping, the strengthening would not be expected to be reversed by annealing. In previous studies at similar irradiation levels, annealing at temperatures of 1200 °C for 24 h allowed for recombination of defects. For higher irradiation levels, annealing caused isolated point defects to aggregate and form stable, large-nanometer-size defect clusters [22,24–26].

In one study, fast neutron irradiation at doses of 10^{26} n/m^2 at temperatures of 650–825 °C produced a high density of dislocation loops in sapphire [27]. In our experiments, the neutron fluence was only 10^{22} n/m^2 and temperatures did not exceed 100 °C during irradiation. After heating to 600 °C to conduct a compression test, no dislocation loops were observed by transmission electron microscopy. The only strengthening mechanism for which we have evidence in our specimens is slip pinning by the isolated defects observed on the twin plane in Fig. 5.

Filtering out slow neutrons with a ^{10}B-borated aluminum shield reduced residual radioactivity in the sapphire so that it could be treated as non-radioactive after 1 month. The dark yellow–brown color of the irradiated sapphire was converted to very pale yellow by annealing at 600 °C for 10 min with little effect on the mechanical strength.

Low levels of ^{10}B doping of sapphire (0.1 wt.% B_2O_3 in Al_2O_3) in conjunction with fission spectrum neutron irradiation enhance displacement damage. ^{10}B-doped sapphire attains the same *c*-axis compressive strength in 35 h of irradiation that requires 70 h for undoped material.

Neutron irradiation is effective for large components, as neutrons uniformly impart point defects (vacancies and interstitials) deep into the sapphire crystal lattice. Neutron processing is not limited to the shallow ranges typically associated with ion implantation because neutrons are not subject to coulombic forces. Their mean free path in sapphire is on the order of centimeters, compared to microns for accelerator-driven charged particles.

In conclusion, we find fast neutron irradiation of bulk sapphire, undoped or doped with ^{10}B, to be an effective treatment for compressive strength enhancement at 600 °C. The origin of this strengthening appears to be slip pinning of *r*-plane twins by radiation-induced defect clusters.

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