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Experimental simulation of the effect of transmuted helium on the mechanical properties of silicon carbide

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Abstract

Experimental results simulating the effects of transmuted helium on the mechanical properties of SiC are presented. High-purity, stoichiometric chemically vapor-deposited SiC bend bars were cyclotron implanted using 37.7 MeV α particles at 590 °C. A uniform implantation to 100 and 1000 appm was carried out, with a maximum implantation depth of ≃0.46 mm. Samples were then neutron irradiated to a dose of ≃8 dpa at 800 °C, thereby simulating atomic displacements at dose rates and temperatures similar to those of a fusion blanket, while in the presence of high helium levels of (≃125 appm He/dpa). Results on as-implanted SiC yield statistically significant changes in bend strength, indent fracture toughness and density. It is clear that these changes are in part due to the ≃0.1 dpa dose coincident with the helium implantation. Following neutron irradiation a larger change in properties occurs, though the difference between the helium pre-injected SiC, and the irradiated control samples was not statistically significant.

1. Introduction

It has been long apparent that ceramics undergo significant gas production, transmutation and material 'burn-up' under high-energy neutron irradiation. For example, the original calculations [1] for pure silicon carbide (SiC) exposed to 10 MW a/m^2 of 14.1 MeV monoenergetic neutrons yielded helium (≃16 000 appm), hydrogen (≃4400), magnesium (≃4500), beryllium (≃2300) and aluminum (≃72 appm), and some less significant transmutants. Clearly, helium is the largest product and, because of its limited diffusivity in SiC [2–4], may cause significant swelling and/or stress in the material. However, there are many mechanical property changes possible due to the fast-neutron transmutation of SiC. The production of the metallic impurities may increase creep as they will tend to migrate to grain boundaries and will, in most cases, be above their melting points for fusion applications. Also, the effect of material burn-up needs to be addressed, especially considering more than one percent of the atoms at the first wall have been transmuted at 10 MW a/m^2, possibly leaving behind gas, vacancies or other fugitive elements in their lattice sites.

Helium and hydrogen production (and corresponding production of Mg, Al and Be) are highly dependent on the neutron energy spectrum. This is demonstrated in Fig. 1, which gives the gas production as a function of the distance through the ARIES IV blanket [5]. Also included in this figure is the gas/dpa ratio. The helium production is ≃2000 appm at the first wall (for 1 MW a/m^2), and drops to <20 appm at the rear of the blanket region. From inspection of the He/dpa curve, the helium production is clearly a strong function of the neutron energy, ranging from 130 appm/dpa near the first wall to about 30 appm/dpa at the rear of the blanket region. In comparison, SiC produces significantly higher helium at the first wall than steel, though are similar at the rear of the blanket region. Specifically, stainless steel produces approximately 20 appm/dpa at the first wall and changes

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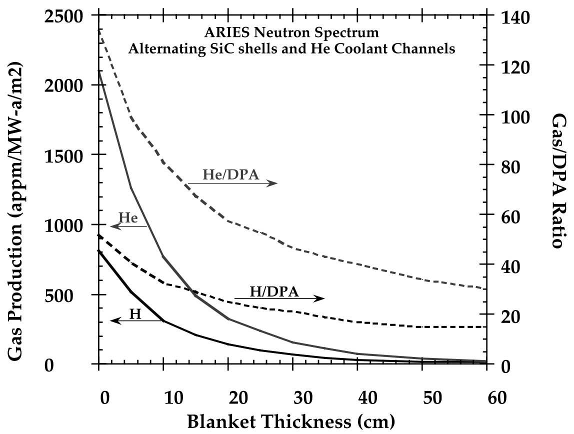

Fig. 1. Effect of fusion neutrons on the gaseous production in SiC [5].

by less than a factor of two at the end of the blanket region [6].

There has been limited study of high levels of helium on the mechanical properties of SiC [7–9] and SiC composites [10–14]. For the case of monolithic materials, helium was produced through the $^{10}B(n,\alpha)$ reaction. Boron acted as a sintering aid and was located at the grain boundaries. In one case, post-irradiation bend strength was seen to decrease [7]. However, this was more likely due to the anisotropic swelling of the SiC and grain boundary phases rather than a response to the presence of helium. For the case of SiC composite materials [10–14], helium was uniformly injected into a CVI SiC/Ceramic Grade Nicalon™ fiber composite and physical properties measured. Decreased bend strength and other fiber/matrix interfacial changes were observed in all cases. However, the amount of degradation (30–40%) is consistent with that expected given the displacement dose associated with the helium implantations for these early grade fiber composites. It was also speculated [12,14] that the helium implantation led to significant swelling (higher than 2% [12]).

The purpose of this work is to understand what effect will have the production of large amounts of helium will have on the mechanical properties of silicon carbide. Specifically, this is simulated by helium implantation followed by neutron irradiation at temperatures of low helium diffusion.

2. Experimental

Samples of Morton (now Rohm Haas) chemically vapor-deposited (CVD) SiC were machined into $1 \times 1 \times 25$ mm bend bars and polished and chamfered on one surface. The chamfer was in a 45° orientation removing $\simeq$0.05 mm from each side of the polished surface. The samples were helium implanted using the CMC-irradiation chamber [12] at the JRC Ispra. Samples were stacked side-by-side with their polished side facing the beam. A beam of 38 MeV helium ions was passed through a staggered, 50 aluminum foil, degrader wheel and rastered at 3 Hz. The approximate depth of uniform implantation was 0.4 mm. The irradiation temperature as measured with thermocouple was 600 °C. The implanted region was 4.5×10 mm^2 such that 10 samples were irradiated at one time over a length of 4.5 mm about the center of the longitudinal axis. The nominal helium implantation levels were 100 and 1000 appm. It is noted that discoloration in the CVD SiC (and a transparent single crystal specimen) was observed over an area of 6–7 mm about the center of the transverse axis of the sample indicating a certain amount of beam drift. Samples were tested in four-point bending at room temperature with a load and support span of 10 and 20 mm, respectively. The implanted side was placed in tension. Indentation hardness and toughness were measured using a Buehler micro-Vickers hardness tester at a load of 2 kg. It is noted that hardness was not measured for indents that caused spalling. Moreover, the effect of the cracking due to indentation was not evaluated. Fracture toughness was evaluated using the Evans–Davis model [15]. The density was measured using a density gradient column technique [16] with a mixture of diiodomethane and tetrabromethane and calibrated glass floats. A 30 min etch in hydrofluoric acid preceded the measurement. The accuracy of the density gradient column technique is on the order of 0.03%. The elastic modulus was measured using a Nanoindenter 2™ in the continuous stiffness mode. Neutron irradiation was carried out in the HFIR 14J experiment in the thermocouple monitored, temperature controlled, 800 °C section.

3. Results

Data on density, bend strength, Vickers hardness, elastic modulus and indent fracture toughness are given in Table 1. The density was measured by grinding away the non-implanted regions and by comparing to non-implanted regions. The non-irradiated density of CVD SiC was measured to be 3.203 g/cm^3. For the as-implanted SiC, the density decrease was found to be (0.26 ± 0.15)% for several samples tested. This variability in swelling is real and may be the result of non-uniform implantation. The swelling of the helium pre-implanted SiC increased to (0.9 ± 0.16)% following neutron irradiation.

3.1. As-implanted mechanical properties of CVD SiC

Bend data were analyzed using a two-parameter Weibull treatment. Due to limitations in obtaining a

Table 1
Physical property data of silicon carbide

	He pre-implanted			He pre-implanted and neutron irradiation		
	Virgin (29 obs.)	100 appm (10 obs.)	1000 appm (9 obs.)	8 dpa (31 obs.)	100 appm (14 obs.)	1000 appm (14 obs.)
Irradiation temperature (°C)	–	590	590	–	800	800
Swelling (%)	0	–	0.26 ± 0.15	0.9 ± 0.03	0.9 ± 0.03	0.9 ± 0.03
Bend strength (MPa)	353 ± 72	474 ± 127	532 ± 122	540 ± 138	585 ± 162	554 ± 130
Indent fracture toughness (MPa/m$^{1/2}$)	1.4	1.2	0.9	1.2	–	–
Vickers hardness (kg/mm^2)	2257 ± 103	2381 ± 120	2516 ± 180	2632 ± 65	2688 ± 230	2574 ± 127
Elastic modulus (GPa)	527	515	490	448	–	–

large number of implanted samples, the number of tests per irradiation condition was less than the 15–30 recommended for Weibull analysis. However, statistical analysis suggests a real increase in bend strength for the as-implanted, and the neutron irradiated material in all cases. The variability quoted is the calculated Weibull standard deviation. Specifically the bend strength has increased $\simeq$34% at the 100 appm injection level, and $\simeq$51% at the 1000 appm level. Elastic modulus for the as-implanted SiC is seen to decrease from a non-implanted value of 527 to 515 GPa for the 100 appm injection level, and to 490 GPa for the 1000 appm level. The Vickers hardness showed a slight increase of $\simeq$5.5 and 11.5% in the 100 and 1000 appm conditions, respectively. However, the statistical variability given as $\pm$1 (normal) standard deviation is a substantial fraction of this change. The indent fracture toughness shows a slight decrease following implantation.

3.2. As-implanted and neutron irradiated properties of CVD SiC

The results of samples implanted with helium and then neutron irradiated are also given in Table 1. Additionally, material was neutron irradiated without helium implantation for comparison. It is seen that the strength of the neutron irradiated, non-implanted CVD SiC has increased 52%, which is comparable to the increase seen in the non-neutron irradiated, 1000 appm helium condition. Again, there is significant intrinsic variability in the data amounting to approximately $\pm$(20–25)% ($\pm$1 Weibull standard deviation.) Following this, no statistically significant difference is seen between the neutron irradiated and the neutron irradiation + helium implanted materials.

4. Discussion

This experiment has attempted to determine what effect the presence of helium in large quantities, and in defect configurations relevant to a fusion application, will have on the mechanical properties of SiC. Obviously, pre-implantation followed by neutron irradiation is not a perfect simulation of what would occur due to exposure to a fusion neutron spectrum. However, the experimental design was to investigate fusion-relevant He/defect configurations by providing lattice displacements in the presence of helium. The typical fusion application temperature for SiC is in the 600–1000 °C range. In determining the helium implantation temperature, 590 °C was chosen as a trade-off between desiring low helium diffusion, and minimization of elastic damage caused by implantation. Fig. 2 gives the helium diffusion coefficient in SiC as a function of temperature [3]. Also plotted on the figure is the temperature-dependent swelling in CVD SiC both from the present and previous [17–19] work. From the data of Fig. 2 it is clear that there is an order of magnitude difference in diffusion between the implantation temperature and

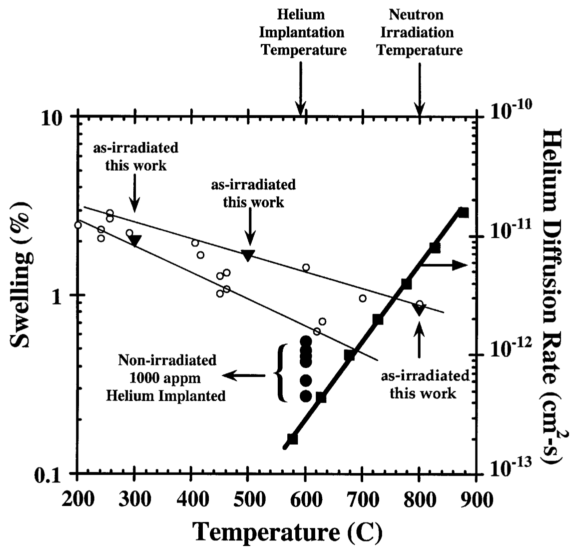

Fig. 2. Saturation swelling and helium diffusivity as a function of irradiation temperature.

neutron irradiation temperature. Separate work [4] on helium release indicates that helium produced in ≃650 °C irradiated SiC reaches its peak release rate at ≃1400 °C with ≃85% of original helium retained in the structure for annealing temperature <1800 °C. It is therefore reasonable to assume that the pre-implanted helium remained in the samples.

The helium implantation produces ≃0.1 dpa elastic damage, based on TRIM [20] calculations (sublattice averaged displacement energy of 30 eV is assumed). The saturation swelling in SiC at 590 °C based on the previous work (see Fig. 2) is ≃1.5%. Katoh [21] has experimentally determined that a dose of 0.5–1 dpa is required to produce saturation swelling at this irradiation temperature. Unfortunately, it was not possible to determine whether the swelling in the as-implanted samples is enhanced due to a helium-induced strain, or is simply due to the point defects caused by the implantation. However, upon annealing of the as-implanted specimen to 1000 °C, density returns to near the non-irradiated value, indicating that the swelling was due to simple point defects produced during the implantation.

Transmission electron microscopy (TEM) performed on the as-implanted samples showed no evidence of helium bubble formation in the matrix or on the grain boundaries. Based on previous TEM studies of bubble formation under helium irradiation and subsequent annealing [9,22], formation of helium bubbles is not expected below ≃1000 °C. Moreover, Sasaki et al. [4] showed that helium bubbles begin to form at ≃1400 °C near grain boundaries for 650 °C neutron irradiated, sintered SiC with ≃2000 appm helium produced via the $^{10}B(n,\alpha)$ reaction. Helium present only near the grain boundaries in the Sasaki et al. [4] work indicates a lack of vacancy mobility at the lower temperatures of the current study, thereby limiting the size of the helium clusters. Reinforcing this point is the work of Allen and Zinkle [23] who used ion channeling analysis on room-temperature he implanted single crystal SiC. In that study, it was further shown that helium is not located randomly in the crystal, but resides singly, or in small clusters, in vacancy sites.

An interesting question is whether the implanted helium was able to diffuse either during implantation, or neutron irradiation, to vacancies and whether these were then stabilized against recombination with migrating interstitials. As pointed out, it is unclear whether the as-implanted swelling of ≃0.26% is entirely caused by the point defect strain from helium elastic collisions, or whether the helium had any synergistic effect. However, the swelling of the as-implanted, neutron irradiated material is consistent with pure neutron irradiation data. Further investigation into the annealing characteristics of these materials would be useful.

From the physical property data of Table 1, there is clearly a change caused by the implantation process. Specifically, the hardness and bend strength are seen to change dramatically. It had been previously speculated [7] that helium produced via the $^{10}B(n,\alpha)$ degrades mechanical properties. However, that study used reaction bonded material with ≃8% free silicon, which had been previously shown [24] to degrade due to irradiation-induced differential swelling of the grain boundary silicon and the SiC grains. Further study is necessary to determine if the elastic damage due to the implantation in the current study was sufficient to induce the observed strength changes. However, it is clear from the data of Table 1 that there is not a significant effect of the presence of helium on the mechanical properties. Furthermore, it is noted that the strength of the non-implanted CVD SiC has shown a significant increase in strength with irradiation. This is contrasted with earlier work [25] on both hot-pressed and CVD SiC materials concluding that SiC underwent significant reduction in strength with irradiation. Results indicating a general increase in strength for CVD SiC over a wide dose and temperature range will be published elsewhere [26].

Another qualitative insight is gained by inspection of the indent following the hardness measurement. In many cases, the 1000 appm implanted material exhibited spalling caused by the indentation process. This was not seen for the non-implanted material, giving a further indication that the helium implantation reduced the fracture toughness.

5. Conclusions

A significant increase in strength, hardness, swelling and indent fracture toughness was observed following uniform implantation of helium in SiC at 590 °C. Bubble formation caused by the implantation was not observed, consistent with a lack of vacancy mobility at this temperature. Annealing to 1000 °C removed the swelling caused by the implantation, leading to the speculation that the helium is not strongly inhibiting the annihilation of migrating interstitials. It is not clear whether the presence of helium has affected the mechanical properties that would occur due to ≃0.1 dpa associated with elastic collisions caused by the helium injection. Neutron irradiation at 800 °C of identically pre-implanted material produced a further increase in strength, hardness and swelling. However, the presence of helium does not appear to affect these properties beyond that what occurs due to the neutron elastic collisions alone. At 8 dpa and 1000 appm He, CVD SiC is seen to increase in strength by more than 50%, the elastic modulus decreases by nearly 19% and the swelling is seen to be within the band typical of neutron irradiated SiC. These findings indicate that the presence of helium to these damage and He levels is not adversely impacting the mechanical properties of stoichiometric SiC.

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