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High Temperature Nanoindentation of Irradiated Silicon Carbide

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ABSTRACT

The demanding environment of future nuclear power systems will require improved irradiation resistance and high temperature mechanical performance from the applied component materials. The refractory ceramic silicon carbide (SiC) possesses excellent properties in this respect and is therefore being investigated for various applications within different reactor concepts. In a monolithic or composite form SiC could potentially replace metallic fuel cladding in commercial light water reactors and within gas-cooled high temperature reactors (HTR) SiC is already used as protective a coating for the safe encapsulation of fission products. For all these applications the accurate understanding of the mechanical properties at elevated temperatures is vital to ensure safe operation.

Here, the temperature evolution of the elastic modulus and hardness of irradiated SiC coatings has been measured by in-situ nanoindentation up to 500°C. The elastic modulus was found to be very stable over this temperature range, whereas the hardness exhibited a pronounced drop. Simulated HTR fuel that was irradiated in the High Flux Reactor (Petten, the Netherlands) at a constant temperature of 1000°C and to a fluence level of 2.05×10^{25} nm^{-2} (E>0.18 MeV) exhibited even slightly higher mechanical property values underlining the exceptional irradiation performance of SiC. Even though nanoindentation has been an established method in materials characterisation; the only lately achieved high temperature capability greatly improves our ability to measure and understand temperature and irradiation effects in materials and hence makes this technique a vital tool for materials development.

INTRODUCTION

Nanoindentation is a depth-sensing indentation technique that can simultaneously deliver values for the hardness and elastic modulus of a material. The measurement volume is typically in the micron-range, which makes this approach excellent to evaluate irradiation effects, since numerous tests can be executed on a small specimen. Thus, reports applying this technique for the characterisation of irradiation effects in various materials have been given in Osborne et al. (1999), Nogami, Hasegawa, and Snead (2002), Hosemann et al. (2012), Egeland, Valdez, and Maloy (2013), Yabuuchi et al. (2014). So far the majority of the nanoindentation studies have been conducted at room temperature, but recent developments have made facilities available that are capable of measuring in-situ up to several hundred degrees Celsius. However, testing reliably at elevated temperatures poses a number of specific challenges (such as thermal drift of the electronics or tip blunting (Everitt, Davies, and Smith (2011), Schuh, Packard, and Lund (2006)) requiring careful mitigation of these issues during the experiments. Hence, reports of irradiation effects on the mechanical properties measured over a temperature range are very limited up until now (Gibson, Roberts, and Armstrong (2015); Huang et al. (2014)).

Silicon carbide (SiC) ceramics exhibit an exceptional mechanical performance at very highly temperatures. Since they are also very resistant to neutron irradiation (Katoh et al. (2012)), recent efforts have sought to develop a new type of fuel cladding for commercial light water reactors (LWR) based on monolithic SiC or in its composite form to replace the currently used metallic materials (Hallstadius, Johnson, and Lahoda (2012)). The application of this refractory ceramic could greatly enhance the accident tolerance of the fuel assembly. In a nuclear context SiC has already been successfully applied in gas-cooled high temperature reactor (HTR) systems. This specific reactor type uses a fuel design where the fissionable material is in the form of a small sphere (500 µm) that is firstly coated with successive layers of low and high density pyrolytic carbon, followed by a SiC

coating (~35 µm thickness) and one further high density carbon layer. These so called tristructural-isotropic (TRISO) fuel particles are then embedded into graphitic blocks or pebbles building the reactor core. SiC coatings in TRISO fuel have been researched and developed over decades and a lot of valuable experience on the fabrication, mechanical performance and behaviour under irradiation has been gained. Although the environment of a HTR differs strongly from that of a LWR the available expertise will be greatly beneficial to the development of SiC fuel cladding.

The small and spherical specimen size of TRISO coatings prevent many standard characterisation methods, but nanoindentation measurements can deliver reliable values for the hardness and elastic modulus. Following we present the temperature evolution of the hardness and elastic modulus of SiC coatings in irradiated TRISO fuel as measured by in-situ nanoindentation measurements up to 500°C. In nanoindentation experiments the specimen is loaded using a sharp indenter tip and the displacement into the surface is recorded during the loading and unloading segment. From the resulting load-displacement curve (see Figure 1) the hardness and elastic modulus can be extracted using the approach by Oliver and Pharr (1992). They assume that unloading occurs fully elastically so the contact stiffness (S) is given by the slope of the unloading curve at any point. With a suitable fitting procedure the contact stiffness can be determined and the contact depth (h_c) is calculated by equation 1:

$$h_c = h_{max} - \varepsilon\beta\left(\frac{P_{max}}{S}\right) \tag{1}$$

The parameters ε and β are related to non-uniformities in the material and the indenter tip geometry, repsectively. With the appropriate area function (A_c) for the specific tip geometry the reduced elastic modulus (E_r) can then be calculated using equation 2. Which in turn gives the elastic modulus of the specimen using equation 3 with the suitable elastic modulus (E_i) and Poisson's ratio (υ_i) for the indenter tip material.

$$E_r = \frac{1}{\beta}\frac{\sqrt{\pi}}{2}\frac{S}{\sqrt{A_c}} \tag{2}$$

$$\frac{1}{E_r} = \frac{1-\vartheta_s^2}{E_s} + \frac{1-\vartheta_i^2}{E_i} \tag{3}$$

The hardness is calculated at the maximum load (P_{max}) with equation 4.

$$H = \frac{P_{max}}{A(h_c)} \tag{4}$$

EXPERIMENTS

The Samples and the Irradiation Experiment PYCASSO

The simulated TRISO fuel used for this experiment had been fabricated by CEA using their custom build fluidized bed chemical vapour deposition (FBCVD) facility and the fabrication conditions, dimensions and density (3.16 g/cm^3) have been reported in Obringer, Mollard, and Bianchini (2008), Perez (2008). As a substrate alumina kernels were used to reduce radiotoxicity of the specimens after irradiation. The irradiation was conducted over four months at the High Flux Reactor (NRG Petten, Netherlands) and a fluence level of 2.05×10^{25} nm^{-2} (E>0.18 MeV) was achieved. Throughout the irradiation campaign the samples were kept at a constant temperature of 1000°C, which was monitored by several thermocouples. A detailed description of the irradiation experiment can be found in Knol et al. (2012), de Groot et al. (2010). From the same fabrication batch pristine samples were available and measured here as well.

Microstructural Characterisation

Scanning Electron Microscopy (SEM) and Raman Spectroscopy was used to characterise the SiC microstructure in the pristine specimens. This was accomplished using a Quanta 650 FEG microscope (FEI) and a Renishaw 1000 Raman system with an Argon laser (514 nm). The elastic modulus evolution with temperature was also determined by Raman Spectroscopy following the approach described in Zhao et al. (2011). Therefore, the specimen (as prepared for the nanoindentation test) were placed on a hot stage and three Raman were taken at each temperature.

High Temperature Nanoindentation

The high temperature nanoindentation experiments were conducted with a nanoindentation facility (Micro Materials, Wrexham, UK) that is equipped with a hot stage and a separately heated diamond indenter tip. The complete facility is situated inside an atmospheric chamber, which was flushed with argon for experiments at 300°C or above to protect the diamond tip from oxidation. Several TRISO particles were dispersed in high temperature resistant cement and polished to the approximate cross-section. They were then fixed onto the hot stage with the same high temperature resistant cement. Three thermocouples were used during these experiments. The first one controls the tip temperature, the second sits inside the hot stage right below the heated surface and a third one was cemented onto the specimen surface. The temperatures were then adjusted so that tip and specimen surface temperature were in equilibrium, which is required to reduce thermal drift of the electronics during the measurement. Measurements were conducted up to 500°C in 100°C intervals. At least 25 indents were taken at each temperature to gain an average and indents were made on different coatings within the specimen to avoid the influence of local variations. The maximum load in all tests was 100 mN and loading and unloading were conducted over 20 s and 10 s, respectively. A holding period of 10 s at maximum load was used and thermal drift was determined before loading and after 90% of unloading was completed. Only measurements with drift rates below 0.15 nm/s were included in the analysis. The load-displacement curves were analysed by the Oliver and Pharr approach with the Poisson's ratio for diamond and SiC of 0.08 and 0.21, respectively. The elastic modulus of diamond is 1139.2 GPa at room temperature and was adjusted for the exact measurement temperature according to the formula given in Wheeler and Michler (2013).

The nanoindentation facility has been extensively calibrated before the start of these measurements using well documented reference samples (fused silica, CVD SiC and tungsten) with strongly differing properties. The contact area function was determined during room temperature measurements on fused silica using the indirect method as described in Herrmann et al. (2000). The same contact area function was used to analyse all indents within one specimen irrespective of the measurement temperature, since earlier investigations had determined that an error in the contact area function caused by the expansion of diamond would be 0.04% or less at 400°C, depending on the indentation depth (Schuh, Packard, and Lund (2006)). For each specimen all temperatures were measured in direct succession without cooling in between the different temperature settings.

RESULTS AND DISCUSSION

A selection of typical load-displacement curves taken at different temperatures is shown in Figure 1. At higher temperatures the loading slope was found to be slightly flatter, whereas the unloading slope appeared to remain unaffected. The maximum load hold of 10 s is necessary to avoid an overlying creep response during the initial part of the unloading section and it was not found to lead to an appreciable additional displacement at room temperature, but for temperatures above 300°C an increase in depth was noticeable and hence h_{max} increased significantly with temperature. This increasing displacement at constant load hold in indentation is customarily referred to as indentation creep. However, due to the very complex hydrostatic stress field in nanoindentation the material behaviour may differ significantly from the creep behaviour observed in standard testing approaches.

So indentation creep can be observed in materials that are usually extremely creep resistant such as SiC which is known to display creep behaviour only above 1400°C (Carter, Davis, and Bentley (1984)).

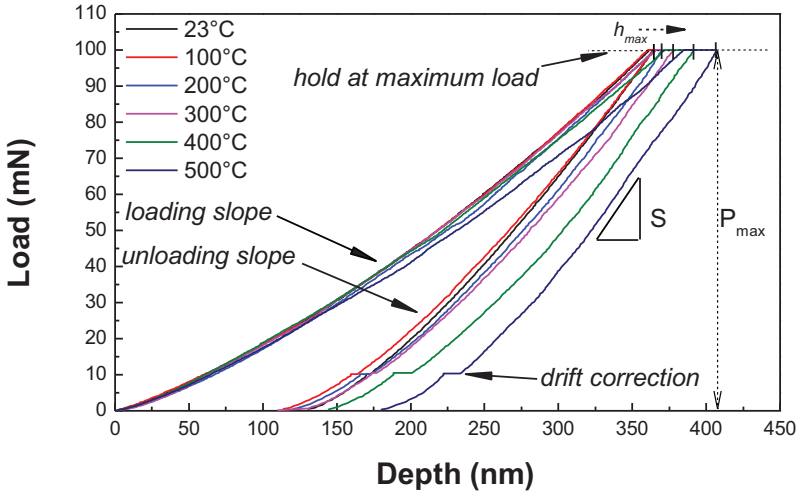

Figure 1: Typical load displacement curves from nanoindentation experiments at different temperatures.

The graphs in Figure 2a and b show the evolution of the elastic modulus and hardness values with temperature as measured by high temperature nanoindentation. The plots give the results obtained from the irradiated as well as the pristine specimens. At room temperature the hardness and elastic modulus were 34.2 ± 1.4 GPa and 369 ± 19 GPa, respectively. Both values are at the lower end of the range reported for SiC coatings in the TRISO fuel (Zhang et al. (2012), Hosemann et al. (2013)). However, fuel performance codes have used 370 GPa in their models (Verfondern (2011)). With increasing temperature the elastic modulus was found to decrease slightly. The elastic modulus of the pristine specimen has also been measured by Raman Spectroscopy and is shown in black in the same graph for comparison. Raman spectra characterise the atomic bonding in the specimen and thus the impact of any microstructural features (such as nanoporosity) on the elastic modulus are not reflected in these results. Hence higher elastic modulus values are determined by this approach. However, the temperature trend observed was found to be similar to the nanoindentation experiments, since only a slight decrease with temperature was detected. The irradiated specimen exhibited a marginally higher elastic modulus, which was within one standard deviation of the measurement. The observed temperature trend was the same in the pristine and irradiated sample.

The hardness decreased noticeably with increasing measurement temperature, which was particularly pronounced above 300°C. The irradiated specimen showed a slightly higher hardness of around 7% at room temperature and the hardness remained higher in the irradiated specimen over the complete temperature measurement range.

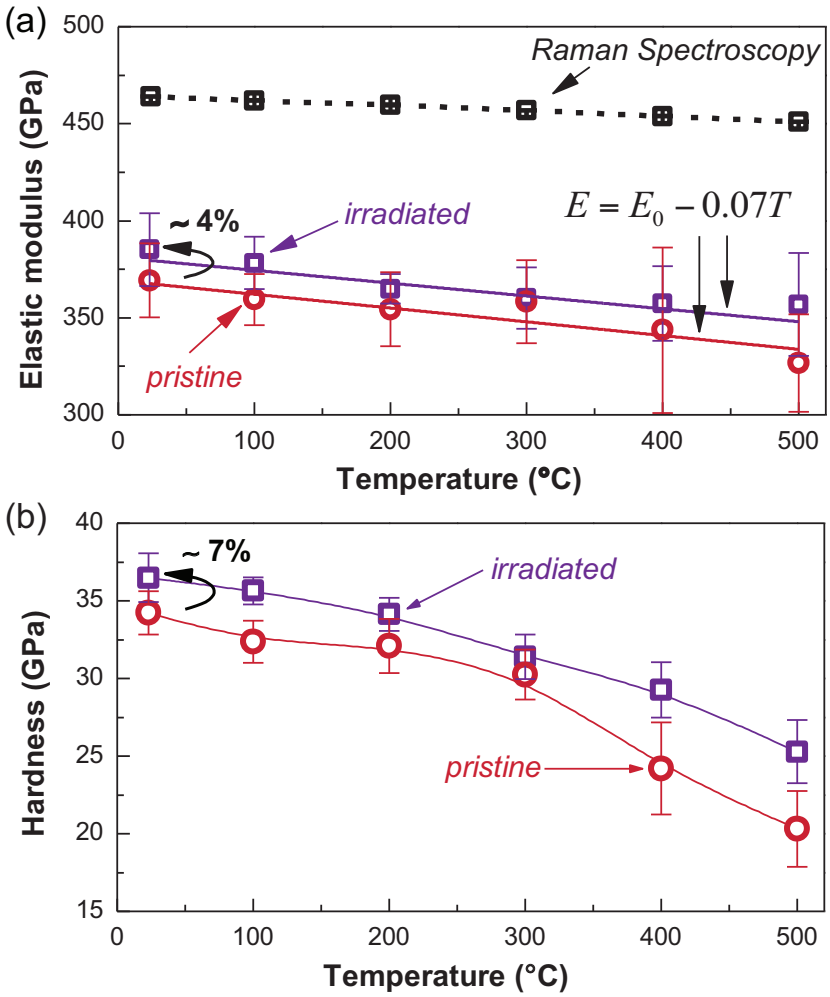

Figure 2: (a) Evolution of the elastic modulus with temperature; (b) Evolution of hardness with temperature. Error bars are one standard deviation.

To date there is little comparable data available. The results of two former studies conducting nanoindentation measurements on irradiated SiC are given in Table I. Both show that irradiation hardening occurs in SiC for different irradiation temperatures and the extent seen is in agreement with the results obtained here. Within their review Snead et al. reported that the irradiation hardening effect could be as high as 20% (Snead et al. (2007)). But the neutron irradiation effect on the elastic modulus is less clear. Very low irradiation temperatures (below 150°C) cause amorphisation in SiC, which in turn reduces the elastic modulus considerably. Also after irradiation around 500°C a decrease in the elastic modulus was detected, which was related to the observed swelling (Osborne et al. (1999)). For the irradiation conditions comparable to the ones of the samples examined here, no change in the elastic modulus was observed (Nogami, Hasegawa, and Snead (2002)). This was attributed to the fact that recombination of the point defects is possible above 1000°C and no swelling was observed in these samples. Considering that the scatter of individual nanoindentation results is in a similar range as the change measured between the pristine and irradiated specimen here, it cannot be established with certainty that the elastic modulus is affected by these particular irradiation conditions.

Table I: Literature data of nanoindentation experiments on irradiated SiC conducted at room temperature.

Elastic modulus (GPa)		Hardness (GPa)		Sample and Irradiation Experiment	Reference
pristine	irradiated	pristine	irradiated		
503 ± 15	421 ± 15 *(T_{irr}= 100 – 150°C)* 447 ± 15 *(T_{irr}= 500 – 550°C)*	36 ± 1	38 ± 1 *(T_{irr}= 100 – 150°C)* 40 ± 1 *(T_{irr}= 500 – 550°C)*	CVD SiC; 2×10^{25} n/m^2 (E > 0.1 MeV)	Osborne et al. (1999)
≈ 490 ± 25	≈ 490 ± 40	37.8	41	CVD SiC; T_{irr}= 1020°C; 1 dpa; 10^{24}-10^{25} n/m^2 (E > 0.1 MeV)	Nogami, Hasegawa, and Snead (2002)

SEM characterisation was executed on the polished cross-section of the coating and one representative image is shown in Figure 3. At the interface to the inner carbon coating the grains are very small, in the nano-metre range, and randomly oriented. Towards the central part of the coating the grains grow in size and develop an elongated shape along the deposition direction. Nanoindentation measurements have always been executed in the central part of the coating to avoid effects caused by the rim. Even though the density of the specimens was reported to be 3.16 g/cm^3 and thus slightly lower than theoretical density (3.21 g/cm^3), no porosity was visible in the SEM characterisation. Raman Spectroscopy was used to evaluate the stoichiometry of the SiC coatings. Raman spectra were taken on various locations within the coating cross-section and no variation was found. All spectra showed fully crystalline β-SiC without and traces of second phase silicon or carbon.

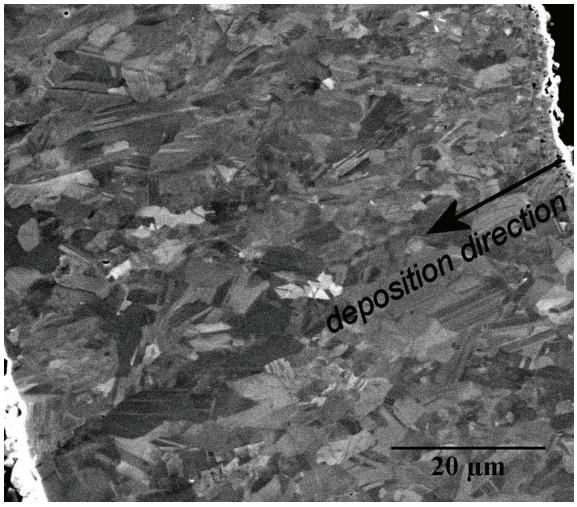

Figure 3: SEM micrograph taken on the polished cross-section of the SiC coating.

The experimental conditions during the "PYCASSO" irradiation were set up as an isolated effect study, hence the specimens were subject to realistic neutron environment but other factors, which are likely to have an effect, were excluded. Most importantly the chemical interactions from the fission products was fully avoided by using surrogate kernels. In respect to a potential application of SiC in an LWR environment the irradiation campaign is only of little resemblance, since LWR conditions vary not only in temperature, but also in coolant chemistry and the present neutron spectrum.

SUMMARY AND CONCLUSION

The presented results show that the elastic modulus of SiC coatings in TRISO fuel was not impaired by the prior irradiation test. A small reduction of the elastic modulus with increasing temperature was detected, which was in agreement with other measurement techniques. A noticeable irradiation hardening was observed, which appeared to be slightly more pronounced at higher measurement temperatures. Overall, the hardness was found to drop substantially over the temperature range measured here.

High temperature nanoindentation shows a great potential in the evaluation of irradiation effects on the mechanical properties of materials. Given a careful experiment conduction, reliable and accurate tests can be executed that will be beneficial to a better understanding of material performance.

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