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Short communication

In-situ nanoindentation of irradiated silicon carbide in TRISO particle fuel up to 500 °C

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ABSTRACT

The evolution of hardness and elastic modulus with temperature for silicon carbide (SiC) coatings in tristructural-isotropic fuel was measured by in-situ nanoindentation from ambient temperature up to 500 °C. Over this temperature range a significant drop in SiC hardness was identified, whereas the elastic modulus decreased only slightly with increasing temperature. The SiC coatings that had been irradiated in the High Flux Reactor in the 'PYCASSO' experiment exhibited irradiation hardening.

1. Introduction

Tristructural-**iso**tropic (TRISO) particles form the integral part of the high temperature reactor fuel design and an accurate knowledge of their mechanical properties is indispensable for the validity of applied fuel performance modelling codes. Even though nanoindentation is an established technique to measure the elastic modulus and hardness of individual TRISO layers at ambient conditions [1,2], in-situ testing at elevated temperatures has not been accomplished up until now. This work is the first to report on the hardness and elastic modulus evolution as measured by high temperature nanoindentation on silicon carbide (SiC) coatings in irradiated simulated TRISO fuel up to 500 °C.

2. Experimental procedure

The TRISO particle specimens were fabricated by CEA (France) in their own custom build fluidized bed chemical vapour deposition facility. The dimensions and characteristics of the different coating layers were determined after fabrication and are given in Table 1 with the respective deposition conditions. Alumina kernels were used as a substrate to minimize specimen activation during the later irradiation. These TRISO particles were irradiated within the PYCASSO I (Pyrocarbon irradiation for Creep and Swelling/Shrinkage of Objects) experiment at the High Flux Reactor (NRG Petten, The Netherlands). The irradiation experiment was set up as a separate effect test optimized to exclude thermal gradients, pressurization or chemical interaction within the fuel [3,4]. A constant temperature of 1000 °C was kept throughout the irradiation, which was assessed by thermocouples placed close to the specimens. Fluence levels were determined at the end of the five months irradiation period at a level of 2.05×10^{25} nm^{-2} (E > 0.18 MeV) in the samples examined here. Also measured in this study were pristine samples from the same fabrication batch.

The microstructural characterization within this work was conducted solely on the pristine samples. For scanning electron microscopy (SEM) and electron backscatter diffraction (EBSD) mapping a Quanta 650 FEG microscope (FEI) equipped with and EBSD detector (Oxford Instruments) was used. The EBSD data was reconstructed using the software channel 5. Misorientations higher than 15° were defined as high angle boundaries, whereas low angle

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Table 1
Coating layer fabrication conditions and specifications of pristine TRISO fuel for PYCASSO I [5,6].

Layer	Deposition temperature (°C)	Deposition gases	Diameter/layer thickness (μm)	Sphericity	Density (g/cm^3)
Alumina kernel	–	–	992	n.a.	3.88
Porous carbon (buffer)	1350	acetylene + argon	187 ± 17	1.030	1.07
SiC	1560	methyltrichlorsilane + hydrogen	59 ± 3	1.028	3.16
Pyrolytic carbon (PyC)	1340	acetylene + propylene + argon	39 ± 3	1.030	2.05

boundaries were between 1.5° and 15°. SiC stoichiometry was evaluated by Raman spectroscopy using the Argon laser (514 nm) of a Renishaw 1000 Raman system.

The high temperature nanoindentation experiments were carried out with a nanoindentation facility of a nominal high temperature capability of 750 °C (Micro Materials Ltd, Wrexham, UK) that allows an individual temperature control of indenter tip and sample. Initially extensive calibration of the facility has been carried out using fused silica, tungsten and commercially available CVD SiC as reference samples. A tip shape determination on fused silica was repeated after each measurement run at elevated temperatures. Three particles of either the pristine or the irradiated specimen were placed in high temperature resistant cement and both samples were polished by standard procedures to the approximate cross-section of the particles. Those were then mounted onto a hot stage using the same cement. Measurements at 300 °C or above were performed in an argon atmosphere. The maximum load in all tests was 100 mN, which was found to produce indent impressions with diagonals >1.5 μm thus always including more than one grain of the finely grained SiC coatings. At least 15 indents were taken at each temperature on different particles within each sample. Thermal drift was measured during a 60 s holding period before loading and after 90% of the unloading cycle was accomplished. Only measurements with drift of less than 0.15 nm/s were included in the analysis. The elastic modulus (E) and hardness (H) were calculated by applying the Oliver and Pharr-method [7] using the temperature adjusted elastic modulus value for diamond [8]. The Poisson's ratio for diamond and SiC were 0.08 and 0.21, respectively.

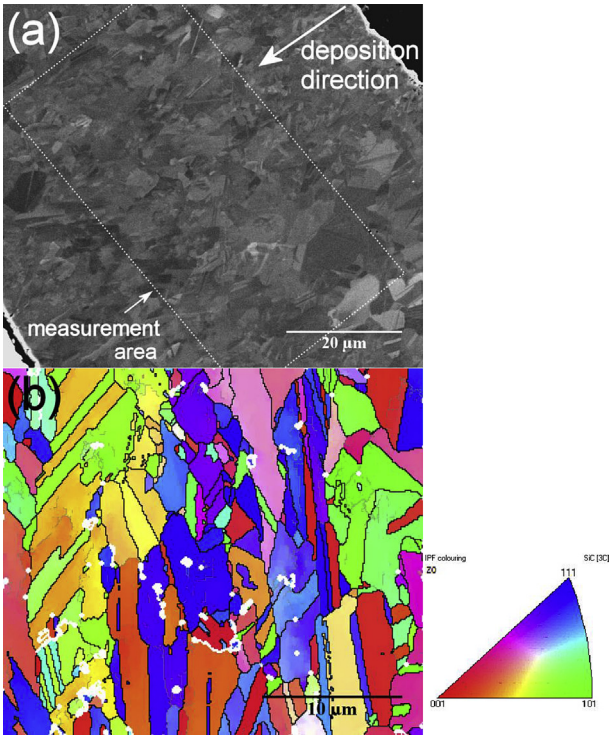

Fig. 1. (a) SEM image of the polished cross-section of the SiC coating layer with illustration of the approximate area for nanoindentation and EBSD measurements; (b) EBSD map of the coating cross-section; the deposition direction is from top to bottom. High angle grain boundaries are represented by thick black lines and low angle boundaries by grey ones (areas where indexing failed were left white).

3. Results and discussion

The grain morphology of the SiC coating layer consisted of radially oriented columnar grains that grow in size along the deposition direction. Indentation was always done in the approximate centre (as indicated by the white rectangle in Fig. 1a) of the coating to exclude potential effects of the rim. EBSD maps (Fig. 1b) were also taken in that central part of the coating and determined an average grain size of 1.4 ± 1.2 μm (only grains with diameters >0.3 μm were included in the analysis). Raman spectroscopy measurements indicated that the coating was fully crystalline and stoichiometric β-SiC containing a comparatively small concentration of stacking faults [9].

At room temperature the hardness and elastic modulus of the pristine specimens were 34.2 ± 1.4 and 369 ± 19 GPa, respectively, and both of these values were within the range reported for SiC coatings in TRISO fuel elsewhere [1,2]. The evolution with temperature as measured here by in-situ nanoindentation up to 500 °C is illustrated in Fig. 2a and b. After measuring the pristine specimens the indenter tip shape area function was adjusted for the occurred tip blunting before the irradiated specimens were mounted and measured. The elastic modulus was found to decrease slightly with increasing temperature, which is expected as the stiffness of the atomic bonds decreases, but the temperature trend was slightly more pronounced when compared with former reports using macroscopic testing techniques [10]. The nanohardness however showed a significant drop over the measurement temperature range. In Fig. 2c these hardness values were normalized to the room temperature hardness so that they could be compared with a microindentation study by Milman et al. [11] showing a somewhat comparable hardness degradation of SiC irrespective of the type (sintered and CVD SiC) or difference in applied load (50 N and 100 mN). The hydrostatic stress field generated during nanoindentation is capable of inducing dislocation mobility at much lower temperatures than seen in conventional mechanical testing and past indentation studies of SiC found micro-cracks and dislocation activity in the deformed volume even at room temperature [13]. The strong temperature dependency of the hardness suggests that dislocation mobility contributed noticeably to the deformation observed here.

The irradiated specimen exhibited slightly higher hardness values over the whole temperature range. No microstructural characterization was carried out on these particular specimens so far, but irradiation at a constant temperature of 1000 °C is expected to cause the creation of point defects and defect clusters [12] that could act as obstacles towards dislocation movement. At higher

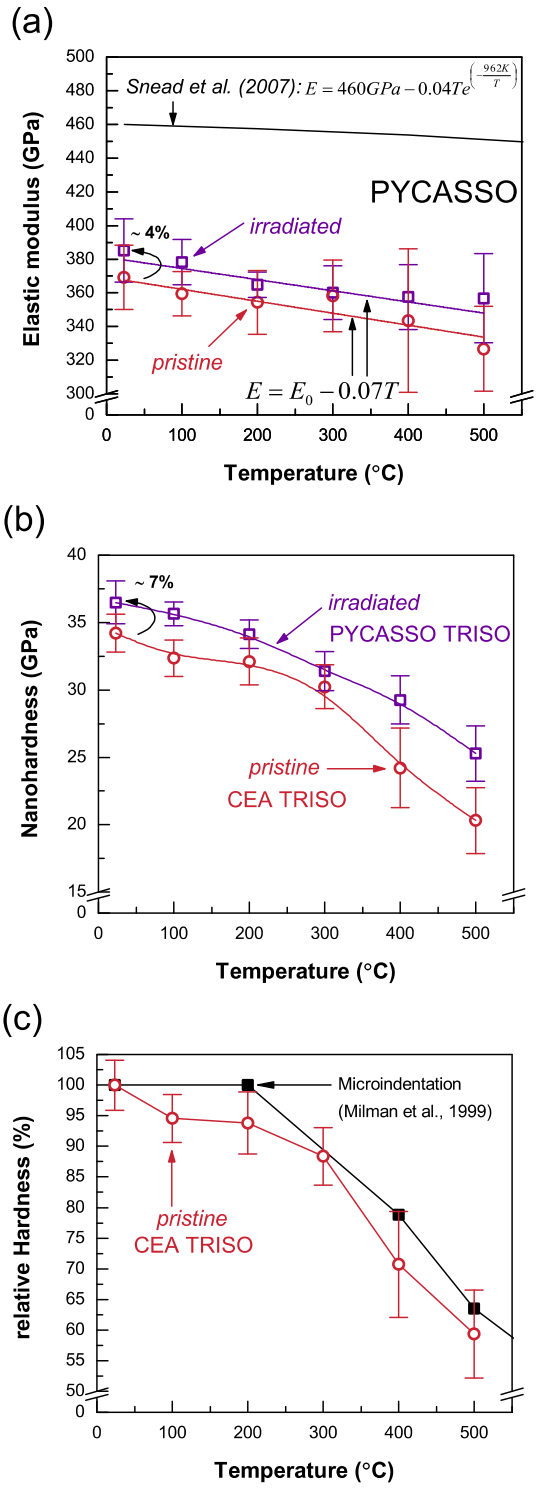

Fig. 2. Results of high temperature nanoindentation measurements of the pristine and irradiated PYCASSO samples (a) Elastic modulus with literature data [10]; (b) Nanohardness; (c) relative hardness compared with literature data [11].

temperatures the mobility of dislocations is enhanced and impeding their movement is more severe thus leading to a more obvious irradiation hardening effect at 500 °C, which was around 20% compared with the 7% at room temperature. Irradiation conducted at 1000 °C has been reported to have little effect on the elastic modulus of SiC [10] and also here the differences between pristine and irradiated samples were found to be minor with approximately 4%. The slightly higher values of the irradiated specimens were mostly within one standard deviation of the measurement. During the nanoindentation experiments, the temperature was significantly lower than during irradiation, thus annealing of point defects is unlikely to have occurred.

4. Summary and conclusion

This is the first report on the nanohardness and elastic modulus evolution of SiC in surrogate TRISO fuel as measured by in-situ high temperature nanoindentation. In the measurement range up to 500 °C the hardness was found to decrease substantially and some irradiation hardening was observed in the irradiated specimens. The elastic modulus showed only a slight reduction with temperature and the temperature dependency was not affected by irradiation.

It was shown that nanoindentation is a suitable technique for in-situ testing at elevated temperatures and a comparable measurement accuracy as in ambient conditions can be achieved if experimental settings are chosen carefully. However, deviations in the exact values obtained by nanoindentation compared with macroscopic testing techniques might arise due to the different stress field.

The presented results confirm the exceptional resistance of SiC against neutron irradiation and highlight its potential for application within a nuclear environment. However, the irradiation campaign “PYCASSO” was a separate effect study using non-active surrogates thus excluding chemical interactions completely. A more complex environment will affect actual HTR fuel in service.

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