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Mechanical properties of irradiated coated particle layers

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Summary

This deliverable describes the high temperature nanoindentation experiments conducted on simulated TRISO fuel that has been irradiated within the PYCASSO project. Within in-situ tests the elastic modulus and hardness were measured up to 500°C. Raman spectroscopy and scanning electron microscopy were used for an additional characterisation of the SiC microstructure. The elastic modulus was found to decrease steadily with temperature over the measured range, while the hardness showed a more pronounced drop, which was in accordance with literature data obtained by other techniques. The elastic modulus of the irradiated samples was slightly higher than in the pristine state, but the decrease with temperature was similar. There was an obvious increase in the hardness of the irradiated samples, which was around 7% at room temperature and more than 20% for the highest measurement temperatures suggesting that irradiation hardening has occurred. This data is the first of this kind and it will help to improve the database for current fuel performance models of HTR fuel. So far these codes had to rely on data generated on dummy specimens that differed from fuel, since the TRISO coating geometry does not allow the application of standardized mechanical testing. Here it was shown that the mechanical properties of hardness and elastic modulus can be measured with accuracy on SiC coatings at elevated temperatures that are closer to the operating conditions.

Approval

Date	By
19/09/2014	Steven KNOL
10/10/2014	Mathias LAURIE
10/10/2014	Steven KNOL

Distribution list

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P. Manolatos	EC DG RTD	Through the EC participant portal
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1. Introduction and Objectives

Within the Archer Project the mechanical properties nanohardness and elastic modulus of the SiC layer in irradiated TRISO particles are to be measured during in-situ tests at elevated temperatures with a nanoindentation facility. The measurements are executed at the University of Manchester (UK) with all the sample preparation carried out at NRG Petten (The Netherlands).

The Nanoindentation technique is well established for measuring the elastic modulus and hardness of thin films and coatings. However, conducting measurements at elevated temperatures poses a number of experimental challenges that complicate in-situ measurements significantly. Thermal mismatch of indenter and specimen can easily cause electronic drift or noise in the depth signal and thus this issue has to be mitigated carefully. Furthermore sample specific characteristics as time dependent plasticity can potentially produce misleading results if this behaviour is not accounted for. Nonetheless this technique is the only feasible experimental method to gain information about the elastic modulus at elevated temperatures in TRISO fuel. The sample geometry of spherical coating layers does not allow any other, more standardized, methods as bending tests. One significant advantage of nanoindentation testing is the high number of individual values that can be obtained within one small sample volume thus allowing a statistical evaluation, while gaining hardness values at the same time.

Two photographs of the High Temperature Nanoindentation facility (Micro Materials Ltd, UK) are shown in Figure 1.1.

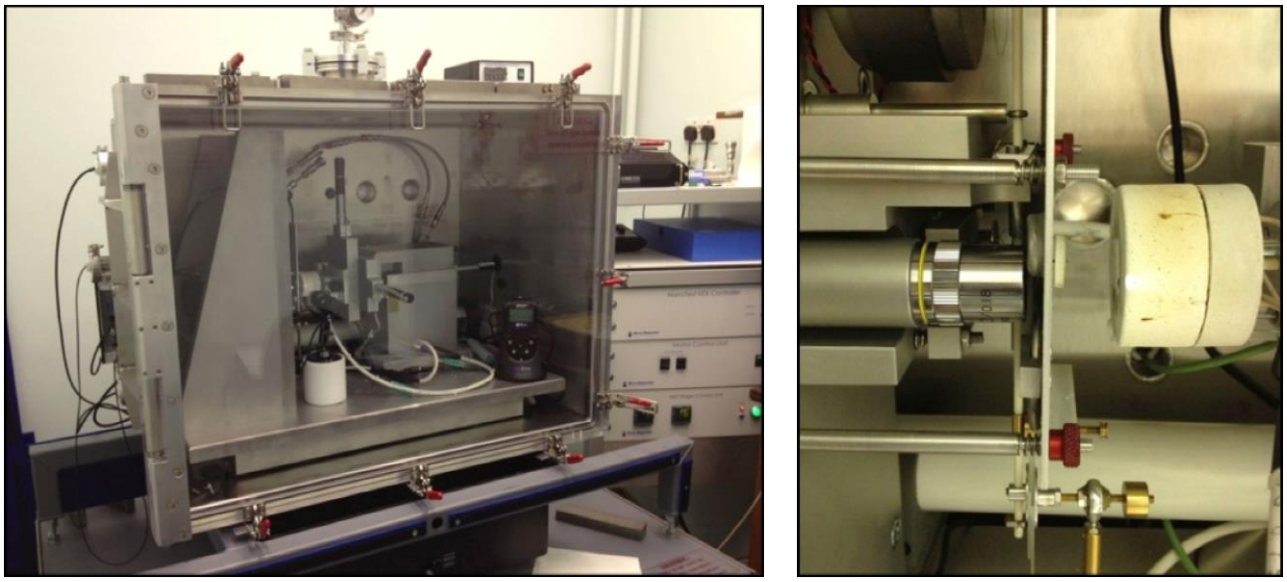


Figure 1.1: High Temperature nanoindentation facility at the University of Manchester. *Left:* The facility is situated inside an atmospheric chamber that is being purged with argon during tests at temperatures above 300ºC. *Right:* Closer view of the pendulum with the heated indenter tip and the hot stage.

2. The PYCASSO Project

The TRISO particles had been fabricated by CEA, France (J. M. Escleine) and consisted of an alumina kernel, buffer, SiC and OPyC layer (1,2). The PYCASSO-I (Pyrocarbon irradiation for Creep and Swelling/Shrinkage of Objects) irradiation campaign foresaw a constant irradiation temperature of 1000°C throughout and was designed specifically to allow accurate fluence determination and minimum specimen activation or chemical interaction. The irradiation campaign in the High Flux Reactor in Petten started in April 2008 and ran for 5 irradiation cycles, for 144 full power days (3).

The samples selected for the indentation measurements are of specimen code “PYC 2 (2/9) B1”, and are irradiated in the high fluence stack, tray 2 of the PYCASSO I irradiation experiment. The samples received a neutron fluence of $19.97*10^{24}$ m^{-2} (for E_n>0.18 MeV).

The primary aim of the PYCASSO-I project was to gain more information about the irradiation effects on pyrolytic carbon, in particular irradiation creep and swelling behaviour. Samples with and without a SiC coating layer were tested to evaluate its influence on the pyrolytic carbon swelling (4). Therefore the experimental design was optimized to exclude other effects in fuel under operation as thermal gradients, pressurization or chemical interactions by fission products. This allowed an isolated study of the pyrolytic carbon as well as the SiC behaviour under irradiation and the obtained data is used for improvement of fuel performance codes.

3. Sample Preparation for High Temperature Nanoindentation Tests and Additional Characterisation

Due to the lack of experience with the High Temperature Nanoindentation technique and the absence of comparable literature data a wide range of experiments on calibration samples have been conducted to ensure the validity of the results.

1.1 Bulk SiC for calibration

For the initial tests larger bulk samples of commercially fabricated CVD SiC were used since they do not require any embedding, which could potentially influence the measurement. Hence a thin disk (~2 mm) was cut from a bulk piece SiC (produced by static CVD (Rohm & Haas, US)) and was polished using standard procedures to a ¼ µm finish by OPS solution. This fully dense CVD SiC sample offers the best resemblance to the properties of the SiC coatings in TRISO fuel and was therefore used extensively here.

1.2 PYCASSO samples (fabricated by CEA, prepared for the experiments by NRG Petten)

Measurements on the TRISO particles were conducted on the polished cross-section of the spherical coating layers. Therefore the full TRISO particles were dispersed inside freshly mixed high temperature cement and

dried. Subsequently they were polished using SiC grinding paper and diamond paste of 1 µm. All polishing steps needed to be accomplished without the use of water, since the cement is water-soluble with the heat generated during polishing. The final sample has a thickness of less than 2 mm and is cemented onto the hot stage (see Figure 3.3).

Some micrographs of the samples as prepared for the tests are given in Figure 3.1 and Figure 3.2. Optical micrographs of the non-irradiated specimens show that the layers are evenly polished and good contact exists along the whole interface between the SiC and pyrolytic carbon layers (Figure 3.1).

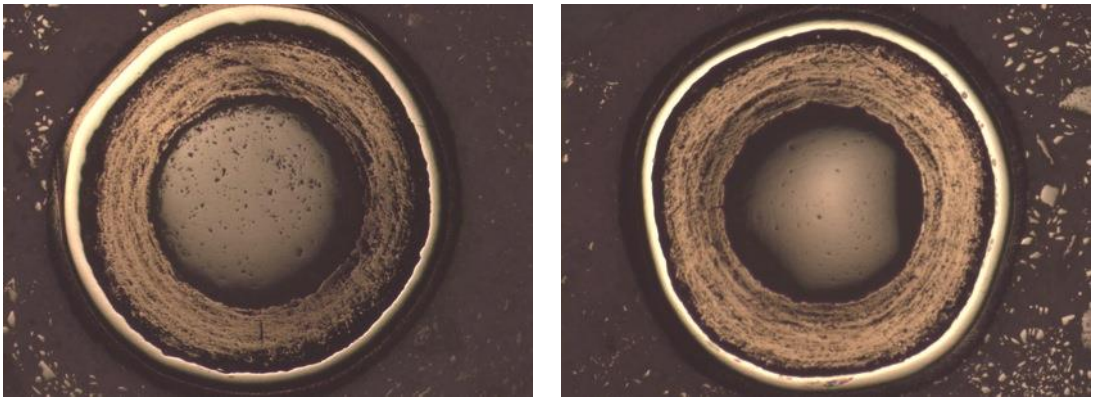
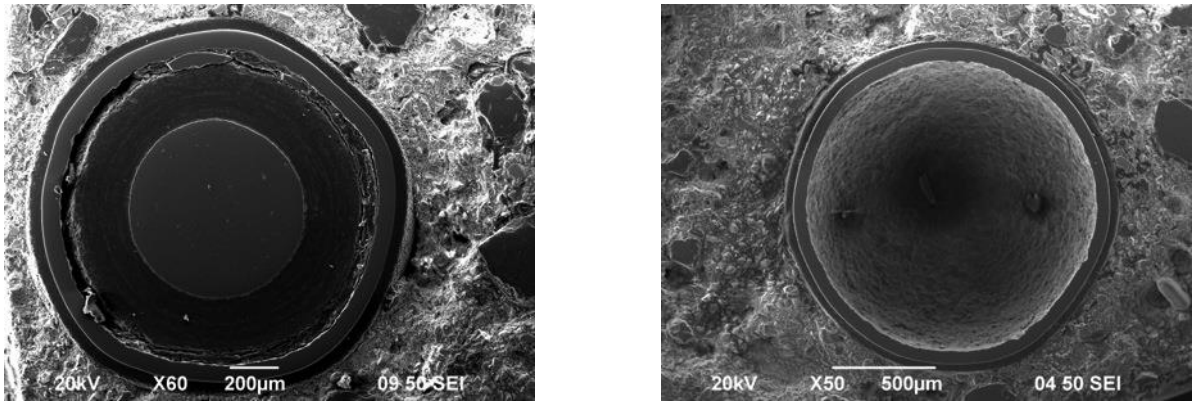


Figure 3.1: Two example optical micrographs of PYCASSO samples (non-irradiated) mounted and polished for HT nanoindentation experiments.

SEM micrographs taken of the irradiated TRISO samples at NRG Petten showed that the inner low density carbon layer had debonded from the SiC coating (Figure 3.2), which was in accordance with observations from tomography tests and not an artefact of the sample preparation here. A small gap (less than ½ µm) between the SiC coating and the OPyC layer was identified as well (Figure 3.2). This gap might have occurred during sample preparation, since it was not noticed within the tomography analysis, however the gap was very small and varied along the SiC and pyrolytic carbon interface.



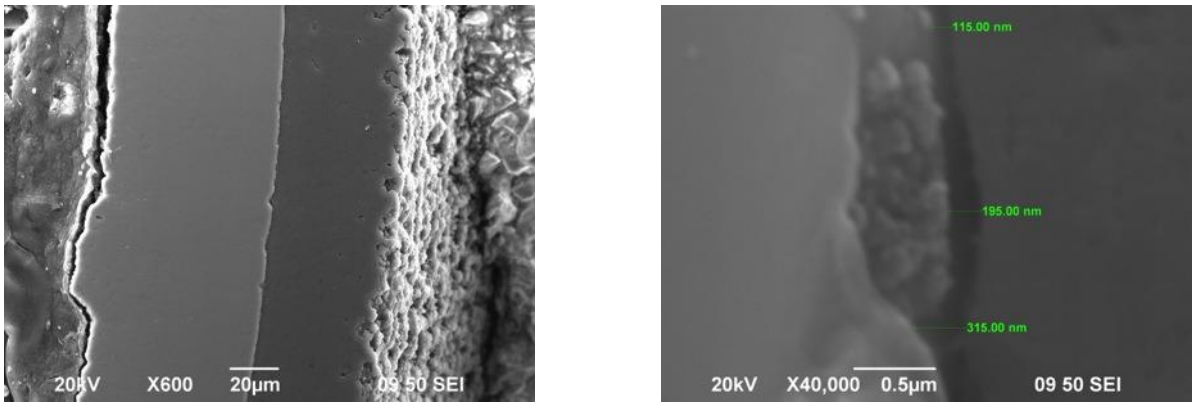


Figure 3.2 : SEM micrographs of the mounted TRISO particles. (taken at NRG Petten)

The sample was shipped to Manchester and upon arrival immediately cemented onto the hot stage by the same high temperature cement used for the embedding of the particles. A photograph of the mounted sample can be seen in Figure 3.3. An additional thermocouple was cemented onto the hot stage next to the sample to control the temperature on the specimen surface.

Figure 3.3: Sample cemented on the hot stage for the nanoindentation experiments.

1.3 Raman Spectroscopy and Scanning Electron microscopy

Additional microstructural characterisation of the pristine TRISO coatings was conducted at UMAN using Raman Spectroscopy and Scanning Electron Microscopy.

Raman Spectroscopy is a powerful tool in determining the stoichiometry of SiC as it easily identifies the typical impurities occurring during CVD of SiC. A number of Raman spectra have been taken on the polished cross-section as well as the coating surface. Measurements were done using the Argon laser of a Renishaw system as an excitation source in the range of 400 to 3000 cm^{-1}. For the measurement of the temperature dependency of the elastic modulus the sample as prepared for the high temperature nanoindentation tests has been placed on a hot stage and 3 Raman spectra were measured at each 100°C interval up to 700°C. The elastic modulus was then calculated according to the peak shift of transversal optical (TO) band of SiC as described by Zhao et al. (5).

Observation by ccanning electron microscopy (SEM) were conducted using a QUANTA 650 FEG SEM (FEI, US). Therefore the TRISO particles had been embedded in copper-containing conductive resin and polished by standard procedure in succeeding steps to a surface finish of ¼ µm.

4. High Temperature Nanoindentation Experiments

One-cycle single loading nanoindentation experiments were conducted with a maximum load of 100 mN using the following settings:

- Loading time: 20 s
- Time at maximum load: 10 s
- Unloading time: 10 s
- Thermalisation time: 180 s
- Drift correction time: 60 s before and after indentation

The load-displacement curves were corrected for initial penetration and thermal drift with the post indentation drift rate and finally analysed using the Oliver and Pharr method. For each condition at least 15 indents were taken and the elastic modulus and hardness values were determined by an average of the individual values.

For the measurements at high temperatures long gaps were programmed to allow indenter and sample to reach similar temperatures. This was achieved by placing the sample in short distance before the indenter without removing it over the course of several hours, which ensured that the thermal transients were reduced during the actual measurement procedure. In addition, before each individual indent a thermalisation time of 180 s was used, when indenter tip and sample surface were kept in direct contact. In some tests the facility did not detect the specimen surface correctly. Those load-displacement curves were easily distinguishable and not included in the analysis.

5. Results

Since the high temperature nanoindentation experiments described here are the first of a kind, numerous calibration tests have been preceding the tests on the irradiated TRISO fuel. There was no literature data available on the hardness evolution with temperature of CVD SiC, but a study using microindentation has been conducted on sintered SiC (6). This data was included in Figure 5.1 showing the hardness evolution with temperature of the bulk CVD SiC sample and the pristine TRISO coating used in the PYCASSO test. The hardness of the sintered SiC is initially lower, but above 200°C the decreasing slope follows a similar temperature trend as the two SiC samples measured here. The bulk CVD SiC piece exhibits a slightly higher hardness at room temperature compared with the coating, but the drop in hardness with temperature is slightly more pronounced and hence they exhibit almost the exact same values from 300°C onwards.

Each data point represents an average of at least 15 individual indents and the error bar is one standard deviation. It was noticed that the coatings frequently exhibited a larger scatter in the values, which was attributed to the sample preparation. Due to the use of the cement for the sample embedding, water could not be used during grinding and polishing. Furthermore, the automatic OPS polishing, usually achieving a submicron surface roughness could not be applied here. Hence the surface finish of the coating was not as good as in the case of the bulk CVD SiC.

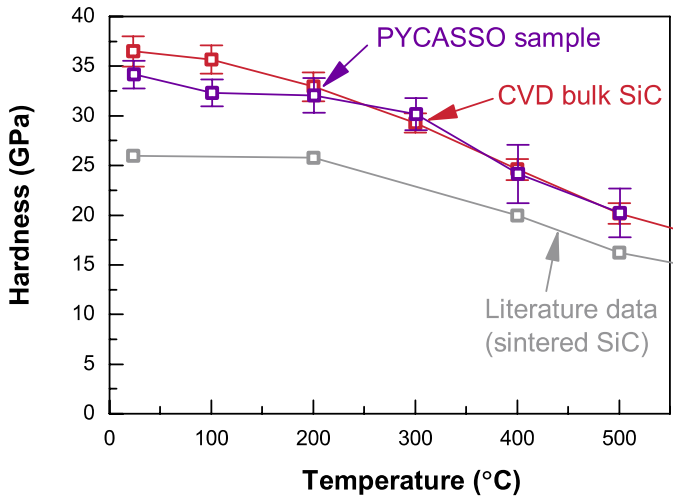


Figure 5.1: Temperature evolution of the hardness of silicon carbide. The pristine PYCASSO sample (purple) and bulk CVD SiC (red) were measured with the High Temperature Nanoindentation facility in this project. The only literature data available was of sintered SiC obtained by Microindentation (6).

During the irradiation programme PYCASSO the CEA particles described before were irradiated inside a test reactor using neutron flux and a constant temperature of 1000°C over the course of five months. As seen in Figure 5.2a the high temperature nanoindentation tests showed that irradiation hardening had occurred. At room temperature the hardness of the irradiated specimen was approximately 7% higher when compared with the pristine sample (36.7 ± 1.6 GPa and 34.2 ± 1.4 GPa, respectively). For higher measurement temperatures this hardening effect became more distinct. So at 500°C the hardness was more than 20% higher in the irradiated specimens.

Also the elastic modulus was found to have increased a few per cent due to neutron irradiation, though the effect was somewhat less pronounced. At room temperature 380 GPa were measured for the irradiated specimens compared with 370 GPa in the pristine state, this amounts to an increase of ~4%. Over the full measurement range the elastic modulus remained slightly higher in the irradiated specimen than in the pristine samples (see Figure 5.2b). The data was fitted according to the formula used by Li and Bradt (7) and the resulting slope suggests that the temperature evolution of the elastic modulus remains unaffected by irradiation.

For comparison the elastic modulus was determined by Raman Spectroscopy on the pristine TRISO sample. The peak position in the Raman spectrum is related to the vibration of the atomic bonds and hence results obtained by this approach do not reflect the impact of local microstructural features as grain boundaries or porosity. This leads to a significantly higher elastic modulus values measured by Raman Spectroscopy compared with the nanoindentation technique. In addition, indentation techniques generate a high hydrostatic stress field underneath the indenter, which might influence the extracted values when comparing it with “stress-free” techniques. Despite these discrepancies the temperature evolution of the elastic modulus over the temperature range here is very similar. Hence it is seen that Raman Spectroscopy provides a good approximation for the temperature dependency, but is incapable to fully characterise the elastic properties of the specific SiC sample incorporating microstructural features.

Sample preparation has to be taken into careful consideration within these types of experiments. Both samples (pristine and irradiated) had been prepared by one technician at NRG Petten following the preparation route as outlined above. The samples had been measured in direct succession to ensure equal tip geometry and the facility had been calibrated extensively on different materials beforehand.

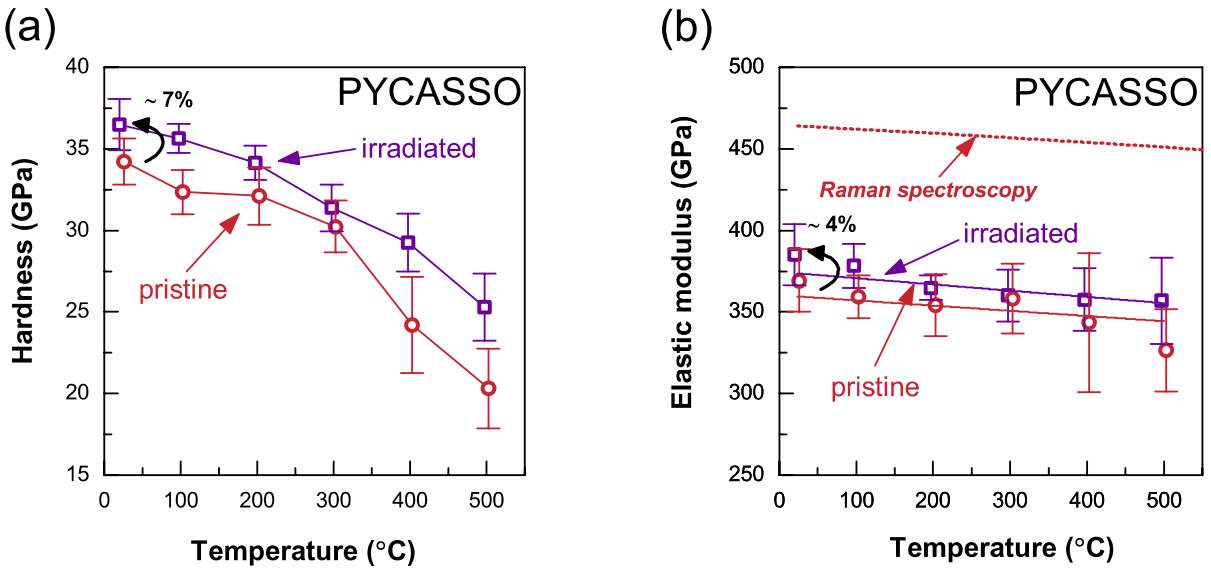


Figure 5.2: High temperature nanoindentation results of the PYCASSO samples. (a) Hardness; (b) Elastic modulus, the elastic modulus evolution with temperature was measured by Raman Spectroscopy on the pristine sample.

The Raman spectrum of the TRISO particle shows that the SiC is highly pure; no carbon or silicon impurities were detected. Only peaks relating to crystalline SiC of the β-modification were found. For comparison the commercial bulk CVD SiC is shown showing that the Raman spectrum is almost identical. A very small peak indicating stacking faults within the cubic SiC matrix is seen; the coating on the other hand does not show any signs of an appreciable stacking fault concentration.

Two SEM micrographs showing the grain morphology of the two samples are given in Figure 5.3b and c. The PYCASSO sample exhibits the grain structure typical for SiC coating layers in TRISO fuel. Towards the inner side the grains are small and grow in size radially with deposition direction. Even the largest grains are only a few microns in length. The bulk CVD has a significantly larger grain size with randomly oriented grains, where some individual ones can be up to tens of microns in diameter.

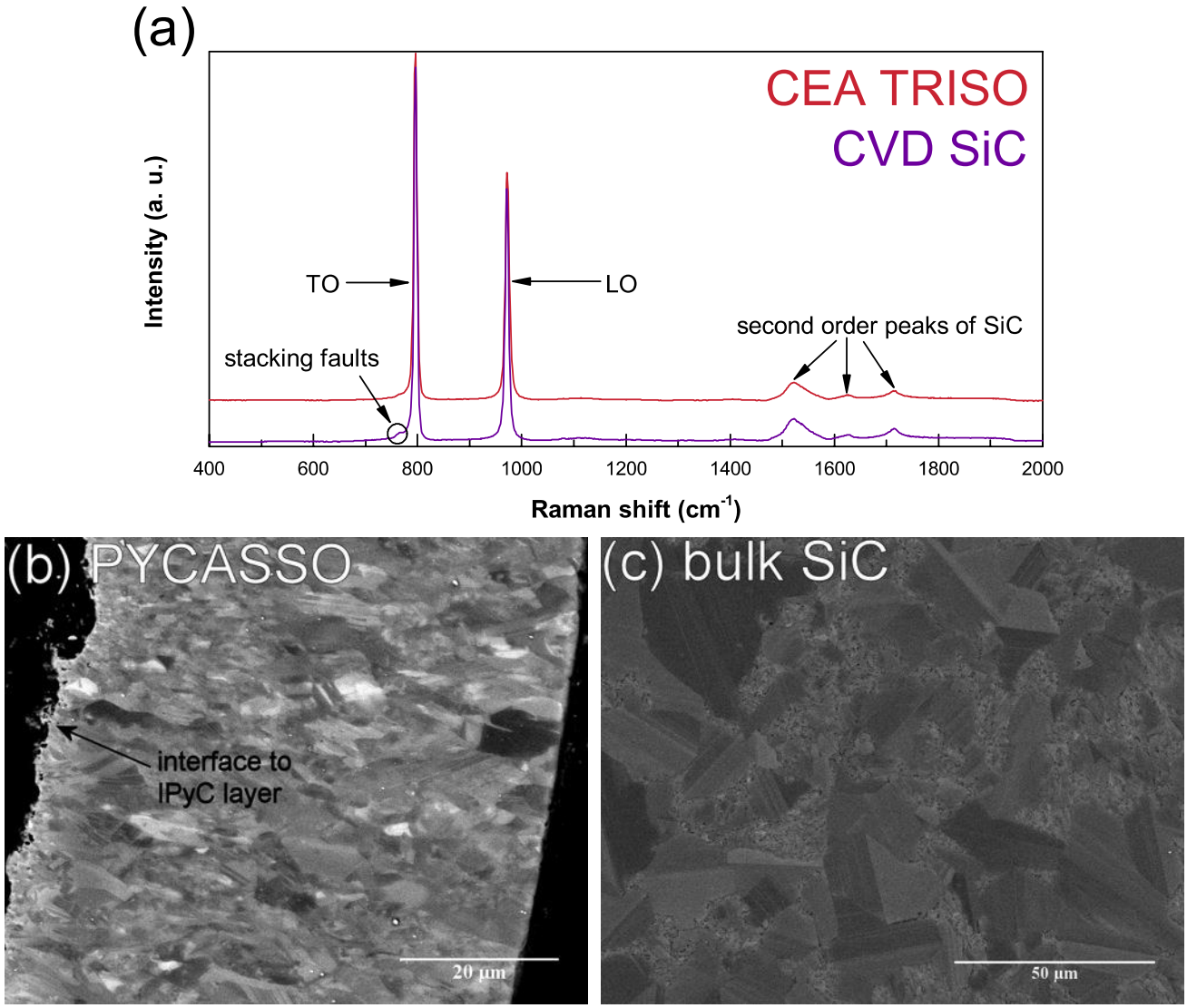


Figure 5.3: **(a) Raman spectra of the pristine PYCASSO sample (CEA) and the bulk CVD SiC; SEM micrographs of the polished samples: (b) TRISO coating (pristine CEA sample); (c) bulk CVD SiC.**

6. Summary and Conclusion

The technique of high temperature nanoindentation tests has been developed to measure the elastic modulus and hardness in TRISO coatings in-situ measurements up to 500°C. Comparative measurements were conducted on pristine and specimen that had been irradiated within the PYCASSO project. They showed that neutron irradiation had let to irradiation hardening and the elastic modulus was slightly increased as well. The hardness dropped significantly over the measured temperature range here, which was found to be slightly less severe in the irradiated SiC. The elastic modulus showed a steady but slight reduction of the elastic modulus, which was in accordance with literature data determined by other techniques on bulk SiC samples. There is no indication that the temperature evolution of the elastic modulus is affected by neutron irradiation.

These experiments are the first of-a-kind and proved the feasibility of measuring the mechanical properties of TRISO coatings. Here the effect of a neutron fluence level of $2*10^{25}$ m^{-2} was measured, however this data is highly beneficial in generating a valid database for fuel performance modelling codes. Currently those rely on estimation based on different samples. The results here can greatly improve the accuracy of their predictions.

7. Annexes

Annex 1 – Activity measurement of disk with 5 embedded TRISO particles as prepared for nanoindentation test

The activity was measured on the May 20th 2014 (NRG Petten); the data was corrected for background radiation.

Table 7.1: List of nuclides detected in the PYCASSO samples as prepared for HT nanoindentation.

Nuclide	Disk with 5 TRISO particles	
	Activity (Bq)	Uncertainty (%)
^{54}Mn	3.489*10^{2}	0.56
^{60}Co	2.096*10^{3}	0.51
^{65}Zn	6.591	11.1
^{125}Sb	4.559	16.9
^{134}Cs	1.735*10	1.98
^{137}Cs	1.542*10	20.0
^{152}Eu	1.021*10	20.0
^{154}Eu	6.252*10	19.4

Annex 2 – Results of the high temperature nanoindentation measurements

T – Temperature

h_{max} – maximum penetration

H – Hardness

E_r – reduced modulus

E – Elastic modulus

creep – Displacement measured over the 5 s load holding period at maximum load

N – number of indents used to calculate the average

Table 7.2: Parameters in Nanoindentation experiments of the CEA TRISO with a maximum load 100 mN (used for PYCASSO experiments).

T (°C)	h_{max} (nm)	H (GPa)	E_r (GPa)	E (GPa)	creep 5 s (nm)	N -
23	373 ± 8	34.2 ± 1.4	289 ± 11	369 ± 19	3.1 ± 0.3	20
100	382 ± 7	32.4 ± 1.3	283 ± 8	359 ± 13	6.4 ± 0.7	28
200	384 ± 10	32.1 ± 1.7	280 ± 11	354 ± 19	9.7 ± 1.5	34
300	390 ± 9	30.2 ± 1.6	282 ± 13	358 ± 21	14.4 ± 2.4	14
400	427 ± 26	24.2 ± 3.0	272 ± 26	344 ± 43	20.7 ± 4.6	21
500	459 ± 24	20.3 ± 2.5	262 ± 15	327 ± 25	26.5 ± 3.9	17

Table 7.3: Parameters in Nanoindentation experiments of the irradiated TRISO with a maximum load 100 mN (PYCASSO experiments of CEA particles).

T (°C)	h_{max} (nm)	H (GPa)	E_r (GPa)	E (GPa)	creep 5 s (nm)	N -
23	357 ± 8	36.5 ± 1.6	298 ± 11	385 ± 19	2.4 ± 0.3	21
100	361 ± 5	35.6 ± 0.9	294 ± 8	378 ± 13	3.7 ± 0.9	21
200	369 ± 5	34.1 ± 1.1	286 ± 4	365 ± 8	6.5 ± 1.1	20
300	380 ± 8	31.4 ± 1.4	283 ± 9	360 ± 16	10.0 ± 2.1	26
400	389 ± 8	29.3 ± 1.8	281 ± 11	357 ± 19	14.9 ± 2.8	18
500	409 ± 14	25.3 ± 2.1	280 ± 15	357 ± 26	20.5 ± 3.5	25

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