WP15ER-PR(17) 18579

M Malo et al.

Stability of porous SiC based materials under relevant conditions of radiation and temperature.

Preprint of Paper to be submitted for publication in
Journal of Nuclear Materials

This work has been carried out within the framework of the EUROfusion Consortium and has received funding from the Euratom research and training programme 2014-2018 under grant agreement No 633053. The views and opinions expressed herein do not necessarily reflect those of the European Commission.

Stability of porous SiC based materials under relevant conditions of radiation and temperature.

Marta Malo[1], Carlota Soto[2], Carmen García-Rosales[2], Teresa Hernández[1]

[1]*CIEMAT, National Fusion Laboratory, 28040 Madrid, Spain*
[2]*Ceit-IK4 Technology Center and TECNUN (University of Navarra), 20018 San Sebastian, Spain*

Keywords: Flow Channel Insert; DCLL blanket; porous SiC; electrical conductivity; radiation damage; thermal stability

Abstract

Porous SiC samples with different percentage of sintering additives have been manufactured by the so-called sacrificial template method at the Ceit-IK4 Technology Center (San Sebastián, Spain). Material stability under ionizing radiation and high temperature conditions considering electrical conductivity and microstructure has been evaluated at Ciemat (Madrid, Spain). Electrical conductivity was measured as a function of temperature before and after irradiation with 1.8 MeV electrons up to 140 MGy (~ $2 \cdot 10^{-5}$ dpa), and radiation induced conductivity (RIC) was also examined during irradiation at 550 ºC for different dose rates (from 0.5 to 5 kGy/s). Electrical conductivity increase with irradiation dose was observed to occur. Posterior XRD analysis allowed interpret radiation induced modification of the electrical conductivity in terms of changes in the SiC crystalline structure. However, neither RIC nor electrical degradation is seen to be an issue when extrapolated to future fusion devices relevant radiation levels.

1. Introduction

SiC based composites are candidates for possible use as structural and functional materials in the future fusion reactors, the main role being intended for the *blanket modules*. In the *blanket*, the neutrons produced in the fusion reaction slow down and their energy is transformed into heat in order to finally generate electrical power. In the blanket design named Dual Coolant Lead Lithium (DCLL), a PbLi alloy for power conversion and tritium breeding circulates inside hollow channels called Flow Channel Inserts (FCIs). These FCI must protect the steel structures against the highly corrosive PbLi liquid and the high temperatures, but also provide electrical insulation in order to minimize magnetohydrodynamic interactions of the flowing liquid metal with the high magnetic field present in a magnetically confined fusion environment [1]. Due to their nominally high temperature and radiation stability as well as corrosion resistance, SiC is the main choice for the flow channel inserts. The significantly higher stability than other sandwich-like structures like steel/alumina/steel layers and the lower manufacturing cost than

SiC/SiC presents porous SiC (dense coating is required in order to assure protection against corrosion and as a tritium barrier) as a firm alternative for this purpose [2-3]. This application requires the materials to be exposed to high radiation levels and extreme temperatures, conditions for which previous studies have shown noticeable changes in both the microstructure and the electrical properties of different types of silicon carbide. Both initial properties and radiation/temperature induced damage strongly depend on the crystal structure, polytype, impurities/additives that are determined by the fabrication process, so the development of a suitable material requires full control of these variables.

Long-term collaborative work between the *Ceit-IK4 Technology Center* (San Sebastián, Spain) and the *Research Centre for Energy, Environment and Technology* (CIEMAT) in Madrid is being carried out first within the Consolider –Ingenio Spanish programme and currently under the framework of the EUROfusion Consortium with the aim of producing SiC with tailored properties which fulfill the specific requirements for the FCI based on the direct feedback between manufacturing and characterization laboratories [4-5].

For this work, several SiC samples with different sintering additives have been manufactured at CEIT, and characterized at Ciemat in terms of radiation and thermal stability. Electrical conductivity was measured as a function of temperature before and after irradiation with 1.8 MeV electrons in the Ciemat HVEC Van de Graaff accelerator up to ~23 MGy. Radiation induced conductivity (RIC) was also examined during irradiation at 550 ºC for different dose rates (from 0.5 to 5 kGy/s). SiC materials in fusion reactors will be subjected to high temperatures expected to exceed 500 ºC, and thermal gradients up to ~200 ºC [6]. Although SiC is foreseen to withstand such conditions and indeed higher temperatures are employed during sintering process, possible degradation at high temperature in different gaseous environments (vacuum, inert gas, oxidizing/reducing/corrosive atmosphere), as well as secondary phases stability should be considered to fully characterize these materials. Thermogravimetric analysis was performed in order to determine volatile or unstable phases in the manufactured material. Finally, XRD analyses were carried out for as-received and tested materials which allowed interpret radiation induced modification of the electrical conductivity in terms of changes in the SiC crystalline structure.

2. Experimental

A fabrication method based on the *sacrificial template* technique has been employed to obtain ~15 x 15 mm^2 and approximately 3 mm thick porous SiC samples with ~ 50 % porosity. For this process, Al_2O_3 and Y_2O_3 powders in 3:2 ratio are added to reduce the sintering temperature.

Samples with different total percentage of additives (2.5 and 5 %) are considered in this study in order to determine their influence on the final material characteristics and behaviour. Manufacturing details and additional characterization tests regarding thermal properties and flexural strength are given elsewhere [7].

Material stability under ionizing radiation and high temperature conditions considering electrical conductivity and microstructure has been evaluated. Gold central and guard electrodes sputtered onto one sample face, and a single earth electrode onto the opposite face allow an electric field to be applied to measure volume and surface electrical conductivity. Electrical conductivity was measured before, and after irradiation with 1.8 MeV electrons in the CIEMAT Van de Graaff accelerator beam line, as a function of temperature between 20 and 550 ºC. Electrical conductivity was also measured during irradiation at 550 ºC (representative operating temperature for this application), and dose rate dependence of radiation induced conductivity (RIC) evaluated for 0.5, 1, and 5 kGy/s up to 23 MGy total dose.

Thermogravimetric analyses were carried out in order to evaluate the as-received material phase stability using a Seiko TG / DTA 6300 equipment. Thermal aging treatments were also performed at 1200 °C for 48 hours in argon to detect either phase transformations and/or polytype changes that may occur during the material operating lifetime. The structural changes between as-received and post-test materials were determined by XRD with a Pananlytical X-Pert diffractometer.

3. Results. Electrical conductivity

Volume electrical conductivity as a function of temperature from 20 ºC to 550 ºC has been measured by applying 500 mV between gold central and earth electrodes before and after electron irradiation up to 23 MGy . Figure 1a shows Arrhenius plots of electrical conductivity for the 5% add. porous SiC unirradiated and following irradiation at 550 ◦C with 1.8 MeV electrons up to ~ 23 MGy. An increase in the volume conductivity is observed after irradiation, the lower the temperature the more pronounced, and essentially stable at temperatures close to the operating levels (see also figure 4).

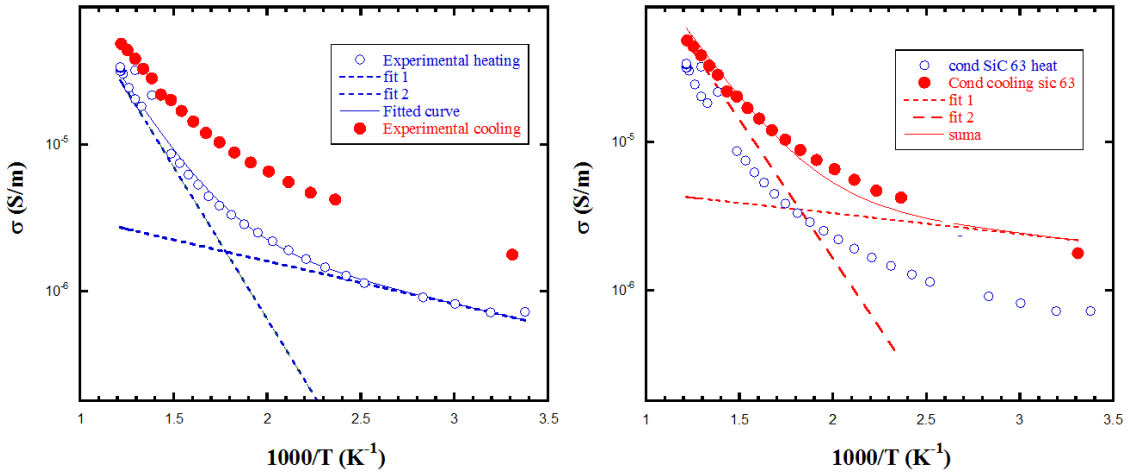

Figure 1. Arrhenius plot of volume electrical conductivity before (heating) and after (cooling) irradiation up to 23 MGy for porous SiC with 5 % additives. Fitting curves to data on heating (a) and cooling (b)

The analysis of these heating/cooling curves provides information about the electrically active point defects originally present in the material and their evolution with irradiation dose. The electrical conductivity in semiconductors exponentially increases with temperature $\sigma \sim e^{-\frac{E_a}{2k_B T}}$, E_a being the required activation energies to overcome the barriers for electron/hole promotion to the conduction band. At least two components for the electrical conductivity in this range of temperature are identified before irradiation (fig. 1a), with activation energies of about ~ 0.1 eV and ~ 0.8 eV. Although further analysis is required in order to determine the main defects electrically active in these complex materials with different phases and microstructures (grains, grain boundaries, pores) the lower energy level is consistent with the activation energy that has been established for substitutional nitrogen in 6H polytype, a common impurity in SiC [8-9]. Slightly lower activation energies are obtained for the cooling curve in figure 1b (0.055 eV and 0.73 eV respectively), the first having being associated also to N but in a cubic structure [10]. As it is shown in figure 2, it is possible to express the data before and after irradiation by the same equation by decreasing the activation energies, while the pre-exponential terms remain unchanged. This modification is possibly due to a structural alteration as a consequence of irradiation, as it is discussed below in section 5.

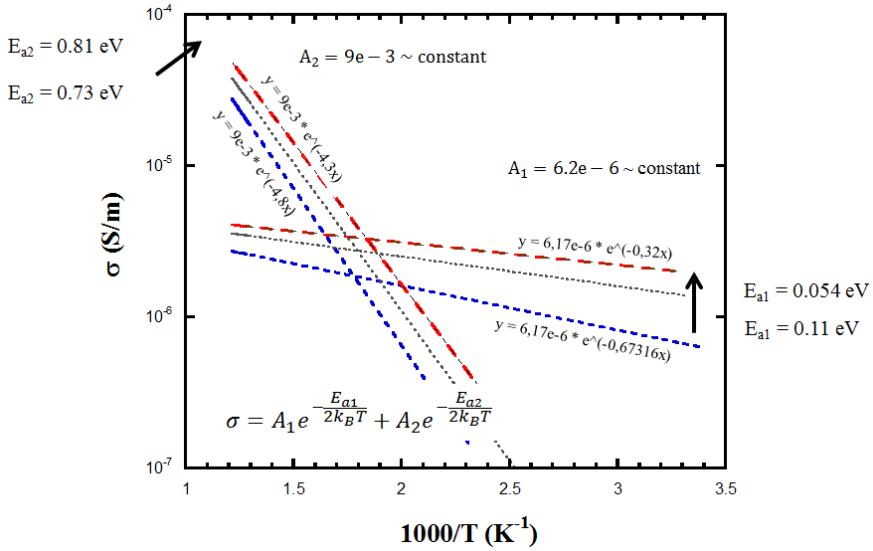

Figure 2**.** Arrhenius plot of volume electrical conductivity before (heating) and after (cooling) irradiation up to 23 MGy for porous SiC with 5 % additives. Fitting curves to data on heating (a) and cooling (b)

Figure 3 shows conductivity for sample with 2.5 % add. as a function of inverse temperature. While the overall behaviour, with an increase of about two orders of magnitude at the maximum temperature, is similar to the 5% add. sample (see figure 1), an abrupt drop in the electrical conductivity takes place on heating at about 300 ºC. Similar problems were found on cooling down after irradiation in about the same range of temperature, what might be related either to the measuring system or sample unstability. Tests should be repeated in order to verify this.

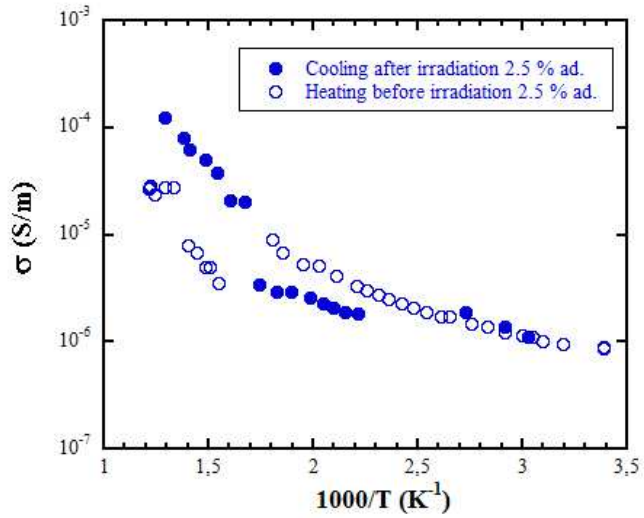

Figure 3**.** Arrhenius plot of volume electrical conductivity before (heating) and after (cooling) 1.8 MeV electron irradiation up to 23 MGy for porous SiC with 2.5 % additives.

The electrical conductivity at 550 ºC has been monitored at intermediate doses (beam off) as a function of dose, as it is shown in figure 4. A continuous linear increase in the volume electrical conductivity of sample with 2.5 % additives is observed, with an increase of about a factor 4 in for ~ 25 MGy. Possible saturation at slightly higher doses, as it has been observed in previous works for similar materials should be confirmed in further experiments [11]. In contrast, higher stability at this temperature is found for material with higher amount of sintering additives, with a slight increase in the onset of the irradiation also detected but saturated in a short irradiation time, after the dose of ~ 2 MGy.

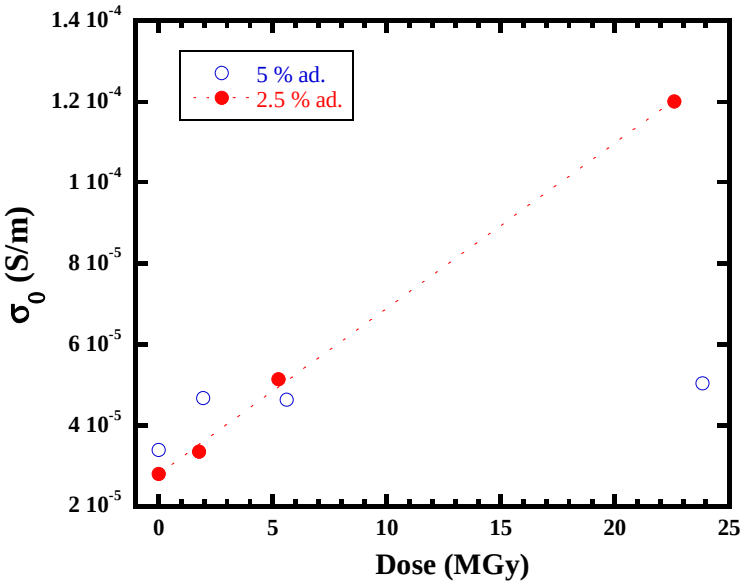

Figure 4 Electrical conductivity at 550 ºC as a function of dose.

One of the critical limitations in the functional materials for fusion applications is expected to be introduced by the increase of the electrical conductivity during irradiation due to the excitation of charge carriers into the conduction band (electron-hole pair production), known as Radiation Induced Conductivity (RIC) [12]. This increase is represented in figure 5 as the conductivity difference when the electron beam is applied ($RIC \equiv \sigma_{Off} - \sigma_{On}$).

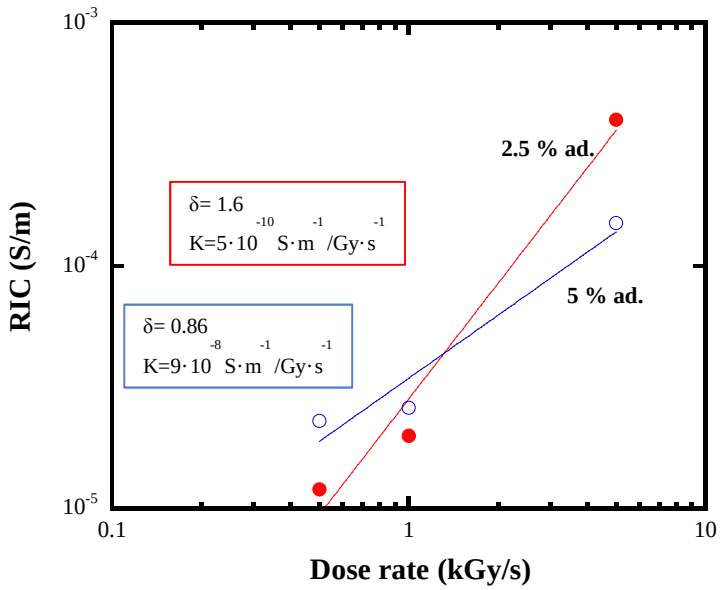

Figure 5 Radiation induced conductivity of measured porous SiC (a) and comparison with results for dense hot pressed and CVD SiC (b)

δ values between ~ 0.9 and 1.6, and K in the order of 10^{-7}-10^{-10} can be considered high if compared with typical values for oxide ceramics for which δ lies between 0.5 and unity and K between 10^{-12} -10^{-9} (S s/Gy m). However, extrapolation to 10 kGy/s, fusion representative dose rate level, still gives electrical conductivity values at 550 ºC in the order of $1\cdot10^{-4}$ S/m, well below the established maximum for the FCI (~100 S/m) [13,14]

4. Results. Thermogravimetric study

Figures 6a and 6b show thermogravimetric (TG) and differential thermal analysis (DTA) curves for samples with 2.5 and 5% add. respectively. Heating was carried out in high purity nitrogen atmosphere (99.9995 %) to prevent oxidation. Similar behaviour is observed irrespectively of the additives content, with less than 1 % weight loss up to 600 ºC and small oscillations (~ 0.1 %) beyond this temperature. Numerical baseline subtraction in DTA curves (figures 6a and 6b, inset) reveals a band-like structure with several exothermal peaks in agreement with the TG variations. We attribute these peaks to thermal decomposition of metal carbonates ($FeCO_3$ → $FeO + CO_2$/$3FeCO_3 \rightarrow Fe_3O_4 + 2CO_2 + CO$) generally occurring at these temperatures [15, 16]. Particularly relevant is the iron (II) carbonate whose decomposition takes place in successive steps producing different oxides above 650 ºC. No indication of these compounds was obtained by XRD, however this can be explained by the limited amount and possibly amorphous structure of these phases.

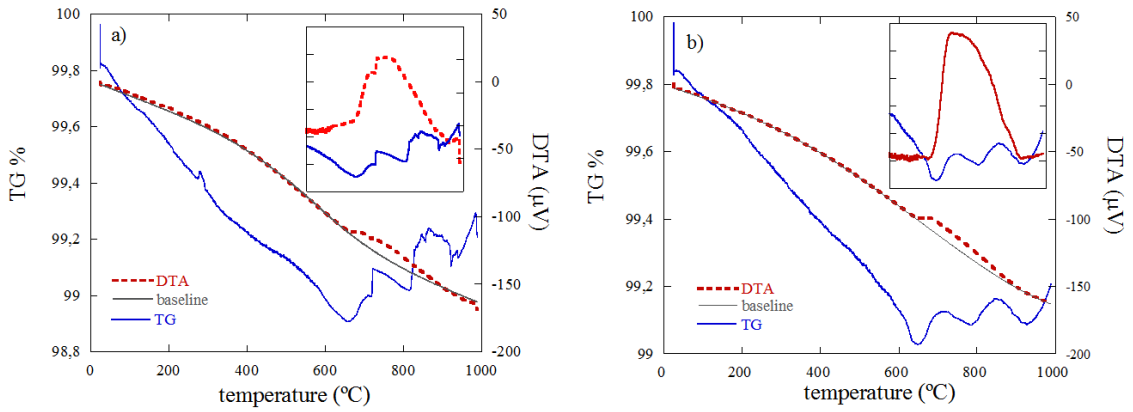

Figure 6 Thermogravimetric (TG) and differential thermal analysis (DTA) curves for 2.5 (a) and 5% (b) additives sample. Insets: DTA after baseline subtraction.

5. XRD analysis and discussion

The crystalline phases for the as-received and tested samples were investigated by XRD. Both 2.5 and 5 % add. materials are crystalline in high degree, with mixed SiC polytypes mainly hexagonal (6H and also 4H in 5% add. sample), and minor rhombohedral SiC phases. Complex compounds based on yttrium and aluminium from initially incorporated powders together with iron oxides and silicates from the iron and silicon impurities commonly present in SiC are found. Due to the diffraction pattern complexity, elemental analysis by X-ray fluorescence (XRF) spectrometry was necessary in order to ease secondary phase determination. Low crystallinity phases related to the added sintering agents were found. Table I compares crystalline phases found in as-received material and after being subjected to thermal aging and electron irradiation.

Table I Crystalline phases for the examined porous SiC

	SiC 2.5 % add.		SiC 5 % add.	
	Main phase	Secondary	Main phase	Secondary
As received	6H-hexagonal SiC	Rombohedral SiC $Y_3Al_2(AlO_4)_3$ Fe_2O_3 SiO_2 $Fe_3(Al_{1.7}Fe_{0.3})(SiO_4)_3$	6H-hexagonal SiC	4H-hexagonal SiC Rombohedral SiC $Y_3Al_2(AlO_4)_3$ Fe2SiO4
Thermal aging	6H-hexagonal SiC	Rombohedral SiC $Y_3Al_2(AlO_4)_3$ Fe_3O_4 SiO_2	6H-hexagonal SiC	4H-hexagonal SiC Rombohedral SiC $Y_3Al_2(AlO_4)_3$
Irradiated*	3C cubic SiC	6H-hexagonal SiC 4H-hexagonal SiC	3C cubic SiC	6H-hexagonal SiC Rombohedral SiC

As it can be observed, the heat treatment does not induce changes in the main but only in the secondary phases of the material. High temperatures tend to improve crystallinity and ease the

removal of volatile products. Such transformations do not imply changes at the microstructural level, but they may have an influence in the electrical conductivity. Once the solid solution limit is reached, the impurities are deposited on the grain boundaries and, depending on their nature might modify (either increasing or decreasing) bulk conductivity.

Phase transition from hexagonal to cubic structure takes place on both samples with irradiation. (Diffraction patterns for the 5% add. as-received and irradiated samples together with 6H and 3C silicon carbide diffractograms are shown in figure 7). While cubic to hexagonal transformation occurs at high temperatures above ~1800 ºC [17] and at lower temperatures under irradiation conditions [18], little information is available on the formation of cubic crystal structure from hexagonal polytype. Studies of this transformation explain it as a diffusion process enhanced by the presence of vacancy-dopant defect complexes [h-c], what is consistent with both the identification of N as possible main contributor to the electrical conductivity and the production of vacancies by irradiation (although very low, in the order of ~10^{-9} dpa/s in the C sublattice for 1.8 MeV electrons at 5kGy/s). However, quantification of nitrogen content would be necessary in order to evaluate its implication in the transformation.

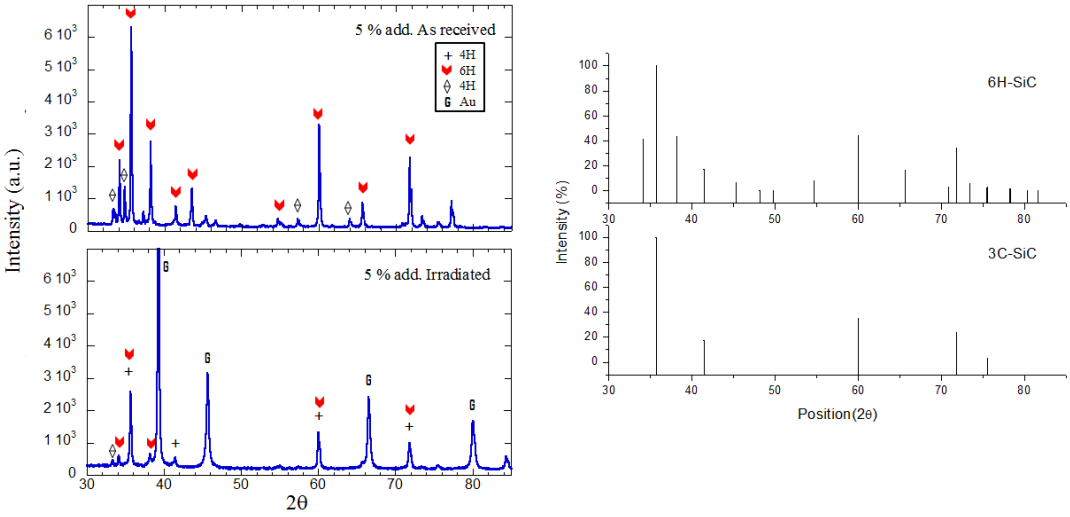

Figure 7 XRD pattern for as-received, and irradiated porous SiC with 5 % additives. 6H and 3C SiC diffraction lines for reference (ICSD codes 015325 and 028389 respectively)

Electrical properties widely differ from polytype to polytype and this phase transition from 6H to 3C with different band gap (3.05 eV and 2.4 eV for 6H and 3C respectively), would explain the increase in the electrical conductivity in the irradiated samples. Secondary phases which in many cases dominate electrical properties of ceramic materials does not seem critiacal in this case, considering the very similar initial electrical conductivity for both 2.5 and 5% add. materials.

Conclusions

Radiation and high temperature effects (~23 MGy ionizing radiation and 1200 ºC thermal treatment respectively) in the microstructure and the electrical properties of porous SiC have been examined as a function of the amount of sintering additives in the material. SiC samples with 2.5 and 5% additives showed room temperature electrical conductivities in the same order (~ 10^{-6} S/m) and similar evolution with temperature (about factor 50 increase up to 550 ºC). Transformation from 6H to 3C structure is observed to occur at this very low ionizing dose and essentially no displacement damage ($3 \cdot 10^{-6}$ dpa), while minor changes take place after thermal aging.

Radiation induced conductivity is higher for the sample with lower amount of additives. Moreover, higher stability with irradiation dose for 5 % ad. sample at elevated temperature (data at 550 ºC) is observed. Thus, the use of higher amount of additives, what significantly improves the sintering process, does not represent any disadvantage in this context but improves material stability. However, further tests are necessary in order to check the reproducibility of these measurements, alternative techniques such as AC complex impedance being also considered for complementary information.

Although no serious RIC was found in general for any of the samples, and electrical conductivity is in all cases bellow the maximum acceptable for FCI (~100 S/m), extended irradiations at representative doses should be performed to fully validate these materials.

Acknowledgements

The authors are indebted to Mr. Javier Valle Paisán and Mr. Francisco Manuel Jiménez Baena for their help in these experiments. This work has been carried out within the framework of the EUROfusion Consortium and has received funding from the Euratom research and training programme 2014–2018 under grant agreement No 633053. The views and opinions expressed herein do not necessarily reflect those of the European Commission. This work has also been supported by Spanish Ministerio de Economía, Industria y Competitividad (MEIC) within the framework of the RADIAFUS IV Project.

References

[1] S. Malang, M. Tillack, C.P.C.Wong, N. Morley, S. Smolentsev. Development of the lead lithium (DCLL) blanket concept. Fusion Sci. Technol., vol. 60 (2011), pp. 249–256.

[2] P. Norajitra. et al., Current status and critical issues for development of SiC composites for fusion applications, Fusion Eng. Des. 58&59 (2001) 629.

[3] S.Sharafat et al., Development Status of a SiC-Foam Based Flow Channel Insert for a U.S.-ITER DCLL TBM, Fusion Sci. Technol., 56 (2009), pp. 883-891,

[4] Manufacturing and characterization of porous SiC for flow channel inserts in dual-coolant blanket designs.*Fus. Eng. Design.*86 (2011) 2526-2529, Ainhoa Bereciartu, Nerea Ordás, Carmen García-Rosales, Alejandro Moroño, Marta Malo, Eric R. Hodgson, Jordi Abellà, Luis Sedano

[5] Testing of porous SiC with dense coating under relevant conditions for Flow Channel Insert application N. Ordás, A. Bereciartu, C. García-Rosales, A. Moroño, M. Malo, E.R. Hodgson, *Fus. Eng. Design.* 89 (2014) 1274–1279

[6] Aoyama, A., Morely, N.B., Sharafat, S., Ghoniem, N., Katoh, Y., & Williams, B. (2007). Status of the flow channel insert development for the US-ITER DCLL TBM. *ICFRM-13: 13 International Conference on Fusion Reactor Materials*, France

[7] C. Soto et al., SiC-based sándwich material for Flow Channel Inserts in DCLL blankets, Fusion Engineering and Design. In Press. https://doi.org/10.1016/j.fusengdes.2017.05.059

[8] G. Pensl , W. J. Choyke, *Optical and Electrical Characteristics of SiC*, Physica B 185 (1993) 264

[9] A. O. Evwaraye, S. R. Smith, and W. C. Mitchel, *Shallow levels in n -type 6H -silicon carbide as determined by admittance spectroscopy*, J. Appl. Phys. 75 (1994) 3472

[10] Properties of silicon carbide, Gary Lynn Harris, IET (1995) ISBN 0 85296 870 1

[11] E. R. Hodgson, M. Malo, J. Manzano, A. Moroño, T. Hernandez, Radiation induced modification of electrical conductivity for three types of SiC, J. Nucl. Mater.417, (2011) 421-424,

[12] V.A.J. van Lint et al., in: Mechanisms of Radiation Effects in Electronic Materials, vol. 1, John Wiley, New York (1980).

[13] M. Malo (2014), Efectos de la radiación en materiales cerámicos para fusión. La luminiscencia como herramienta de caracterización y diagnóstico (doctoral thesis). Universidad Complutense de Madrid.

[13] C. Mistrangelo, A. R. Raffray, and the ARIES Team, MHD Analysis of Dual Coolant Pb-17Li Blanket for ARIES-CSC, Fusion Sci. Technol. 52 (2007)

[14] Y. Katoh et al., Current status and critical issues for development of SiC composites for fusion applications, Journal of Nuclear Materials 367–370 (2007) 659–671

[15] Ozlem Sel, A.V. Radha, Knud Dideriksen, and Alexandra Navrotsky , Amorphous iron (II) carbonate: Crystallization energetics and comparison to other carbonate minerals related to CO2 sequestration, Geochimica et Cosmochimica Acta 87 (2012) 61–68.

[16] El-Bellihi, A.A., Kinetics of thermal decomposition of iron carbonate, Egyptian Journal of Chemistry 53 (2010) 871-884.

[17] S.I. Vlaskina et al., 3C-6H transformation in heated cubic silicon carbide 3C-SiC Semiconductor Physics, Quantum Electronics & Optoelectronics, 2011. V. 14, N 4. P. 432-436.

[18] Chad M. Parish et al., Irradiation-induced β to α SiC transformation at low temperature, Sci Rep. 7 (2017) 1198.

[19] S.I. Vlaskina, Mechanism of 6H-3C transformation in SiC, Semiconductor Physics, Quantum Electronics & Optoelectronics. 2002. V. 5, N 2. P. 152-155.