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C Garcia-Rosales et al.

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SiC-based sandwich material for Flow Channel Inserts in DCLL blankets: manufacturing, characterization, corrosion tests

Carlota Soto[a], Carmen García-Rosales[a], Jon Echeberria[a], José M. Martínez Esnaola[a], Teresa Hernández[b], Marta Malo[b], Ernests Platacis[c], Faina Muktepavela[c]

[a] *Ceit-IK4 and TECNUN (University of Navarra), 20018 San Sebastian, Spain*
[b] *CIEMAT, National Fusion Laboratory, 28040 Madrid, Spain*
[c] *Institute of Solid State Physics, University of Latvia, Salaspils 2169, Latvia*

Flow Channel Inserts (FCIs) are key elements in a DCLL blanket concept for DEMO, since they provide the required thermal insulation between the He cooled structural steel and the hot liquid PbLi flowing at ≈ 700°C, and the necessary electrical insulation to minimize MHD effects. In this work a SiC-based sandwich material is proposed for FCIs, consisting of a porous SiC core covered by a dense CVD-SiC layer. A method to produce the porous SiC core is presented, based on combining a starting mixture of SiC powder with a spherical carbonaceous sacrificial phase, which is removed after sintering by oxidation, in such a way that a microstructure of spherical pores is achieved. Following this technique, a porous SiC material with low thermal and electrical conductivities, but enough mechanical strength was produced. Samples were covered by a 200 μm thick CVD-SiC coating to form a SiC-sandwich material. Finally, corrosion tests under static PbLi were performed, showing that such a dense layer offers a reliable protection against static PbLi corrosion.

1. Introduction

The Dual Coolant Lead Lithium (DCLL) blanket is one of the most attractive concepts for its application in a future DEMO reactor. In the high temperature DCLL design a eutectic Pb-15.7Li alloy flows through long poloidal channels acting as self-cooled breeder, absorbing the neutron flux energy and reaching temperatures around 700 °C. Helium is used to cool the blanket structure, made of reduced activation ferritic-martensitic (RAFM) steel, that has a maximum allowable PbLi interface temperature of around 470 °C due to corrosion issues [1]. Such a blanket concept provides net efficiencies around ≈ 45%, considerably higher than those achieved in other blanket designs [2].

Flow channel inserts (FCIs) are key elements in the DCLL design; they consist of hollow channels containing the flowing PbLi and being separated from the RAFM steel wall by a thin gap, also filled with PbLi. The thicknesses typically proposed for the FCI's wall and gap in the high temperature DCLL are 5 and 2 mm, respectively [3]. FCIs serve as electrical insulators, to reduce MHD effects, and as thermal insulators, to avoid heat loses from the hot metal to the steel walls. To fulfill these functions, FCI's materials must have low thermal and electrical conductivities, good PbLi corrosion resistance, low activation and degradation by neutrons and excellent high temperature performance. Besides, FCIs will be subject to mechanical stresses during operation due to high thermal gradient across its walls [4]. For this reason, FCI's materials must exhibit enough mechanical strength to withstand this thermal stresses.

At present, SiC is the main candidate material for the FCIs in the high-temperature DCLL, thanks to its excellent stability at high temperatures, low thermal expansion, high thermal shock resistance, low activation and low corrosion by PbLi [5]. However, the need for low electrical and thermal conductivities requires substantial R&D efforts in the development and fabrication of new SiC-based materials, and different possibilities are being considered. One promising option is a SiC-sandwich material formed by a core of porous SiC covered by a dense SiC coating fabricated by chemical vapor deposition (CVD): the porous core provides the insulating properties while the dense layer offers protection against PbLi corrosion and infiltration. However, a reliable method to produce porous SiC with the required characteristics for FCI application has to be developed, and the resulting sandwich material should be characterized and tested under relevant conditions.

In this work, a method to produce porous SiC based in the *sacrificial template* technique is presented. In this method a sacrificial phase is introduced in the initial powder mixture, being removed after sintering and leaving spherical pores instead. Materials produced by this method and their characterization in terms of microstructure, thermal and electrical conductivities, and flexural strength are presented.

A previous thermomechanical study of the basic heat transfer problem of FCIs described in [4] provides a guideline for the material's development. The first objective marked by this study was to produce a material with thermal conductivity ≤ 7 W/(m·K) and flexural strength well above 25 MPa to offer reliable protection against thermal stresses. The achieved materials properties are compared with the requirements marked by this study, to determine their suitability as porous SiC core of a sandwich FCI.

Another important point to determine the viability of the SiC sandwich concept for FCIs is to study the reliability of the dense CVD-SiC coating covering the porous core, in terms of quality (lack of defects) and corrosion resistance. According to the mentioned thermo-mechanical study [4], a coating thickness resulting in reasonable mechanical stresses would be 200 μm. Thus, porous SiC samples produced in this work were covered by a dense CVD-SiC coating of ≈ 200 μm. In order to test

if such a dense coating offers effective protection against PbLi corrosion, laboratory tests have been performed on SiC-sandwich samples under static PbLi at ≈ 700 ^{0}C during 1000 h.

2. Production of porous SiC

2.1 Experimental procedure

SiC powder (Superior Graphite, 0.5 µm) was mixed with 2.5 wt. % Al_2O_3 (0.4 µm) and Y_2O_3 (1 µm) powders as sintering additives, added in a 3/2 relation. The sacrificial phase proposed in this work is a graphitized powder of spherical mesocarbon microbeads (MCMB, 15 µm). 3 wt. % of an aqueous polymer dispersion was used as binder. Additives, SiC and binder were mixed in ethanol during 16-18 h, being the MCMB subsequently added to the solution and mixed during 30 min. The resulting blend was dried and uniaxially pressed to the required geometries at 100 and 200 MPa. The green compacts were sintered at 1850 ^{0}C during 1h. The sintered samples were heated at 700 ^{0}C in air during 5h to burn out the carbonaceous sacrificial phase.

Density of the samples was determined, in green state and before and after the oxidation treatment, by geometrical measurements, and porosity was calculated from relative density and theoretical density, which were obtained by the rule of mixture. Microstructure was studied by field emission gun scanning electron microscopy (FESEM) and energy dispersive X-ray spectroscopy (EDS). Thermal conductivity as a function of temperature was determined from the heat capacity (obtained from [6]), density of the samples and their thermal diffusivity, measured by the Laser Flash method. Flexural strength was determined at room temperature by three point bending tests (3PBT) using 4 samples for each condition. The electrical conductivity was measured in high vacuum between 15 and 550 ºC. The corrosion test was carried out under static eutectic PbLi at ≈ 700 ºC, immersing the samples during 1000 h in a niobium container placed in a vacuum chamber.

2.2 Results

In fig. 1 the final porosity of the samples pressed at 100 and 200 MPa as well as the increase of relative density during sintering are shown as a function of three different initial amounts of MCMB (sacrificial phase): 0, 15 and 20 wt. %. It can be observed that the porosity increases in an exponential way with increasing MCMB content while the variation of relative density during sintering decreases. The sintering process is less effective in presence of the MCMB phase (since it is external to the SiC-Al_2O_3-Y_2O_3 sintering system): the MCMB does not suffer any change in composition or volume during sintering, being rather an obstacle in the shrinkage of the SiC matrix and, possibly, in the diffusion of the liquid phase formed by additives. Besides, the sintering process seems to be less effective on samples pressed at 200 MPa; this may indicate the presence of internal stresses inside the green samples caused by end-capping, usually appearing in ceramics during uniaxial pressing [7].

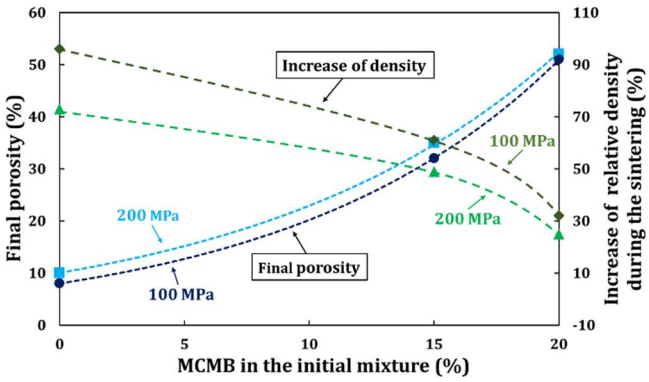

Fig. 1. Total porosity of the samples after sintering and oxidation, and increase of their relative density during sintering, as a function of the initial amount of sacrificial phase

Fracture surfaces of the materials produced are shown in fig. 2. The final porosity of the samples with initial MCMB is formed by smaller pores (≤ 1 µm) present in the SiC matrix caused by partial sintering, and by spherical pores (≈10-15 µm) formed by burn out of the sacrificial phase, as can be seen in b) and c). The higher sintering grade of b, the sample with less initial MCMB, can be appreciated. Micrographs in a) show the pores present at the surface of a sample sintered without any sacrificial phase, where pores due to partial sintering are more abundant than inside, as has been reported in other SiC materials sintered with Al_2O_3-Y_2O_3 as additives [8].

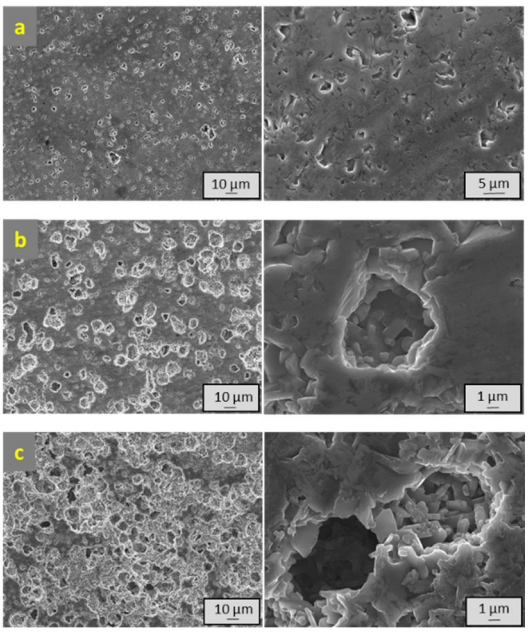

Fig. 2. FESEM micrographs of samples fabricated with: a) 0% MCMB; b) 15% MCMB and c) 20% MCMB in the initial powder mixture, pressed at 100 MPa

One crucial property of the porous SiC material for application as core of FCIs is its thermal conductivity. In fig. 3. a) the thermal conductivity as a function of temperature can be seen for samples of different initial MCMB content and thus of different final porosity. As expected, the thermal conductivity decreases with temperature and with porosity. The thermal conductivity of the samples at 700 ^{0}C (the expected operation temperature of a FCI in the high temperature DCLL)

versus its porosity is shown in b), resulting in an exponential relationship. A similar trend has been noticed in a previous work [9].

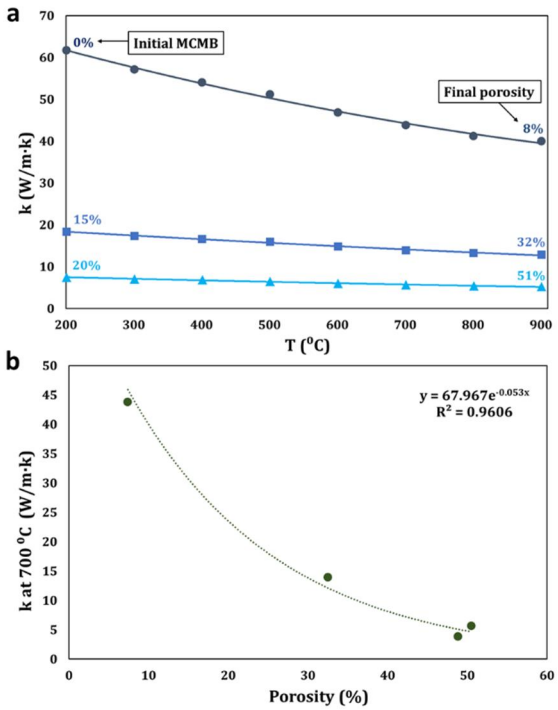

Fig. 3. a) Thermal conductivity as a function of temperature for different initial MCMB contents; b) Thermal conductivity at 700 °C versus porosity

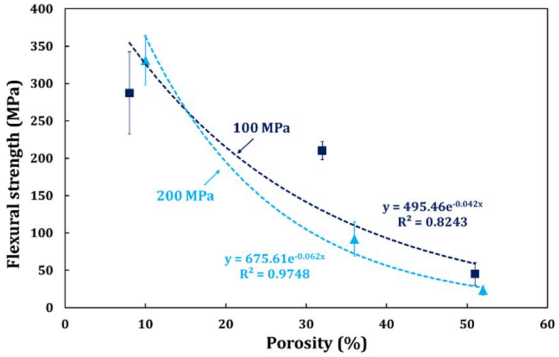

Fig. 4. Flexural strength versus porosity for samples pressed at 100 and 200 MPa

In fig. 4, the flexural strength versus the porosity of the samples is shown for the two used compaction pressures: 100 and 200 MPa. Different results are obtained depending on the compaction pressure; this behavior, together with the important dispersions of the measured values, seems to confirm the hypothesis that end-capping cracks or other defects were present in the samples. For this reason, the flexural strength is possibly infra-estimated in some of these results, especially in the case of the densest samples. The flexural strength values of the samples pressed at 200 MPa fit better to the exponential behavior usual in ceramic materials [10][11], while the flexural strength in middle-porous samples seems higher in the 100 MPa samples. In any case, more work should be done to produce samples free of defects with required geometry for 3PBT, to measure the real strength avoiding high dispersions.

Finally, the electrical conductivity of a 50% porous sample has been measured as a function of temperature until 550 °C. Results are shown in fig.5, being similar to those obtained in a previous work [9].

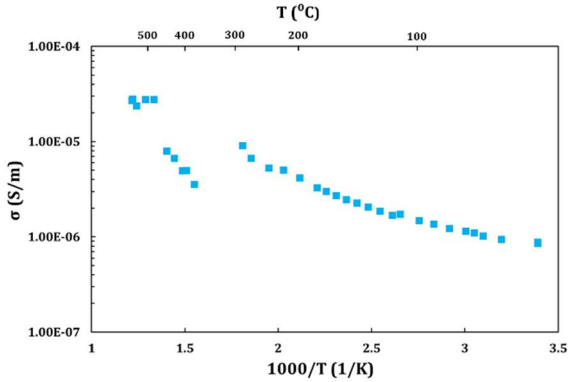

Fig 5. Electrical conductivity versus the invers of temperature of a 50% porous SiC sample, before and after a 1.8 MeV irradiation up to 130 MGy

3. Corrosion test of coated samples

In order to study if a dense ≈ 200 µm thick CVD-SiC layer offers a reliable protection against PbLi corrosion at 700 °C, 14x14x5 mm³ porous SiC samples with ≈ 50% porosity were covered by a dense SiC coating produced by Archer Technicoat Ltd, UK. Cross-sections of the produced sandwich samples are shown in fig. 6. The thickness of the dense layer is near 180-200 µm in all areas and no cracks or other damages were found.

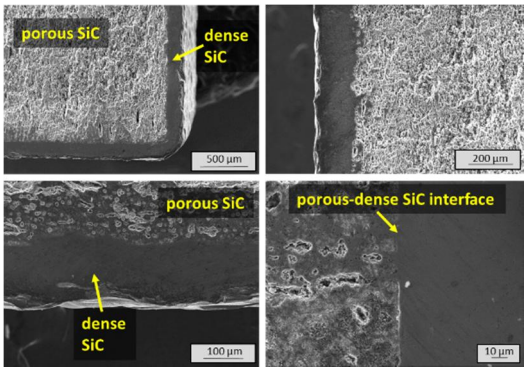

Figure 6. Cross-sections of SiC-sandwich samples formed by a ≈ 50% porous SiC and a dense CVD-SiC coating of ≈ 200 µm thickness (secondary electrons)

The covered samples were immersed in static PbLi at ≈ 700 °C during 1000 h. After the experiment the samples seemed undamaged, although pieces of the dense layer were detached from some samples during their manipulation after the test, as shown in the photographs of fig. 7. No metal infiltration or deposition was detected on the surface of the damaged samples, confirming that detachments did not occur during the experiment.

SEM and EDS analysis were performed inside the samples; micrographs of samples after the experiment can be seen in fig. 8. No lead was detected inside them and no cracks or damages in the dense CVD-SiC coating were found, being the thickness of the coating the same as before the experiment in all samples. Contamination observed by backscattered electrons in the interior of the

sample (fig. 8) is superficial and is assumed to originate from the cutting procedure.

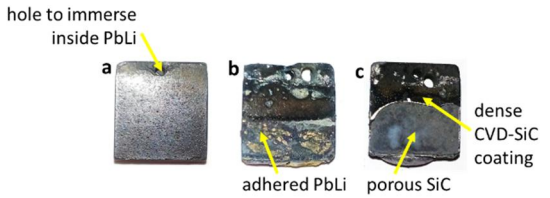

Fig. 7. a) Sample before the corrosion experiment; b) Undamaged sample after the experiment, conserving its whole CVD-SiC coating with metal adhered to the surface; c) Damaged sample after the corrosion experiment

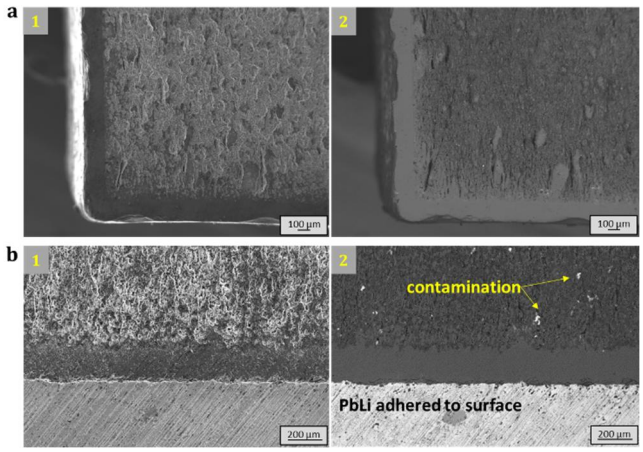

Fig. 8. SEM micrographs of: a) A corner of a sample after the corrosion experiment; b) Detail of the CVD-SiC layer of another sample after the experiment, with PbLi adhered to the outer surface (1 – secondary electrons; 2- backscattered electrons)

4. Discussion

Assuming a porous sandwich core of ≈ 5 mm thick and following the guidelines of the thermomechanical study mentioned in the introduction [4], a porous SiC with a porosity around ≈ 43% would have the required thermal conductivity of ≈ 7 W/m·K, as can be deduced from the relationship showed in fig. 3 b). Such a material can be produced with the proposed method by adding ≈ 18 wt. % of sacrificial phase in the initial powder mixture, as can be inferred from the relationship between the initial MCMB and the final porosity of the samples showed in fig. 1. With the values of flexural strength obtained (in the range 50-80 MPa), it seems that such a porous sample would have enough strength to support the expected thermal stresses. However, it would be desirable to improve the flexural strength of the developed materials with high porosity, in order to assure its integrity in service. On the other hand, the high dispersion obtained in the flexural strength values, especially in the more dense samples, indicates that more work is required to produce free-of-defect samples to not infra-estimate these values. Regarding the electrical properties, the measured electrical conductivity is well below the most restrictive requirements for FCIs found in literature ($\sigma \approx 1$ S/m for inboard blankets [2]). Although the values showed in fig. 5 correspond to the porous material, an important increase in the electrical conductivity due to the dense CVD-SiC layers is not expected due to their reduced thickness compared to the one of the porous core.

5. Conclusions

The following conclusions can be drawn from this work:

- With the proposed method, a porous material with required thermal conductivity and enough mechanical strength to form the core of a SiC-sandwich FCI has been produced. The properties of the material can be varied in a wide range by tailoring its porosity.
- The electrical conductivity of the produced porous SiC is sufficiently low to assure the FCI insulation.
- A 200 µm thick free-of-defects dense CVD-SiC coating offers a reliable protection against static PbLi corrosion.

References

[1] C. P. C. Wong, M. Abdou, M. Dagher, Y. Katoh, R. J. Kurtz, S. Malang, E. P. Marriott, B. J. Merrill, K. Messadek, N. B. Morley, M. E. Sawan, S. Sharafat, S. Smolentsev, D. K. Sze, S. Willms, a. Ying, and M. Z. Youssef, "An overview of the US DCLL ITER-TBM program," *Fusion Eng. Des.*, vol. 85, no. 7–9, pp. 1129–1132, 2010.

[2] S. Smolentsev, N. B. Morley, M. a. Abdou, and S. Malang, "Dual-coolant lead–lithium (DCLL) blanket status and R&D needs," *Fusion Eng. Des.*, pp. 1–11, 2015.

[3] S. Smolentsev, N. B. Morley, C. Wong, and M. Abdou, "MHD and heat transfer considerations for the US DCLL blanket for DEMO and ITER TBM," *Fusion Eng. Des.*, vol. 83, no. 10–12, pp. 1788–1791, 2008.

[4] C. Soto, J. M. Martínez-Esnaola, and C. García-Rosales, "Thermomechanical analysis of a Flow Channel Insert based on a SiC-sandwich material concept," *Nucl. Mater. Energy*, vol. 7, pp. 5–11, 2016.

[5] B. Riccardi, L. Giancarli, A. Hasegawa, Y. Katoh, A. Kohyama, R. H. Jones, and L. L. Snead, "Issues and advances in SiCf/SiC composites development for fusion reactors," *J. Nucl. Mater.*, vol. 329–333, no. 1–3 PART A, pp. 56–65, 2004.

[6] K. H. O. Knacke, O. Kubaschewski, *Thermochemical properties of inorganic substances*, 2nd ed. Düseldorf: Springer, 1991.

[7] A. Singh and N. F. Complex, "End-capping and other defects in pressed ceramic compacts," no. October, pp. 196–200, 1996.

[8] T. Grande, H. Sommerset, E. Hagen, K. Wiik, and M. a Einarsrud, "Effect of Weight Loss on Liquid-Phase-Sintered Silicon Carbide," *J. Am. Ceram. Soc.*, vol. 80, no. 4, pp. 1047–1052, 1997.

[9] N. Ordás, A. Bereciartu, C. García-Rosales, A. Moroño, M. Malo, E. R. Hodgson, J. Abellà, S. Colominas, and L. Sedano, "Testing of porous SiC with dense coating under relevant conditions for Flow Channel Insert application," *Fusion Eng. Des.*, vol. 89, no. 7–8, pp. 1274–1279, 2014.

[10] R. W. Rice, "Evaluation and extension of physical property-porosity models based on minimum solid area," *J. Mater. Sci.*, vol. 31, no. 1, pp. 102–118, 1996.

[11] J. Magdeski, "The porosity dependence of mechanical properties of sintered alumina," *J. Univ. Chem. Technol. Metall.*, vol. 45, no. 2, pp. 143–148, 2010.