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Interface reactions between silicon carbide and interlayers in silicon carbide–copper metal–matrix composites

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Abstract

Novel copper matrix composites reinforced with silicon carbide fibres are considered as a new generation of heat sink materials for the divertor of future fusion reactors. The divertor is exposed to intense particle bombardment and heat loads of up to 15 MW m^{-2}. This component consists of the plasma-facing material which is bonded to the actively cooled heat sink. Due to its high thermal conductivity of about 400 W m^{-1} K^{-1} copper is a promising material for the heat sink. To increase the mechanical properties of copper at working temperature (823 K), silicon carbide fibres with a diameter of 140 μm are used to reinforce the interface area between the plasma-facing material and the heat sink. Push-out tests show that the adhesion between SiC fibre and Cu matrix without any interlayer is very low. To increase the fibre-matrix bonding the fibres are coated with Cr and W with a thickness of 300–400 nm before Cu deposition by magnetron sputtering. Push-out tests on these modified fibres show a significant increase in adhesion compared to the fibres without interlayer. XRD investigations after a heat treatment at 923 K show a chromium carbide ($Cr_{23}C_6$, Cr_3C_2) formation and the absence of chromium silicides. In the case of a W interlayer a W_2C formation is detected and also no tungsten silicides. Single-fibre tensile tests were performed to investigate the influence of the reaction zone on the ultimate tensile strength of the fibres. The ultimate tensile strength for fibres without interlayer remains constant at about 2200 MPa after annealing at 923 K. The fibres with chromium and tungsten interlayers, respectively, show a decrease of about 30% of the ultimate tensile strength after the heat treatment at 923 K.

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1. Introduction

The divertor component will play an important role in a future fusion device. However, the material selection is still an open question, especially for the heat sink [1]. In the current experimental reactors, like Tore Supra or W7-X and the planned ITER, the copper alloy CuCrZr is used for this application [2]. A high thermal conductivity, low swelling under neutron irradiation and sufficient strength at operation temperature were the main reasons for this choice. In the next reactor beyond ITER, the DEMO reactor, the divertor component will operate at a higher temperature [1,3]. The interface temperature between the plasma-facing material and the heat sink will then be in the range of 823 and 873 K [2]. In this

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temperature region the currently used copper alloy, CuCrZr does not own acceptable mechanical strength [4]. Therefore a fibre-reinforced copper metal–matrix composite is investigated to be used as an additional interlayer between the plasma-facing material and CuCrZr. This material will combine the excellent thermal conductivity of copper with the high temperature strength, creep resistance and low induced radioactivity of silicon carbide [5]. In earlier performed experiments silicon carbide fibres with a thin carbon layer (SCS-6, Specialty Materials) were used as reinforcement element. These investigations had shown that the fibres and the copper matrix have a very low adhesion. It was also shown that a thin Ti interlayer as a coupling agent between fibres and copper matrix increases the bonding significantly [6–8]. With this titanium interlayer the fibre itself is the weak point of the composite. Due to this result and the fact that carbon causes problems under neutron irradiation like swelling [9] for further experiments a SiC fibre without the outer carbon layer (SCS-0, specialty materials) is used. Preliminary experiments with this fibre type showed a weak bonding at the copper–silicon carbide interface. To optimize the adhesion between matrix and fibre two different carbide forming interlayers are investigated in this paper: thin crystalline layers of chromium and tungsten.

2. Experimental

For the different investigation methods two kinds of samples were used: planar silicon carbide substrates and SCS-0 SiC fibres (Specialty Materials; fibres without carbon-enriched surface).

The planar samples for investigation of the interaction between the different interlayers by RBS and XRD were prepared by magnetron sputtering in a discovery 18 device with two cathodes (Denton Vacuum).

In the first step, a graded layer of SiC and the interlayer are deposited (Fig. 1). This transition layer with a total thickness of about 150 nm is divided in three 50 nm thin layers with the compositions: (1) SiC/interlayer 3/1, (2) SiC/interlayer 1/1 and (3) SiC/interlayer 1/3. The transition layer is followed by the interlayer (pure Cr or W) with a thickness of 300–400 nm. A 150 nm graded cross-over between the interlayer and Cu was deposited following the same procedure as the first gradient: (1) interlayer/Cu 3/1, (2) interlayer/Cu 1/1 and interlayer/Cu 1/3. Finally a 200–300 nm thin copper layer was deposited on top to prevent the interface from oxidation (Fig. 1).

The preparation of the SiC fibres is performed in the same way except that in a final step an additional 80 μm copper layer is deposited galvanically (Fig. 1). This thick copper layer acts as the matrix material in the SiC/Cu composite and leads to a fibre volume fraction of about 20% in the composite. To reduce the hydrogen and oxygen content in this galvanically grown layer a heat treatment at 823 K for 2 h with a low heating rate of 0.5 K min^{-1} followed the deposition. After this process the single-fibres were packed into a copper capsule (inner diameter of 2 mm; outer diameter of 8 mm; total length 40 mm) as dense as possible and then pressed hot isostaticly (temperature of 1123 K and a pressure of 100 MPa for half an hour).

Heat treatments of the planar substrates and single-fibres were performed in a vacuum of 10^{-5} Pa at 823, 923 and 1123 K for 1 h. The inter-diffusion and microstructure of the as-deposited and the annealed planar substrates is studied by Rutherford backscattering spectroscopy (RBS) with 4 MeV ^{4}He ions, X-ray diffraction (XRD) and scanning electron

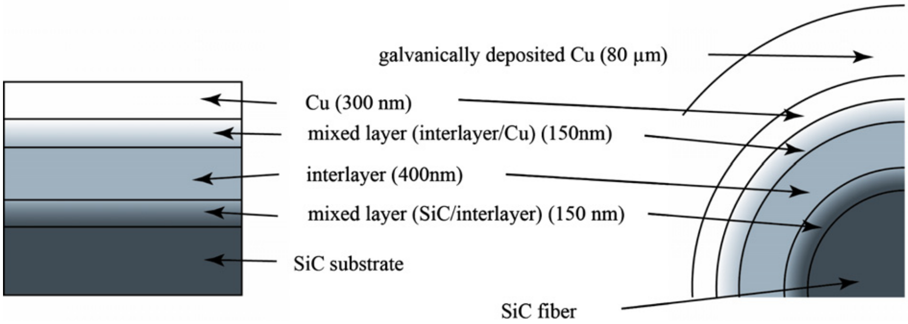

Fig. 1. Schematic view of the layer composition of coated planar samples and fibres.

microscopy (SEM). The phase formation correlation was done by the PCPDFWIN database version 2.1 by ICDD [10]. The adhesion of fibre and matrix is investigated by Push-out tests described by Brendel et al. [6]. Additional single-fibre tensile tests were performed to investigate the influence of the different reaction zones to the ultimate tensile strength of the as-received and the modified fibres. For these experiments a universal test machine (Tira GmbH) is used. To protect the fibres against damage through the clamping, the fibres were embedded in small pieces of paper.

3. Results and discussion

In the system SiC and Cu, which acts as the reference system for the optimization process, RBS measurements show no inter-diffusion up to 923 K. At 1123 K the silicon carbide disintegrates and the free silicon diffuses into the copper layer (Fig. 2) towards the surface of the sample. After 1 h of annealing there is a content of about 15% of silicon in the copper layer. The X-ray diffraction pattern shows no phase formation after annealing at 1123 K. Referring the Cu/Si phase diagram a lot of different phases exist in this temperature range [11]. Therefore the formed crystals can be too small to be found by XRD after annealing for 1 h.

The wetting of Cu and SiC follows complex mechanisms, described by Rado et al. and is for untreated copper and silicon carbide, respectively very poor [12]. To obtain a sufficient reaction zone between silicon carbide fibres and copper anyway the hot-isostatic pressing temperature will be 1123 K. However, Push-out tests on a composite with fibres without interlayer showed no reaction between fibre and matrix and the force to push the fibres out of the matrix lies in the range of 1.5–25 N for the different sample thicknesses (Fig. 3). This indicates that the adhesion between fibre and matrix is very poor and has to be increased to obtain acceptable mechanical properties for the composite. Therefore two carbide forming elements W and Cr respectively were sputtered between fibre and matrix.

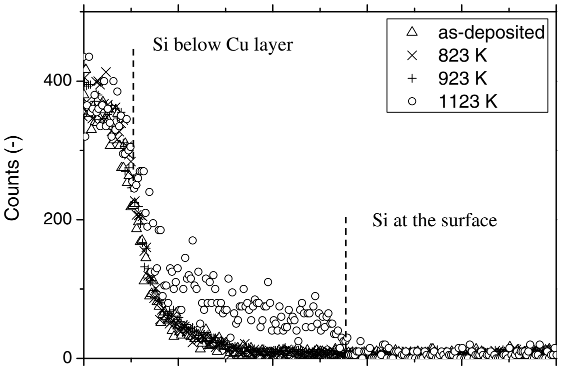

Fig. 2. Silicon edge of the RBS spectra before and after different heating steps in the system SiC–Cu (4 MeV ^{4}He).

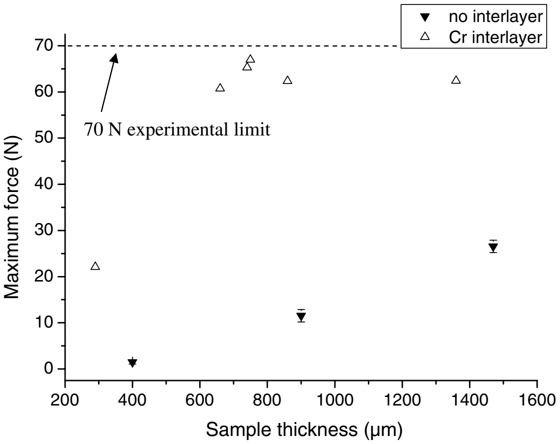

Fig. 3. Comparison between push-out results of SiC–Cu composites with as-received and Cr coated fibres; no error bars are given for Cr because the experiments were cancelled manually at the force limit.

For samples with a W interlayer RBS measurements show no diffusion between the different layers up to 923 K. No results can be obtained for 1123 K because due to high stresses, caused by the different thermal expansion coefficients, the Cu layer flaked off the substrate after annealing the planar samples.

XRD measurements show that a W_2C formation starts during the heat treatment at 923 K. This behaviour corresponds to results obtained by Linsmeier and co-workers who showed that not the carbide (WC) with the higher enthalpy forms first during a heat treatment but the sub carbide W_2C [13]. These results indicate that at temperatures up to 923 K only a reaction at the interface between SiC and W occurs. No diffusion of silicon and copper starts through the W layer.

The strongest diffusion processes appeared in the system SiC–Cr–Cu. In the corresponding RBS spectrum a mixture of all layer and substrate elements is visible. There is a strong diffusion of carbon and silicon towards the sample surface, while chromium and copper diffuse to the interface. This strong diffusion of the elements into the matrix material can lead to a reduced thermal conductivity of the whole composite. Additional investigations have to answer this question.

Investigations by X-ray diffraction of this system show the formation of $Cr_{23}C_6$ and Cr_3C_2 after annealing the samples at 923 K. Between 923 and 1123 K no new phases are observed which shows that all forming processes starts below 923 K and are stable up to 1123 K.

Push-out tests with composites made of chromium coated fibres show a very strong bonding of fibre and matrix, presumably due to the large reaction zone (Fig. 4). Fig. 4(a) shows a SEM image of a push-out sample with the fibre protruding from the matrix. During the push-out the copper matrix is strongly deformed plastically. In Fig. 4(b) an EDX map shows the same area indicating the elements silicon (bright) and chromium (dark). Due to the good adhesion the fibre disintegrates. Parts of the SiC fibre are found on the copper matrix. To prevent the indenter, made of tungsten carbide, from damage the experiments were limited to the force of 70 N. This means that for the Cr interlayer only qualitative results can be achieved. With a sample thickness less than 600 μm the deformation of the copper matrix dominates the push-out process. If the thickness is greater than 600 μm the maximum force reaches values in the range of the limit and the experiment is stopped manually (Fig. 3).

Push-out tests for the system SiC–W–Cu are presently not available.

With this outstanding data it is possible to say which reaction type plays the dominant role for the adhesion of fibre and matrix in the SiC–Cu composite: the carbide formation at the interface with simultaneously diffusion of the elements in greater depths (Cr interlayer) or only the interface reactions of the W interlayer.

To investigate the damage to the fibres due to reactions between silicon carbide and the interlayers at the fibre surface single-fibre tensile tests were performed with fibres as-deposited and annealed at 923 K. As Fig. 5 shows, the ultimate tensile strength (UTS) for the as-received fibres and the fibres without interlayer (only copper coating) remains constant at about 2200 MPa before and after the heat treatment. For both interlayers the UTS decreases by approximately 30% after the heat treatment. Due to the high negative enthalpy of formation of $-338.6\,\mathrm{kJ\,mol^{-1}}$ for the sub carbide $Cr_{23}C_6$ [14] fibres with a chromium interlayer have even at room temperature (as deposited) a reduced tensile strength of about 1750 MPa (Fig. 5) that means only the deposition process of Cr damages the SCS-0 fibres significantly.

Taking into account that tungsten and chromium have a different diffusion behaviour but almost the same reduction of the ultimate tensile strength, only

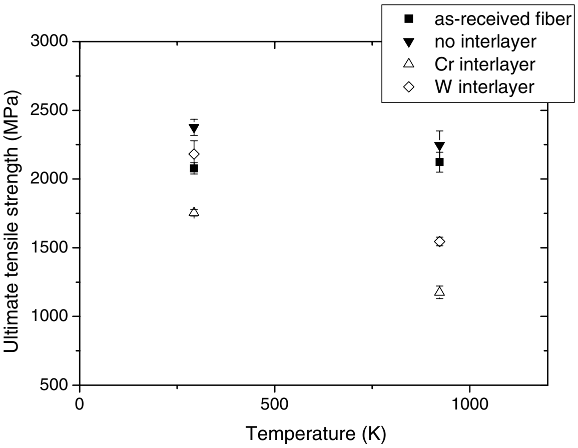

Fig. 5. Comparison of the ultimate tensile strength (UTS) of the different coated and uncoated fibres.

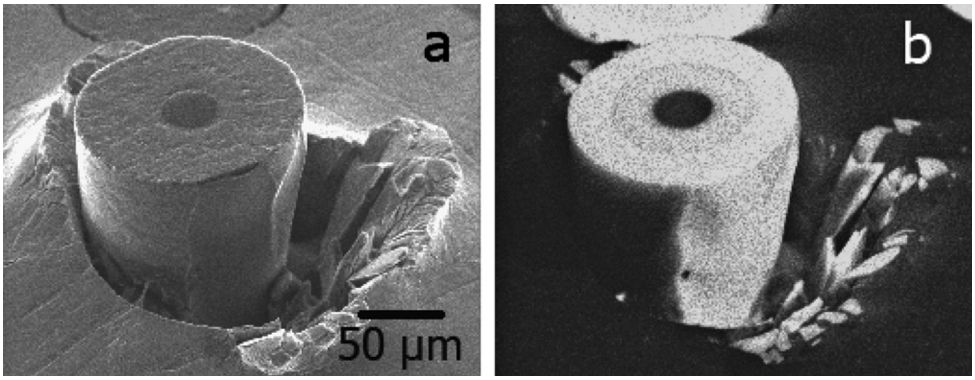

Fig. 4. (a) SEM image of a fibre push-out, (b) EDX map of the same detail where the white colour indicates Si and the black colour Cu.

the carbide formation at the interface influences the tensile strength of the fibres.

4. Conclusion

The results of the investigation on the SiC–Cu system show that an optimized metal–matrix composite only can be obtained with a reactive interlayer between copper and silicon carbide. Push-out tests indicate that without this interlayer the adhesion of the fibre is very poor.

The results of thin W and Cr interlayers in contrast show on the one hand the possibility to use carbide forming elements to increase the bonding between SiC fibres and a copper matrix. In both cases carbides had been formed after annealing at 923 K. This reaction leads in the case of chromium to a strong bonding as push-out tests showed. For the tungsten interlayer these tests are in progress.

On the other hand the single-fibre tensile tests show that the reaction zone at the fibre surface influences the ultimate tensile strength of the fibres significantly. This is an important point which has to be optimized in future work.

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