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Effect of tungsten matrix on the mechanical property of SiC fiber reinforced tungsten composites with foils fabricated at 1700 °C

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ABSTRACT

The SiC fiber reinforced tungsten (W) composites were prepared by hot press process at 1700 °C for 1 h under a pressure of 20 MPa with W foils as matrix. The effect of thickness of W foils on the phases, microstructure, and mechanical properties of the composites were investigated in this work. In addition, the recrystallization temperature of W foil used in this work was confirmed. The results demonstrated that the composites with 0.08 mm foil exhibited better mechanical property with 197 MPa and high pseudo ductility than those of the 0.05 mm foil composites of 129 MPa. In addition, the used foils after sintering have recrystallized, and W can be identified by XRD. Therefore, SiC fiber can be an effective reinforcement to toughen W and dense foils as matrix can prevent the reaction partially.

1. Introduction

The divertor environment in the fusion reactor is extremely harsh for materials owing to heat load and sputtering by plasma and neutron. Tungsten (W) is the most promising candidate for divertor, but its brittleness properties caused by high ductile–brittle transition temperature (DBTT) and further embrittlement in a neutron irradiation environment are restrictions. In addition, the toughness deteriorates caused by the recrystallization behavior, causing the narrow operating temperature window of W between DBTT and recrystallization temperature.

To improve the toughness of brittle materials, fiber reinforcement has been developed as a successful method for decades, in which SiC fiber is widely used because of its extraordinary mechanical properties even at temperature [1] higher than the recrystallization temperature of W. In this study, a completely new method, to strengthen W with SiC ceramic filaments by hot press that can obtain excellent fracture toughness, was to give more choices for divertor application retaining excellent W features including stability to plasma sputtering and high thermal conductivity. Since tungsten and SiC have very close thermal expansion coefficients, and the swelling of SiC at the operating temperature window of W (800 °C to 1300 °C [2]) by neutron irradiation is lower than 1% [3], so it is considered that the stress generated at the interface is minor. In addition, SiC materials also exhibit excellent mechanical properties in a neutron irradiation environment[4]. Besides, both Si and C are light elements. Thus the heat removal in loss-of-coolant accident is relatively easy.

The significant reactions were identified between W powder and SiC fiber genetating tungsten silicides (W_5Si_3 and WSi_2 (47 $W/m^{-1}/K^{-1}$ [5])) and tungsten carbides (WC (63 $W/m^{-1}/K^{-1}$ [6]) and W_2C), lower than the themmal conductivity of SiC and W. Therefore, we consider using dense W foil as matrix to reduce the reaction and improve the strength of composites. Based on this, the mechanical property of two kinds of W foils with thickness as matrix at RT, phase changes during fabrication, and the recrystallization behavior were examined in this work.

2. Experimental

Continuous Hi-Nicalon Type S SiC fibers (NGS Advanced Fibers Co., Ltd.) were utilized as reinforcement to fabricate fiber reinforced W composite, in which W foils with 0.05 and 0.08 mm thick foil (99.95 % purity, E-metals Co. Ltd.) were used as matrix in this work. In addition, W powders with 0.6 μm grain size (99.9% purity, Kojundo Co. Ltd.) were filled in the fiber bundle to connect the foils and fiber and improve the density.

To fabricate SiC_f/W composites, SiC fibers were desized at 500 °C to remove sizing agent firstly. Meanwhile, W powder and polyvinyl butyral (PVB) were dispersed in acetone to prepare the slurry. Then the slurry

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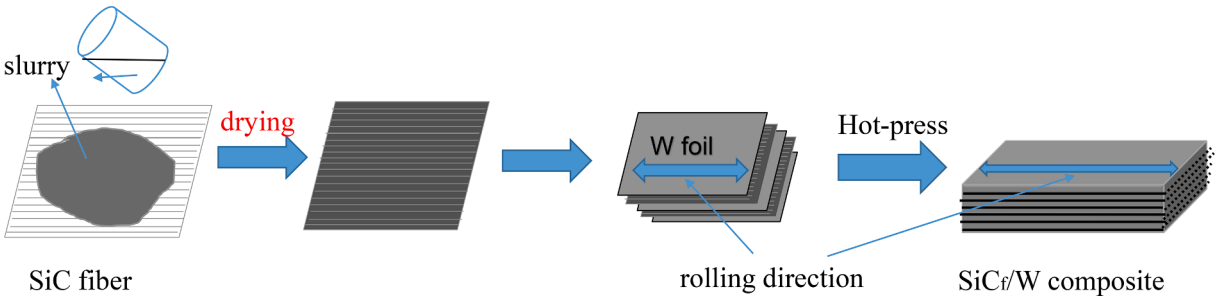

Fig. 1. Method of preparation SiC fiber reinforced W composite with foils.

Table 1
Density and porosity of sintered composites with W foils.

composites	Vf/%	ρ_s / g/ cm^3	ρr / g/ cm^3	Po / %	Pc / %	R.D / %
composite0.05	46.68	10.49	11.68	10.15	2.92	86.93
composite0.08	43.39	11.06	12.44	11.09	1.09	87.81

Note: Vf is fiber volume ratio; ρs is density calculated by geometric method; ρr is density measured by AccuPyc II 1340; Po and Pc is open and closed porosity of composites; R.D is relative density of composite.

was poured into the desized fibers. Afterwards, the fibers filled in the slurry were dried for 24 h at room temperature (RT). After drying, they were cut to 40 × 22 cm^2 slices and staked together with W foil of the same size in a graphite die. Herein, the direction of the fiber arrangement was sustained parallel to the rolling direction of foil. Subsequently, they were sintered by the hot press with 20 MPa pressure at 1700 °C for 1 h in argon atmosphere (see Fig. 1). Moreover, W foils were annealed from 600 °C to 1200 °C for 1 h (every 200 °C) to verify the recrystallized temperature of W foils used in this work. In addition, the pure W specimen was also sintered at the same condition as composites. W foils were washed in NaOH solution (0.98 wt%) using ultrasonic cleaning to remove oxide on the surface of W foil.

The real density (ρr) and volume (Vr) is measured by Shimadzu AccuPyc II 1340 using helium gas. Before voulume test, the weight (m1) was measured firstly. Besides, to understand the open porosity (*Po*), the mass in pure water (m2) and the mass (m3) of the same specimen filled with water were also measured. Thus, *Po* can be cacluted by $Po = \frac{m3-m1}{m3-m2}$. Then the relative density (RD) in this work is from the equation of $RD = 1 - \frac{Vr}{Vs}$ (Vs is volume calculated from size.), and the close porosity (*Pc*) can be from $Pc = 1 - \frac{Vr}{Vs} - Po$. The mechanical property assessment was examined by tensile test at RT by Instron-5581. The size of the testing bar is 40 × 3 × 1.5 mm^3, two pieces of strain gauge were pasted to 40 × 3 mm^2 surface respectively before measurement. Scanning electron microscopy (SEM) was used to observe the microstructure of fabricated composites and the W/SiC couples. Elements were analyzed by electron probe micro analyzer (EPMA). The phases in composites after sintering were identified by X-ray diffraction (XRD) with Co target.

3. Results and discussion

3.1. Density and porosity

Table 1 displays the density and porosity as well as other information of composites. Herein, 1500 °C 0.08 means the composite with 0.08 mm foil sintered at 1500 °C. The relative density is 86.93 % and 87.81 % for composite with 0.05 mm foils and 0.08 mm foils respectively, in which the low density is from high open porosity of approximately 10 % for both composites because the slurry do not disperse uniformly in the fiber bundle. Besides, the fiber volume fraction is about 43.4 % in 0.08 mm foils fabricated composites, lower than that of composites with 0.05 mm W foil of 46.7 %.

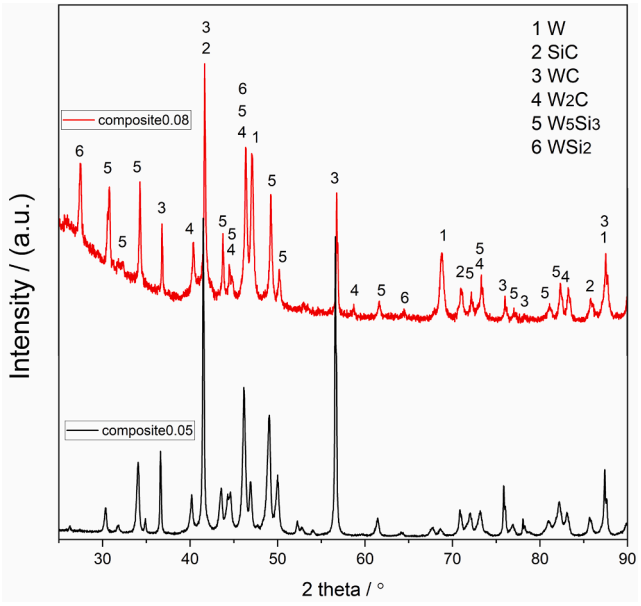

Fig. 2. The XRD pattern of sintered composites with W foils of different thickness.

3.2. Microstructural characterization

The XRD pattern of the fabricated composites is shown in Fig. 2, displaying the phases in the composites. Herein, it is clear to identify the W's peaks in both composites with two kinds of foils sintered at 1700 °C, although the stable reaction products of silicides (W_5Si_3 and WSi_2) and carbides (WC and W_2C) can be found. However, no W remained after sintering at 1700 °C for composite with powders as matrix, illustrating that dense foil can lessen the raction rate between SiC and W. Besides, the intensity of W peaks in 0.08 mm foil fabricated composite is stronger than that of composites with 0.05 mm foil W and without foils fabricated at 1700 °C, indicating that more W remained in composite with 0.08 mm foil.

The SEM images of the cross-section and element analysis by EPMA mapping of 1700 °C sintered composites with foils are exhibited in Fig. 3. It is easy to recognize the remained W and the damaged SiC fibers. In addition, the content of non-reacted W in composites with thicker foil is more than that in composite with 0.05 mm foil, and approximately 10 μm W matrix remained in 0.05 foil, illustrating that dense matrix can decline the reaction rate. Besides, it is easy to observe columnar grains tungsten silicides in composites. Moreover, the diffusion path of Si and C atoms to W were much larger than the one of W into SiC caused by the difference of atoms' size. According to the reported results [7], the possible reactions bwteen W and SiC during the the sintering process up to 1700 °C are shown as follows, and such reactions leading to the degration of fiber.

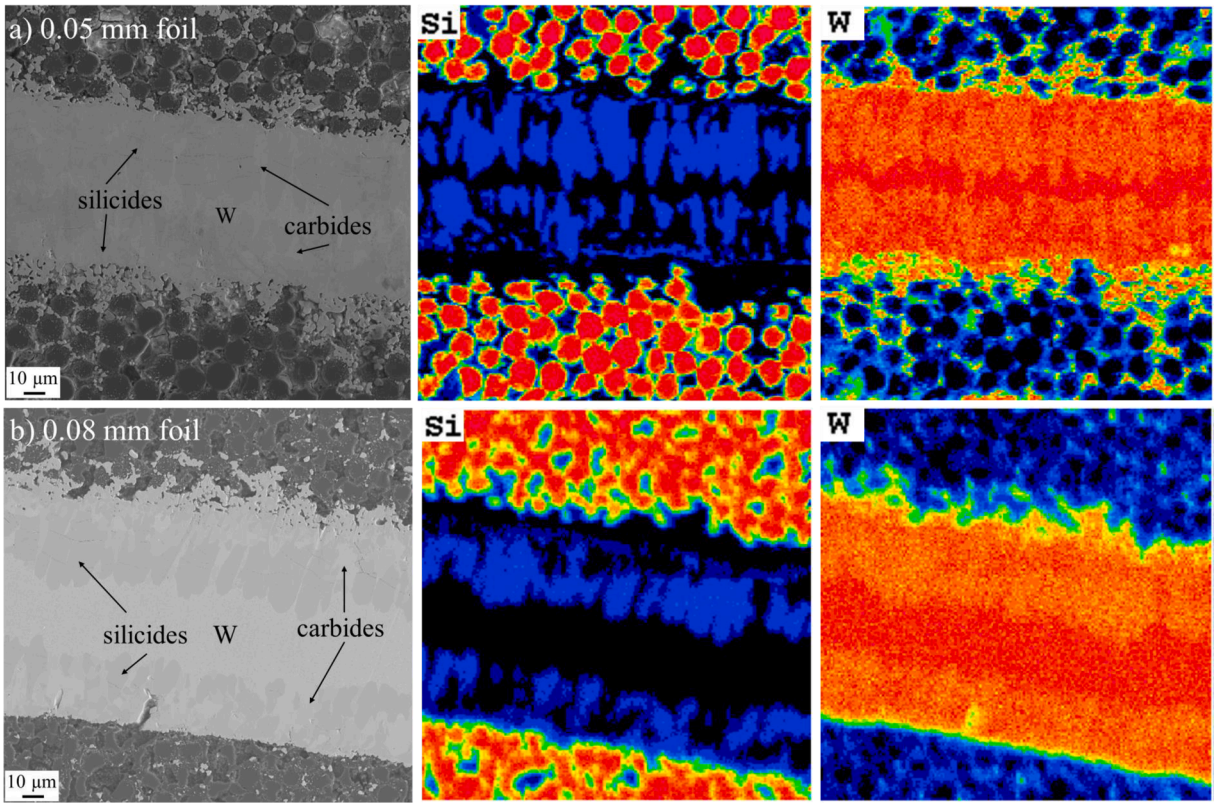

Fig. 3. The cross-sectional SEM images and element analysis by EMPA of composite fabricated with different thicknesses of W foils. a) 0.05 mm foil; b) 0.08 mm foil.

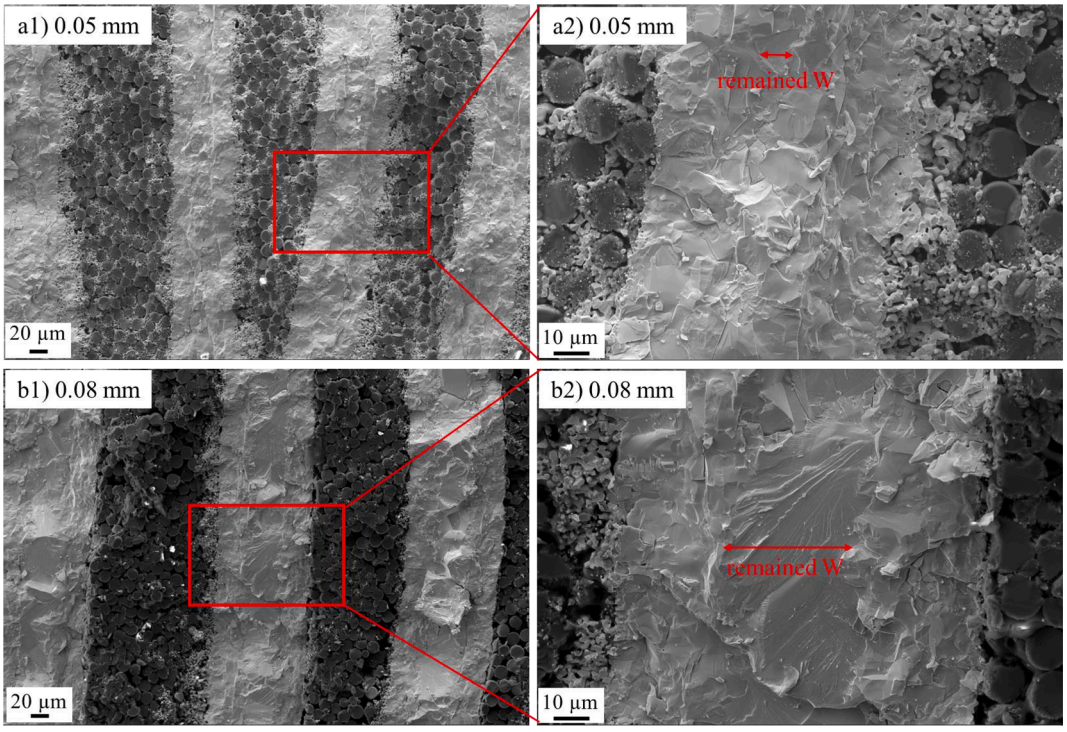

Fig. 4. The cross-sectional SEM images of composites sintered at 1700 °C after tensile test measured at RT. a1) and a2) are composite fabricated with 0.05 mm-thick foils in various magnifications; b) composite with 0.08 mm-thick foils.

$SiC + 5/3\ W \rightarrow 1/3\ W_5Si_3 + C.$
$SiC + 5/2\ W \rightarrow 1/2\ WSi_2 + W_2C.$
$SiC + 3/2\ W \rightarrow 1/2\ WSi_2 + WC.$
$SiC + 8/3\ W \rightarrow 1/3\ W_5Si_3 + WC.$
$SiC + 8/3\ W_2C \rightarrow 1/3\ W_5Si_3 + 11/3WC$
$SiC + 3/7\ W_5Si_3 \rightarrow 8/7\ WSi_2 + WC.$

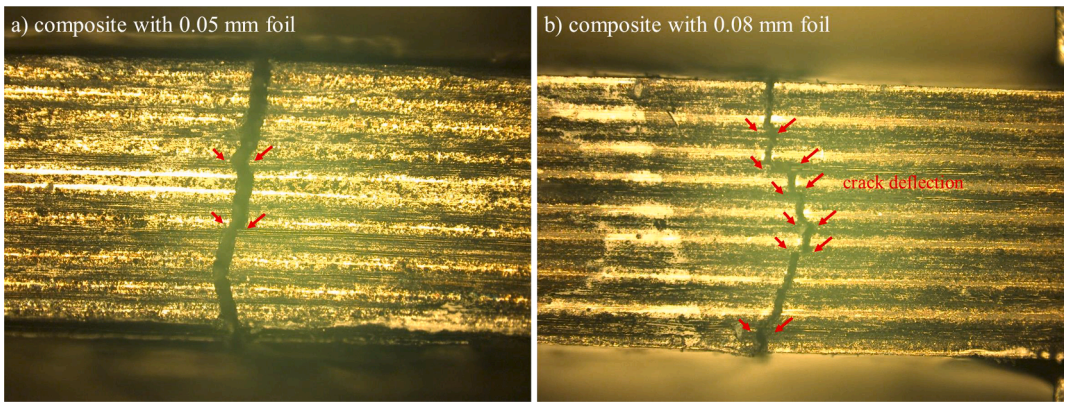

Fig. 5. Optical image of the fracture surface side of composite with foils. a) 0.05 mm; b) 0.08 mm.

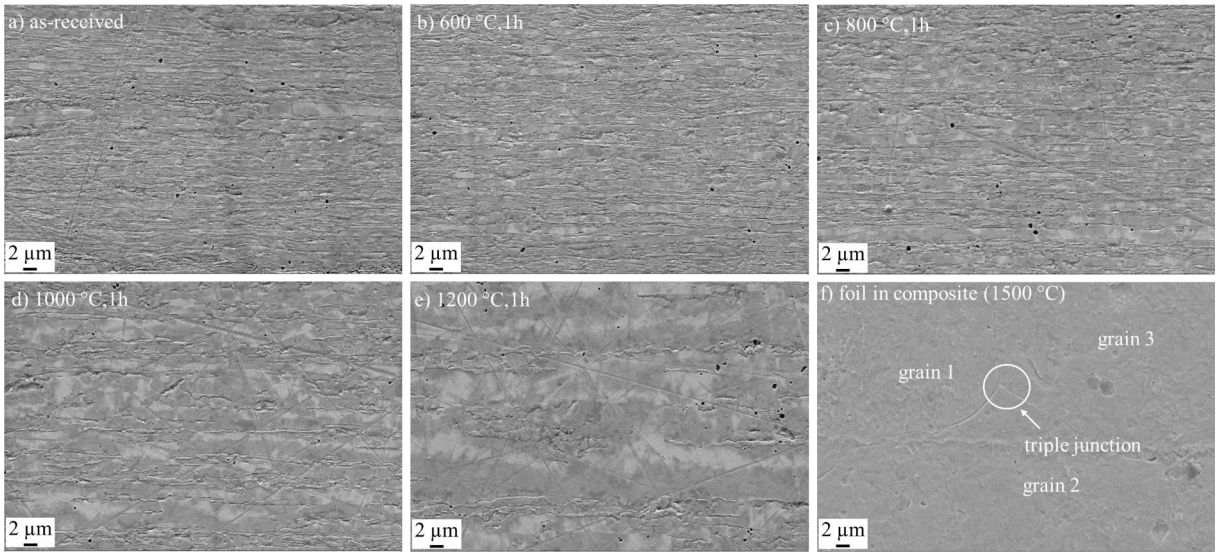

Fig. 6. SEM images of microstructural changes of 0.08 mm W foils heat-treated at different temperatures. a) as-received W foil; b) 600 °C, 1 h; c) 800 °C, 1 h; d) 1000 °C, 1 h; e) 1200 °C, 1 h; f) 0.08 mm W foil in composite (1500 °C).

Fig. 4 reveals the SEM images in SE mode of the cross-section of fabricated composites containing W foils after tensile test at RT with different magnification. No pull-out fiber can be observed from these images in both composites. In addition, most grains in fracture surface show transgranular fracture at RT. Besides, it was also found that the SiC fibers were damaged after sintering at 1700 °C. Moreover, for both composites, small pores in matrix in W powders area near fiber tow can be observed, and these unsintered regions should be carbides because of the high melting point of tungsten carbides combined with the EPMA results.

The optical photographs of the side of fracture surface of composite with foils are revealed in Fig. 5. It is easy to identify the short foil pull-out behavior from image b) due to weak bonding between SiC fiber and W matrix caused by the relatively open porosity, leading to crack deflection. In contrast, only limited crack deflection can be found in composite with 0.05 mm foils. Therefore, we think the pull-out effect from foil contributes to the pseudo ductility in this work.

Fig. 6 displays W's recrystallization behavior, in which 0.08 mm foils were annealed at elevated temperatures for 1 h from 600 °C to 1200 °C for every 200 °C, etched by plasma using CF4 and O_2 mixture gas with the ratio of 90% and 10% before observing [8]. Furthermore, the SEM images of the foil in 1500 °C fabricated composite with 0.08 mm foil is shown in Fig. 6 f), in which the reaction between SiC fibers and W foil is limited. It can be found that the W grains have no noticeable change

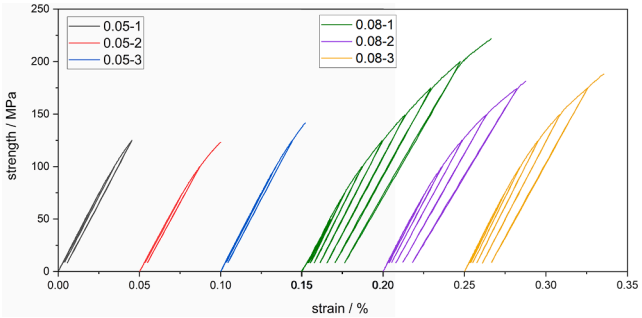

Fig. 7. Tensile test results of fabricated composites with different thick foils measured at RT.

below 800 °C, while they start recovery from 1000 °C. In addition, a typical triple junction can be found in 1500 °C heat treatment W foil, indicating that the grains have completely recrystallized at 1500 °C. Therefore, we think both foils in composites have recrystallized even after 1700 °C sintering. The recovery temperature is slightly higher than the value reported in K-doped W and K-doped W-Re materials [9]; however, both rolled W recrystallized completely as well after 1500 °C, 1 h annealing [9], causing the significant variation of properties like

reducing the Vicker hardness [9] and increasing the DBTT [10].

3.3. Mechanical property

The tensile test results of SiC_f/W composites with different thick foils tested at RT sintered at 1700 °C are illustrated in Fig. 7. The loading direction is parallel to the fiber direction and rolling direction of foil. It can be found that both composites with foils exhibited pseudo ductility tested at RT, although the temperature of tensile tests was room temperature, which is lower than the DBTT of W and the fabrication temperatures are higher than recrystallization temperature. However, the composite with thicker foils displayed a better mechanical property with the more evident pseudo ductile behavior. The result is consistent with the optical images, in which more pull-out short can be found in composites with 0.08 mm. Furthermore, it maintains a high strength of 197 MPa, although it has a comparatively low fiber volume fraction. Besides, the strength is much higher than that of composite fabricated with 0.05 mm foil of 129 MPa. Thus, it can be assumed that the composite with 0.08 mm foils without reactions between fiber and foils should exhibit better UTS and pseudo ductility, in which fiber is responsible for ductility and the W matrix is for strength. However, the UTS of both composites are lower than that of pure W of 478 MPa at RT shown in Fig. S1. But no ductility can be found. In addition, we think both foils have no contribution to ductility because they have recrystallized after 1700 °C sintering (see Fig. 6), and it is reported that the recrystallized W has no ductility below 200 °C even though the as-received W displayed ductile behavior at RT [9]. Therefore, the pseudo ductility in this work is from the SiC fiber and pull-out foil (see Fig. 5), and considering that the lower volume fiber fraction in composites with thicker foil exhibit higher ductility, the contribution for the pseudo ductility from the pull-out effect is higher than SiC fiber itself.

4. Conclusion

Continuous SiC fiber reinforced W composites with 0.05 mm or 0.08 mm foil as matrix were fabricated at 1700 °C successfully. Foils have recrystallized after sintering in this work based on the results of annealing evaluation. Therefore there is no contribution for ductility of composites from foil. The tensile test measured at RT, lower than the DBTT of W, implies that the composites obtained with 0.08 foil showed better apparent pseudo-ductile behavior due to the short pull-out foil and higher UTS of 197 MPa owing to high relative density and more remained W, suggesting that using dense foil as matrix is an efficient way to reduce the reaction rate. Thus SiC fiber as reinforcement is one of the successful methods to ameliorate the embrittlement of W, and it is dispensable to consider the DBTT and recrystallization temperature. Moreover, it is expected that pseudo-ductile behavior will be obtained even if tungsten is brittle caused by neutron irradiation.

CRediT authorship contribution statement

Yina Du: Writing – original draft. **Tatsuya Hinoki:** Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.nme.2022.101142..

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