Production of tungsten-fibre reinforced tungsten composites by a novel continuous chemical vapour deposition process

H. Gietl[a,b], J. Riesch[a,*], J.W. Coenen[c], T. Höschen[a], R. Neu[a,b]

[a] *Max-Planck-Institut für Plasmaphysik, 85748 Garching, Germany*
[b] *Technische Universität München, Boltzmannstrasse 15, 85748 Garching, Germany*
[c] *Forschungszentrum Jülich GmbH, Institut für Energie und Klimaforschung, Partner of the Trilateral Euregio Cluster (TEC), 52425 Juelich, Germany*

Abstract

The brittleness below the ductile-to-brittle transition temperature and the embrittlement during operation are the main drawbacks for the use of pure tungsten in plasma facing components of fusion reactors. Tungsten fibre-reinforced tungsten composites overcome this problem by utilizing extrinsic mechanisms to improve the toughness. Dense samples (>99%) have been successfully produced by a step-wise chemical deposition process of single layers of equally spaced fibres. The sequential deposition process with intermediate vents for the fibre placement leads, however, to inhomogeneities and internal interfaces in the deposited tungsten matrix. A new set-up utilizing a continuous deposition process was developed and used for the fabrication of first samples. These samples were examined by microstructural analysis and compared to material produced by the standard technique. It is shown that this advanced set-up in combination with tungsten fabrics allows the productions of tungsten-fibre reinforced tungsten composite in a more controlled and considerably faster way.

Keywords: tungsten, chemical vapor deposition, fibre-reinforced composite, continuous fabrication

1. Introduction

Tungsten (W) is a promising candidate for the use as a plasma facing material in a future fusion device (DEMO) due to its unique properties such as a low sputter yield, high melting point and moderate activation [1]. The brittle behavior of tungsten below the ductile-to-brittle transition temperature (DBTT) [2, 3] and the embrittlement during operation e.g. by overheating [4] and/or neutron irradiation [5, 6] are the main drawbacks for the use of pure tungsten. This limitation is mitigated by using tungsten fibre-reinforced tungsten composites (W_f/W) [7, 8, 9] which utilizes extrinsic mechanisms to improve the toughness similar to ceramic fibre-reinforced ceramics [10]. W fibres made of commercially available W wire (OSRAM GmbH) are used as reinforcements [11, 12, 13, 14] in combination with a tungsten matrix produced either by a chemical deposition [7, 15] or by a powder metallurgical process [16, 17]. It has been shown that this idea in principle works in as-fabricated state [7, 18] as well as after embrittlement [19, 20].

Recently a stepwise chemical vapour deposition (CVD) process allowing the production of bulk samples was established [15]. In this process single layers of equally spaced, long fibres are sequentially ingrown into the chemically deposited matrix. For the placement of the individual layers the deposition process is frequently stopped. Enhanced performance was shown for this material in Charpy impact [15, 21], tensile [18] and three-point-bending tests [20, 19]. However, during the frequent interruptions of the deposition process interfaces are formed which are suspected to weaken the matrix material [18]. These interfaces are caused by the stop and re-initiation of the growing process but also due to surface contamination as the fibre layer placement makes a break of the vacuum necessary. As the deposition takes places at elevated temperatures cooling down is necessary for each step leading not only to a significant extension of the process time but also to an increased risk of the formation of thermal stresses. In this contribution, we give a detailed description of a novel continuous chemical vapour deposition process for the production of W_f/W avoiding these drawbacks.

2. W_f/W Production

2.1. Standard process

A layer-wise CVD process consisting of three repeating process steps is the standard process for the W_f/W production at the moment [15]. At first, the fibre preform consisting of a single layer of equally spaced long tungsten fibres is placed on a heatable plate inside the process chamber. Then, the plate and thus the preform is heated up and tungsten is deposited until the fibre layer is fully ingrown. Finally, the process chamber is opened to place the next preform layer on top of the already formed solid composite. This process is repeated until the desired thickness is reached. The fibre volume fraction of the specimens is up to 30 % (depending on the distance between the fibre layers) with an overall density of up to 99,7 % [15, 22]. In Fig. 1 the grain structure of material produced with the described layer-wise process is shown. During the process CVD

*Corresponding author: johann.riesch@ipp.mpg.de

tungsten (CVD-W) is growing columnar on all hot surfaces. These can be either be the newly put fibres or CVD-W from the previous steps. In the figure the transition between two layers is shown in detail. Three main growing zones are clearly distinguishable. The first one is marked with 1 and develops during the ingrowing of the first fibre layer. During the deposition of the second fibre layer, new W grains nucleate on the already existing first layer (2a) as well as on the surface of the newly placed fibres (2b). The growth of 2a) stops when either the gas path is blocked or the two growing fronts meet. From that point on, only growing zone 2b) increases in thickness. The red and blue lines in Fig. 1 mark the different interfaces which develop during the deposition.

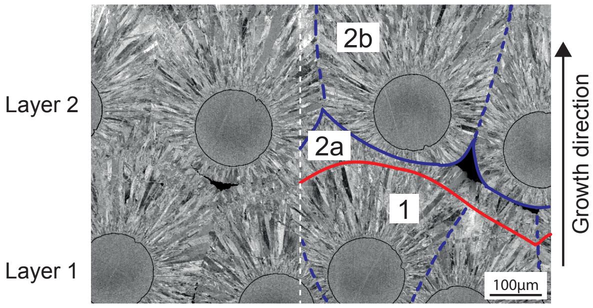

Figure 1: Grain structure of W_f/W produced with a layer wise CVD process. Three growing zones (1, 2a and 2b) are distinguishable. Interfaces in the grain structure are marked with lines in the right part of the figure (separated by dotted white line). The red line marks the interface formed by the restart of the growth process (type I), the blue lines interfaces where growth-fronts meet (type II).

There are two types of interfaces present. The interface between 1 and 2a) (type I, red line) is formed by the restart of the growth process on the already grown CVD material. Here the newly growing small grains are in contact with large grains formed in the previous deposition step. As the material is exposed to air during the placement of the next layer this interface can contain impurities like oxygen. The interface between 2a) and 2b) (type II, blue line) is formed where growth-fronts meet. Here the grains are of similar size. By a premature blocking of the gas access to the surface typically triangular shaped pores are formed at this interface as shown in Fig. 1 and discussed in [23]. This interface is similar to the interface found within the individual layers (dashed blue line).

2.2. *Concept of continues manufacturing*

A continuous process would allow to avoid type I interfaces and due to the obsolete cooling down and venting of the system the risk of contamination, thermal stresses as well as the process time are reduced. For this purpose a continuous manufacturing routine based on the layer-wise process was designed as schematically shown in Fig. 2. In contrast to the standard process, the whole manufacturing process takes place under vacuum. At first, the fibre preform (W-fabric [22]) is wound onto a heatable tube. After a system check this tube is heated up and by providing the reaction gas, W is deposited on the hot fibre preform. By turning the tube the next fabric layer is placed on the already produced composite and is also ingrown. This is repeated until the desired thickness is reached.

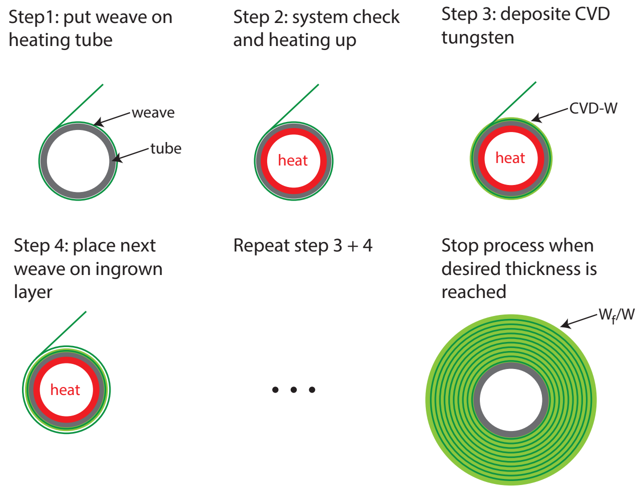

Figure 2: Concept for the continues manufacturing of W_f/W.

2.3. *Technical realisation*

For the technical realisation of the continues manufacturing routine a set-up called FRED (**F**or **R**otary **E**nhanced **D**eposition) was constructed and implemented in the already existing reactor for the chemical depositon of tungsten - WILMA (**W** **I**nfi**L**tration **MA**chine [15]). The set-up is shown in Fig. 3 where in b) a detailed view of the inner parts is given. The system consist of two rotatable tubes (see Fig. 3 b)). On one the fabric is stored (fabric tube) and on the other one (heatable) the CVD reaction takes place (composite tube). The fabric tube needs to be protected from heat to avoid undesired deposition. For this purpose a heat shield is placed between the two tubes. The composite tube is heated from the inside by cartridge heaters. By this the process gases do not have direct contact with the heating elements. On this tube a shell (two parted for mounting purpose) of a tungsten heavy alloy (HPM1850, H.C. Stark [24]) is clamped on which the formation of the composite itself takes place. By this thermal stresses during the mounting/unmounting and fabrication are minimized as the coefficient of thermal expansion of this tungsten heavy alloy is similar to W. By turning the composite tube the fibre preform is rolled onto it. In the first stage of the installation the turning of the tube is performed manually. During the manual turning of the composite tube the fabric is strained and the fabric tube is turning passively. The friction in the bearings of the fabric tube ensures that the fabric remains under tension and uncurled. On three sides of the composite tube a gas inlet for the process gases (WF_6 and H) is placed (not shown in the picture). These inlets are fed from the same gas supply pipe.

For the first test deposition the heater was set to 650°C which resulted in a surface temperature for the deposition of 600°C. The reaction gas was 1500 sccm H_2 and 400 sccm WF_6 at a pressure of 100 mbar. As fibre preform a fabric with a fibre distance of approximately 270 μm [22] was chosen. A deposition time of 45 min was defined for each layer. After that time the composite tube was manually rotated for 360° to place a new fibre layer.

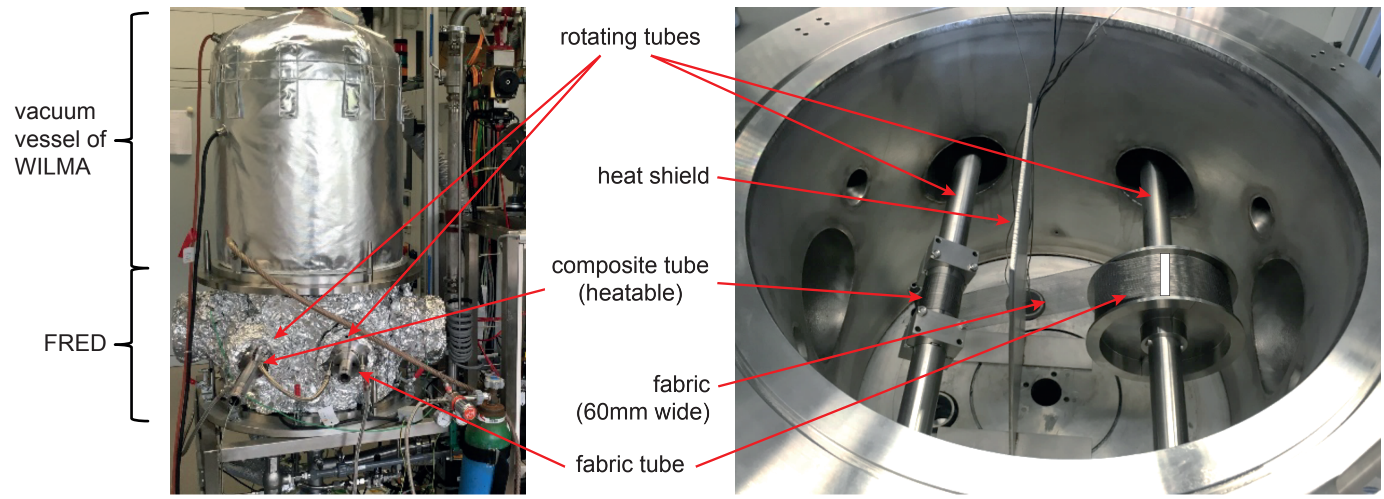

Figure 3: Experimental set-up of FRED a) FRED implemented in WILMA b) detailed view of the inner parts.

3. Results

Fig. 4 shows the result of the first deposition in FRED. Here, the produced W_f/W material and the composite tube are still in one piece. The deposition is not homogenous around the tube. Whereas at the top (where the gas inlet was coming from above) a relatively homogenous layer is visible the fabric is still visible on the other parts (where the gas inlet was placed at the side).

Figure 4: Sample produced during the first deposition in FRED. The deposition was not homogenous with a thick coating at the top part and still visible fibre fabric in the other parts.

Samples for the micro structural analyses were cut out of the dense top part of the tube. The grain structure of the produced material is shown in Fig. 5. There are two fibre layers visible (marked with 1 and 2). The matrix material is pore free and shows a columnar grain structure starting at the W-fibres. The shape of the grains is an indication for the growth direction. During growth-initiation very small grains are formed (see fibre surface) and the longer the deposition takes place the larger the grains get. Between layer 1 and 2 only one interface is visible. The reason for that seems to be that after placing layer 2 new grains start to grow on the newly placed fibres but at the same time the growth of the grains of layer 1 is not stopped. The two growing fronts meet at some point forming a type II interface. The blue line in Fig. 5 marks this interface.

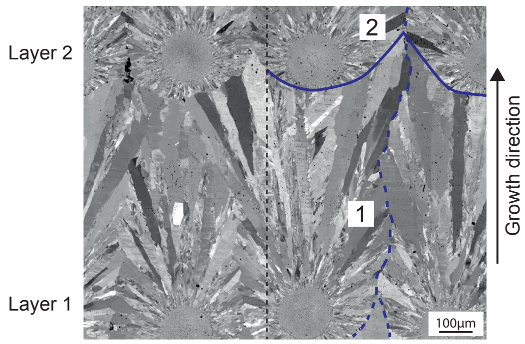

Figure 5: Grain structure of the continuously produced W_f/W. Two growing zones (1 and 2) are distinguishable. Interfaces in the grain structure are marked with lines in the right part of the figure (separated by dotted black line). Only interfaces where growth-fronts meet are present (type II).

4. Discussion

A non uniform coating in circumferential direction of the composite tube was observed in the first deposition. The reason for that is probably the gas supply. Although it was anticipated that the gas will be distributed uniformly to the three inlets it seems that due to gravity the heavy WF_6 gas was directed mainly through the top inlet and that there was only minor gas flow through the other two inlets. Therefore the deposition rate was also highest next to the top inlet. The high deposition rate most probably led to a depletion of the reaction gas preventing the coating of the other parts. At the moment FEM simulations are ongoing trying to understand this depletion in more detail. To avoid this problem the cross-sections of the supply pipes to the inlets could be adjusted in a way that a uniform flow in all three inlets is achieved. In another solution only the upper gas inlet in combination with a continues rotation of the heated tube would be used. By the continues rotation all hot surfaces of the fabric would be moved trough the WF_6 flow. For this the set up needs to be geared up with a motor and the rotation needs to be adjusted to the growth rate of the CVD-W.

In a layered W_f/W manufacturing routine the grain growth is in general columnar, i.a. perpendicular, on every hot surface. The grain growth starts with small grains and ends up with a few large grains (Fig. 1, Fig. 5 and Fig. 6). In Fig. 1 the interface caused by the stop of the grain growth and the nucleation of new grains on all surfaces, which are the already existing deposited W-grains and the newly placed fibres, is visible. This nucleation on the already existing W-grains is a result of the preceding stop of the deposition during cooling down and ventilation of the system. As in the deposition with FRED these steps are not existent this interface is not formed. The grains of the first layer does not show growth interruption although the tube was rotated by 360°. An interface is only formed when the growing front of the first fibre layer meets the growing front of the second fibre layer (Fig. 5 and Fig. 6). To illustrat this difference the grain growth of the standard process and the continues process is schematically shown in Fig. 7.

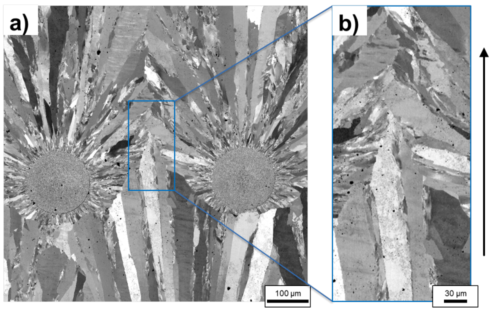

Figure 6: Detailed grain structure of W_f/W produced with FRED.

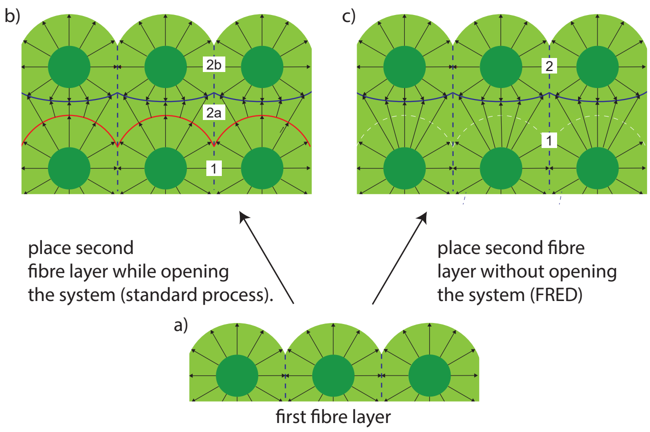

Figure 7: Difference in grain growth with layered deposition with and without ventilation.

On the one hand, the interface free growth of the tungsten microstructure might have a positive effect on the mechanical properties of the W-matrix in W_f/W due to the reduction of contamination and thermal stresses. On the other hand, the grains produced with the continuous process are much bigger. As fine grained W shows in general better mechanical properties than coarse-grained or recrystallised W [3, 14] it is possible, that these large grains show reduced mechanical properties. Mechanical tests on the produced material will be used to investigate the actual performane.

5. Conclusion and Outlook

The layered deposition for the production of long fibre reinforced W_f/W was for the first time performed continuously. The W grain structure was pore free with large columnar grown W grains and internal interfaces could be reduced.

It is planned to produce a mock-up for high-heat flux tests [25] with the continuous deposition process in the near future and to compare it with mock-ups produced with the conventional technique. A possible production routine for such a mock-up is shown in Fig. 8. The W_f/W is directly produced on a CuCrZr tube which will later be used as the cooling tube. The final geometry of the mock-up can be cut out with electric discharge machining. With respect to the results the set-up of the system and the process design will be adopted e.g. by the incorporation of W yarns allowing for sharper winding angles and thus more complex geometries.

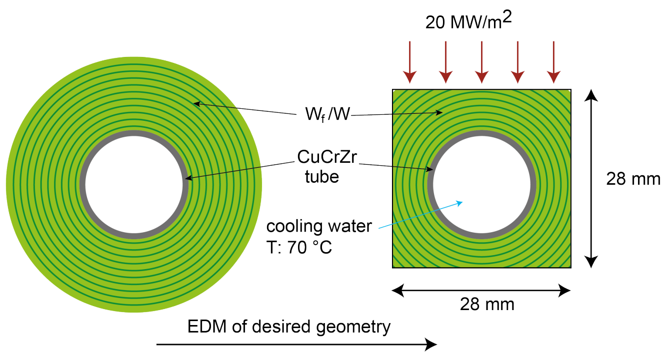

Figure 8: Mock-up production routine with FRED

Acknowledgement

The authors want to acknowledge the Osram GmbH, Schwabmünchen, Germany for providing the tungsten wire and the whole W_f/W team. 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.

References

[1] J.W. Coenen, S. Antusch, M. Aumann, W. Biel, J. Du, J. Engels, S. Heuer, A. Houben, T. Höschen, B. Jasper, F. Koch, J. Linke, A. Litnovsky, Y. Mao, R. Neu, G. Pintsuk, J. Riesch, M. Rasinski, J. Reiser, M. Rieth, A. Terra, B. Unterberg, Th. Weber, T. Wegener, J-H. You, and Ch. Linsmeier. Materials for DEMO and reactor applications boundary conditions and new concepts. Physica Scripta, T167:014002, 2016.

[2] C. Gandhi and M.F. Ashby. Overview no. 5: Fracture-mechanism maps for materials which cleave: F.C.C., B.C.C. and H.C.P. metals and ceramics. Acta Metallurgica, 27(10):1565–1602, 1979.

[3] E. Lassner and W.-D. Schubert. Tungsten - Properties, Chemistry, Technology of the Element, Alloys, and Chemical Compound. Springer, 1999.

[4] W. Yih and C. Wang. Tungsten: Sources, Metallurgy, Properties, and Applications. Springer US, 1979.

[5] V. Barabash, G. Federici, M. Rödig, L. Snead, and C. Wu. Neutron irradiation effects on plasma facing materials. Journal of Nuclear Materials, 283-287:138–146, 2000.

[6] J.M. Steichen. Tensile properties of neutron irradiated TZM and tungsten. Journal of Nuclear Materials, 60:13–19, 1976.

[7] J. Riesch, T. Höschen, Ch. Linsmeier, S. Wurster, and J.-H. You. Enhanced toughness and stable crack propagation in a novel tungsten fibre-reinforced tungsten composite produced by chemical vapour infiltration. Physica Scripta, T159:014031, 2014.

[8] J.W. Coenen, Y. Mao, J. Almannstötter, A. Calvo, S. Sistla, H. Gietl, B. Jasper, J. Riesch, M. Rieth, G. Pintsuk, F. Klein, A. Litnovsky, A.v. Müller, T. Wegener, J-H. You, C. Broĉkmann, C. Garcia-Rosales, R. Neu, and C. Linsmeier. Advanced materials for a damage resilient divertor concept for demo: Powder-metallurgical tungsten-fibre reinforced tungsten. Fusion Engineering and Design, 124:964–968, 2017.

[9] R. Neu, J. Riesch, A.v. Müller, M. Balden, J.W. Coenen, H. Gietl, T. Höschen, M. Li, S. Wurster, and J-H. You. Tungsten fibre-reinforced composites for advanced plasma facing components. Nuclear Materials and Energy, 12:1308–1313, 2017.

[10] A.G. Evans. Perspective on the development of high-toughness ceramics. Journal of American Ceramic Society, 73:187–206, 1990.

[11] J. Riesch, J. Almannstötter, J.W. Coenen, M. Fuhr, H. Gietl, Y. Han, T. Höschen, Ch. Linsmeier, N. Travitzky, and P. Zhao. Properties of drawn w wire used as high performance fibre in tungsten fibre-reinforced tungsten composite. IOP Conference Series: Materials Science and Engineering, 136:012043, 2016.

[12] J. Riesch, Feichtmayer A., M. Fuhr, J. Almannstötter, J.W. Coenen, H. Gietl, T. Höschen, A. Manhard, C. Linsmeier, and R. Neu. Tensile behaviour of drawn tungsten wire used in tungsten fibre-reinforced tungsten composites. Physica Scripta, (T170):014032, 2017.

[13] A.v. Müller, M. Ilg, H. Gietl, T. Höschen, R. Neu, G. Pintsuk, J. Riesch, U. Siefken, and J. H. You. The effects of heat treatment at temperatures of 1100 °C to 1300 °C on the tensile properties of high-strength drawn tungsten fibres. Nuclear Materials and Energy, 16:136–167, 2017.

[14] P. Zhao, J. Riesch, T. Höschen, J. Almannstötter, M. Balden, J.W. Coenen, U. Himml, U. von Toussaint, and R. Neu. Microstructure, mechanical behavior and fracture of pure tungsten wires after different heat treatments. International Journal of Refractory Metals and Hard Materials, 68:29–40, 2017.

[15] J. Riesch, M. Aumann, J.W. Coenen, H. Gietl, G. Holzner, T. Höschen, P. Huber, M. Li, Ch. Linsmeier, and R. Neu. Chemically deposited tungsten fibre-reinforced tungsten - the way to a mock-up for divertor applications. Nuclear Materials and Energy, 9:75–83, 2016.

[16] Y. Mao, J.W. Coenen, J. Riesch, S. Sistla, J. Almannstötter, B. Jasper, A. Terra, T. Höschen, H. Gietl, M. Bram, J. Gonzalez-Julian, C. Linsmeier, and C. Bröckmann. Development and characterization of powder metallurgically produced discontinuous tungsten fiber reinforced tungsten composites. Physica Scripta, T170:014005–, 2017.

[17] Y. Mao, J.W. Coenen, J. Riesch, S. Sistla, J. Almanstötter, B. Jasper, A. Terra, T. Höschen, H. Gietl, Ch. Linsmeier, and C. Broeckmann. Influence of the interface strength on the mechanical properties of discontinuous tungsten fiber-reinforced tungsten composites produced by field assisted sintering technology. Composites Part A: Applied Science and Manufacturing, 107:342–353, 2018.

[18] H. Gietl, J. Riesch, J. Coenen, T. Höschen, C. Linsmeier, and R. Neu. Tensile deformation behavior of tungsten fibre-reinforced tungsten composite specimens in as-fabricated state. Fusion Engineering and Design, 124:396–400, 2016.

[19] H. Gietl, J. Riesch, J. Coenen, S. Olbrich, T. Höschen, G. Holzner, L. Raumann, Y. Mao, H.A. Rost, and R. Neu. Fracture toughness for tungsten fibre-reinforced tungsten composites utilising different estimation techniques. In Preperation, 2018.

[20] R. Neu, J. Riesch, J.W. Coenen, J. Brinkmann, A. Calvo, S. Elgeti, C. Garcia-Rosales, H. Greuner, T. Höschen, G. Holzner, F. Klein, F. Koch, Ch. Linsmeier, A. Litnovsky, T. Wegener, S. Wurster, and J-H. You. Advanced tungsten materials for plasma-facing components of DEMO and fusion power plants. Fusion Engineering and Design, 109-111: Part A:1046–1052, 2016.

[21] H. Gietl. Weiterentwicklung von wolframfaserverstärkten Wolfram-Verbundwerkstoffen für den Einsatz in der Fusion. PhD thesis, Technische Universität München, 2018.

[22] H. Gietl, A.v. Müller, J. Riesch, J. Coenen, T. Höschen, Ph. Huber, M. Decius, D. Ewert, M. Milwich, and R. Neu. Textile techniques for tungsten fibre-reinforced composites production. Journal of Composite Materials, Article first published online, 2018. https://doi.org/10.1177/0021998318771149.

[23] J. Riesch, T. Höschen, A. Galatanu, and J-H. You. Tungsten-fibre reinforced tungsten composites: A novel concept for improving the toughness of tungsten. In Proceedings of the Eighteenth International Conference on Composite Materials, Jeju, South Korea, 2011.

[24] R. Neu, H. Maier, M. Balden, S. Elgeti, H. Gietl, H. Greuner, A. Herrmann, A. Houben, V. Rohde, B. Sieglin, and I. Zammuto. Investigations on tungsten heavy alloys for use as plasma facing material. Fusion Engineering and Design, 124:450–454, 2017.

[25] H. Greuner, B. Bswirth, J. Boscary, and P. McNeely. High heat flux facility gladis: Operational characteristics and results of w7-x pre-series target tests. Journal of Nuclear Materials, 367–370:1444–1448, 2007.