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Tungsten-Based Composites for Nuclear Fusion Applications

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Abstract

This chapter provides a comprehensive knowledge about the potential role of tungsten-based composites in fusion reactors and the research work which has been done in this very important area of nuclear materials. The characteristics of tungsten, which make it the most potential candidate for plasma-facing applications, have been presented along with the shortcomings in pure tungsten. The research work that has been done so far in the field of tungsten-based composites to overcome the problems with pure tungsten has been included. The fabrication, characterization, types of reinforcements and the classes of composites have been reviewed. The behavior of tungsten-based composites under various kinds of loads (i.e. mechanical and thermal) and environments (radiations and oxidizing etc.) has been summarized.

Keywords: tungsten-based composites, nuclear fusion, plasma-facing materials, metal matrix composites, oxide dispersion

1. Introduction

Engineering materials for nuclear applications must be able to withstand extremely harsh service conditions. Among the various areas of nuclear engineering, the fusion reactor system presents a great challenge for materials engineering. The fusion environment, i.e., with high temperatures and high neutron and particle flux, steps up the degradation and alters the mechanical and thermal behavior of the fusion reactor materials, jeopardizing the dimensional stability and integrity of the materials [1]. The selection of proper materials for certain applications has always been somewhat difficult, and the fusion environment, involving high temperatures and likely radiation damage, makes this task more difficult [1].

As a result of extensive research, tungsten (W) has emerged as a highly useful plasma-facing material (PFM) [1–3]. Its high melting point, high thermal conductivity, low coefficient of thermal expansion, high sputtering threshold energy, low tritium retention and low neutron activation make W a potential candidate for fusion applications [4–6]. Previously, applications of W were rare and were limited to experimental purposes only in tokamaks due to the formation of high-Z dust, which originates from materials eroding on the surfaces of the plasma-facing components. This dust has detrimental effects on the plasma parameters [7], but research has revealed the feasibility of plasma operations with W [1, 8]. The plasma impurity problem associated with W may be eliminated by ensuring that the energy of the plasma particles remains lower than the sputtering threshold (~ 700 eV for tritium) [9]. In fusion applications, an increase in the future utilization of W is foreseen [9, 10], as it is considered as a first wall [11] and a divertor surface [1] material for future fusion reactors, as illustrated in **Figure 1**.

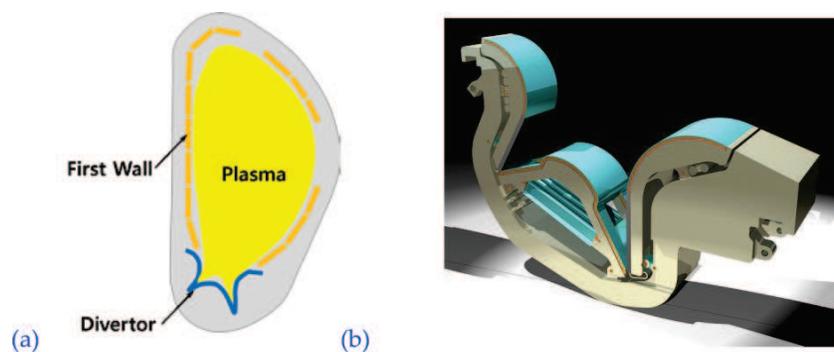


Figure 1. (a) A schematic cross-section of tokamak and (b) a solid model illustration of divertor (commons.wikimedia.com).

As compared to other high-temperature applications, which require good physical and mechanical properties such as high thermal conductivity, good thermal shock resistance and high-temperature strength, toughness and stiffness [12], fusion reactors impose very complex requirements on plasma-facing materials (PFMs) [1]. While PFMs are assumed to be able to sustain high mechanical, thermal and magnetic loads for prolonged periods of time [8], irradiation effects are particularly important in plasma-facing components [13]. Transmutation and ballistic damage, which alter the composition and microstructure of materials due to the interaction between the materials and the high-energy neutron flux (~ 14 MeV), reduce the mechanical properties of PFMs. The interaction of neutron flux with materials forms dislocation loops and clusters of transmutation products from non-equilibrium phases [14].

The energetic ions and neutral atoms in the service environments of fusion reactors cause sputtering erosion in plasma-facing components [1], which is a major concern associated with these materials [8]. The free atoms can be ionized and form contaminants. These contaminants can then be deposited at various locations on the chamber wall. The erosion and re-deposition create new layers which can shorten the service lifetime of the fusion reactor by enhancing tritium retention and morphology variations [8].

Appropriate mechanical, thermal and physical properties are commonly required in plasma-facing components [15]. The hydrogen isotope retention of the materials is also one of the essential considerations when selecting appropriate materials [9]. In the future, the challenges associated with PFMs are expected to increase due to the continuous increase in the thermal loads of upcoming fusion reactors. For example, PFMs may experience very high amounts of localized energy in a very short period of time during transient conditions. Plasma disruption, vertical displacement events (VDEs) and the edge-localized mode (ELM) cause these high localized thermal loads [16], and the inner and outer plates of the divertor may experience loads of $\sim 7\text{--}40\text{ MJ/m}^2$ and $\sim 4\text{--}25\text{ MJ/m}^2$ due to plasma disruption. Considering VDEs, the energy deposition on the outer wall blanket modules may increase to $\sim 20\text{--}30\text{ MJ/m}^2$ in $\sim 0.1/0.3\text{ }\mu\text{s}$. The ELM, if it is controlled, may impose loads of 0.5 MJ/m^2 and 0.3 MJ/m^2 on the inner and outer plates, respectively, of the divertor, whereas the ELM if uncontrolled may be more severe as it can impart corresponding loads of 10 MJ/m^2 and 6 MJ/m^2 on the inner and outer plates of the divertor within ~ 0.25 to $0.5\text{ }\mu\text{s}$ [17].

2. Properties of W for fusion applications

2.1. Advantages of W and drawbacks of using pure W in fusion applications

In order to be considered as a potential candidate for plasma-facing and high-temperature applications, more specifically for the divertor and the first wall in a fusion power reactor, a material must fulfill all of the requirements of plasma-facing applications noted in the above section. W has unique characteristics, which have increased its value relative to other materials. The properties which confer this valuable status in nuclear engineering include its refractoriness, high melting point, high thermal conductivity, low thermal expansion coefficient, good chemical stability, high heat resistance, high sputtering threshold energy, low sputtering rate, low erosion rate at edge plasma temperatures of less than $40\text{--}50\text{ eV}$, low deuterium/tritium retention rate, low tritium permeability, high moduli of elasticity, good thermal shock resistance, lack of hydride formation and adequate corrosion resistance [12, 15, 18–30]. The use of W is associated with other advantages as well. For instance, under neutron irradiation, the thermal conductivity of W does not decrease sharply [12]. Moreover, it is not greatly affected by high activation [19]. Taken together, these properties increased the usefulness of W in plasma-facing and high-temperature applications.

However, W has a number of shortcomings as well, which need to be addressed. The behavior of W is undoubtedly advantageous for fusion applications, but the few drawbacks of W create areas for further research to make W more reliable. Inherently, W possesses a high ductile-to-brittle transition temperature (DBTT), low ductility and poor fracture toughness, low machinability and fabricability, low-temperature brittleness, radiation-induced brittleness, and a relatively low recrystallization temperature compared to its operation temperature [5, 15, 21, 26, 29]. The use of W above its recrystallization temperature interminably can be unsafe because its mechanical properties decrease in such an environment [19, 21]. W is also associated with high embrittlement due to irradiation at low temperatures [4, 22, 24], and the DBTT of W

increases with an increase in the radiation level [29]. Low-temperature brittleness imposes restrictions on the application of tungsten as a structural material [25, 27, 28].

The development of a melt layer due to an intense thermal transient condition stimulates the generation of highly activated dust particles. Due to the interaction with high-energy ions, W can undergo additional erosion [1]. W shares a common disadvantage with other high-Z materials, i.e., very low acceptable impurity concentrations in the plasma, thus requiring almost perfectly controlled plasma [1]. The recombination rate coefficient for H₂ is very high in W, and the high hydrogen content results in bubbles and blisters. Keeping W at an elevated temperature will increase the blisters and the inventory problem [9]. He bubbles are also observed when W samples are exposed to He plasma [31–33].

Due to its high hardness, high brittleness, and poor machinability, the manufacturing of W parts is very costly and time-consuming [20]. The joining of W to a Cu-based (CuCrZr) heat sink is troublesome, owing to the large difference in the CTEs of these two materials [18]. Considering all of these shortcomings, it can be said that further enhancements of the properties of W are essential prior to its commercial use [4, 18].

2.2. Recent trends to enhance the performance of W

Pure W shows favorable behavior for applications to high-temperature and plasma-facing applications. Regarding the aforementioned limitations, research is in progress to improve W and make it useful in future fusion reactors [4]. Currently, research in the field of plasma-facing materials focuses on determination of the impacts of ion irradiation on the properties of W [4]; improvements of its mechanical properties [1], such as its ductility [19] and fracture toughness [15]; methods to mitigate its brittleness [26]; and clarifications of the activation of this material [2].

Various options are being utilized for modifications and improvements of these properties. Some of these techniques involve (i) W-based composites [19], (ii) nanocrystalline W-based materials [1, 5, 34], (iii) W–X (X=Ta, Re, Mo, V, Ti, etc.) alloys created by powder metallurgy [15, 35–39], (iv) the dispersion of ductile fibers in W by mechanical synthesis [25], (v) the dispersion of ceramic particles of transition metals [13], (vi) the addition of rare-earth oxide particles into W [26], (vii) effective energy dissipation caused by controlled cracking and friction at fiber/matrix interfaces [28], and the utilization of functionally graded materials (FGMs) as an efficient solution to the joining problem of W to copper-based heat sinks [34], (viii) the creation of laminated hybrid composites [18], (ix) the post-processing of W to obtain full densification [21], and (x) the addition of a sintering activator to obtain high density levels [21].

All of the abovementioned methods and techniques have some influence on the properties of W. For instance, equal-channel angular pressing (ECAP) reduces the brittleness and improves the toughness and strength of ultrafine (0.9 μm) equiaxed grains of W [21], as ECAP ultra-fine-grained W exhibits much smaller cracks as compared to coarse-grained W around dents produced by microhardness tests even at 250°C [30]. Plasma spraying offers high adhesion

and stability of thick W coatings on EUROFER steel [1]. Among all of these options, W-based composites are of great importance due to their diverse range of useful properties.

3. Development of W-based composites for nuclear applications

Conventional alloys of W exhibit brittle behavior [40]; therefore, the development of W-based composite materials is considered to be advantageous for incorporating W with desirable properties [40]. A number of additives [36, 41–47] have been examined for the production of W composites with enhanced high-temperature mechanical properties [48–50] and good irradiation resistance [51–53].

3.1. Types of W-based composites

The research focusing on incorporating W with enhanced high-temperature properties and irradiation resistance via composite materials is multidimensional. Various types of W-based composites, including dispersion-strengthened, particle-reinforced, fiber-reinforced, and laminated composites, as illustrated in **Figure 2**, are being developed and investigated.

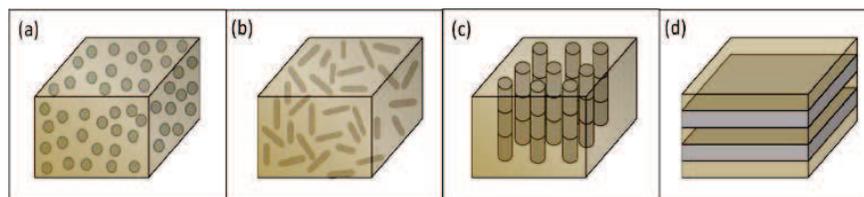


Figure 2. (a) ODS and/or ceramic particles reinforced composites, (b) whisker reinforced composites, (c) fiber reinforced composites and (d) laminated/3D composites.

3.1.1. Oxide-dispersion-strengthened (ODS) alloys

The dispersion of oxides increases the creep strength, which is an important property for high-temperature structural materials [27, 28]. Therefore, ODS W composites have caught the attention of researchers due to their improved high-temperature mechanical properties. Extensive research work is in progress to develop ODS-W composites with optimized high-temperature and plasma-facing properties. An important aspect of the R&D work to realize ODS W composites is to explore materials which may maintain a suitable microstructure after irradiation without grain growth or recrystallization [1].

Y_2O_3/W ODS composites have been investigated by many scientists [5]. When a Y_2O_3/W ODS composite was produced by powder metallurgy, it revealed lower brittleness between 400 and 1000°C, but a Charpy test at 500–1000°C revealed a reduced ability to absorb energy at 500–1000°C [19]. Itoh et al. and Kim et al. also investigated Y_2O_3/W ODS composites, finding enhanced densification in the Y_2O_3/W ODS composite due to the addition of yttria [10]. Grain refinement, which increases the strength of the material, was also observed from 18.8 to 3.7

μm , in ODS-W [23]. Liu et al. and Zhou et al. also reported improved mechanical properties and grain refinement due to the addition of 1wt% Y_2O_3 to W [5]. The grain refinement of $\text{Y}_2\text{O}_3/\text{W}$ by adding Ti has also been reported [54].

The characteristics of $\text{Pr}_2\text{O}_3/\text{W}$ composites were investigated by doping via a wet chemical method. Pr_2O_3 increased the tensile strength of the composite. The wet chemical method, which differs from conventional solid-state synthesis approaches such as mechanical alloying, produces a combined powder using liquid phases. The wet chemical method produces the powder with relatively fine grains and no residual stress [26].

Another important additive which has captured the attention of many researchers is La_2O_3 [55–58]. The addition of 1% La_2O_3 in W can enhance its machinability and recrystallization temperature [55]. 1wt% La_2O_3 W also shows refined grains and improved mechanical properties when prepared either by mechanical alloying (MA) and spark plasma sintering (SPS) or microwave sintering [5]. The behavior of La_2O_3 -doped W has also been investigated by producing this composite via a hydrothermal-hydrogen reduction process [57].

Given the findings of research conducted thus far, ODS W composites are expected to show good high-temperature mechanical properties and resistance to irradiation [19]. Therefore, ODS W composites may serve in parts of fusion reactors, such as in a gas-cooled divertor, where pure W is joined with a $\text{La}_2\text{O}_3/\text{W}$ composite [1].

3.1.2. Ceramic particle-reinforced composites

Like oxides, carbides are also drawing much attention as a candidate dopant to produce dispersion-strengthened W composites [5]. Many types of carbide are being investigated, including TiC, TaC [20], WC [23], ZrC [59] and SiC [11].

WC/W composites, when sintered at 1800°C after an addition of 5 and 10%vol WC, are converted into 8.9vol% $\text{W}_2\text{C}/\text{W}$ and 17.8vol% $\text{W}_2\text{C}/\text{W}$ by the $a\text{W}+b\text{WC}\rightarrow(a-b)\text{W}+b\text{W}_2\text{C}$ reaction. The material may retain a high-temperature W_2C phase if cooled at a high cooling rate ($\sim 150^\circ\text{C}/\text{min}$), but conventional sintering, in which the cooling rate is low, also resulted in W_2C , indicating that the decomposition of the W_2C phase may be challenging. Grain refinement and densification were observed as a result of an addition of WC [23].

The lower neutron activation of SiC [11] has granted the SiC/W composite a unique place among other high-temperature PFMs. SiC/W exhibits a good combination of thermal, mechanical and physical properties. SiC/W composites when fabricated by hot pressing or spark plasma sintering between 626 and 1926°C have reaction phases of WSi_2 , WC, W_5Si_3 and W_2C [12]. These reaction phases can cause the material to fail; therefore, W-SiC requires additional attention [11]. The formation of reaction phases in W-SiC can be avoided with plasma spraying at a high temperature (5000 – $12,000^\circ\text{C}$) and at high velocities (200 – 700 m s^{-1}), as was done by Kang and Fahim, who prepared 50wt% and 12wt%SiC/W composites without reaction phases. The porosity of their composite was increased due to the oxidation of W and the decomposition of SiC [11]. The oxidation of tungsten along with structural imperfections have significant effects on the thermal and mechanical properties of W-SiC composites, as observed when a 12wt%W-SiC composite was prepared using a gas-tunnel-type plasma spray; the composite

was fully dense and showed a gradual decrease in its hardness due to the formation of WO_3 [12].

2wt%TaC/W and 8wt%TaC/W samples were developed via powder injection molding. The powder mixtures, with a required proportion, were dried and mixed with a 50vol% polyolefine-based binder to produce feedstock for injection molding. The green compacts of W-TaC composites, produced by injection molding, were sintered in an H_2 atmosphere after removing the binder, the impurities and the residual stress by debinding. High agglomeration of TaC particles and brittleness in the resultant composites were observed [20]. In addition to powder injection molding, attempts to produce TaC/W composites with enhanced properties using SPS, hot rolling followed by annealing [60] and mechanical alloying with subsequent hot isostatic pressing have been used [61].

Due to its high melting point and comparable mechanical and thermal properties with W, ZrC is also a dopant of interest in the effort to develop a W-based composite having good high-temperature properties. In the search for a suitable W-based composite, 35vol%ZrC/W was produced by reaction sintering via the heating ZrO_2 and WC together up to a temperature of 2100°C with subsequent evaluation of physical and mechanical properties [62]. A sol-gel method followed by precipitation, drying, hydrogen reduction, and sintering was also utilized to develop more than 99% dense ZrC/W composites. The improvement in the high-temperature thermophysical and mechanical properties upon an addition of ZrC was also observed by producing 30vol%ZrC-W via hot pressing under a vacuum at 2000°C [63]. While fabricating ZrC/W, close control over the dimensions and process parameters is required to establish uniform effects of the process parameter on the feed materials. ZrC/W composites containing 20vol%ZrC and fabricated by hot pressing, when subjected to laboratory investigations, reveal ZrC_xO_y in addition to (Zr, W)C in the core of sample which resulted in inhomogeneous structure and properties [64].

Another important W-based composite, which can improve strength, microstructural stability, and irradiation resistance and can solve the embrittlement problem of W, is the TiC/W composite. The TiC/W composite, when prepared by the wet chemical method and spark plasma sintering at 1800°C , showed a relative density of 99.0% and improved thermal stability at elevated temperatures. The grains and grain boundaries both showed the presence of TiC particles, and the sample showed a mixture of inter- and transgranular fracturing [65]. In contrast, the 0.1wt%TiC/W composite produced by a different synthesis technique, i.e., wet chemical processing with polyvinylpyrrolidone (PVP) as a dispersion agent and SPS, showed the well-dispersed presence of TiC particles inside the grains only. The bending strength of the composite with PVP was 562.24 MPa, whereas without PVP it was 486.67 MPa [66]. Another approach to avoid the agglomeration of TiC particles and to obtain good phase stability, protection of the core from the environment, and good physical and chemical properties is the synthesis of core-shell structured TiC/W powders, by immersion of TiC in aqueous solution of hydrofluoric acid and ammonium fluoride followed by cleaning, deionizing, drying and then a reduction step [67]. The ongoing research to explore TiC/W composites has led to the production of 0–40%TiC/W composites via milling in ethanol, with the milled powder hot pressed at 20 MPa and 2000°C in a vacuum. The increasing amount of TiC increases the

modulus of elasticity, hardness, and coefficient of thermal expansion of the TiC/W but decreases thermal conductivity. Indifferently, toughness and flexural strength increases with TiC up to 20% then again decreases [68]. The addition of 0.1wt%TiC to W produces a composite having a recrystallization temperature of 1500°C [69] but 0.1wt%TiC and 1.1wt%TiC/W don't affect deuterium retention capabilities of W [69, 70].

3.1.3. Fiber- or whisker-reinforced composites

Fibers play a very effective role in the enhancement of the mechanical properties of materials by transmitting and bearing loads while stretching. By absorbing energy, fibers prolong or deflect the paths of cracks as they propagate while also improving the strength and toughness of fiber-based composites [24]. By frictional sliding and debonding of the fiber/matrix interface, fibers control cracking and enhance the load-bearing capacity of composite materials. As fibers suppress cracks, a greater load is required to pull out the fibers, and when the load is increased further, the metal cracks propagate again, but in a controlled manner [27, 28]. In several industrial applications, the toughness of composites was significantly improved by the addition of fibers [27].

The effects of carbon fibers (C_f) on W were studied by adding 0.5wt% and 2wt% C_f with an average diameter of ~7–8 μm to W powders with a grain size of 1.2 μm , with 1%TiC also added to the composite. All samples showed relative density levels exceeding 97%, and the density of the TiC/W with 0.5wt% C_f sample was 98.36% [24]. A mechanical load moves dislocations and concentrates stress, also rupturing TiC particles or dislocating/detaching TiC from W to nucleate. Micropores then grow, coalesce and fracture. However, these phenomena are rarely observed in TiC/W with 2wt% C_f composites [24].

W wires, which are ductile and usually have a tensile strength which exceeds 2.7 GPa, can be added to the W matrix to produce W_f/W composites. The W fibers can withstand a fusion environment until they lose their toughness and become brittle. The effectiveness of W_f with regard to the properties of W_f/W composites depend upon the volume fraction of the fibers [27]. Intermediate fracture energy of W_f/W interface is needed to obtain maximum toughness in fiber-reinforced composites. The interface should be able to debond such that it can deflect cracks, and it should be strong enough to absorb energy and transfer a load. Interface coating is suggested to achieve this requirement of the interface in a W_f/W composite [27, 28]. The effects of such interface coatings of carbon and ZrO_x -based materials on shear strength, debonding strength and fracture energy have already been studied [27, 28].

A Ta (fiber/powder)-W composite was also effectively developed by hot isostatic pressing. Pulse-plasma sintering can also be used, as it imparts a high density to a composite. Ta shows high affinity for O_2 , and a Ta-Ta₂O₅ eutectic mixture forms in the composite [15].

W/Cu composites, which are typically developed by infiltration, can scarcely achieve full density owing to the differences in their thermal expansion coefficients and their poor solubility. In order to increase the density of W/Cu composites, high temperatures can be used to improve the wettability. A W_f -reinforced W/Cu composite was prepared for use as an intermediate layer between a CuCrZr heat sink and plasma-facing W in a fusion reactor [18].

3.1.4. Laminated or 3D composites

In addition to their other properties, plasma-facing materials require good toughness in order to be successfully utilized as structural materials in fusion plants. Cold working can shift the DBTT to a lower value; in an extreme case, it may be -120°C . W foils produced by cold working processes such as rolling and forging can exhibit fracture toughness levels of $70\text{ MPa m}^{1/2}$ and can sustain 1000 bar of pressure during burst tests at room temperature [71]. Laminated W composites consisting of multiple layers of W foils can be used as a structural material, as they demonstrate ductile behavior because W foils are ductile at room temperature [72, 73]. The behavior of a W-foil laminated composite under a mechanical load revealed that this material has the potential to serve in fusion reactors as a structural material [73].

W laminates, which were produced by assembling several layers of W foils together, when subjected to Charpy impact test, absorbed 2 J, 5 J and 10 J of energy at room temperature, at 100°C , and at 300°C , respectively. The laminates, which were developed from the recrystallized foils at 1800°C for 1 hour, showed an increase in DBTT to 500°C as compared to a recrystallized W plate [74, 75].

The properties of W laminates depend upon the types of interlayers, the joining methods and materials, and the microstructure of the foil and interface. The brazing of foils with a silver-copper filler material does not affect the microstructure; this method can be used to develop a sharp interface between the foil and the filler. This type of laminate is best in terms of low-temperature toughness [72]. Copper is also used to join the interlayers of tungsten foils, but it slightly alters the microstructure and produces a sharp interface. Laminates that utilize Ti for brazing show large grains and a diffusion zone between the Ti and the W. Zr, if used for brazing, reacts with W excessively and produce small bands of W [72].

A laminated W composite was synthesized using ultrafine W foils. Diffusion bonding between the W laminates and the Ti interlayer was used. The changes in the mechanical properties during annealing at 1000°C for 10 to 1000 hours were examined, with the results demonstrating the inappropriateness of this material in structural applications at 1000°C [76].

Laminated W pipes find structural applications in fusion reactors, where they serve to carry He coolant and bear impingements. For this and other similar applications of laminated W, composites with low DBTTs are required [77]. Laminated composites with a copper foil interlayer were developed by rolling and brazing. As compared to pure W, the laminated W-Cu composite showed extraordinary behavior when subjected to impact and burst tests. In the burst tests, this material did not explode up to 1000 bar [77]. In addition to copper, palladium, titanium, zirconium, vanadium and other materials have also been used to create interlayers, and the choice of the interlayer material and the interface properties significantly affect the overall behavior of the resulting laminated composites [77].

In fusion reactors, W-based composites employed in a He-cooled divertor are joined to other structural materials. A W/Cu laminated composite can be joined to steel by brazing [77]. A laminated, functionally graded W/Cu composite with layers of a W/Cu composite materials with varying compositions was also investigated for its possible application in a plasma-facing environment [34].

In order to meet the requirements of high-temperature strength and reasonable ductility at low temperatures for plasma-facing applications, bonded layers of high-strength and high-ductility materials in the form of hybrid composites were analyzed. W/Cu and W/AgCu laminates were studied, and their low melting points and low strength levels diverted the attention of researchers towards V due to its sufficient high-temperature strength, good irradiation resistance, and much higher melting point, exceeding 1300°C. A hybrid W/V composite was produced by the diffusion bonding of thin layers of W and V at 700°C under a compressive stress of 97 MPa with a dwell time of 4 hours under a vacuum. A continuous increase in the hardness from the V (2 GPa) to the W side (8.5 GPa) was observed. The W/V hybrid composite also showed increased toughness. The layered structure of a hybrid composite was found to be highly resistant to crack propagation [78]. A W/V laminated composite with significant high-temperature creep resistance and good fracture toughness at low temperatures was produced. As compared to pure W and pure V, the laminated W/V composite shows a wide operating temperature window [79].

3.2. Fabrication methods of W-based composites

A number of techniques are used to fabricate W-based composites, such as (i) mechanical milling and alloying [26], (ii) conventional sintering [19], (iii) hot pressing (HP) and hot isostatic pressing (HIP) [21], (iv) spark plasma sintering (SPS) [26], (v) plasma pressure compaction (PPC) [23], (vi) microwave sintering [23], (vii) resistance sintering under ultrahigh pressure (RSUHP) [33], (viii) rolling [14], (ix) powder injection molding [20], (x) hot forging [19], (xi) combustion synthesis with centrifugal infiltration [18], (xii) polymer infiltration and pyrolysis (PIP) [11], and (xiii) a wet chemical process. The selection of any one technique depends on the type of composite, and it has great influence on the density, microstructure and other properties of the resultant composites [21].

Due to the sufficiently high melting point of W, mechanical milling is preferred for the fabrication of metallic W. It is a high-energy procedure which produces a uniform, homogeneous and controlled microstructure by repeated welding, fracturing and rewelding [80]. Ultrafine-grained (UFG) tungsten, which exhibits improved ductility, is also produced by mechanical milling [73].

To create nanosized ODS W powders, mechanical milling and mechanical alloying are commonly used [26]. Wang et al. found that the mechanical milling improved the sinterability of nano W powder when used prior to consolidation by pressureless sintering [23], HIP, and the SPS of PPS [15]. Improvements in the density as a result of milling have also been observed [15]. In addition to the advantages of mechanical milling and mechanical alloying, as noted earlier in this section, there are some disadvantages as well. During milling, dopant/additive particles tend to agglomerate due to high surface energy, and some contamination is also possible due to wear of the milling media and equipment. To avoid these detrimental effects of mechanical milling and alloying, milling is sometimes replaced by wet chemical processes, which develop composites with high purity and homogeneity levels [26]. After milling of the powder, conventional sintering (CS) is used to generate dense and refined microstructures in W-based composites [21, 26]. In the HP and SPS approaches, the samples are compressed

during the sintering step. As a result, these techniques require a low sintering temperature and a short dwell time as compared to those used in CS. The short sintering time and optimum temperature help to prevent grain growth [21]. However, plasma/microwave sintering, as well as HIP, cannot be used for mass production because these techniques lack the ability to fabricate relatively large components [5].

SPS, being less time consuming and less prone to grain growth [15], and porosity [26], has numerous applications. In addition to particle-reinforced tungsten composites, fiber-reinforced composites such as TiC/W with (0.5–2)wt% C_f [24] and tantalum fiber/powder-nano-structured W composites can be consolidated by SPS [15].

Microwave sintering may also be used to sinter W-composites. Jain et al. utilized microwave sintering followed by HIP to sinter submicron W powder. After sintering, the density was 91.3%, which was raised to 98.5% after HIP [23].

Another technique, known as gas-tunnel-type plasma spraying (GTPS), has also been used to develop several W-based composites, such as W/SiC [12]. In order to fabricate functionally graded W/Cu composites, resistance sintering at ultrahigh pressure levels (RSUHP) has been utilized. The synthesis of laminated W/Cu composites having six layers of W/Cu with different volume ratios has been reported in studies which use RSUHP [33].

To produce bulk components of laminated W, rolling is used, as this process can result in a nano-structured microstructure as well [14]. The powder injection molding (PIM) process for joining W and materials doped with W was used to eliminate any further need for brazing or welding [20]. In order to produce small composite pellets, injection molding is used. Injection molding, which produces green pellets, is followed by debinding to remove impurities and residual stress [20].

A 2% Y_2O_3 /W composite, when produced by pressing and then sintering at 2000°C followed by hot forging [4, 19], results in a relative density of 99.3% and a grain size of 1–2 μm . The pressing, sintering, and hot forging process were also utilized to produce pure W or 2% Y_2O_3 /W composites. A composite with a density exceeding 99% was obtained because yttria particles strengthened the grain boundaries and reduced the porosity [22].

A novel method, termed combustion synthesis with centrifugal infiltration, has been proposed to produce W-fiber-reinforced W/Cu composites. In this combustion synthesis, Cu melt produced through a thermite reaction at 2000°C was infiltrated into W powder and a fiber bed by gravity. The high temperature causes the sintering of W particles and binds the W fibers [18].

Polymer infiltration and pyrolysis (PIP) is used to fabricate other important high-temperature plasma-facing candidate materials, e.g., W–Si–C. The pyrolysis of raw powders followed by infiltration and a heat treatment are carried out to obtain composite materials with W, W_2C , and W_5Si_3 phases. PIP is a low-temperature process which requires an additional heat treatment to promote densification and crystallinity [11].

The wet chemical process is utilized to produce composite powder of high purity and homogeneity levels [26]. The development of TiC/W ultrafine powder via chemical reduction has also been reported. In the chemical process, tungsten hexachloride serves as the raw

material, ethyl alcohol as a solvent, lactic acid as a complexing agent, hydrazine hydrate as a reducing agent, 2,2-dipyridyl as a stabilizer, and ammonia water as a pH controller. The reduction process is carried out in an H_2 atmosphere to avoid oxidation; after the reduction step, SPS is carried out to produce a bulk composite [13]. The preparation of ODS-W composites by another wet chemical process, i.e., the reaction of a W precursor with praseodymium salt in water at room temperature, has also been reported [26]. This method produced highly homogeneous Pr_2O_3/W which was consolidated by SPS. The microstructure of the ODS-W composite showed dispersed oxide particles both in the interior of the ultrafine grains and at the grain boundaries [26].

In practical applications, composites are joined with other materials in high-temperature and plasma environments. Electron beam welding, diffusion welding and vacuum electron beam welding are commonly used joining techniques for W-based composites. The properties of the joint may not be as good as those of composite materials depending on the filler metals used or on the presence of pores and/or cracks [81].

A good number of techniques are available for the development of W-based composites, with more developments, customized and novel methods yet to be developed. Some advantages and disadvantages are associated with each technique. Each technique imparts characteristic effects on any particular W-based composite. In order to develop any one composite, multiple techniques can be used, such as powder metallurgy in conjunction with infiltration. In addition, plasma spray and cold spray techniques have been utilized to fabricate tungsten-based composites [81].

4. Performance of W-based composites in a fusion reactor environment

4.1. Mechanical behavior

Researchers are in search of W-composites which can withstand high-temperature and plasma environments without losing their mechanical integrity. This section summarizes the mechanical behavior of several W composites reported in various publications.

The DBTT of pure W lies between 120 and 250°C. Many approaches to reducing the DBTT in this case, such as alloying or/and doping, to produce W-based composites are being considered [14]. A reduction in the brittleness of W is observed by producing bulk materials with W laminates, brazed using copper brazing. This technique produces W composites with DBTTs of less than 500°C [14].

W-based composites produced by doping with La_2O_3 and TiC show brittle failure up to 350°C. This brittleness is sustained up to 500°C when Y_2O_3 and TaC are used as additives [20]. The addition of 1wt% TiC in the W matrix results in stronger materials, but no change in the DBTT is observed [20]. However, Kurishita et al. observed decreases in the DBTT by preparing 0.25–0.8wt%TiC/W via mechanical alloying and hot isostatic pressing [5].

The DBTT of 2% Y_2O_3/W is between 400 and 1000°C, better than certain other composites. In 2%Y/W produced by mechanical alloying in an Ar atmosphere and HIP, yttrium was trans-

formed into yttria, and the resulting composites showed DBTTs between 1000 and 1200°C. The ductile behavior of 2% Y_2O_3/W at temperatures higher than 400°C is due to the plastic deformation of the grains [19].

W-yttria composites undergo a ductile-to-brittle transition between 500 and 600°C, as it absorbs more energy when the temperature is increased in this range. However, the low values of the absorbed energy result in poor ductility of this composite, even at an elevated temperature [19]. An analysis of 2% Y_2O_3/W composite samples after irradiation at 300 and 700°C reveals the formation of voids. The material showed improved stiffness, a reduction in its ductility, and improved mechanical properties [4].

An analysis of the fracture surface of 1wt%TiC/W revealed transgranular fractures in less porous areas and a highly dense composite material. Pure W fractures via the intergranular mode due to its weak grain boundaries, indicating that the addition of TiC strengthens the grain boundaries. The average grain size was 3 μm , lower than the grain size of pure W, which is 10 μm [13].

The powder metallurgical route was adopted to produce a 2% Y_2O_3/W composite. This material exhibited improved hardness up to 4.9 GPa, which is higher than that of pure W (i.e., 4.5 GPa [22]) produced by an identical method. It is important to note here that another researcher reported that the hardness of 2% Y_2O_3/W was identical to that of pure W, i.e., 4.78 GPa [4]. A separate publication reported an increase in the hardness of 2% Y_2O_3/W to 4.9 GPa when it was produced by the same method [22]. However, the hardness of a 2% Y_2O_3/W composite was found to be lower than those of 2%Y/W and 1% Y_2O_3/W when developed by mechanical alloying [19]. The improved density and grain-stabilizing ability of yttria allow this material to enhance the mechanical properties of materials [22]. The hardening capacity of a W-yttria composite depends on the temperature, as the storage of dislocations during permanent deformation decreases with an increase in the temperature. The hardening capacity of W-yttria decreases from 0.658 to 0.32 when the temperature increases from 673 to 1273 K [19]. A hardness test of irradiated samples of 2% Y_2O_3/W was performed; considering a depth of the irradiation damage of 3 μm , the load during the hardness test was kept low (from 1 to 2 N). The irradiation effect on the hardness of the samples at 300 and 700°C was identical [4].

In an effort to improve the hardness, other composites, such as WC/W, TiC/W, and Ta/W, were also produced and analyzed. The addition of WC in W produced a composite with an increased hardness level, and the hardness values follow the WC, i.e., the hardness increases with an increase in the WC content, due to the high hardness of WC [23]. The hardness of TiC/W (471 Hv), developed by chemical reduction, was also found to be greater than that of pure W [13]. Similar behavior was noted by Kurishita et al. when they prepared 0.25–0.8wt%TiC/W through mechanical alloying and HIP [5]. Pr_2O_3 also contributes to the production of W composites with improved hardness. 1wt% Pr_2O_3/W synthesized by a wet chemical process and SPS shows Hv equal to 377.2, higher than that of pure W [26]. A Cu layer was bound with Cu/W via a novel method consisting of combustion synthesis and infiltration. The hardness of the Cu/W and the Cu layer was 75 HRB and 21 HRB, respectively [81].

W-Si-C composites produced by pyrolysis at 1800°C exhibit a flexural strength level of approximately 400 MPa. When such a composite is heat-treated at 1700°C, the flexural strength is reduced to ~350 MPa. The hardness and indentation modulus of post-heat-treated W-Si-C were found to be 7.8 GPa and 250 GPa, respectively [11]. The fractural strength is a function of the porosity/density; thus, to develop high-strength W composites, researchers have focused on low porosity and high density [21].

Yttria particles produce W-based composites with improved high-temperature strength. The Young's modulus of 2%Y₂O₃/W was found to be 400 GPa, which is higher than those of pure W, 2%Y/W and 1%Y₂O₃/W [19, 4, 22]. Larger yttria particles and a low porosity level resulted in improved mechanical behavior [22]. However, the Young's modulus of a W-based composite was found to decrease when a composite with 1wt%TiC was prepared by chemical reduction [13]. The strength may also be improved by producing W composites with 1wt%Pr₂O₃ [26] and 0.25–0.8wt% TiC [5]. Moreover, W_F-reinforced Cu/W composites prepared via combustion synthesis followed by centrifugal infiltration show a 12.7% improvement in the bending strength due to the well-bonded W, Cu powder and W fibers [18].

The conventional sintering of W-based composites containing V, Ti, Nb, Ta, Fe, and Ni caused hydrogen embrittlement because the dissolution of H₂ dissolves into the composite due to the negative formation energy of the vacancy-hydrogen complexes. Hence, conventional sintering in a hydrogen environment is not recommended [21].

4.2. Thermal properties

Fine-grained W-based composites produced by doping with rare-earth oxides such as Y₂O₃ and La₂O₃ and carbides such as TiC and ZrC were subjected to transient heat flux tests. It was observed that a high heat flux of 200 MW/m² can be sustained by these materials, which is nearly 100% higher than conventionally sintered pure W. This promising behavior may be the result of the processing route, i.e., a sol-gel method, heterogeneous precipitation, spray drying, hydrogen reduction and ordinary sintering in sequence [5].

However, oxide- and carbide-doped W composite samples, when subjected to a thermal shock, showed cracks. However, pure W sintered at 2400°C withstands thermal shocks well [20].

The responses of W composites consisting of 20%-80% porous W and infiltrated by Cu, Al or Si and then exposed to a high-temperature environment have been thoroughly studied. These composites exhibit good strength, conductivity and good melt layer stability at high temperatures. In contrast with pure W, some W-based composites can withstand plasma edge temperatures in excess of 200 eV [82].

The thermal conductivity of TiC/W composites and pure W produced by chemical reduction followed by SPS at 1800°C decreases when the temperature is increased from ambient to 827°C. However, the conductivity remains above 120 W/m-K at RT [13]. The effect of the temperature on the thermal conductivity of ODS-W composites prepared by adding 1wt% Pr₂O₃ was examined, and the behavior of pure W was compared with that of pure W. The conductivity of both materials decreased when the temperature was increased from 25 to 800°C, but the conductivity of these materials exceeds 150 W/m-K at room temperature [26].

4.3. Oxidation resistance

In fusion reactors, W-based materials will be exposed to high-temperature and plasma environments; therefore, their high-temperature oxidation resistance is of great concern in the case of loss of vacuum accident. Attempts to develop W-based composites with enhanced high-temperature oxidative ablation resistance have been made by incorporating ZrN_p into a W matrix. 10–30% ZrN_p/W samples, when tested using an oxyacetylene torch, showed enhanced oxidative ablation resistance. The rate of ablation was found to decrease with an increase in the ZrN_p content. The microstructure of the ablated samples lacked a uniform protective film due to the insufficient amount of ZrN_p [83]. Improved oxidative ablation resistance and a reduction in the ablation rate were also found by adding HfC to W up to 30%. A protective layer of HfO_2 was found on post-ablated samples [84].

An analysis of the ablation properties of W-based composites suggests that composites with high oxidative ablation resistance can be developed by the incorporation of a W matrix with secondary phase particles having low thermal conductivity, a high melting point, and good oxidation resistance [84].

4.4. Behavior of composites in radiation and plasma environments

Pure W also faces transmutation damage, and in DEMO full-power operations, W may be transformed into W-3.8at%Re-1.4at%Os. These chemical variations alter the mechanical properties of pure W [14]. At the end of the lifetime of the blanket, 5–8 at% of W may be transmuted; moreover, transmutation below 1% has no significant effect on the physical properties of W alloys [2]. The transmutation of W is mainly a function of the neutron's spectrum and fluence [2]. Neutrons in a fusion environment may be absorbed by W with a consequent release of alpha and beta particles and the production of impurities such as Re, Ta, and Os. The change in the chemistry of the material degrades its mechanical (and other) properties [2].

ODS-W composites when prepared by adding Y_2O_3 also show irradiation hardening when subjected to 24 and 2 MeV Fe and He ions, respectively, up to a damage level of 5 dpa at 300 and 700°C. Irradiation resulted in radiation loops in W and voids in Y_2O_3 particles, which caused the hardness to increase [4]. No voids or cracking were found on the grain boundaries, demonstrating the capability of the grain boundaries of Y_2O_3/W composites to accommodate heavy ions [4]. In another study in which a W-yttria composite produced by a powder metallurgical method was subjected to 24 and 2 MeV Fe and He ions, similar changes in the microstructure and hardness were observed [22].

An improvement in the ion irradiation damage resistance of W by doping with TiC was observed by Kurishita et al. In their study, mechanical alloying and HIP were used to produce 0.25–0.8wt%TiC/W composites. He ions at 500°C were used to irradiate TiC/W. The irradiation vacancy defect density was only 1/3 to 1/4 of the density of commercially pure W [5].

The interaction between plasma-facing materials, such as W and its composites, and a single hydrogen beam, a single helium beam and an electron beam results in a rough surface and a fine scale. This modification of the surface can affect the mechanical properties along with the

thermal conductivity and tritium retention capabilities of the material [22]. The sputtering threshold energy may be increased from 2.5 KeV to more than 10 KeV by applying an alkali monolayer onto a W composite surface. Alkali metals having a higher mass are more useful for reducing sputter-induced erosion [82].

4.5. Hydrogen retention

The addition of 0.1wt%TiC to W does not cause significant differences in the deuterium retention behavior [69]. The deuterium retention behavior of a 1.1wt.%TiC/W composite was also investigated by exposing 1.1%TiC/W composite samples to D₂ gas at 527–690°C and 100 kPa or by irradiating the 1.1%TiC/W composite via 38 eV/D ions at 527°C. Thermal desorption spectroscopy revealed slightly higher deuterium retention in 1.1%TiC/W as compared to pure W after exposure to D₂ gas. However, it was significantly higher after D ion irradiation [61]. The deuterium retention properties of TiC/W when examined by irradiating TiC/W composite samples with 200 eV/D ions at fluence levels ranging from 1×10^{22} to 1×10^{24} D/m² at a temperature of 37°C or with 38 eV/D ions at fluence levels ranging from 6×10^{22} to 6×10^{24} D/m² at temperatures of 27 and 327°C were examined. At 37 and 27°C, no significant differences in the deuterium retention of TiC/W and pure W were observed. However, at 327°C, deuterium retention was higher in TiC/W than in pure W [70].

5. Conclusion

In order to understand the feasibility of W-based composites for nuclear fusion applications, the fabrication processes, properties and performances of W-based composites in the forms of oxide dispersion strengthened alloys, ceramic particle reinforced composites, fiber- or whisker-reinforced composites, and laminated 3D composites were reviewed. Many advantages in mechanical properties, oxidation resistances, and radiation resistances were identified while more attention should be given to enhancing further thermal properties and hydrogen retention resistance. To address the materials challenges in the development of plasma-facing materials like first wall or divertor in fusion reactors, the selection of the reinforcement phase and the structures of W-based composites should be optimized through the wide range of performance evaluation calculations and experiments.

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