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Methods for Improving Ductility of Tungsten - A Review

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Abstract

Pure tungsten and tungsten alloys with minor alloying additions are known to be brittle at room temperature and have high ductile-to-brittle transition temperatures (DBTT). Improving the ductility of tungsten can have significant impact on both the manufacturing of and the range of applications of tungsten. Although there has been a significant volume of reported research on improving the ductility of tungsten over the span of several decades, it remains a difficult challenge. This is at least partially attributable to the fact that the understanding on the mechanical properties of tungsten and their dependence on microstructure has been insufficient. This article attempts to offer a critical review of the methods that have been reported in the literature for improving the ductility of tungsten in order to understand the critical factors that control the ductility (or lack thereof) in tungsten. It is clear from the literature that all tungsten materials that have been reported to be ductile at room temperature, or to have drastically reduced DBTT, are the result of thermomechanically processed (TMP) material with deformed and textured microstructures. Alloying tungsten with rhenium is essentially the only known method to improve the ductility of tungsten by alloying (excluding the class of alloys known as heavy alloys which are composites of tungsten with nickel and iron). Although there have been a large number of research reports in recent years on the effect of additives, including oxides, carbides, and others, the results are inconclusive to date or insignificant with respect to the effects of those additives on the ductility of tungsten independent of the effects of thermomechanical working. Using ultrafine-grained or nanocrystalline microstructure to improve the ductility of tungsten is another approach that has appeared promising. However, the results to date have not shown that the ductility of tungsten can be improved by reducing the grain size alone, without the benefits of thermomechanical processed or deformed microstructures. Another objective of this review is to examine the correlation between the ductility of tungsten and different microstructures resulting from different processing methods and compositions.

Keywords: Tungsten; Powder Metallurgy; Microstructure; Mechanical Properties; Ductility

1. Introduction

Tungsten is a refractory metal with a unique set of properties including: the highest melting point among all elements, high elastic modulus, high density, high thermal conductivity, and excellent mechanical properties at elevated temperatures. These exceptional properties make tungsten the choice of material for many applications, such as incandescent light bulb filaments, heating elements, and kinetic energy penetrators. In recent years, tungsten has also been identified as one of the candidate materials for plasma facing components in fusion reactors, owing to its high melting point, low sputtering yield [1], and high plasma sputtering erosion resistance [2]. However, a major drawback of tungsten is its near non-existent ductility at room temperature and its high ductile-to-brittle transition temperature (DBTT). The poor ductility of tungsten causes serious challenges for both its workability and its performance in demanding applications. Improving the mechanical properties of tungsten could have significant impact on its manufacturing and its range of applications.

In order to improve ductility, an in-depth understanding of the origin of tungsten's brittleness is essential. It is widely accepted that there are two primary contributing factors: an intrinsic lack of close-packed planes and the poor cohesion of grain boundaries. The former is indicative of the body-centered cubic (BCC) crystalline structure and on the slip systems of tungsten. As a BCC metal, the plastic deformation of tungsten depends on the mobility of non-planar ½<111> screw dislocations [3]. The dislocation cores of tungsten spread into three {110} planes of the <111> zone and result in a very high Peierls stress [4,5], which is defined as the stress needed to move a dislocation within a plane of atoms by glide at 0 °K. The spread of a ½<111> dislocation core makes a three-dimensional structure that is difficult to move along a slip system in a BCC structure[6]. This is the basic factor limiting deformation in tungsten and the main reason for its brittle behavior.

In addition to the lack of operable slip planes, tungsten also suffers from poor grain boundary cohesion. Inter-granular fracture has been shown as the most prominent failure mode of tungsten. Up to 95.9% of fracture surfaces are intergranular for essentially pure tungsten samples (>99.97%) [7]. These experimental observations have been corroborated by theoretical simulations [8]. It has also been recognized that impurities concentrated on grain boundaries play a significant role in inter-granular fracture, and in the brittleness of tungsten. Among various types of impurities, carbon, oxygen, potassium, and phosphorous are most notable in the literature [9-11]. It is generally believed that grain boundary segregation of contaminants, such as potassium and nickel, can weaken the grain boundaries, increase the amount of inter-granular fracture, and lead to the embrittlement of tungsten [12-16]. However, in contrast, Gludovatz et al. [7] reported that even high purity tungsten can fail by inter-granular fracture and that impurities generally are not observed on the fracture surfaces. Except at high levels of impurities, grain boundary cohesion is not the deciding factor, but the limited ductility is more generally the result of strain incompatibilities between grains [7]. The true mechanism of tungsten's intergranular fracture and brittleness is still under investigation.

Over the past several decades, researchers have worked on improving the ductility and decreasing the DBTT of tungsten. Among various approaches, thermomechanical processing has been found to be the most effective approach. Rolling at temperatures below recrystallization temperature can reduce the DBTT of tungsten from above 700 °C to less than 300 °C [17]. There are several main factors contributing to the improvement in ductility of deformed tungsten, including the laminated microstructure after rolling and high dislocation density. Contrary to intuition, and the tendency of most metals, annealing and recrystallization of deformed tungsten generally leads to rapid degradation of the ductility [18,19]. Research by Reiser et al. [18] reported that deformed tungsten foil is ductile at room temperature in the as-deformed state. However, both texture and dislocations will gradually disappear during high temperature annealing, resulting in an increase of the DBTT. Similar results were also observed by D. Terentyev et al. using high temperature tensile testing [19]. The results showed that the recrystallization of rolled tungsten at 1600 °C for 1 hour can lead to dramatic decreases in both ultimate stress and strain during tensile testing, even at test temperatures as high as 500 °C.

To minimize the consequences of recrystallization during high temperature processing, cold working based on conventional deformation techniques has also been used to improve the ductility of tungsten. Due to tungsten's very high recrystallization temperature, "cold" working can be performed up to about 1400 °C [20]. By doing so, recrystallization and grain growth of tungsten during the deformation process is prevented, resulting in a finer laminated microstructure and higher dislocation density in the material. Compared to high temperature rolled materials, tungsten cold rolled at 400 °C showed increased dislocation density, more low angle grain boundaries, and significant improvements in strength, as well as a lower DBTT [21,22]. The relationships correlating the microstructure of deformed tungsten and its mechanical behavior are fundamental issues that must be understood.

Another well-known approach for improving the ductility of tungsten is to alloy with rhenium. This approach was first developed in the 1950s by G. Geach et al. [23]. Reportedly, the Peierls stress in tungsten can be reduced and additional slip planes like {112} can be promoted by the formation of solid solutions of tungsten and rhenium through so-called solution softening [24,25]. However, rhenium is a high cost rare element, making these alloys prohibitively expensive for many applications. Significant research effort has been directed at replacing rhenium with tantalum [26], vanadium [26,27], titanium [28,29], or other elements to accomplish similar results. However, to date, there has been little experimental evidence that has demonstrated the effectiveness of those other alloying elements.

In recent years, based on advances in the research of both metals and ceramics, nanocrystalline or ultrafine-grained structures have been explored as a way to improve the ductility of tungsten. In order to produce nanocrystalline or ultrafine-grained tungsten, both top-down and bottom-up approaches have been studied. The top-down approach refers to the refinement of grain size by thermomechanical means, such as rolling, extrusion, and severe plastic deformation techniques. The bottom-up approach refers to powder metallurgy processes

during which nanosized tungsten powder is compacted and sintered to obtain fully, or near fully, dense bulk tungsten with an ultrafine grain microstructure. In general, it has been reported that ultrafine grain tungsten made by the top-down approach exhibits improved ductility [30], while there is little data about the mechanical properties of tungsten made by the sintering of nanosized powder. Research reports have shown improvements in hardness and fracture toughness by having the ultrafine grain structure [31]. However, there is no evidence of the ductilization of tungsten in the as-sintered state. The effects of grain size on the ductility of tungsten, independent of that of thermomechanical processing, thus remains a question to be explored.

The above summary suggests that although there are a number of ways by which the ductility of tungsten can be improved, it is far from clear how the ductility of tungsten is affected by various microstructural factors. The objective of this article is to examine the literature for correlations between the ductility of tungsten and different processing methods, including alloying, in order to understand the dependence of the mechanical properties of tungsten on the microstructures resulting from those different processing methods and compositions. The article begins with a review of conventional and novel alloying approaches, and then considers the state of understanding of mechanical working of tungsten and its effects on ductility and DBTT, before considering the current state of research on ultrafine grain microstructures and tungsten with additives, and their consequences to mechanical properties of tungsten.

2. Tungsten Alloying

The most common alloy additions for tungsten are designed to improve ductility. This is generally accomplished by improving dislocation mobility [3], scavenging interstitial impurities [32,33], refining microstructure or increasing the recrystallization temperature [34-39]. As mentioned in the introduction of this review, recrystallization, recovery and grain coarsening will generally increase the DBTT in tungsten, but dislocation mobility is fundamental for improving the ductility of tungsten-based alloys. This portion of the review will focus on the effects of alloy additions and impurities that have a direct influence on the mobility of dislocations (e.g. tungsten-rhenium alloys), in addition to the alloy additions and additives that affect the microstructure and dislocation structure of tungsten.

2.1 Tungsten-Rhenium Alloys

In 1955, Geach and Hughes [23] were the first to report that the ductility of tungsten can be increased by alloying with rhenium. They prepared tungsten-rhenium alloy with 35 at.% rhenium using arc-melting. They then cold rolled the alloy at room temperature and measured the reduction in thickness that could be sustained before the material fractured. The results showed that the 35 at.% rhenium alloy could be rolled at room temperature up to 11% reduction without cracking, while the pure tungsten specimen cracked at the beginning of the rolling process. This demonstrated that the tungsten-rhenium alloy system is far more workable than

pure tungsten. They also reported tungsten can be worked without difficulty at a few hundred degrees Celsius, although no data were provided to support this statement.

Further characterization of arc-melted and hot worked tungsten-rhenium alloys was reported by Klopp et al. [40,41], using 3-point bending, tensile, and creep tests. The results showed that the addition of as little as 1 wt% rhenium is sufficient to obtain a noticeable decrease in tungsten's DBTT. An increase in rhenium content up to a composition near its solid solution limit led to much more significant decreases in DBTT [40,41]. For example, compared to rolled pure tungsten with DBTT of 113 °C, arc-melted and rolled tungsten with 1.9 wt% rhenium had a DBTT of 25 °C, while the DBTT of tungsten with 26 wt% rhenium showed a DBTT as low as -101 °C [40,42]. Klopp et al. [40] also showed that the other mechanical properties of tungsten-rhenium solid solution alloys have a strong dependence on the rhenium content. They used step-load creep tests to show that the high-temperature creep properties of arc-melted tungsten-rhenium alloys extruded at 1871 °C changes with rhenium content. The creep strength reaches a maximum at about 6-8 wt% rhenium [40,43-46]. The most studied tungsten-rhenium alloys have either relatively low rhenium content (3-10 wt%) for optimum combinations of strength and ductility, or concentrations nearing the solubility limit (25-27 wt%) to maximize ductility.

The addition of rhenium to arc-melted or electron-beam-melted tungsten also refines its grain size and increases the recrystallization temperature. The minimum grain size and minimum grain growth rate occur when the rhenium content is above 6 wt% [40]. The changes in grain size have a direct effect on the properties of tungsten. Figure 1 shows the DBTT as a function of grain size for arc-melted tungsten and tungsten-rhenium alloys, as characterized by bending tests [47]. In addition to the improvement of the DBTT, studies by Raffo et al. [48,49] showed that the yield strength of swaged tungsten alloys with up to 20 at% rhenium increases with increasing rhenium content when tested at 327 °C. Improvements in the fracture toughness of sintered and forged tungsten alloys with 5, 10, and 26 wt% rhenium using 3-point bending tests at temperatures up to 800 °C were reported by both Gludovatz et al. [50] and Mutoh et al. [51]. This simultaneous increase in both strength and ductility by solid solution alloying using rhenium in BCC metals, including tungsten, molybdenum, and chromium is an abnormal behavior and is often referred to as the "rhenium effect" [52].

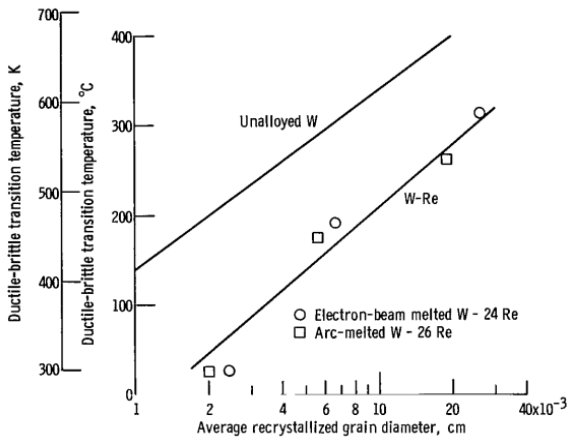

Figure 1 Bend transition temperature for recrystallized tungsten and tungsten-rhenium alloys as a function of grain size (used with permission from [47]).

It should be noted and emphasized that most of the reported studies cited above on the ductility of tungsten-rhenium alloys were performed using thermomechanical processed material. The effects of the deformation process and the resulting deformed microstructures are mixed with those of rhenium alloying. It should also be noted here that improvements of tungsten-rhenium by thermomechanical processing generally degrade significantly with recrystallization. Wurster et al. [53,54] reported that the room temperature fracture toughness of forged W - 26 wt.% Re dropped from 54.2 to 22.8 MPa-$m^{0.5}$ after annealing at 2000 °C for 2 h.

Despite the fact that many tested tungsten-rhenium alloys had been worked, reports do show that tungsten-rhenium is more ductile than tungsten with or without thermomechanical processing. As an example, Mutoh et al. [51] compared the fracture toughness of tungsten samples with 0, 5, and 10 wt% rhenium. They showed rhenium alloying led to a more significant increase in facture toughness (K_{IC}) as temperature increased without thermomechanical processing, and that the fracture toughness improves as the Re content increases [51].

In addition to arc-melting, powder metallurgy processes have also been used to prepare tungsten-rhenium alloys. In studies reported by Ivanov and Oda et al. [55,56], high energy ball milling was used to process the powder, and sintering was done using a two-step hydrogen sintering technique. The sintered alloy showed formation of homogeneous W(Re) solid solutions with rhenium compositions up to 25 wt% [37,55-59]. Field assisted sintering techniques such as Spark Plasma Sintering (SPS) were applied in more recent studies on these alloys [57,60,61]. Using a high temperature creep test, Stephenson [62] compared arc-melted and sintered alloys with 25 wt% rhenium after they had been rolled from 25.4 to 1.524 mm in thickness (94% reduction) at 1600 °C. He showed that the sintered tungsten-rhenium had lower rupture ductility at 1650 °C, but higher ductility at 2200 °C [62].

It should be noted that, in the above examples, sintered tungsten-rhenium was also thermomechanically worked. To understand the properties without thermomechanical processing, Luo et al. [63] reported that the addition of rhenium to as-sintered tungsten can have a strong solid solution softening effect. They reported the room temperature hardness decreased by as much as 16% at about 3.6 wt.% rhenium [63]. Similar alloy softening effects have also been reported by Ramalingam [64] and Stephen et al. [65].

Rhenium is a rare element and the major drawback of alloying using this element is cost. Aside from this, rhenium has limited solid solubility in tungsten. At rhenium composition above 27%, the brittle intermetallic σ-phase will form at room temperature and significantly decreases the alloy's mechanical performance. For fusion reactor applications, rhenium addition also has to be restricted, because rhenium can transmute into osmium or tungsten under neutron radiation and generates high-level waste with high disposal ratings [66].

Despite the rarity and high cost of rhenium [67], and over fifty years of research to find a suitable analog for ductilizing tungsten, rhenium remains the most industrially relevant alloying addition for enhancing the ductility of tungsten [68]. Historically, this "rhenium-effect" has been attributed to several different mechanisms including: scavenging and trapping impurities (particularly oxygen) in the lattice thus mitigating grain boundary segregation and embrittlement [69], improving grain boundary cohesion [8], or by directly modifying the mechanical response [70,71]. Specifically, modifying the mechanical response is done by reducing the Rice-Thompson Parameter ($b\mu/\gamma$) [26,70,71], where b is the magnitude of the Burgers vector, μ is the shear modulus, and γ is the shear strain. While each of these factors could influence the ductility of tungsten-rhenium alloys, the most complete picture for the effect of rhenium have been described based on the mechanism of solid solution softening [63,72-77], or modification of the dislocation core structure [78]. Both of these mechanisms improve the low-temperature mobility of screw dislocations.

2.2 Other Alloying Elements

Given the significant positive effects of rhenium on the mechanical properties of tungsten, there has been a great deal of research directed at exploring other possible beneficial alloying elements that may be less costly. Two approaches of alloying are solid solution alloying and compositions that create second phases in the alloyed microstructure. Concerning the solid solution approach, only a limited number of elements can form solid solutions with tungsten at room temperature, based on the binary phase diagrams. In this regard, tantalum, niobium, vanadium and molybdenum are the only elements that are fully miscible with tungsten in the solid state [79], while rhenium, titanium, technetium and osmium exhibit limited solubility in tungsten. Additionally, metastable alloys of tungsten with copper have been synthesized, and although a range of lattice strains have been reported, no reports on mechanical properties have been made and improvements in ductility seem unlikely [80,81]. The formation of intermetallic χ- and σ-phases limits the solubility of rhenium and titanium in tungsten to 27 wt% and 12 wt%,

respectively [82,83], as the presence of these secondary phases generally leads to a significant decrease in ductility. Additionally, iridium, hafnium and rhodium have minor solubility in tungsten with maximum values of 2 at.%, 4 at.% and 4 at.%, respectively [79]. There were some promising results in terms of the effects of those alloying elements on mechanical properties. For example, experimental studies on arc-melted and annealed tungsten with 0.4 and 0.8 wt% iridium showed tungsten-iridium has similar behavior to tungsten-rhenium in terms of room temperature tensile elongation results [63,84]. Since iridium, as well as technetium, osmium, hafnium and rhodium, are all rare elements and are unlikely to offer cost advantages over rhenium at high concentration, the studies of these rare elements at very low concentrations are limited. Therefore, for a wide range of alloying concentrations, tantalum, niobium, vanadium, molybdenum and titanium are the only remaining possible substitutes for Re for the solid solution alloying of tungsten.

Alloying tungsten with either tantalum or vanadium has not been shown to decrease tungsten's DBTT. Wurster et al. [26] reported no improvement in the fracture toughness of forged tungsten by the addition of up to 10 wt.% tantalum. Additionally, Wurster et al. [26] showed that high-pressure torsion (HPT) is necessary in order to obtain high fracture toughness with 30% Ta or 20% V. Additionally, an increase in tantalum content from 1 to 5 wt% was reported to lead to a significant decrease in Charpy impact energy in the temperature range from 700 to 1100°C, with no sign of improvement in the DBTT in the work by Rieth et al. [27]. Alternatively, titanium alloying has shown slight improvements in toughness and strength in bending tests on as-sintered tungsten with up to 4 wt% Ti [28,29]. These improvements were attributed to a change in the fracture initiation mechanisms in the large tungsten grains. However, the behavior of tungsten-titanium was still generally, brittle with no improvement in the alloy's DBTT. Recent research into alloying tungsten with large amounts of molybdenum (30 wt%) through sintering also did not show promising results in room temperature compression tests in terms of improving ductility [85]. In short, to date, little in the way of promising results has been presented on novel solid solution compositions.

Alloying additions of K, Zr, Hf, Ti, Y_2O_3, La_2O_3, TiC, TaC, and ZrC have all been studied and/or used in production of tungsten for various applications [28,32,38,45,66]. Notable examples of the oxides and carbides are discussed in section 3.2. Potassium as a minor alloying element, often with trace aluminum and silicon, has been used in the range of 100-160 μg/g in creep-resistant alloys for incandescent light bulb filaments [68]. These are commonly referred to as non-sag alloys. Although new fabrication routes and compositions have been investigated, significant improvements in ductility have not been realized.

Alloying with minor amounts of elements such as zirconium, titanium, or several of the rare earth elements that can bond with oxygen and increase grain boundary strength has gained attention [7,8,86-88]. An investigation of the thermal shock behavior of yttrium doped tungsten alloys prepared by spark plasma sintering was done by Lemahieu et al. [86], and indicated that yttrium in the range of 0.25-1.0 wt% increased grain boundary strength and improved thermal

shock and cycling resistance from ambient temperature. Further testing from 400°C, however, indicated that yttrium may have raised the DBTT of the material. The incorporation of zirconium by spark plasma sintering in the range of 0.2 – 1.0 wt.% Zr, both with and without additional yttrium oxide dispersions, has also been recently investigated. Liu et al. [87] showed a decrease in the DBTT of approximately 200 °C over pure tungsten with the addition of 0.2% Zr alone, while strength was improved with the additional incorporation of Y_2O_3 particles, which also resulted in a small decrease in corresponding ductility. Meanwhile, Xie et al. [88] showed that there was an optimum of approximately 0.2 wt.% ZrH_2 in tungsten, which dehydrogenated during processing and bound with oxygen forming ZrO_2 particles of approximately145 nm diameter, and resulted in significant increases in both strength and fracture energy. At higher compositions of zirconium, larger oxides were formed, which did not facilitate strength or fracture energy beyond 0.5 wt% Zr. In their works [87,88], by showing an increase in transgranular fracture on fracture surface and increase in tensile fracture energy, they claimed tungsten's grain boundary cohesion has been improved by zirconium micro-alloying and nano-sized yttria dispersion strengthening. However, there appears to be a limit to the more direct experimental evidence on the effect of additives on strengthening grain boundaries.

Tungsten heavy alloys generally have concentrations of iron and nickel between 2 and 10 wt.% (4.8 and 21.4 vol.%), and sometimes contain other elements [68]. These alloys rely on a second phase structure to improve ductility and are considered beyond the scope of the present article.

2.3 Simulation Studies

The basic mechanism of rhenium-induced ductilization has been extensively studied and several hypotheses have been established in recent years to explain mechanisms for achieving and analyzing ductility in tungsten. Based on density functional theory (DFT) calculations, alloying rhenium with tungsten modifies screw dislocations from a symmetric to an asymmetric core structure，decreases the Peierls stress, and reduces resistance in shear [3,78]. Another first principle calculation studies also reported that the incorporation of rhenium improves the mobility of ½<111> screw dislocations, which reduces the critical stress required to start plastic deformation [89,90]. As mentioned in the introduction, few experimental studies on tungsten and tungsten-rhenium single crystals have supported these DFT results, as rhenium additions promote slip on {112} planes at room temperature [24,25]. However, the absolute determination of active slip planes remains unclear, and other minor slip planes such as {110} have also been reported, based on micro-compression tests of tungsten single crystals [91,92].

The effects of transition metals on ductility in binary tungsten alloys have also been investigated using DFT [3,78,93,94]. Results suggest that alloying W with transition metals with a higher number of *d* electrons changes the dislocation core structure, reduces the Peierls stress, and lowers the barrier for ½<111> screw dislocation movement. However, the elastic shear constants decrease steadily with Ta content as it depletes the *d* band [94]. However, a simulation

study by Qi et al. [95] showed contrary conclusions. They showed that alloying tungsten with group IV or V transition metals can transform intrinsic failure modes of tungsten into ductile behavior, thereby failing in shear under [100] tension [95]. Recently, Hu et al. [96,97] also focused on systemic screening of alloying elements using a computed first principles approach, and proposed aluminum and manganese to be promising substitutes for rhenium [96,97]. However, the high processing temperatures required to consolidate tungsten presents a significant technical hurdle for incorporating these specific alloy additions, which have much lower melting point.

Brittle fracture along grain boundaries is well known in tungsten materials. Scanning Auger results reported by Tran-huu-loi et al. [13] clearly showed that the propagation of cracks follows the path of lowest energy and the reason for intergranular embrittlement of tungsten can be phosphorous segregation. Therefore, strengthening grain boundaries is another proposed mechanism for alloying elements to improve the mechanical properties of tungsten. Studies by Setyawan et al. [8] and Scheiber et al. [98] revealed cohesive effect of transition metals on tungsten grain boundaries via first-principle calculations. They found that both lower and higher valence elements enhance cohesion at different positions; the sixth-row transition metals are more vigorous strengtheners than the fifth-row elements [8], and strengthening elements belong to the middle of the *d*-band, while the embrittling elements are located at the boundaries of the *d*-band [98].

2.4 Summary on Alloying of Tungsten

Table 1 summarizes the reported results on the effect of alloying elements on tungsten's DBTT. The tungsten-rhenium alloys are, of course, the most well-known tungsten alloy system enhancing ductility [23,40,41]. Most reported research on tungsten-rhenium alloys shows the combined effects of rhenium alloying and thermomechanical processing [40,41,48,50]. The effect of thermomechanical processing will be examined in more detail in the next section. Sintered tungsten-rhenium without thermomechanical processing has been reported. Although direct evidence on decreases of the DBTT in the as-sintered state is not readily available, a clear solid solution softening effect has been reported by several groups [63,65]. Although there have been efforts to find substitutions for rhenium, no successful experimental work has been reported to date.

Table 1. Reported DBTT results on tungsten alloyed with secondary elements.

Alloy Type	Alloying Composition	Processing Method	Testing Method	DBTT (°C)	Reference

W-Re	1.9 wt% Re	Arc-melted, extruded and rolled	3-point bending	24	[40] W. Klopp et al., 1966
W-Re	26 wt% Re	Arc-melted, extruded and rolled	3-point bending	-101	[40] W. Klopp et al., 1966
W-Re	7 at.% Re	Arc-melted, extruded and swaged	Tensile test	177	[48] P. Raffo et al., 1969
W-Re	25 at.% Re	Arc-melted, extruded and swaged	Tensile test	77	[48] P. Raffo et al., 1969
W-Re	5 wt% Re	Sintered	3-Point bending	600	[51] Y. Mutoh et al., 1995
W-Ti	4 wt% Ti	HIPed	3-point bending	Above 600	[28] M. Aguirre et al., 2009
W-Ir	0.8 wt% Ir	As-melted (?)	Tensile test	Room temperature	[63] A. Luo et al., 1991

3. Effects of thermomechanical processing on tungsten's ductility

3.1 Thermomechanical Processing of Tungsten

For most ductile metals, plastic deformation causes an increase in dislocation density within the material, which in turn causes an increase in strength and a decrease in ductility. This phenomenon is referred to as work hardening [99]. Unlike work hardening in ductile metals, mechanical work can improve the ductility of tungsten. Rolled tungsten, which is commercially available from several major refractory metal companies, is known to be less brittle than W without thermomechanical processing, and the DBTT of commercial tungsten can be as low as 200 °C. Various deformation techniques, including: rolling, forging, swaging, and severe plastic deformation (SPD) techniques, such as equal-channel angular pressing (ECAP) and high pressure torsion (HPT), are all reported to have positive effects on the ductility of tungsten [17,100-108].

In 1963 and 1964, Bodine [109] and Maykuth [11] were among the first to publish systematic studies on the effects of deformation on the mechanical properties of tungsten. By using bending tests to determine the DBTT, they compared tungsten samples that had been rolled in the temperature range from 1150 to 1450 °C and then annealed at 1100 °C for 10 min. Based on their results, the DBTT of rolled tungsten decreased to 149 and 104 °C as the rolling reduction increased to 38 and 73%, respectively. The DBTT further decreased to about 82 °C after removing the 1100 °C annealing step [109,110].

A study by Rupp et al. [100] compared samples made of rolled pure tungsten subjected to 65% reduction. As shown in Figure 2, samples were fabricated with pre-crack notches that were orientated either parallel, radial, or tangential to the rolling direction. The samples were tested using a 3-point bending test at temperatures up to 725 °C [100]. The parallel and radial specimens (Figure 2 – type I and II) failed predominantly by intergranular fracture, and the tangentially oriented specimen (Figure 2 – type III) exhibited almost exclusively transgranular cleavage. The tangentially oriented specimens also showed fracture toughness of approximately 20 MPa-$m^{0.5}$ at 227 °C compared to about 10 and 13 MPa-$m^{0.5}$ for the radial and parallel specimens, respectively [100]. The DBTT of the tangential specimens also decreased to below 275 °C [100]. There results highlight the importance of texture and grain morphology in describing ductility and the DBTT.

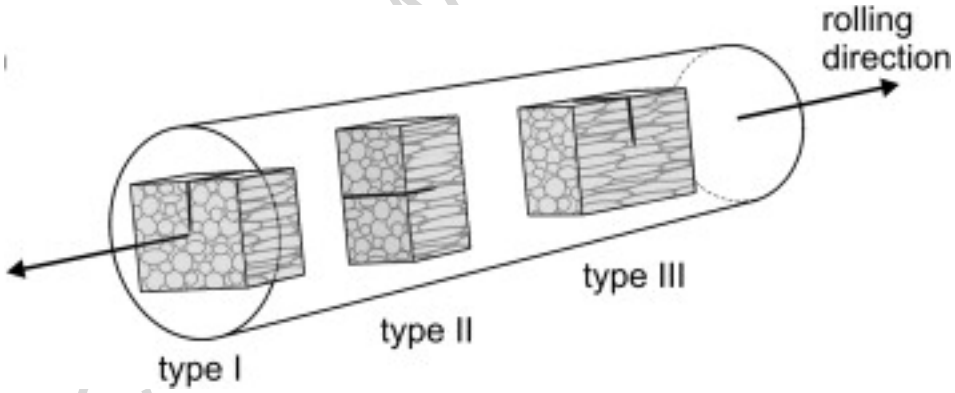

Figure 2 Schematic of types and crack orientations of 3-point bending samples. Type I: radial, type II: parallel and type III tangential to the rolling direction (used with permission from [100]).

In another study, T. Shen et al. reported that the DBTT of tungsten rolled at 1450 °C decreased from 300 °C to 250 °C as the tensile test sample's orientation changed from transverse to parallel to the rolling direction [17]. Similarly, in regard to the dependence of ductility on the orientation of rolling, Reiser et al. [22] reported on cold-rolled tungsten using Charpy impact testing. As the sample orientation changed from transverse to parallel to the rolling direction, the DBTT of cold-rolled tungsten decreased from 250 °C to only 125 °C [22]. In addition to orientation, the mechanical properties of rolled tungsten are also sensitive to the amount of deformation and to the rolling temperature [21,101]. Work by Zhang et al. [101] reported a study

of the evolution of texture in pure tungsten produced under various rolling reductions. It was observed that grains could be broken up, and new grains completed nucleation before reaching 40% reduction with a high initial rolling temperature at 1500 °C. There was substantial grain growth prior to 60% reduction. A fibrous microstructure appeared at about 80% reduction as a result of the further rolling process at lower temperature. By using Charpy impact testing, it was found that the DBTT of tungsten decreased from above 927 °C for sintered sample to 577 °C for a 60% rolling reduction and to 527 °C for samples with a 90% rolling reduction [101]. These reported DBTTs [101] are relatively high compared to conventional thermomechanically processed tungsten [22], which is probably due to their high rolling temperature and the 1100 °C annealing step.

All the examples discussed above demonstrate a strong sensitivity of tungsten to the deformed microstructures. The general trend is that DBTT increases as the thermomechanical processing temperature increases, and as the average grain size increases. This trend was also shown by the work of Wei et al [21] by tensile tests of tungsten specimens rolled at temperature from 400 to 800 °C. They showed that the ductility of rolled pure tungsten increases as the rolling temperature decreases, and an excessively high final rolling temperature can diminish the benefits of a lower temperature rolling process [21]. Regarding the microstructure, Wei et al. [21] reported that low temperature rolling leads to much finer grain sizes compared to higher temperature processing. They suggested that the thickness of the laminates is a function of rolling temperature, lowering the rolling temperature resulted in further smoothing of tungsten filaments, which are able to plastically deform significantly before final failure [21].

In addition to high temperature rolling, similar results were shown by Reiser et al. [22] in their work on cold-rolled pure tungsten materials [22]. This study indicated that low temperature rolling increased the cleavage resistance stress and resulted in a decrease of the DBTT [22]. A clear increase in the occurrence of low angle grain boundaries was observed as the rolling temperature decreased, where segments of dislocation networking formed boundaries, and can act as dislocation sources [22,111]. Figure 4 compares EBSD maps of annealed, high temperature rolled and cold-rolled material (<1200 °C), showing tungsten's microstructures reported by J. Reiser et al. [22]. Compared to the annealed condition, rolled tungsten showed very clear deformed grains with elongation parallel to the rolling direction. A significant amount of additional grain boundaries were also introduced into the microstructure due to both deformation and grain refinement. As a result of rolling, the DBTT of tungsten decreased from 675 °C for annealed condition to 375 °C and 125 °C for high temperature rolled and cold rolled conditions, respectively [22]. To date, besides single crystal tungsten [112-114], the only pure tungsten materials with appreciable room temperature ductility are highly deformed filaments or foils [115-117], for example the cold-rolled 100 μm thick tungsten foil samples reported by Reiser et al. [115] and Wei et al [21]. With its microstructure of severely deformed grains and strong {100}<011> texture, the tungsten foil specimens were able to reach a maximum of 4 to 7%

strain in a tensile test at room temperature [21,115]. This property was attributed to the high amount of mobile edge dislocations and to the small grain size.

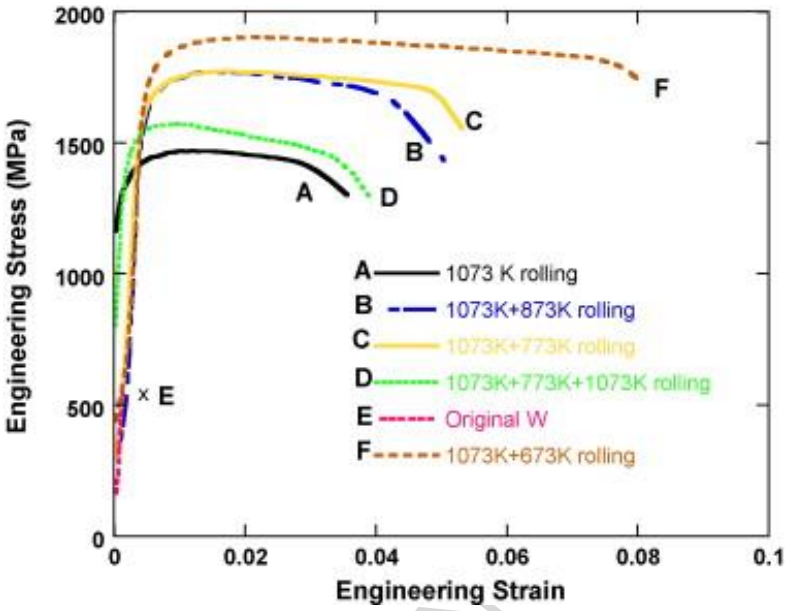

Figure 3 Room temperature tensile engineering stress–strain curves of tungsten rolled at different temperatures (used with permission from [21]).

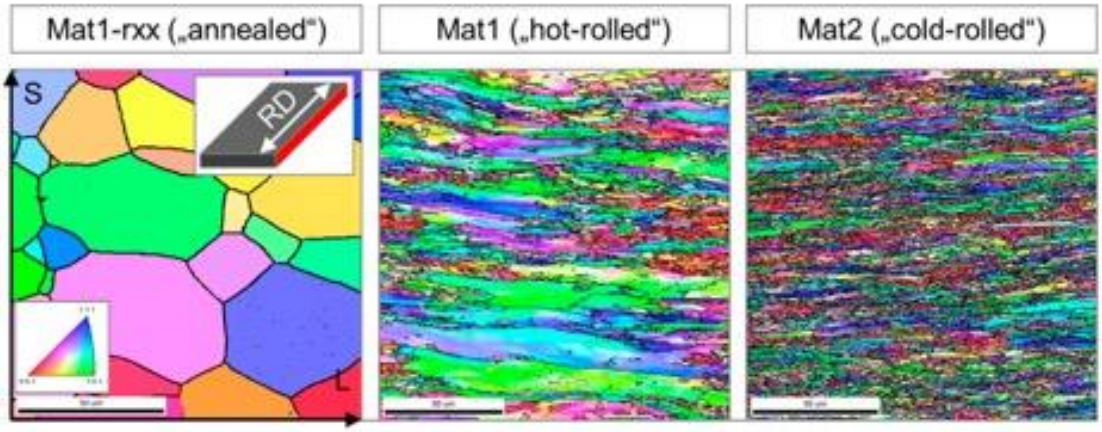

Figure 4 EBSD maps of annealed, high temperature rolled and cold-rolled tungsten (L = Longitudinal Direction, S = Short Transverse Direction.) (used with permission from [22]).

Other deformation processes, such as forging and equal-channel angular pressing (ECAP), have shown similar abilities to improve tungsten's ductility and decrease its DBTT. A study by Shen et al. [17] reported the ductility of tungsten rolled at 1650 °C is greater than that of material forged at 1700 °C. Using a tensile test, the DBTT was measured at about 250-300 °C for the rolled tungsten and about 350 °C for the forged tungsten [17]. Another study by J. Habainy et al. [118] showed that at 480 °C, the tensile strain level is up to 17.6% for rolled and up to 25% for

forged tungsten. Compared to conventional thermomechanical processing techniques, such as rolling and forging, ECAP has the advantage of being able to generate ultrafine-grained tungsten with an average grain size of about 0.3 – 2 μm. Based on Charpy test results, the DBTT of tungsten ECAPed at 800 °C and 950 °C decreased to 386 °C and 322 °C, respectively [102].

The effect of annealing on mechanical properties of rolled tungsten is another important topic, and has been studied by several researchers. A study by Briant reported that after rolling at 1300 °C, tungsten annealed at 1600 °C decreased its grain length to width aspect ratio from 35 to 11 [119]. Similar work by Alfonso et al. [120,121] also showed that following rolling at 1000 °C, the Vickers hardness dropped from 430 to 350 after tungsten was annealed at 1100 °C. In related work, Reiser et al. [22] also showed that annealing rolled tungsten at 2000 °C for 1 h recrystallized the deformed tungsten grains, which increased the DBTT from 375 °C to 675 °C [22]. In general, the positive effects on ductility and DBTT in tungsten gained from mechanical work are partially or totally lost with subsequent annealing at temperature above tungsten's recrystallization temperature.

3.2 Effects of Additives on the Properties of Thermomechanically Processed Tungsten

Over recent decades, there have been a significant number of reported efforts to improve the mechanical properties of tungsten using oxide and carbide additives through refining grain size and inhibiting recrystallization. These additives include, but are not limited to: Y_2O_3, La_2O_3, TiC, TaC, and ZrC. In most of these reported studies, tungsten alloys with additives were prepared using thermomechanical processing as a part of the process to produce the material. As an example, without thermomechanical processing, Miao et al. [32] reported on the addition of 0.2 wt% TaC to tungsten, sintered using the SPS process, which decreased the DBTT from 700 to 650 °C. Further increase of TaC content to 0.5 wt% and rolling with a 70% reduction led to a DBTT of approximately 250 °C [32]. Similar behavior was reported for thermomechanically processed W with other types of additives, such as La_2O_3 [122], K [31], ZrC [123] and TiC [124]. For example, Z. Xie et al. [125] reported on the addition of 0.2 wt% Zr and 1 wt% Y_2O_3 to tungsten that was rolled at 1650 °C, which significantly decreased the fraction of intergranular fracture from 25% to only 5%. The DBTT, as determined by tensile tests, also decreased from 200 °C to 150 °C by adding 0.2 wt% Zr and 1.0 wt% Y_2O_3 to W [125].

In an intriguing study, Kurishita et al. [66,126] developed a process called the superplasticity-based microstructural modification (SPMM) process. This process is based on the superplasticity caused by grain boundary sliding in an ultrafine-grained W-TiC alloy. It was stipulated that the SPMM process can lead to recrystallized, equiaxed fine grain tungsten with significantly strengthened grain boundaries due to the segregation of TiC [127]. The W-1.1 wt% TiC samples with 80% reduction during SPMM processing were found to have the highest elongation, exceeding 160% at temperatures from 1500 to 1700 °C in tensile testing among all W-TiC materials [128,129]. It was attributed to a grain boundary strengthening effect that converts the brittle W material to a toughened, fine-grained, and recrystallized (TFGR) W-

1.1TiC. As shown in Fig. 5, the W-1.1 wt% TiC material had a fracture strength as high as 3.3 GPa in 3-point bending tests and about 0.8% strain after the yield point, even at room temperature [128]. Additionally, room temperature bending ductility has also been reported on other materials, including W – 0.3 wt.% TiC rolled at 1497 °C [130,131], and W – 1 wt.% Y_2O_3 rolled at 1600 °C [132]. Besides tungsten foil, wire or single crystal, the combination of rolling and additives appears to be the only known approach to manufacture bulk tungsten material with detectable room temperature ductility.

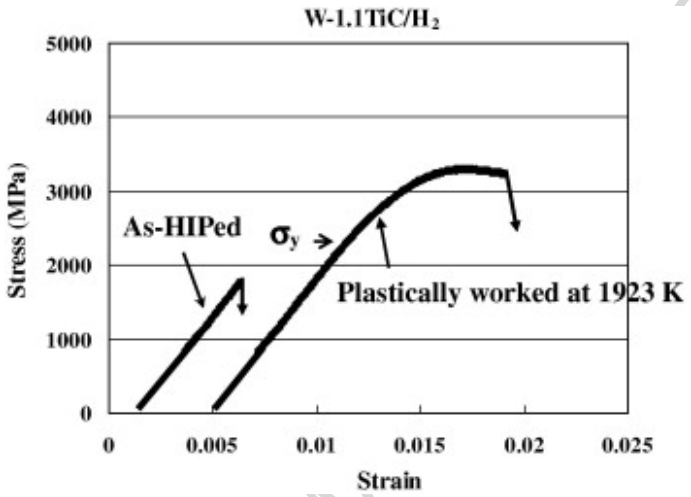

Figure 5 The 3-point bend stress-strain curves for W–1.1 wt% TiC before and after compression formed by approximately 80% reduction at 1650 °C (used with permission from [128]).

3.3 Tungsten Composites

As discussed in the previous section, the DBTT of tungsten decreases with an increasing degree of deformation; and without additives, foils and fibers are the only polycrystalline tungsten materials with reliable room temperature ductility. To extend this desired mechanical behavior of tungsten foils to bulk shapes, fabrication of tungsten laminate composites by assembling multilayers of ductile W foils has been proposed and investigated by Reith et al. [133-135]. This tungsten laminate contains 20 layers of 0.1 mm thick rolled tungsten foils, which are joined by a eutectic Ag-Cu brazing filler. Charpy impact test results showed a significant increase in impact energy as testing temperature increased from room temperature to 300 °C [134,135]. This result indicates the DBTT of the tungsten laminate is below 300 °C, which is much lower than most reported pure tungsten materials.

Another proposed approach is tungsten fiber reinforced tungsten composites, developed by Du et al. [136-138]. In their work, 150 μm diameter tungsten wire covered with multilayer ZrO_x or carbon films were wound and further coated with tungsten by CVD processing to form a dense matrix mantle [136,137]. Three-point bending tests proved that, rather than catastrophic failure, these fiber reinforced tungsten composites showed stable crack propagation. Even during a fiber fracture event, the sample only experienced a large load drop instead of a total fracture

[139]. Similar work was done on tungsten composites with a tungsten matrix and mixed short tantalum fibers produced via the SPS method, in which energy released by crack propagation was absorbed by the deformation of relatively ductile tantalum fibers [140]. A pseudo toughness mechanism has been proposed for these fiber reinforced tungsten composites, a concept that has been widely used in fiber reinforced ceramic matrix composites [139,141]. By using this type of approach, crack propagation is deflected at the fiber/matrix interfaces, which leads to the dissipation of stored energy by interface debonding and friction [139,141].

3.4 Discussion of the Mechanisms of Tungsten Ductilization through Thermomechanical Processing

According to most of the reported work on thermomechanically processed tungsten, the microstructure of rolled W exhibits strong texture, of which the lamellar structure shown in Fig. 4 [22] is most common. It has been shown that the thickness of lamellae decreases as the rolling temperature decreases [101]. Work by Zhang et al. [101,124] suggested that the fracture surface of samples with a laminate structure tested in tension at 300 °C showed necking with up to 38.94% area reduction and 19.3% elongation, which indicated plastic deformation before failure. As shown in Figure 6, Rupp et al. [100] explained that during fracture of tungsten with a lamellar or elongated grain structure, cracks initiated in front of the notch tip in the rolling direction, and cracks only propagated by shear fracture of the ligaments [100]. This is clearly different from the catastrophic failure in recrystallized tungsten caused by rapid intergranular cracking. This crack propagation mechanism may increase fracture toughness of W and make the fracture behavior more controllable.

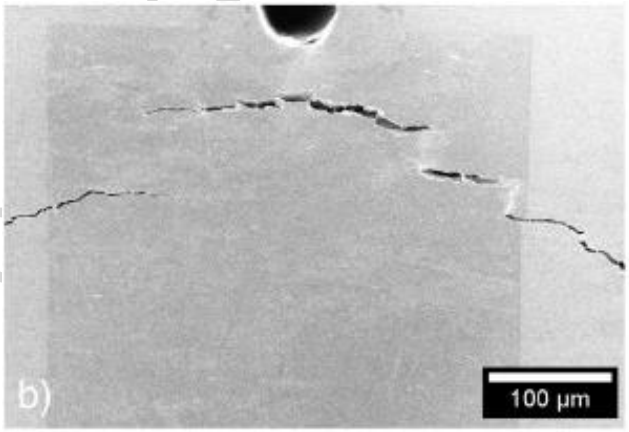

Figure 6 Crack initiation and propagation with increasing applied load during in situ fracture testing at 350 °C (used with permission from [100]).

In addition to the effects of texture, thermomechanical processing may also strengthen tungsten grain boundaries by minimizing the presence of segregation on the grain boundaries [68]. Wei et al. [142,143] proposed that, based on their observations from compression tests, the grain refinement as a result of the thermomechanical processing can improve the ductility, because

impurities are redistributed such that the impurities and defects are spread over larger areas of grain boundaries. However, direct experimental evidence of the decrease in impurity level and its relationship to ductility is still lacking.

The migration of dislocations is another widely proposed factor affecting the DBTT of tungsten. Several published studies conducted on single crystal [144], polycrystalline [145], coarse grain and ultrafine-grained tungsten materials [146] have discussed the effect of screw dislocation glide on the DBTT. Recent studies by Reiser et al. [22,147] on low temperature rolled pure tungsten showed a significant increase in low angle grain boundaries after rolling. They proposed that the availability of the sources of dislocations is responsible for the shift of DBTT, and these sources could be either dislocation boundaries or grain boundaries [22,147].

Mechanisms have been proposed in a number of studies for how the improvement of tungsten's ductility through thermomechanical processing is accomplished. These can be summarized as: 1) thermomechanical processing increases the density of tungsten, eliminates porosity, which may function as strain concentration locations; 2) thermomechanical processing results in crystallographic texture and a lamellar microstructure with high factions of small angle grain boundaries, which facilitates dislocation movement across such boundaries, 3) low temperature thermomechanical processing increases the number and fraction of edge and mixed dislocations, which have higher mobility and improve tungsten's fracture toughness at low temperature; 4) thermomechanical processing increases the density of both dislocations and dislocation sources, which decreases the energy necessary for dislocation migration; 5) the microstructure texture also helps to control cleavage planes and the crystallographic orientation of crack front propagation; 6) average grain size decreases as the deformation ratio increases, which generally leads to an increase in the fracture toughness of tungsten; 7) thermomechanical processing increases grain boundary density through grain refinement, decreases the impurity concentration at grain boundaries, and thus improves grain boundary cohesion. To date, the overall mechanism and relative contributions from each of these possible mechanism is yet to be fully understood, and more experimental evidence is needed to elucidate the effect of thermomechanical processing on tungsten's ductility.

3.5 Summary on the Effects of Thermomechanical Processing

It is widely recognized that thermomechanical processing is currently a necessary processing step to obtain ductile tungsten or reduce the DBTT of tungsten. Thermomechanical processing can lead to strong anisotropic microstructures with deformed grains and elongated grain boundaries with high fractions of small angle grain boundaries. Thermomechanical processing also increases dislocation density, eliminates pores, and improves grain boundary cohesion. When combined with the effects of alloying with Re or the effects of using additives, such as oxides and carbide particulates, tungsten exhibits the best mechanical properties and workability. Table 2 summarizes the reported studies on rolled pure tungsten materials, with detailed information on the rolling temperature, average grain size and DBTT.

Table 2 Reported DBTT results on rolled pure tungsten materials.

Sample Description	Rolling Temperature (°C)	Average Grain Size (μm)	Testing Method	DBTT (°C)	Reference
0.1mm film	400	0.8	Tensile	Below room temperature	[21] Q. Wei et al., 2008
0.1mm film		0.5	Tensile	Below room temperature	[115] J. Reiser et al., 2013
Rolled plate	Below 1200	1 – 4	Charpy	125	[22] J. Reiser et al., 2016
Rolled plate	2100	5 – 50 bimodal	3 point bending	180 – 230	[148] V. Krsjak et al., 2014
Rolled plate	1450 – 1650	100 x 400	Tensile	<280	[118] J. Habainy et al., 2015
Rolled plate	1450 – 1650	140 x 330	Tensile	250 – 300	[17] T. Shen et al., 2016
Rolled plate	1500	100	Charpy	577	[101] X. Zhang et al., 2016.

4. Ultrafine-Grained and Nanocrystalline Tungsten

4.1 Ultrafine-Grained and Nanocrystalline Metal Alloys

In general, the potential of nanocrystalline microstructure for improving the mechanical behavior of metallic materials has attracted a great deal of attention from the research community since the early 1980s. In 1981, Gleiter [149,150] presented the initial concept for developing nanocrystalline materials to obtain special thermal, electrical, and mechanical properties. In the early 1990s, R. Valiev [151-154] first reported the production of ultrafine-grained metals using the severe plastic deformation (SPD) method, invented by V. Segal [155,156]. By deforming an Al alloy at room temperature using ECAP to reduce the average grain size from 10 μm to 200 nm, they showed an increase in 1420-Al alloy's tensile yield stress from 330 to 550 MPa and maximum elongation from 5 to 6% [154]. Subsequently, many different SPD processing techniques have been used for manufacturing ultrafine-grained metals [157], for example: high-

pressure torsion (HPT) [106,158-160], multi-directional forging [161,162] and accumulative roll-bonding [105,163].

As another example, Yamashita et al. [164] reported on a Mg – 0.9 wt.% Al alloy with 17 μm equiaxed grains after ECAPing at 200 °C for 2 passes. These samples showed an increase in room temperature ultimate tensile stress from about 70 MPa to 240 MPa and an increase in the elongation to failure from 2.5% to 15% as the ECAP pressing increased from 0 to 2 passes [164]. Work by Stolyarov et al. [165] also showed, compared to coarse-grained samples, that after 8 passes of ECAP at 400 °C on pure titanium, a 68 to 89% improvement in room temperature tensile yield stress was realized, while the samples maintaining good ductility with 10 to 14% elongation. Similar behavior has also been reported on other SPDed alloys like Al-6061, copper and steel [166-168].

4.2 Ultrafine-Grained Tungsten and Techniques

Based on the previous successes on various types of metal alloys, the use of nanocrystalline microstructures has also been considered as a promising approach to improve the ductility of tungsten and decrease the DBTT [30]. Figure 7 shows the result of a recent TEM study by Cheng et al. [169] on high-pressure torsion (HPT) processed ultrafine-grained molybdenum. Molybdenum is very similar to tungsten, indicating that a decrease of grain size leads to a decrease in screw dislocation density and an increase in edge/mixed dislocation density. Based on studies on iron, tantalum and vanadium, gliding of edge dislocations in BCC metals is much faster than slip of screw dislocations [170-172]. Therefore, deformed samples with finer grain size should have improved ductility as a result of increased density of gliding dislocations. Furthermore, in relation to the use of tungsten in irradiative environments, ultrafine-grained and nanocrystalline tungsten have been proven to be more radiation resistant than coarse grained tungsten as the irradiation induced point defects can be absorbed by the larger total volume of grain boundaries [173-175].

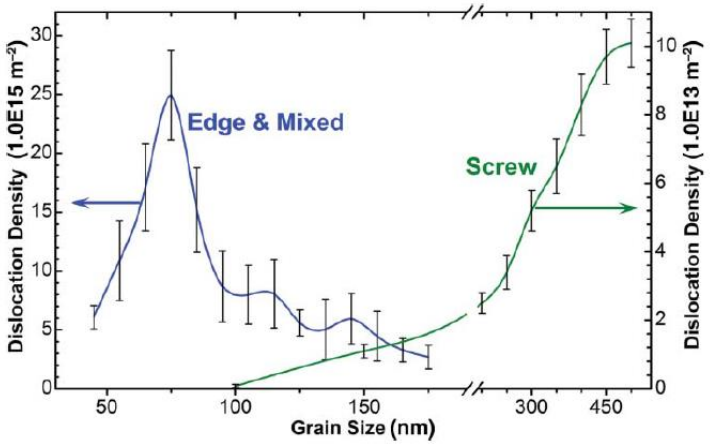

Figure 7 The variation of dislocation densities with grain size for ½<111> screw dislocations and for ½<111> edge and mixed dislocations measured by HRTEM in HPT processed ultrafine-grained molybdenum (used with permission from [169]).

There are two main categories of approaches to manufacture ultrafine-grained or nanocrystalline tungsten: the top down approach, and the bottom up approach [176]. The top-down approach of manufacturing nanocrystalline tungsten is generally completed by the same severe plastic deformation (SPD) techniques as used in other metal alloys [177-179]. A study by Zhang et al. [107] reported on commercial-purity tungsten rod produced by ECAP at 1150 °C with a DBTT between 250 °C to 350 °C based on microhardness testing. Another study by Wei et al. [108] produced nanocrystalline W samples using a high-pressure torsion technique at 500 °C with deformation strains of up to 90%, and showed an extremely high strength for this material at about 3.0 GPa under quasi-static compression and about 4.0 GPa under dynamic compression. However, it should be noted that a common drawback of these SPD techniques is that it is very difficult to scale up these processes for production and it is also difficult to fabricate complex shapes with various geometries.

4.3 Ultrafine grain W by Sintering of Nanocrystalline Powder

The bottom-up approach uses powder metallurgy techniques, involving synthesis of nanosized tungsten powders followed by a consolidation process. Several research efforts have been undertaken in order to obtain ultrafine-grained tungsten using bottom-up approaches.

The control of grain growth during the consolidation process is the most challenging process for the bottom-up approach, since elevated temperatures are used. Several types of consolidation processes, such as hot isostatic pressing (HIP), spark plasma sintering (SPS) and microwave sintering have been applied to overcome this challenge. A study by Monge et al. [180] reported consolidating planetary ball milled tungsten powders at 1700 °C using HIP, and obtained sintered tungsten samples with 4.4 μm average grain size and a relative density of 92.7%. Additionally, Kim et al. [181] improved the relative density of sintered W to 96% by first tubular ball milling of tungsten powders and then SPS at 1700 °C at the cost of average grain size, which increased to 18.8 μm. Research using microwave sintering at 1500 °C reported more promising results for pure tungsten samples with an average grain size of 3.2 μm and relative density of 96.9% [182]. All of this work on consolidation of pure tungsten showed clear improvements over conventional tungsten sintering, which employs temperatures above 2000 °C, and where the average grain sizes are in the range of 10 to 30 μm with a sintered density less than 95% [183]. The high densification rate of these consolidation processes suppresses the influence of the grain growth mechanism during a normal sintering process, and ultrafine-grained microstructures can be obtained. However, most of the reported grain sizes of the as-sintered materials are still larger than the ultrafine-grain range, which is generally defined as less than 500 nm, and relatively low sintered densities are still common.

Dispersing small amounts of thermally stable particles as grain growth inhibitors into tungsten has been reported as another method for controlling grain growth during sintering. Yttrium oxide is a popular choice as an additive for oxide dispersion strengthening (ODS) of tungsten. Liu et al. [182] reported on tungsten materials with Y_2O_3 additive prepared using microwave sintering at 1500 °C for 30 min in vacuum by a 2.45 GHz microwave generator. By adding 1% Y_2O_3, the average grain size of tungsten was reduced from 3.2 μm to 0.7 μm, while the relative density was maintained at about the same level, 96.8% [182]. Spark plasma sintered tungsten also showed similar behavior with the addition of 2% Y_2O_3, which led to a 29.3% decrease in average grain size and a 1.5% increase in sintered density [181]. Aside from the grain growth inhibiting effect, using yttrium as an additive in tungsten was also reported, where yttrium transformed into Y_2O_3 during mechanical alloying, and reduced the excess oxygen content in the milled powders [141]. Additionally, La_2O_3 is another reported ODS additive [182,183]. The same microwave sintering research by Liu et al. [182] also reported that the addition of 1 wt% La_2O_3 to tungsten led to a reduction in grain size from 3.2 μm for W to 1.4 μm for W-La_2O_3, while the relative density also decreased from 96.9% to 95%. Titanium carbide, TiC, another thermally stable particle has also been used to inhibit grain growth in tungsten. Work by Ding et al. [184] on spark plasma sintering of W-1 wt% TiC at 1800 °C reported an average grain size of 3 μm and a relative density of 98.6%. The extensive work performed by H. Kurishita et al. reported densified W – x wt% Ti ($x \leq 1.5$) samples produced by ball milling and HIP with 50-200 nm tungsten grain sizes by using up to 40 nm sized TiC particles that were effective at pinning grain boundaries [185-187]. Yamazaki et al. [188] reported on tungsten wire with 0.01 – 0.06 wt% Co and incorporating 0.1, 0.4, and 0.55 wt% of Al_2O_3, SiO_2 and K_2O, respectively. The maximum tensile elongation of this tungsten wire increased with increasing amounts of Co, and reached 26 % elongation with 0.06 wt% Co content [188]. By combing the above mentioned pressure assisted consolidation, and grain growth inhibitors, W – 0.5 wt.% TiC with a submicron grain size and up to 97.6% relative density has been reported [186].

Park et al. [189] reported their study on W–15 at% Cr alloy which showed material with nearly full density (>98%) after pressureless sintering at temperatures around 1500 °C. They also showed sintered W–35at.%Ti–10 at.% Cr with near full density and a grain size of 100 nm [189]. Based on TEM analysis and atomistic modeling, the accelerated sintering was attributed to the diffusion of tungsten through the chromium phase during the densification [190-191]. However, all of these reported materials are tungsten with large amount of secondary phase alloying element (15 to 45 at.%) which inevitably lead to significantly lower density that that or pure or near-pure tungsten. Therefore, they fall outside the scope of this manuscript.

High-energy ball milling, including planetary or vibratory milling, is the most common method for preparation of nanosized tungsten powder. However, the sol-gel method has been used in several recent studies as a novel route to synthesis of nanosized ODS tungsten powders [192-194]. Work by R. Liu et al. [182] reported that W-1 wt% Y_2O_3 samples with 3.2 μm average grain size and 99% relative density can be obtained by sol-gel production of nano-

tungsten powders and SPS at 1800 °C. By using the sol-gel method, Y_2O_3 particles with sizes as fine as 52 nm can be dispersed homogeneously at grain boundaries and even grain interiors, which leads to both reduced grain size and mechanical behavior improvement [87,193].

Recent work by the C. Ren et al. [195-197] and X. Wang et al. [198] revealed a new approach for obtaining ultrafine-grained tungsten using pressureless sintering of planetary ball milled nano-tungsten powder. Pure tungsten samples with 98.3% density and average grain sizes less than 2.5 μm were obtained by sintering at temperatures as low as 1300 °C for 1 hour [195]. By using a titanium additive as a grain growth inhibitor and a low temperature sintering approach, the average grain size of tungsten was further decreased to 500 nm with no decrease in relative density [196]. This is one of the finest grain sizes reported to date for tungsten with near full density. The sintering atmosphere was demonstrated to have a critical effect on sintered density and also the densification mechanism of tungsten, where sintering in argon led to much higher density with finer grain sizes than sintering in H_2 atmosphere [195-197]. During sintering, the titanium additive not only functioned as a grain growth inhibitor, but also absorbed oxygen from adjacent tungsten grains or grain boundaries [197].

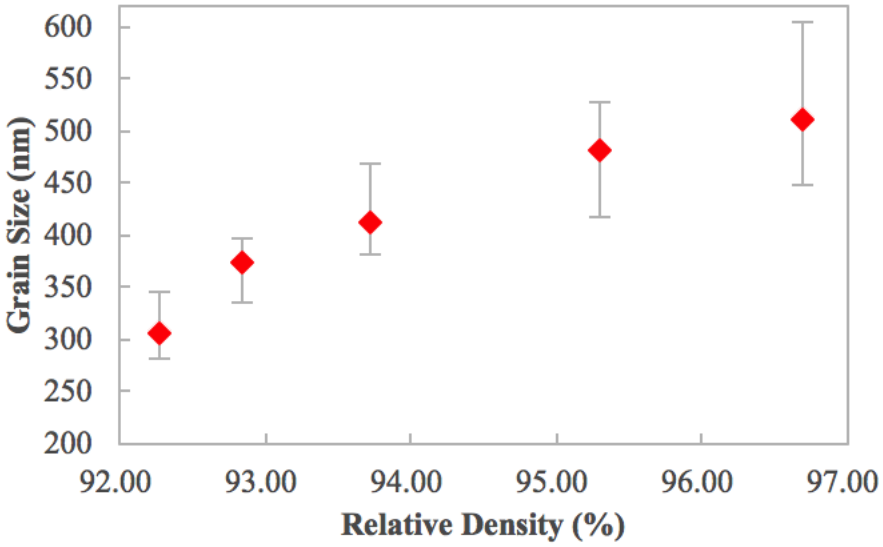

Figure 8 Tungsten grain size vs. relative density for W-1wt.% Ti samples sintered at 1100 °C from 1 to 16 h in an argon atmosphere (used with permission from [197]).

Table 3 summarizes the reported results of ultrafine-grained tungsten work. Based on the table, the addition of ODS or titanium additives leads to finer grain size with only a slight decrease in the relative density of sintered parts. Traditionally, pressure assisted sintering techniques, such as HIP or SPS, are required to obtain near fully dense tungsten material at temperature below 2000 °C. The average grain size of sintered materials is still generally above 1 μm, with two exceptions, reported by Y. Kitsunai et al. [186] and C. Ren et al. [197] on their W-TiC and W-Ti materials, respectively. Due to the nature of field assisted sintering, these

approaches may not be amenable to manufacturing large bulk tungsten materials with near net shaped structures. In this respect, to date, the only successful work reported on pressureless sintering of ultrafine-grained tungsten is that by C. Ren et al. [197], in which near full density tungsten with an average grain size as small as 512 nm was obtained.

Table 3 Reported results on ultrafine-grained tungsten materials.

Material Type	Additive Composition	Processing Method	Consolidation Temperature (C)	Relative Density	Grain Size (μm)	Reference
W	0%	Planetary Mill and HIP	1700	92.7%	4.4	[180] M. Monge et al., 2009
W	0%	Commercial Powder and SPS	1800	96.1%	6.3	[199] J. Ma et al., 2013
W	0%	Planetary Mill and Pressureless Sintering	1300	98.3%	2.4	[195] C. Ren et al., 2016
W-Y_2O_3	1% Y_2O_3	Planetary Mill and SPS	1800	99.5%	3.9	[193] R. Liu et al., 2016
W-Y_2O_3	1% Y_2O_3	Sol Gel and SPS	1200	92.0%	2.3	[194] M. Yar et al., 2011
W-TiC	0.2% TiC	Ball Mill and HIP	2000	97.6%	0.4	[186] Y. Kitsunai et al., 1999
W-La_2O_3	1% La_2O_3	Planetary Mill and Microwave Sintering	1500	95.0%	1.4	[182] R. Liu et al., 2012
W-Ti	1% Ti	Planetary Mill and Pressureless	1100	96.7%~98.3%	0.5~1	[197] C. Ren et al.,

		Sintering				2017

4.4 Mechanical Behavior of Ultrafine-Grained Tungsten

Although extensive work has been done on reducing grain size and increasing the sintered density of tungsten materials, studies concerning the changes in mechanical behavior of tungsten solely caused by grain refinement are relatively lacking. At the same relative density, ultrafine-grained tungsten usually has higher hardness than commercial tungsten as a result of the finer grain size [182,194,200]. Decreasing grain size from 3.2 μm to 0.7 μm in 1500 °C microwave sintered tungsten by adding 1% Y_2O_3 led to a 37% increase in Vickers hardness (from 5.04 to 6.91 GPa) [182]. Aside from hardness, fracture toughness is another property which can be significantly affected by grain refinement. Based on disk shaped compact tension and single edge notched bend tests, Faleschini et al. [31] reported that decreasing the grain size of sintered tungsten by the addition of 1% La_2O_3 and 0.005% K led to an approximately 63% increase in fracture toughness (from about 26 to 42.5 $MPa*m^{0.5}$), and the fracture toughness difference of tungsten samples with and without additives increases as test temperature increases up to 600 °C. The only improvement on the DBTT of ultrafine-grained tungsten was reported by Liu et al. [87,201] on their studies of W-Zr and W-ZrC samples made by planetary ball milling and consolidation by SPS at 1800 °C. With the addition of less than 0.5% Zr or ZrC, the DBTT of tungsten can be reduced from above 600 °C to a range of 400 – 500 °C or 500 – 600 °C, respectively. This effect was attributed to the nanosized Zr or ZrC particles, which could capture the residual oxygen and strengthen the grain boundaries, and the ZrC dispersed in the grain interior could pin dislocations [87,201]. Although these are important results, the report did not provide any details of the processing, nor any specifics of the testing methods. The effects of grain size and Zr or ZrC additives on mechanical properties remain to be clarified.

Despite the indications of higher hardness and possible higher fracture toughness, there are no data reported to date that shows any improvement in ductility of sintered ultrafine-grained tungsten at room temperature, or lower DBTT, without the benefits of thermomechanical processing. There are several possible reasons for this. First, the randomly oriented tungsten grains in the as-sintered state lack the beneficial texture or lamellar structure of hot or cold worked material [188]. Second, unlike deformation processed materials, sintered tungsten is not expected to have a higher density of mobile and mixed dislocations. Third, as a result of the Hall-Petch effect [99], ultrafine-grained structures usually lead to extremely high yield strength [141], which means a high barrier for slipping. Fourth, the existence of residual pores may also have significant detrimental effects on ductility.

4.5 Summary of Ductility Improvements in Ultrafine-Grained Tungsten

Improving mechanical properties through ultrafine-grained or nanocrystalline microstructures have been used in many metal alloy systems since the 1980s [149,150,154,164,165]. Based on the successes in other alloys, ultrafine-grained or nanocrystalline approaches have also been considered as a promising method to improve tungsten's ductility. Two main approaches have been reported: the top-down and the bottom-up [176]. The top-down approach, using the same SPD techniques, has shown both an increase in compression strength and a decrease in the DBTT [107,108]. The bottom-up approach uses powder metallurgy techniques, which include using nano-sized initial tungsten powders and various types of consolidation techniques. Additives, such as metal oxides or carbides, may be incorporated at grain boundaries as grain growth inhibitors, which minimizes the grain size in the sintered samples. By combining nano-sized starting powders and grain growth inhibitors, ultrafine-grained tungsten with near full density and grain sizes as small as 500 nm can be sintered without the use of assisting pressure.

Although extensive research has been performed on manufacturing ultrafine-grained tungsten by the bottom-up approach, the studies on mechanical behavior of this material are very limited. However, there are many promising avenues of research based on the changes in dislocation character and mobility in deformed BCC microstructures with ultrafine grain sizes [169].

5. Conclusions

The ductilization of tungsten is highly desired for many of tungsten's applications and is one of the main research objectives for the refractory metal community. Several remarkable successes have been achieved in the last sixty years, which enable the production of tungsten materials with room temperature ductility. However, a comprehensive understanding of the fundamentals of the ductility of tungsten, as well as the processing factors controlling the ductility of tungsten, are still sorely needed for not only expanding the applications of tungsten, but also improving the manufacturability of tungsten.

Alloying with Re is still the only proven and dependable method for ductilizing tungsten through alloying. However, the low availability and high cost of this element inhibits its applications. Encouraging simulation results have been obtained for alloying tungsten with other solid solution elements, but the few experimental results have thus far shown contrary results. Much of the reported tungsten alloying research other than tungsten-rhenium has shown clear formation of secondary phases, which are known to increase tungsten's brittleness.

Thermomechanical processing of tungsten is the only commercially scaled method for producing tungsten with ductility and relatively low DBTT. For pure tungsten, deformation using rolling, forging, or ECAP usually results in a significant decrease in the ductile-to-brittle transition temperature. The combination of deformed and ultrafine-grained microstructure has been demonstrated as an effective method for ductilization of polycrystalline tungsten at room

temperature, aside from rhenium alloying. The specific advantages of microstructure texture, strengthened grain boundaries, lamellar structure, and high dislocation density with improved dislocation mobility make rolling an effective method for tungsten ductilization.

Ultrafine-grained or nanocrystalline microstructures have been proposed as another approach to ductilize tungsten. Ultrafine-grained tungsten with submicron grain size and near full density can be obtained through the use of nano-sized starting powders and grain growth inhibiting additives. It was shown that ultrafine-grained structure leads to measurable improvements in hardness, fracture toughness, and radiation resistance. However, there are no data to date that could show the effects of ultrafine grain size on the ductility of tungsten without the benefits of thermomechanical working. Poor grain boundary cohesion, residual porosity, lack of dislocations, and the lack of a lamellar grain structure in these as-sintered materials appear to present serious obstacles to ductilization.

Although rhenium alloying and deformation have been proven to effectively ductilize tungsten, the fundamental understandings underlying the ductility of tungsten remain insufficient. A range of approaches including additives and ultrafine microstructure that are utilized to improve tungsten is effective only when they are used in combination with thermomechanical working. In this regard, one of the challenges or directions for future research is to find compositions without rhenium, processing routes without thermomechanical working, and microstructures that can yield ductility in tungsten. This would enable near-net-shape manufacturing of ductile tungsten, or at least lower the temperatures required for thermomechanical working of tungsten.

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Highlights

- Review of the methods for improving the ductility of tungsten in order to understand the critical factors that control the ductility in tungsten.
- All reported tungsten materials with room temperature ductility were thermomechanically processed.
- Rhenium is the only known effective alloying element to improve the ductility of tungsten.
- No evidence has yet shown reducing grain size alone improves the ductility of tungsten.
- Correlations are presented between the ductility of tungsten and microstructures that result from different processing methods and compositions.