DENSIFICATION MECHANISM AND MECHANICAL PROPERTIES OF TUNGSTEN POWDER CONSOLIDATED BY SPARK PLASMA SINTERING

G. Lee^{1,2}, J. McKittrick², E. Ivanov³, E.A. Olevsky^{1,4,*}

¹Mechanical Engineering, San Diego State University, San Diego, USA

²Mechanical and Aerospace Engineering, University of California, San Diego, La Jolla, USA

³Tosoh SMD Inc., Grove City, USA

⁴NanoEngineering, University of California, San Diego, La Jolla, USA

ABSTRACT

The dominant densification mechanism of a tungsten powder processed by spark plasma sintering (SPS) is revealed by the continuum theory of sintering-based regression of the experimental data on the powder consolidation carried out at the temperatures from 1600 °C to 1800 °C and pressure levels of 60 MPa and 120 MPa. The strain rate sensitivity is determined to be 0.39 and the sintering activation energy is 412 kJ/mol. It appears that the main mechanism of tungsten powder densification compaction is grain boundary sliding controlled by dislocation climb with the dislocations moving along grain boundaries. The evidence of the superplastic-like behavior of the tungsten powder during SPS is also supported by electron backscatter diffraction microstructure analysis of the compacted specimens. The relative density of the compacted pellets reaches 81~95%, depending on the SPS temperature conditions. The experimental outcomes indicate that the carbon uptake during SPS results in the formation of tungsten carbide at the surface of compacted specimens. Based on the experimental data, the diffusion coefficient of carbon in tungsten is obtained and is found to be similar to literature values.

Keywords: tungsten, superplasticity, grain boundary sliding, tungsten carbide, spark plasma sintering, field-assisted sintering

* Corresponding author: e-mail: eolevsky@mail.sdsu.edu

1. Introduction

Tungsten (W) components find a broad spectrum of applications in automotive and aerospace industry, in furnace elements, in electronics, in medical devices, in sports equipment, in welding electrodes, and in nuclear power plants. Due to the high melting temperature, manufacturing of tungsten parts is frequently attempted through powder metallurgy routes. However, consolidation of tungsten powders by traditional powder processing technologies, such as sintering and pressing, presents significant challenges. It has been reported that 2.3 μm W powder had to be sintered at 2500 °C for 1 hour in a hydrogen atmosphere to get specimens with the relative density close to 90 % [1]. In a different study Bewlay *et al.* showed that 50 hours of free sintering were required to obtain 90.2 % density under 1800 °C [2].

Pressure-assisted sintering methods were also utilized for the consolidation of W powders. Karpinos *et al.* reported that W powder could be sintered to 94 % under 2300 °C and 24.52 MPa using hot pressing (HP) [3]. Hot isostatic pressing (HIP) using 14 μm W powder achieved 92.7 % with the processing conditions of 1277 °C and 195 MPa [4].

To lower the consolidation temperature and pressure, alternative sintering methods have been pursued to compact the dense W components. Spark plasma sintering (SPS) utilizes the low voltage DC pulsed electric current for the consolidation of a powder under elevated temperature and pressure. In comparison with conventional sintering methods, SPS has the advantages of lower processing temperature, higher heating rates and shorter holding times [5-7].

W consolidation by SPS showed that 91.5 % relative density was achieved within 8 min holding time at 2327 °C and 47 MPa in the air [8]. This study indicated clean grain boundaries formed due to the interface cleaning effect by the SPS method [5, 9]. Cho *et al.* tested various SPS sintering conditions and

revealed the effects of the powder size, pulsed current, holding temperature and pressure on the final density and microstructure of W specimens [10].

Under free sintering, the densification mechanism of W powders has been investigated for different consolidation approaches for micro- and nano-powders. Hayden and Brophy [11, 12] measured the linear shrinkage of a W powder body as a function of time and concluded using the two sphere sintering model that grain boundary diffusion was the rate limiting mechanism over the temperature range of 1050 °C to 1200 °C with activation energy of 380 kJ/mol [13]. Based on the rate of volume change in terms of the diffusion constant, Kothari found the activation energy of 420 kJ/mol for cold-pressed W powders (3 µm) under vacuum conditions [14, 15]. This study revealed that densification occurred by grain boundary diffusion for temperatures between 1100 °C to 1500 °C. Vasilos and Smith studied W sintering kinetics between 1300 °C and 1750 °C and found that the activation energy was 465 kJ/mol, which was in agreement with the activation energy of the grain boundary diffusion [16]. Chen investigated the sintering kinetics with dilatometric analysis and concluded that the rate controlling mechanism was the grain boundary diffusion [17].

There are few reports on the determination of the sintering mechanisms of W by pressure assisted methods (HP and SPS). Karpinos *et al.* [3, 18] investigated W densification using HP and used a sintering kinetics model, which had been earlier employed by Kothari [14]. Densification mechanisms were subdivided into three regions with respect to the relative density. The dominant mechanisms identified for each region were (i) particle rearrangement (45 - 58%), (ii) plastic flow (58 - 75 %), and (iii) grain boundary diffusion (> 80%). Gao *et al.* studied the kinetics of W compaction by SPS using an initial stage model of sintering and found that diffusion along the grain boundaries leading into interparticle neck regions was the rate controlling mechanism for W sintering in the temperature range of 1250 °C to 1500 °C and under 16 MPa pressure [19].

It is known that power-law creep is the main mass-transfer mechanism of crystalline powder at intermediate to high temperatures [20]. Robinson and Sherby reported that low temperature ($< 2200\text{ }^{\circ}\text{C}$) creep of W had a strain rate sensitivity (m) of 0.14 (subgrains are not formed during creep) or 0.21 (subgrains are formed during creep). They discovered that the rate controlling step was dislocation diffusion for temperatures in the range $0.4 - 0.65 T_m$ (T_m = melting temperature of W) and lattice diffusion for temperatures over $0.65 T_m$ [21].

Superplastic behavior was reported for coarse ($> 10\text{ }\mu\text{m}$) grain size pure W powder subjected to creep test conducted under near $0.5 T_m$ or higher temperatures [22]. Also, W powder mixture with Re showed superplasticity with $m = 0.2 \sim 0.4$ rendering substantially larger elongation to failure ($200\% \sim 400\%$) compared with that of $m = 1$ [23-26]. Nieh *et al.* indicated that superplasticity in W-Re alloys may be the result of a solid solution behavior governed by the solute atom diffusion with dislocation glide [27]. Kurishita *et al.* controlled the mechanical milling conditions of a mixture of W and TiC powder, which showed superplastic behavior with $m = 0.2$ and $m = 0.5$ for in hydrogen and argon atmospheres, respectively [28]. Recently, SPS of powder mixtures containing W (nano-) powder has been reported, where the W-phase was contributing to the overall power-law mechanism of mass transfer [29].

In the present study, micron size W powders were consolidated using SPS. In order to obtain the densification kinetics of W compacted by SPS, for the first time, the constitutive model of powder hot pressing (based on the continuum theory of sintering [30]) was applied assuming the dominance of power law creep, a mechanism which contributes, and often prevails in HP [20]. The present study indicates that grain boundary sliding controlled by dislocation climb with dislocations moving along grain boundaries is the main densification mechanism of the W powder compaction by SPS method. Also, the microstructure and mechanical properties of the compacted W pellets were examined in close correlation to the powder material processing conditions.

2. Experimental Procedures

2.1. Tested Materials

Fig. 1. (a) and (b) Scanning electron microscope images of W powders : 2500X, 20000X, respectively. (c) X-ray diffraction results for as- received W powders.

W powders (99.999%, body centered cubic, Im-3m) produced by Buffalo Tungsten Inc. were employed. The powder morphology and size (Figs. 1(a) and (b)) were observed using the scanning electron microscope (SEM) (FEI Quanta 450, USA). The powders had a faceted shape with a tendency to form agglomerates. Based on the manual size measurement of 200 particles using an image analysis program (Image J), it was determined that the powders had various size particle distributions, which were composed of about 1 μm to 12 μm size particles. The purity level of the powders was obtained by measuring 12 regions by energy-dispersive X-ray spectroscopy (EDS, Oxford Instruments, UK).

The crystal structure and lattice parameters were evaluated by X-ray diffraction (XRD) (Phillips X'Pert Pro), utilizing CuK_α radiation at room temperature. In Fig. 1(c), the measured and reference W (ICSD collection code # 76151) [31] diffracted pattern are presented by hollow circles and a solid line, respectively. The diffracted (hkl) planes are shown on the top of each peak. The dashed lines indicate the intensity difference between the measured and reference peaks. The lattice parameter of the powders is found to be 0.3168 nm, which is very close to the reported value of 0.3165 nm [31].

2.2 Spark plasma sintering processing regimes

The sintering experiments were carried on the SPS device manufactured by SPS Syntex Inc., model Dr. Sinter SPSS-515 with a graphite tooling setup generally made from Isocarb Graphite I-85 (Electrodes Inc., CA), except for the selection of silicon carbide punches for high-pressure SPS tests. The detailed information on the tooling setup and SPS device can be found elsewhere [7].

Most of the experiments used the 0.3 mm-thick graphite paper for wrapping the powder to prevent adhesion and contamination between the specimen and the tooling. For some specimens, boron nitride was sprayed onto the graphite paper, which surrounds the inner hole of the graphite die in order to block the carbon diffusion from the graphite (specimens W3BNC_1660_H30, W6BNC_1660_H30, and W9BNC_1660_H30 in Table 1).

For 60 MPa or 120 MPa, the measured initial green (after pre-cold-compaction) densities of the powder compacts were ~ 54% and ~ 65%, respectively. The sintering conditions were a heating rate of 100 °C/min from 600 °C to the maximum temperature (1600 °C, 1700 °C or 1800 °C) with dwell times of 0, 6, 30 or 60 min.

The SPS device was set to apply the periodic sequence of 12 ms of DC pulses followed by a pause of 2 ms. Most experiments were conducted under ~20 Pa, except the experiments carried out at 1800 °C when argon gas was purged in the SPS chamber.

3. Spark Plasma Sintering Results

The densified specimens were ground by a 125 µm diamond disk and subsequently by a series of gradually finer SiC grinding papers (36 µm, 21.8 µm, and 15.3 µm). Afterwards, the specimens were dried in an oven (Neyo 2-1350, USA) at 120 °C for 20 min. The relative density was estimated by the Archimedes' immersion method, which required the samples to be coated with paraffin wax prior to the

measurements to prevent the access to the open porosity, which resulted in a non-negligible amount of the overall porosity in several specimens.

For electron backscatter diffraction (EBSD) analysis, the specimens were ground and polished using an automatic polishing machine (Struers, Germany). The polished samples were analyzed by scanning electron microscopy (Hitachi S3600N, Hitachi, Ltd., Japan) utilizing the Hikari Pro series EBSD camera (EDAX, USA). The respective pole figure has been constructed by means of TSL OIM Analysis 5.31 software (EDAX, USA) (see section 3.2 below.)

3.1. W powder densification map

The physical and mechanical properties of the W specimens are listed in Table 1, which indicates that the highest value of the relative density ($\sim 95.18\%$) was achieved at $1600\text{ }^{\circ}\text{C}$ under 60 MPa.

Fig. 2. (a) Relative density dependence on SPS maximum temperature, holding time and pressure, measured by Archimedes immersion method. (b) Relative density variation with the temperature at a fixed pressure of 60 MPa.

For 60 MPa, the relative density generally increased with increasing temperature and holding time, as shown in Fig. 2 (a). Some experimental conditions such as those used for sintering of W6_1760_H30, W9_1860_H30 and W10_1860_H60, show decreasing relative density with increasing the temperature or holding time. This can be explained as follows: during characterization of the samples, a tungsten carbide layer was observed at the periphery of the specimens and the carbide layer thickness

increased with the holding time and temperature. Because the theoretical density of W (19.25 g/cm^3) is used for the relative density calculations, the lower density of tungsten carbide (15.63 g/cm^3) layer renders lower final relative density. Carburization of W is analyzed in section 4 in more detail.

At a fixed temperature and holding time (1700 °C and 6 min), the pressure effect on the relative density was examined using the double die setup as shown in the Fig. 2(a). The higher pressure of 120 MPa (Fig. 2(a): star shape symbol) renders ~95% relative density which is ~5% higher compared with that obtained when applying 60 MPa. However, considering the different green densities provided by applied pressures of 60 MPa and 120 MPa, respectively, a total increase of the relative density was ~ 36% and ~ 30%, respectively. **Specifically, the net density increase is smaller when using the high-pressure double die setup; slower densification at higher relative density may be the reason for this phenomenon. Also, the lower thermal and electrical conductivity of SiC punch can affect the densification environment during SPS, which has been discussed in our earlier study [7].**

Fig. 2(b) shows the effect of the maximum sintering temperature on the relative density as a function of temperature under 60 MPa and 6 min holding time. The fast heating rate (100 °C/min), results in ~ 15 °C of overheating are shown on the plots at each final sintering temperature. The vertical portions of the curves show the increase of the relative density during the holding stage. All the three plots show similar densification rate during the ramping stage. Fig. 2(b) indicates that the final sintering temperature is the major factor controlling the final relative density of the processed specimens.

Name	T	P	Holding time	Atmosphere	Relative density	Grain size	Vickers micro-hardness of W (HV1)	Vickers micro-hardness of W ₂ C (HV0.5)
	°C	MPa	min		%	μm	Kgf/mm ²	Kgf/mm ²
W1_1660_H0	1600	60	0	Vacuum	81.18	8.56	354	-
W2_1660_H6	1600	60	6	Vacuum	88.46	6.96	311	-
W3_1660_H30	1600	60	30	Vacuum	95.93	6.48	292	-
W4_1760_H0	1700	60	0	Vacuum	86.68	6.03	278	-
W5_1760_H6	1700	60	6	Vacuum	90.37	7.91	323	-
W6_1760_H30	1700	60	30	Vacuum	94.38	11.06	358	1755

W7_1860_H0	1800	60	0	Argon	91.33	5.82	220	-
W8_1860_H6	1800	60	6	Argon	92.25	16.13	359	1671
W9_1860_H30	1800	60	30	Argon	93.50	30.15	363	1875
W10_1860_H60	1800	60	60	Argon	92.98	39.46	397	1885
W11_1712_H6	1700	120	6	Vacuum	95.18	-	394	1890
W3BNC_1660_H30	1600	60	30	Vacuum	94.11	19.11	-	-
W6BNC_1760_H30	1700	60	30	Vacuum	94.61	22.38	-	-
W9BNC_1860_H30	1800	60	30	Argon	95.04	85.09	-	-

Table 1. Physical, chemical and mechanical properties of W specimens prepared by spark plasma sintering.

3.2. W powder densification kinetics

In the present study, the constitutive equation of the continuum theory of sintering [30] is used to determine the densification kinetics of W powder subjected to SPS. The mass transfer constitutive parameters include strain sensitivity m (or its reciprocal - stress exponent n) and activation energy of creep Q , as summarized elsewhere [27, 32, 33].

The flow stress for high-temperature deformation of crystalline materials can be described as a function of strain rate ($\dot{\epsilon}$) and absolute temperature (T) as expressed by the Dorn equation [27]:

$$\left(\frac{\sigma}{G}\right)^n = \frac{\dot{\epsilon} k T}{A_{cr} D G b} \left(\frac{d}{b}\right)^p \quad (1)$$

where $\dot{\epsilon}$ is the steady-state creep rate (1/s), k is the Boltzmann's constant (J/K), D is the diffusion coefficient (cm^2/s), G is the shear modulus (MPa), T is the absolute temperature (K), b is the Burgers vector (m), σ is the applied stress (MPa), A_{cr} is the material constant for creep (unitless), d is the grain size (m), p is the grain size exponent, and n is the stress exponent (n is equal to $1/m$, where m is the strain rate sensitivity).

The dependence of the diffusion coefficient D on temperature T can be expressed through:

$$D = D_0 \exp\left(\frac{-Q}{RT}\right) \quad (2)$$

where D_0 (cm²/s) is the diffusion constant, Q (KJ/mol) is the activation energy for the creep, and R is the gas constant.

Eqn. (1) can be converted to power-law relationship in terms of strain rates as follows:

$$\sigma = A_m \dot{\epsilon}^m \quad (3)$$

The m -dependent constant A_m (Pa·m·s), which is a function of strain rate sensitivity (m) and microstructure, is expressed as:

$$A_m = A_{m0} G^{(1-m)} \left(\frac{d}{b}\right)^{pm} T^m \exp\left(\frac{mQ}{RT}\right) \quad (4)$$

Here, A_{m0} (Pa·s/K) is a material constant not dependent on m :

$$A_{m0} = \frac{k}{A_G b D_0} \quad (5)$$

Following Munro [34] the shear modulus should be simultaneously dependent on porosity and temperature:

$$G(T, \theta) = G_T(T) G_\theta(\theta) \quad (6)$$

The porosity dependence of the shear modulus can be approximated by linear fitting of the empirical porosity-shear modulus curves [35]. The temperature-shear modulus relation can be obtained from the Ashby's deformation mechanism map of W [36].

Therefore, the constitutive equation for the W powder high temperature deformation processing can be re-written as [30]:

$$\dot{\theta} = - \left[\frac{\sigma_z}{\left\{ G_0 (1 - 1.973\theta) * \left(1 + \frac{(T - 300) T_M}{T_M G_0} \frac{dG}{dT} \right) \right\}^{(1-m)}} \right]^{1/m} \left(\frac{b}{d} \right)^p (A_{m0} T)^{-1} \exp \left(\frac{-Q}{RT} \right) \left(\frac{3\theta}{2} \right)^{\frac{m+1}{2m}} (1 - \theta)^{\frac{m-3}{2m}} \quad (7)$$

For W, shear modulus at 300K (G_0) is 160 GPa, T_m is 3683 K, b is 0.274 nm and $\frac{T_M}{G_0} \frac{dG}{dT}$ (temperature dependence of shear modulus) is -0.38 [36].

Fig. 3. Experimental porosity evolution curves of W specimens ((a) W3_1660_H30 and (b) W6_1760_H30) processed by spark plasma sintering fitted by constitutive equation (7).

All experiments with 30 min holding time were chosen for finding the densification kinetics. Fig. 3 shows constitutive equation-based fittings of the porosity time evolution under (a) 1600 °C and (b) 1700 °C with 60 MPa during holding stage. The experimental densification curves were drawn by the scattered square symbols, while the curves defined by a solid line denote the fitting curve using Eq. 7. The best fit corresponds to $A_{m0} = 1.5 \times 10^{-24}$ Pa·s/K, $m = 0.39$ and $Q = 412.27$ kJ/mol.

Fig. 4. W powder densification rate change as a function of porosity, conducted at 1600 °C (squares), 1700 °C (triangles) and 1800 °C (circles).

To confirm the sintering mechanism, the activation energy was also calculated by modifying Eqn.

(1). If it is assumed that G , A_{cr} , D_0 and m are same for different temperatures (T_1 and T_2), Then Eqn. (1) can be simplified as follows:

$$\ln \left[\frac{\frac{\dot{\epsilon}_2 T_2}{\dot{\epsilon}_1 T_1}}{\left(\frac{d_1}{d_2}\right)^p} \right] = \frac{Q}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \quad (8)$$

In this equation, p should be close to zero when grain growth is not significant. The powders show the grain growth when relative density is $> 90\%$, so $p=2$ was used to include the grain growth effect [27]. By comparing the densification rate for the three different sintering temperatures of 1600°C, 1700 °C and 1800 °C, the apparent activation energy Q for powder consolidation was obtained. Grain sizes for each temperature are estimated by Eq. 9 (see below) [37]. Using the densification rate change as a function of porosity and temperature during the holding stage (Fig. 4), Q was found to be 433.76 kJ/mol. This value is in the same range as the values assessed by Kothari (418 kJ/mol) [14], Vasilos and Smith (463 kJ/mol) [16] and Karpinos *et al.* (418 kJ/mol) [3, 18] and with the activation energy value of the grain boundary diffusion (385 kJ/mol) determined by the tracer diffusion method in the temperature range of 1400 °C to 2200 °C [38]. This finding supports the view of the grain boundary diffusion as the rate

limiting mechanism. A number of other studies [13, 17] also suggested the grain boundary diffusion to be the main sintering mechanism for pressure-less and pressure assisted sintering of W in the vicinity of 0.5 T_m .

Each of the mechanisms for powder material high temperature creep has specific values of m and Q by which the mechanism can be defined uniquely [39].

The obtained in the present study results match well the mechanism of grain boundary sliding accommodated by dislocation slip governed by dislocation climb [27]. The superplasticity of coarse-grained (10 ~ 20 μm) W was reported in the past [22]. Both the obtained from the SPS constitutive equation-based fitting and the value of the activation energy obtained from the Dorn method indicate that the grain boundary diffusion is the rate controlling mechanism. The calculated m is in between the dislocation climb and glide behavior ($m = 0.1$ to 0.33) and superplastic behavior ($m = 0.5$ to 1)[40]. This may indicate that SPS of W powder is affected by the contribution of two or more mass transfer mechanisms. Kapinos *et al.* speculated that dislocation climb controlled by diffusion ($m = 0.2$ to 0.25) was the consolidation mechanism for HP of W during the final stage of sintering [3, 18]. Therefore, one can conjecture that the two mechanisms (dislocation slip and grain boundary sliding) affect the densification of the W powder processed by SPS. The electric current effect during SPS may also affect the plastic deformation of W powder, inducing superplasticity of W. However, the analysis of the contributions of the field effects is an object of future investigations beyond the scope of the present work.

Fig. 5. Pole figures showing the grain orientation of the sample subjected to SPS at 1700 °C for 0 min, 6 min, and 30 min recorded along the surface perpendicular to the applied uniaxial pressure.

The results of the EBSD texture analysis also support the notion of grain boundary sliding contributing to the densification mechanism. When polycrystalline structures are subjected to largely tensile plastic deformation, close-packed crystallographic planes have the trend to be aligned with the tensile direction. Previous results show that cold pressed or extruded W have $(001)\langle 110 \rangle$ texture [41]. In Fig. 5 the pole figures of the main crystallographic directions of the specimens sintered at 1700 °C for 0 min show a relatively strong $(001)\langle 110 \rangle$ texture along the uniaxial pressure direction when EBSD scanned along the surface perpendicular to the applied uniaxial pressure. Pole figures (200) are equivalent to (100). The reduction of the texture by increasing the holding time under 1700 °C is very prominently represented by the pole figures. Most likely the initial cold pressing of the powders in the SPS chamber aligns the (110) grains perpendicular to the specimen axial direction; and this alignment can be retained until the holding stage due to the fast heating conditions. However, it is also possible that the grain orientation is changed by the mechanism of cold pressing during the ramping stage which showed over 25% densification. Detailed study on the grain orientation imposed by cold pressing and affecting sintering shrinkage anisotropy is within the scope of future publications.

Grain rotation associated with grain boundary sliding produces predominantly random texture after deformation [42], which would make the degree of texture decrease with increasing holding time. The small equiaxed grain structure of the specimens also support the concept of the grain boundary sliding being one of the components of the overall densification mechanism (Table 1 and Fig. 6). However, there is a low probability of grain boundary sliding under the sintering temperature of 1800 °C, which showed large grain growth, thereby shifting the dominant mechanism from grain boundary sliding to dislocation creep during densification.

Uniaxial compression of 60 MPa renders the normalized shear stress value (σ_s / G) of 2.58×10^{-4} . Based on the deformation mechanism map of W with 1 μm grain size [36], this processing condition corresponds to the grain boundary diffusion mechanism. On the other hand, from the deformation mechanism map of W with 10 μm grain size [36], this processing condition matches the low-temperature power law creep range. The average grain size of 8 μm in the present study is between these above-mentioned two values. Therefore, it appears that the processing conditions utilized in the present work should render densification mechanisms near the boundary between power law creep and diffusional flow. Indeed, Gao *et al.* [19] studied the W compaction by SPS using 16 MPa applied pressure and pointed out the grain boundary diffusion as the major densification mechanism. However, some studies have shown that the grain boundary sliding region can be at lower stress levels associated with lower creep strain rates in the power law creep region in deformation maps [43-45]. Therefore, according to the values of the normalized shear stress and the average grain size of the processed W specimens, the utilized SPS processing conditions may cause some grain boundary sliding too. It appears that the small particle size of W powders and different processing conditions may result in the change of the major contributing densification mechanism, as demonstrated by the results of the present study.

4. Processed Specimens Characterization

4.1. Microstructure characterization

The morphologies and the grain area distribution of the etched surface of the W samples were extracted from the EBSD scans using OIM software. Mean grain sizes were calculated from the total 0.38 mm² cross section area of each of the W samples.

Fig. 6. (a) Plot of the grain size time evolution for W powder consolidated at 1700 °C and 1800 °C by spark plasma sintering. The grain growth exponent for each temperature plot is shown on the right side of the fitting curves. Scanning electron microscopy images of W specimens processed at 1800 °C with holding time of (b) 0 min, (c) 6 min, (d) 30 min and (e) 60 min.

The grain growth kinetics can be described as [37]:

$$D^s - D_0^s = kt \quad (9)$$

where s is the grain growth exponent, D_0 is the average initial grain size, D is the final average grain size after annealing time t , k is the temperature dependent rate constant. The s value can be 2 for normal grain growth conditions (high purity metal at a high homologous temperature). The s value can be deviated from 2, when the grain growth inhibiting factors, such as solute dopants or impurities, the liquid phase at the grain boundaries, and inclusions (pores or second phase particle), are present [15, 19, 46].

Fig. 6 shows the relationship between the isothermal grain growth and the annealing time. The values for s for 1700 °C and 1800 °C are found to be 3.70 and 2.58, respectively. Parameter s values from Eq. 9 are decreased with increasing temperature and tend to converge to 2. This is in a good agreement with previous studies on the grain growth of W using conventional sintering [15] and SPS [25]. The change of the grain growth exponent s with sintering temperature implies that grain growth is affected by a combination of a number of various grain growth mechanisms. Decreasing s values in the present work are possibly related to the removal of the grain growth inhibiting factors such as the pinning by pores when the sintering temperature was increased.

Fig. 7. A cross-sectional view of W specimen processed by SPS at 1800 °C and 60 MPa for 30 min (a) without boron nitride coating, and (b) with boron nitride coating. (c) XRD patterns of W processed by SPS at 1800 °C and 60 MPa with different holding times of 0 min, 6 min, 30 min, and 60 min. W peaks (circle) and $W_2C_{0.85}$ peaks (diamond).

Although W densification using SPS is carried out during short time compared with conventional sintering methods, diffusion of carbon into specimens is observed. For W powder consolidation by SPS at 1800 °C and 60 MPa for 30 min, the respective SEM image reveals a clear interface between the two different zones (A and B) as shown in the Fig. 7(a). The average thickness of the A zone is about 253 μ m. The cross-sectional hardness was measured at both locations. The average Vicker's hardness values were 1875 MPa and 363 MPa in A and B zones, respectively, which indicates that the two zones may contain different material phases. From EDS analysis, the A zone contains W atoms and carbon (2.20 wt%), while B zone is pure W. Fig. 7(c) showed the diffraction patterns of the cross section of the W specimens

processed at 1800 °C for 0, 6, 30 and 60 min. Circle and diamond symbols indicate W and $W_2C_{0.85}$ peaks, respectively. The tungsten carbide peak increased with holding time, which shows that the tungsten carbide phase is thickened with time. From the SEM, EDS and XRD results, the carburized zone A can be assumed to contain hexagonal $W_2C_{0.85}$. Carbon can diffuse from the graphite die, punch, and paper, which surround the W powder during the SPS. The carburization of W in HP and SPS has been explained also elsewhere [47-50].

The presence of carbon near the processed W powder does not guarantee the carbide layer formed during SPS consolidation. The solubility of carbon in W is the main factor for carbide layer formation [51]. The carburized layer is assumed to grow in a parabolic manner with holding time, which allows an approximate estimation of the diffusion coefficient of carbon in W (D_C). If it is assumed that the concentration of carbon at the interface is constant, D_C can be obtained by the following equation.

$$x \sim (D_C t)^{0.5} \quad (10)$$

where x is the tungsten carbide thickness, D_C is the diffusion coefficient of carbon into W (cm^2/s) and t is time. D_C is estimated to be $3.86 \times 10^{-7} \text{ cm}^2/\text{s}$, which is in a good agreement with a literature value [49].

To minimize the carbon diffusion, some experiments (used for fabrication specimens W3BNC_1660_H30, W6BNC_1660_H30, and W9BNC_1660_H30, Table 1) the graphite paper was coated with a boron nitride spray ((MR-97, ZYP Coating, Inc., Oak Ridge, TN) before the powder was loaded. Boron nitride is known to block carbon diffusion during SPS [52]. However, a large reduction of the thickness of tungsten carbide layer is not achieved in the present study, which may be attributed to the high solubility of carbon in W. The thickness of the tungsten carbide layer was 191 μm (Fig.7(b)) when boron nitride coated graphite paper was used, which can be compared with 253 μm (Fig.7(a)) of the non-boron nitride coated case.

4.2. Mechanical properties characterization

Fig. 8. Vickers micro-hardness dependence on porosity of W specimens consolidated by spark plasma sintering.

The polished specimens were subjected to Vickers micro-hardness test (M-401-H1 Hardness testing machine, Leco, Michigan) by applying a load of 1 kg for 10 s. The mean Vickers hardness of each sample was determined by averaging 4 different indents at different locations of the sample. Fig. 8 shows that hardness is generally increased with decreasing porosity. The measured maximum hardness is 397 kg/mm² and this is similar to the reference value (407.9kg/mm² for 96.10% relative density) [53].

The transverse rupture strength (TRS) was obtained with a Universal Testing System (5982 Instron, USA), by applying a load through a tungsten carbide ball-shaped indenter onto the disk-shaped W specimens. The equation utilized to calculate the TRS is given as follows:

$$\sigma_{\text{max}} = \frac{P}{h^2} [(1+\nu)(0.4851 \log \frac{a}{h} + 0.52) + 0.48] \quad (11)$$

where P is the measured load, h the specimen thickness, a the specimen radius and ν the Poisson ratio (0.28 for W, as reported in [54]). A more detailed explanation of the TRS setup and procedures can be

found in Ref. [55]. TRS values for 91% and ~ 95% specimens (W7_1860_H0, W6BNC_1760_H30) were found to be 705 MPa and 1006 MPa, which are larger than the three point bending strength value (< 658MPa for 94.85% to 98.22 % relative density specimens) of W compacted by resistance sintering under ultra-high pressure (RSUHP) [56]. The higher strength found here can be attributed to longer holding time compared with that (30s to 60s) of RSUHP method which may cause the formation of metastable W-based phases.

5. Conclusions

For the first time, the densification mechanism of tungsten consolidated by spark plasma sintering was analyzed by the constitutive equation of sintering considering the applied pressure using the power-law creep model of mass transfer. A strain rate sensitivity of 0.38~0.40 and sintering activation energy of ~ 410 ~ 431 kJ/mol were obtained. These values indicate that one of the densification mechanisms may be grain boundary sliding accommodated by dislocation climb controlled by the grain boundary diffusion, which is also supported by the electron back-scattered analysis. Increasing the sintering temperature causes the reduction of the grain growth exponent and tends to be converged to the ideal grain growth exponent of 2, possibly due to the removal of the grain growth inhibiting factors such as the pores. A tungsten carbide external shell is generated on the specimen surface with increasing holding time due to the presence of carbon wrapping paper and die. The diffusion coefficient of carbon in the tungsten was obtained and is similar to the literature values. Using boron nitride coating on the graphite paper did not block the carbon uptake from the die and graphite paper, but it slowed down the diffusion of carbon. Vickers micro-hardness was measured for the processed tungsten specimens and showed the porosity dependence. Further investigation is necessary in order to reveal the electric field effect on W powder densification mechanisms during the SPS process.

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Table Captions

Table 1. Physical, chemical and mechanical properties of W specimens prepared by spark plasma sintering

Figure Captions

Fig. 1. (a) and (b) Scanning electron microscope images of W powders : 2500X, 20000X, respectively. (c) X-ray diffraction results for as- received W powders.

- Fig. 2. (a) Relative density dependence on SPS maximum temperature, holding time and pressure, measured by Archimedes immersion method. (b) Relative density variation with temperature at a fixed pressure of 60 MPa.
- Fig. 3. Experimental porosity evolution curves of W specimens ((a) W3_1660_H30 and (b) W6_1760_H30) processed by spark plasma sintering fitted by constitutive equation (7).
- Fig. 4. W powder densification rate change as a function of porosity, conducted at 1600 °C (squares), 1700 °C (triangles) and 1800 °C (circles).
- Fig. 5. Pole figures showing the grain orientation for the sample subjected to SPS at 1700 °C for 0 min, 6 min, and 30 min recorded along the surface perpendicular to the applied uniaxial pressure.
- Fig. 6. (a) Plot of the grain size time evolution for W powder consolidated at 1700 °C and 1800 °C by spark plasma sintering. The grain growth exponent for each temperature plot is shown on the right side of the fitting curves. Scanning electron microscopy images of W specimens processed at 1800 °C with holding time of (b) 0 min, (c) 6 min, (d) 30 min and (e) 60 min.
- Fig. 7. A cross-sectional view of W specimen processed by SPS at 1800 °C and 60 MPa for 30 min (a) without boron nitride coating, and (b) with boron nitride coating. (c) XRD patterns of W processed by SPS at 1800 °C and 60 MPa with different holding times of 0 min, 6min, 30 min, and 60 min. W peaks (circle) and $W_2C_{0.85}$ peaks (diamond).
- Fig. 8. Vickers micro-hardness dependence on porosity of W specimens consolidated by spark plasma sintering.