Effect of heating mode on sintering of tungsten

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1. Introduction

Tungsten belongs to Group VIB of periodic table. As a refractory metal, tungsten is characterized by its very high melting point (3420 °C), high density (19.3 g/cm³), low coefficient of thermal expansion (4.4 ppm/K at 20 °C) and superior mechanical properties at elevated temperatures, which render it highly suitable for many engineering applications such as lighting, electric arc welding, resistance heating, aerospace, electronic devices, sports and military uses, etc. [1]. Owing to very high fusion point, the consolidation of a conventional microcrystalline W powder is difficult and generally requires a temperature in excess of 1700 °C through solid-state sintering in electrical resistance sintering furnace under hydrogen atmosphere.

Achievement of near theoretical sintered densities for pure tungsten at temperatures below 1650 °C is typically not feasible [2]. Densification of refractory metals, such as tungsten, can be enhanced greatly by activating the sintering process wherein the sintering temperature is appreciably lowered. Activated sintering refers to combination of processing approaches that reduce the activation energy for sintering. One such technique to activate sintering is by addition of small amounts (< 1 wt.%) of Group VIII transition metals [3–6]. It has been reported that the sintering temperature of tungsten powder can be brought down from 2800 °C to 1400 °C by less than 1 wt.% addition of transition metals, such as palladium and nickel [6]. German and Munir [5,6] have extensively investigated the role of various transition metal additions in densification activation of tungsten powder compacts. From their study, it is quite evident that some transition metals (e.g., Pd, Ni) enhance densification, while others (e.g., Ag, Cr) have little influence. Densification enhancement in tungsten by transition metal additives was attributed to enhanced solubility and mass transport kinetics. The additives which remain segregated to the W–W powder interface and in which tungsten has appreciable solubility, act as short-circuit diffusion pathways, thereby promoting densification.

Another important approach to activate sintering of tungsten is through selection of submicron or nano-sized precursor tungsten powder. However, such powders are expensive and are prone to contamination [7]. Many studies have shown that sintering temperature is related to the powder size, when the size is in nano-scale, the sintering temperature can be decreased up to several hundreds of degrees. The reduction of sintering temperature for nano tungsten has been reported by several researchers [7–10]. Bose et al. [7] have also shown that pressure assisted process such as plasma pressure compaction helps in the reduction of process temperature. The reported sintering temperature of nano-sized tungsten produced by high energy mechanical milling was drastically decreased from conventional temperature of 2500 °C to 1700 °C [8]. Other processes such as hot-isostatic processing [10], and spark plasma sintering [11], too result in further reduction in the processing temperature.

Because of the characteristic feature and obvious advantages, application of microwave energy in consolidating particulate materials has become a preferred method over conventional (resistant heating) technique. The application of microwave energy in consolidating tungsten powders was first studied by Jain et al. [12]. A comprehensive study on microwave sintering of tungsten and its alloys were also conducted by several researchers [13–21]. This paper reports the consolidation of nano-sized tungsten powder through microwave and conventional sintering methods. To evaluate the interaction of microwaves, tungsten powder with a median particle size of 72 nm was subjected to 2.45 GHz microwaves in a multimode furnace. For comparing the effect of heating mode, in a parallel set of experiments, tungsten powder compacts pressed to similar green density levels were consolidated in a conventional furnace.
2. Experimental procedure

Tungsten of average crystallite size of 72 nm powders was supplied by NEI Corporation, New Jersey, USA. The as-received powders were pressed in a die of 1.6 cm inner diameter to make the green compacts of approximately 0.3 to 0.4 cm in height. The green density was around 49% of theoretical. To study the densification behavior the green (as-pressed) compacts were sintered using conventional and microwave furnace. The conventional sintering of green compacts was conducted in a MoS2 heated horizontal tubular sintering furnace (model: OKAY 707T-7, supplier: Bysak, Kolkata, India). Microwave sintering of the green compacts was carried out using a multimode cavity 2.45 GHz, 6 kW microwave furnace. Further details of the microwave furnace and experimental arrangements have been described elsewhere [19]. For each set of experiments (conventional and microwave sintering) four samples were investigated and the as-sintered samples were characterized for sintered density through both dimensional measurements as well as Archimedes density measurement techniques. To take into account the influence of the initial as-pressed density, the compact sinterability was also expressed in terms of densification parameter which is calculated as follows:

\[
\text{Densification parameter} = \frac{(\text{sintered density} - \text{green density})}{(\text{theoretical density} - \text{green density})} \tag{1}
\]

Metallographic techniques were employed on the sintered samples. The sintered samples were wet polished in a manual polisher (model: Lumn Major, supplier: Struers, Denmark) using a series of 6 µm, 3 µm and 1 µm diamond paste, followed by cloth polishing using a suspension of 0.04 µm colloidal SiO2 suspension. Murakami’s reagent was used for etching the sintered tungsten samples. The scanning electron micrographs of as-polished samples were obtained by a scanning electron microscope (model: FEI quanta, Netherlands) in the secondary electron (SE) and back scattered (BSE) mode. Bulk hardness measurements were performed on polished surfaces of sintered cylindrical compacts at a load of 5 kg using Vickers hardness tester (model: V100-C1, supplier: Leco, Japan).

3. Results and discussion

3.1. Effect of heating mode on sintering of tungsten

Fig. 1 compares the thermal profiles for tungsten powder compacts heated in conventional and microwave furnace. It is interesting to note that W compact couples with microwaves and gets heated up quite rapidly. Tungsten powders owing to their fine size are susceptible to oxidation and hence need to be processed in reducing (hydrogen) atmosphere. Due to the poor thermal shock resistance of the alumina tube used, the heating rate of the conventional sintering was restricted to 5 °C/min. Furthermore, to ensure homogenization of the temperature, isothermal hold at intermediate sintering temperatures was provided. Unlike conventional sintering, in a microwave furnace, the tungsten powder compact per se acts as a source of heat since it couples directly with microwaves. Consequently, the overall heating rate achieved in microwave furnace was ~25 °C/min for the tungsten compacts. Taking into consideration the lower heating rate and the intermittent isothermal holds in conventional furnace sintering, there is about 90% reduction in the overall processing time during microwave sintering.

Unlike ceramic materials microwave interaction with metals is restricted to its surface only. This depth of penetration in metals, also known as skin depth (δ), is defined as the distance into the material at which the incident power drops to 1/e (36.8%) of the surface value. The skin depth is mathematically expressed as follows:

\[
\delta = \frac{1}{\sqrt{\pi f \mu \sigma}} \tag{2}
\]

where, \( f \) is the microwave frequency (2.45 GHz), \( \mu \) is the magnetic permeability, \( \sigma \) is the electrical conductivity, and \( \rho \) is the electrical resistivity of the metals. From Eq. (2), it is evident that metals with higher electrical conductivity have lower skin depths. For metals, as the resistivity increases with increase in temperature, the skin depth too increases. Resistivity as a function of temperature has been considered from the literature [22] and Fig. 2 plots the effect of temperature on the skin depth of tungsten. For the sake of comparison similar graphs have been plotted for various other conductive metals as well. It is interesting to note as compared to some other metals, the skin depth of tungsten is relatively higher. Since the initial tungsten powder size is lower hence the compacts undergo relatively homogenous heating despite the heating rate being so high. Since the objective of the present work was to restrict the temperature to 1600 °C, owing to the small size of the initial powder the temperature was achieved in just applying 900 W of power. In comparison, to heat the similar compact in a conventional furnace wherein the heat transfer was indirect and limited by the radiative losses, the input power was on an average 2.1 kW. While it is possible to increase the heating rate in the conventional sintering by increasing the power throughput, it will be at the expense of overall furnace life. One such experiment was tried; however, the as-pressed compact could not withstand the thermal gradient and pulverized during processing.

Recently, Prabhu et al. [14] too have reported microwave sintering of tungsten powders prepared by high energy milling. However, as compared to our study, they could achieve 93% theoretical density at 1800 °C with a heating rate of 7.8 °C/min and at a power throughput.

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of 16 kW. Furthermore, they did not compare their sintering results with the conventionally sintered W powder compacts.

3.2. Densification response of sintered tungsten

Fig. 3a compares the effect of heating mode on the sintered density and densification parameter of tungsten powder compact. It is worth noticing that irrespective of the heating mode the compacts undergo significant densification during sintering. This can be attributed to the ultra-fine particle size of the powder used for this investigation. Elsewhere, Wang et al. [10] too reported similar sintering response of ultra-fine sized tungsten powder. The sintered density of the W powder compacts in microwave increased from 90% to 95% for pure tungsten compacts when compared with conventional heating. The densification parameter is a normalized parameter which takes into consideration the initial variation of the green density on the densification response. Since, the initial density of the W powder compact was kept the same hence the densification parameter follows a similar trend as the sintered density.

Usually, the sintering characteristics of the tungsten powders have been investigated in micron-sized powders [10]. For achieving small sizes, these powders were usually milled [8]. Due to the contamination from the milling media and high defect structure within the crystallites, proper evaluation of the sintering response of the tungsten powder is usually difficult. However, the general consensus in the literature has converged to the fact that for submicron/nano particle sizes the onset of densification occurs at lower temperatures of 0.2–0.4T_m (T_m — melting temperature in K) as compared to 0.5–0.8T_m for micron-sized powders [23]. Moreover, it has been established that for nano-structured powders, grain boundary sliding and rotation and viscous flow significantly contribute to densification enhancement [24–27]. In the present study, due to the chemical processing route, the tungsten powders were prepared in nano-scale in strain free condition. The sintering temperature selected for the present study corresponds to 0.46T_m.

Jain et al. [12] also reported about 10 to 12% higher density in case of microwave sintered compacts over the conventional heating. More recently, Prabhu et al. [14] have also investigated microwave sintering of high energy milled tungsten powder compacts. However, in their experiments the compacts were sintered under nitrogen atmosphere and at a high temperature (1800 °C). Despite consolidating at such a high temperature, the sintered density was less than that achieved in this study. It can therefore be inferred that for effective utilization of the microwave heating, the powder compacts must be sintered in reducing atmosphere.

Fig. 3b shows the axial and radial shrinkage of the cylindrical tungsten compacts sintered in a conventional and microwave furnace. Due to the low green density (49%), the compacts heated in both the modes undergo substantial shrinkage. In case of conventional sintering, however, the radial shrinkage is more than that observed in the longitudinal (axial) direction. In contrast, the shrinkage in both the directions is nearly similar for microwave sintered compacts.

![Fig. 3a](image1.png)  ![Fig. 3b](image2.png)

Fig. 3. Effect of heating mode on (a) the sintered density and densification parameter and (b) the axial and radial shrinkage of tungsten compact. All compacts were pressed at 100 MPa and sintered at 1600 °C in reducing atmosphere.

![Fig. 4](image3.png)

Fig. 4. SEM photomicrograph of (a) the as-pressed tungsten powder and the powder compact sintered at 1600 °C for 30 min in (b) conventional and (c) microwave furnace.
which indicates more isotropic shrinkage behavior. This further confirms that the compact heating in microwaves is more uniform despite the high heating rate. This is attributed to the volumetric heating microwave provides.

### 3.3. Effect of heating mode on microstructure and hardness

To investigate the effect of heating mode on the microstructural coarsening and its homogeneity, the as-sintered compacts were metallographically prepared. Fig. 4a shows the SEM micrograph of the as-pressed tungsten powder. Fig. 4b and c shows the photomicrographs of compacts sintered in conventional and microwave furnace, respectively. It is worth noticing that as owing to the initial low as-

density pressure, sintering results in significant microstructural coarsening in tungsten powder compacts. For both the heating modes, the as-sintered compacts attain well-developed polyhedral grains. The average tungsten grain size was measured using intercept method and is summarized in Table 1. From Fig. 4 and Table 1, it is evident that varying heating modes have not significantly influenced the microstructures.

Table 1 also compares the effect of heating mode on the bulk hardness of the sintered tungsten compacts. As expected, the microwave sintered compacts have higher hardness. This can be attributed to the higher density and a more refined microstructure of the tungsten grains in case of microwave sintering. The hardness of W compact achieved through microwave sintering in this study is higher than those reported earlier by Upadhyaya et al. [15] and Kim et al. [28]. The hardness results achieved in microwave sintered W compacts in the present study is 30% higher than the best values (303VHN) achieved by Prabhu et al. [14] by microwave sintering tungsten compact at 1800 °C.

### 4. Conclusions

In this study, tungsten powder compact was successfully consolidated through microwave sintering. It is interesting to note that tungsten compact strongly couples with microwaves and gets heated very rapidly. This result in the drastic reduction in the sintering cycle time over the conventional process: up to as high as 90%. Despite being heated at high heating rates, none of the tungsten powder compacts displayed any distortion or cracking during microwave heating. This underscores the volumetric heating aspects of microwaves. Moreover, due to the low thermal mass, microwave heating was less energy (power) consuming as compared to the equivalent volume of material being consolidated conventionally. Another common observation is that the microwave sintered compacts undergo more densification as compared to their conventionally processed counterparts. Because of the rapid heating rates achieved in microwave furnace, the microstructure coarsening was relatively lower. Consequently, as compared to conventional sintering, the mechanical properties of the microwave sintered compacts were higher.

### References