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Sintering behavior and mechanism of tungsten powders prepared by solution combustion synthesis combined with hydrogen reduction

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Abstract
Nanosized tungsten powders were fabricated by solution combustion synthesis combined with hydrogen reduction. The powder had a size of 20 nm but possessed a large numbers of lattice defects. The fracture surface images at different temperatures show that the as-synthesized tungsten powder could be sintered via a pressureless process to relative density up to 95.78% at 1773 K. Kinetic analysis suggests that grain-boundary diffusion is one of the primary mechanisms of mass transport during the intermediate stage of sintering. The sintering properties are attributed to the ultrafine grain and the high sintering activation caused by the effect of the solution combustion synthesis method. It reveals in detail that the as-synthesized tungsten powder has a lower sintering activation energy compared to commercial nanosized tungsten powder, with a measured hardness of 633 HV.

1. Introduction

Tungsten is a strategic material that has received much attention due to its excellent properties. It exhibits high thermal conductivity, low tritium inventory, high stability, low sputtering yield and high hardness/strength, properties which are appealing for many important high-temperature applications such as plasma-facing materials (PFMs) in future fusion reactors [1]. However, it is difficult to sinter this kind of refractory metal to full density because of its high melting point. Temperatures exceeding 2273 K need to be employed to yield bulk tungsten-based materials with a high density. For example, Blagoeva et al [2] used a powder metal injection molding (PIM/MIM) technology with sintering temperatures above 2273 K to obtain pure tungsten and oxide dispersion strengthened (ODS) tungsten materials; both these materials were found to display high strength with high density.

Several methods have been proposed to improve the sintering ability of tungsten [3–10]. One approach is to add appropriate transition metals such as Ni and Fe which can lead to the liquid-phase sintering; however, the element additions can have a negative influence on certain properties including the melting point [3] and their magnetic behavior [4]. High pressure or fast sintering has also been utilized to achieve full density, but these processes often need special requirements of equipment, such as hot isostatic pressing (HIP) [5], and/or spark plasma sintering SPS [6]. Refining the powder particles is another effective method to yield high density tungsten products with an excellent sintering ability [7, 8]. For example, Wang et al [9, 10] employed a chemical method to prepare tungsten oxide with a unique ultrahigh-energy planetary ball milling technique to reduce the tungsten powder down to the ~20 to 30 nm size range. They found that the ultrafine powder exhibited an outstanding sintering ability such that it could be readily densified at 1373 K. Indeed, controlling and minimizing the initial particle size is one of the most effective approaches to manufacture bulk materials with excellent properties. However, milling inevitably introduces impurity elements into the material, which can serve to diminish the performance of the final component or product.
Here we present a chemical method, called solution combustion synthesis (SCS), that needs to prepare a tungsten oxide precursor ($\text{W}_18\text{O}_{49}$) to procure nanocrystalline tungsten powder by a reducing reaction with hydrogen. Solution combustion synthesis is a versatile and energy-efficient method which can generate crystalline nanomaterials in a single step. Some researchers $[11, 12]$ have used this method to prepare highly active metal oxides which are helpful for subsequent reduction, nitriding and other reactions. Here we investigate, with an accompanying theoretical analysis, the sintering behavior of the nano-sized tungsten powder created by solution combustion synthesis combined with hydrogen reduction. As a detailed characterization of the combustion reaction was reported in our previous work $[11]$, here we are present a comparative study using commercial 400 nm sized tungsten powder.

2. Experimental procedures

2.1. Synthesis of nanosized tungsten oxide precursor
All chemicals were purchased in analytical grade and were used as received without purification. In a typical sample preparation procedure from SCS, 0.01 mol ammonium paratungstate, 0.24 mol ammonium nitrate and 0.1 mol glycine were dissolved into 150 ml deionized water, and then stirred to obtain a homogeneous solution. The pellucid solution was placed in a platinum crucible and heated to $\sim$523 K inflow of air in a controllable muffle furnace, where the combustion reaction took place. As a result, the whole process of swelling and combustion appeared to undergo a self-propagating and non-explosive exothermic reaction within several minutes.

2.2. Synthesis of nanosized tungsten powder
The dehydration of precursors was performed in a tube furnace in a hydrogen gas with the flow rate of $200 \text{ ml min}^{-1}$: the samples were heated to 873 K at an increasing rate of 10 K min$^{-1}$ with 2 h temperature hold at 873 K, prior to being heated to 973 K at the same rate with 2 h hold now at 973 K. The as-synthesized powder (SP) and commercial powder (CP) samples were then uniaxially pressed at 650 MPa into green pellets with the size of $\phi 15 \times 5 \text{ mm}$ which were then calcined at 1473 K, 1623 K, 1773 K, 1923 K, 2073 K for 2 h, respectively, in a hydrogen gas atmosphere.

2.3. Structural and mechanical characterization of the products
The morphology and particle size of the powders were characterized by field emission scanning electron microscopy (FESEM, ZEISS ULTRA 55 Field-Emission Scanning Electron Microscope) and a Tecnai G$^2$ F20 transmission electron microscopy (TEM) at an acceleration voltage of 200 kV. The density of the samples was analyzed using the Archimedes’ immersion method and the hardness was measured with a Vickers MH-6 microhardness tester under a load of 300 gf for 15 s. At least three samples for each condition were tested.

3. Results and discussions

Figure 1 shows the morphology of the as-synthesized and commercial tungsten powders. The size of the raw powder is a key point for the sintering densification. The size of the SP is about 20 nm (figure 1(a)), $\sim$20 times less than the 400 nm size of the CP, (figure 1(b)). Both nanopowders trended to agglomerate due to the high specific surface energy caused by their nanoscale size, which naturally can affect the resulting properties. To solve this problem, we used cold isostatic pressing to achieve a homogenized structure. The detailed configuration of the SP shown in the inserted TEM picture at the top right of figure 1(a), which illustrates that the particles are anisometric; indeed, they inherit the needle-like nanostructure of tungsten oxide and present a chain-like structure. Thus, in accordance with theoretical analysis of the tungsten reduction process $[13]$, we believe that we have synthesized tungsten powder which maintains its structure with large numbers of lattice defects.

As reported in several previous studies $[9, 14]$, the sintering of nanopowders can be divided into initial, intermediate and final stages, which is exactly what we observed in the current experiments. Fracture surface analysis of the tungsten samples sintered at different temperatures is presented in figure 2. The morphology of fracture surface from the synthesized tungsten powder in the figures corresponds well to the three sintering processes. In the initial stage, the powder coarsened at 1473 K from its initial size of $\sim$20 nm to $\sim$200 nm with the grain shape changing from spherical to polyhedral. Neck-like connections - sintering necks - were formed between the particles, leaving a significant degree of porosity remaining in the samples. Therefore, many surfaces have been consumed due to particles bonding and coarsening. The grain boundary energy gradually replaces the surface energy as the main driving force for the process. When the sintering temperature was increased to 1623 K, the porosity was markedly reduced with an increase of the grain size to $\sim$500 nm in figure 2(b). The appearance of this phenomenon indicates that sintering has entered the intermediate stage, at which increasing
density and strengthening are the main features. However, a significant change took place at a temperature of 1773 K (figure 2(c)), the samples became more compact with a decreasing grain size to $\sim 2 \mu m$. Such phenomenon of the rapid coarsening grains has been reported previously [10, 15]; the prevailing mechanisms are discussed below. As the sintering temperature increased to 1923 K and 2073 K, the densification was further enhanced along with the continuous growth of the grains, as shown in figures 2(d), (e), with an indication of entering the final stage. Distinct from the SP, the CP grain grew up to about 1 $\mu m$ at 1473 K (figure 3(a)) and formed a large number of sintering necks. As the temperature increased, the grains of CP gradually became equiaxed at 1773 K (figure 3(c)) before growing to $\sim 20 \mu m$ when the temperature reached 2073 K, as shown in figure 3(e).

The relationship between grain growth and sintering temperature is shown in figure 4(a), and illustrates that above 1623 K, the grains in the CP had a higher growth rate (1.73%) than grains in the SP (0.6%), which indicates that less energy dissipation is needed to obtain SP samples comparing to the same grain size of CP. Figure 4(b) shows the evolution of the sintered densities with progressively increasing temperature. At 1473 K, the SP sample has a relative density of 84.27%. As the temperature increases, the density remained at $\sim 95.7\%$ between 1773K and 1973K and reached to 97.5% at 2073 K; in contrast, the relative density of the CP reached 87.1% at 1473 K, higher than that of SP, but increased to 97.5% at 2073 K, as high as that of SP. The relative density curve suggests that the entire sintering process of CP is similar to the SP; however, the analysis of grain size (figure 4(a)) clearly shows that the SP attains a smaller grain size and a higher relative density than that of CP after sintering at the same temperature. This strongly suggests that the SP has better mechanical properties, consistent with fact that strengthening is provided by the finer grain sizes [16, 17].

These experimental results provide evidence that the sintering behavior of nanosized powders significantly relates to its initial size. First, in the low-temperature heating stage, because of the agglomeration, both the SP and CP coarsen into larger powders. Then with further increase in temperature, the sintering process with three stages can ensue. In the initial stage, the fundamental driving force for coarsening is the reduction of surface energy or grain boundary energy, so it is necessary to investigate the grain growth in the non-isothermal process by the kinetic analysis. As such, it is appropriate to employ the widely known grain growth powder law [10] as shown in equation (1), viz:

$$G^n - G^n_0 = kt,$$

where $G$ is the free energy of the system, $n$ is the order of the reaction, $t$ is the time, $k$ is the rate constant, and $T$ is the temperature. The rate equation can be rewritten as:

$$\frac{dG}{dt} = \frac{K}{nG^{n-1}} = \frac{k_G(T)}{TnG^{n-1}},$$

where $k_G(T)$ is the temperature-dependent rate constant.
where $t$ represents the sintering time, $G$ and $G_0$ are the average grain size at time $t$ and time $0$, respectively, $n$ is the grain-growth exponent and $k$ is a rate constant. $T$ is the absolute temperature. However, for non-isothermal grain growth, the integrating Equation (2) is non-trivial; accordingly, we used mathematical methods for the kinetic analysis. Substituting $\beta = \frac{dT}{dt}$ in equation (3), we obtain:

$$\frac{dG}{dT} = \frac{k_G}{\beta T n G^{n-1}} = \frac{k_G}{\beta T n G^{n-1}} \exp\left(-\frac{Q}{RT}\right)$$

where $Q$ represents the activation energy for grain growth, $R$ is molar gas constant, $T$ is absolute temperature, $\frac{dG}{dT}$ was measured from figure 3(f) by taking derivatives of the curve (as shown in the inset to figure 4(a)).

By using differential (taking the natural log of both sides of this formula) and integral (integrating with respect to $T$) methods respectively, equation (3) can be rearranged to analyze the initial coarsening of nanotungsten powder, which yields the following expressions [9]:

Differential method (DM):

$$\ln\left[\frac{dG}{dT} - (1 - n)\ln G\right] = -\frac{Q}{R} \left(\frac{1}{T}\right) + \ln\left(\frac{k}{\beta n}\right).$$

Figure 2. Images of the fracture surface of the synthesized tungsten powder at (a) 1473 K, (b) 1623 K, (c) 1773 K, (d) 1923 K and (e) 2073 K, (f) grain growth at the different temperatures.
Figure 3. FESEM images of the fracture surfaces of the commercial tungsten powder at (a) 1473 K, (b) 1623 K, (c) 1773 K, (d) 1923 K and (e) 2073 K.

Figure 4. Density of (a) the synthesized powder (SP) and (b) the commercial powder (CP) at different sintering temperature.
The corresponding plots according to the equations (4), (5) are shown in figure 5. By taking the grain-growth exponent $n$ for the best linear regression and sintering activation energy $Q$ from the slope of linear line in figure 5, we obtained the results for both integral and differential methods for $n$ values ranging from 1 to 5, as shown in table 1. By comparing the data in the table, we found that $n = 2$ is the appropriate value when the difference in the data calculated in integral and differential methods are closest for both the SP and CP, as shown as the best fit lines in figure 5. From equations (4) and (5), when $n = 2$, the average activation energy of the SP is $314$ KJ mol$^{-1}$ (DI) or $316$ KJ mol$^{-1}$ (IM), and that of the CP is $349$ KJ mol$^{-1}$ (DM) or $340$ KJ mol$^{-1}$ (IM); these values are close to the activation energies of the grain-boundary diffusion process [10], which strongly implies that grain-boundary diffusion is one of the salient mechanisms of mass transport during the intermediate stage of sintering. Since the size of SP is such smaller than that of CP, the activation energies of grain boundary diffusion for the CP are lower than that for the SP.

Table 1. Regression fitting coefficient ($R^2$) using different grain growth exponent values for both integral method and differential method.

|     | $n = 1$ | $n = 2$ | $n = 3$ | $n = 4$ | $n = 5$ |
|-----|---------|---------|---------|---------|---------|
| SP  | Integral method | 0.9294  | 0.986   | 0.9651  | 0.9463  | 0.9364  |
|     | Differential method | 0.9065  | 0.992   | 0.9862  | 0.9797  | 0.9695  |
| CP  | Integral method | 0.9202  | 0.9363  | 0.865   | 0.8588  | 0.8566  |
|     | Differential method | 0.9266  | 0.9999  | 0.9876  | 0.9701  | 0.9553  |

Integral method (IM): 
\[
\ln \left( \frac{G^n - G^n_0}{T} \right) = - \frac{Q}{R \left( \frac{1}{T} \right)} + \ln \left( \frac{Rk}{Q} \right), \tag{5}
\]

Based on the preceding experimental results and kinetic analysis, the key finding in this work is that the sintering behavior of tungsten powders is significantly affected by the size of the powder and the precise synthesis method. At present, some studies suggest [18–20] that the basic mechanism of grain growth is that grains start to coarsen in the initial stage because of surface diffusion, and then further densify through grain-boundary diffusion in the intermediate stage. Since finer powders have a larger surface area, the more surface atoms that are active promotes the rate of diffusion. Li et al. [21] prepared spherical tungsten nanoparticle, using a radio-frequency induction thermal plasma, to create particles of a size of $\sim 50.5$ nm and achieved a relative density of 91.3% at 1773 K. Rahimian et al. [22] reported that Al-Al$_2$O$_3$ compacts with finer grains could reach a higher density at the same sintering temperature and time. In our work, the reaction using the solution combustion synthesis method was performed in a relatively short time, which effectively hinders the full growth of the grains as a large amount of gas released rapidly and it formed a porous precursor which further inhibits grain growth. Therefore, the size of the powder was significantly reduced and can be sintered to densification at relatively low temperature.

On the other side, according to the recent study [23, 24], the activation of the powder contains surface activity and lattice activity. The former is determined by the particle size and shape of the powder and the latter depends on the crystal size, lattice defects, internal stress and so on. In our work, we first used the solution
combustion synthesis method to prepare the nanosized W₁₈O₄₉ which has needle-like structure with large amounts of lattice defects in the crystal, which has been proved in previous paper [11]. The obtained W₁₈O₄₉ was reduced in the hydrogen at a low temperature as 750 °C. Thus the tungsten powder we achieved at last had the size of 20 nm with abundant lattice defects which possessed high sintering activation. As a result, we could find the sintering neck formed at temperature as low as 1200 °C. Similar results were also reported in earlier publications by Qin [25] and Chu [26]. Qin prepared W powder by solution combustion synthesis and claimed that relative density of the sintered W pellet, calcined at 1650 °C for 2 h with pressureless and additive free sintering, was found to be 98.5% of its theoretical density.

To evaluate the mechanical properties of the compositions, Vickers micro-hardness testing was performed; results are shown in figure 6. Both of SP and CP obtained the highest hardness at 1773 K, specifically at 633 HV and 538 HV, respectively. The hardness increased from 1473 K to 1773 K because of the densification and grain growth of the samples, yet decreased from 1773K to 2073 K due to grain coarsening and a consequent diminished grain boundary surface. By comparison, the hardness of CP is generally lower than that of the SP, especially at low sintering temperatures. Through the above comparisons, we can conclude that nanometer tungsten powder prepared by SCS has certain advantages in sintering densification. Specifically, densification can be achieved at lower temperatures for low cost and energy saving.

4. Conclusions

The sintering behavior of nanosized tungsten powders was investigated. The powders were prepared by solution combustion synthesis combined with hydrogen reduction. The resulting nanosized SP powder exhibited large numbers of lattice defects. Compared to the commercial nanosized tungsten powder (CP), the as-synthesized tungsten powder could be sintered via a pressureless process to relative density as high as 95.78% at 1773 K for 2 h. Kinetic analysis suggests that grain-boundary diffusion is one of the primary mechanisms of mass transport during the intermediate stage of sintering. The potent mechanisms for such excellent sintering properties are the ultrafine grain and the high sintering activation attributed to the effect of the solution combustion synthesis method. Accordingly, the hardness of the synthesized powder treated at 1773 K was measured to be as high as 633 HV. Our results suggest that solution combustion synthesis combined with hydrogen reduction can be used as a new strategy to design ultrafine nano-materials with excellent sintering ability and mechanical behavior.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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