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Fine grain tungsten produced with nanoscale powder

Tao Lin, Fang Zhao, Liying Zhang, Chengyi Wu, and Zhimeng Guo

Materials Science and Engineering School, University of Science and Technology Beijing, Beijing 100083, China

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Abstract: Nanoscale tungsten powder was prepared by reducing nanoscale tungsten trioxide in hydrogen to $WO_{2.90}$ and further to W powder. After compacted with a rubber die, the nanoscale tungsten powder was sintered in a high-temperature dilatometer to investigate its shrinkage process. The results show that the compact of the nanoscale tungsten powder starts to shrink at 1050°C and ends at 1500°C. The shrinkage rate reaches the maximum value at 1210°C. The relative density of sintered samples is 96.4%, and its grain size is about 5.8 μm.

Key words: tungsten; nanometer; sintering; compaction

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1 Introduction

The melting temperature of tungsten is up to 3410°C, which is the highest one in metals. Furthermore, tungsten has an excellent strength at high temperature. With these characteristics, tungsten is very useful for applications at high temperature. With the development of tungsten and tungsten-based alloys (*e.g.*, W-Cu, W-Ni/Fe), there exit requirements for uniform microstructure, superfine grains and good plastics. However, conventional techniques can not meet these requirements [1].

The nano-related technology can provide a new process for producing ultrafine grain materials. In recent years, ultrafine grain cemented carbides with high performance can be prepared using nanoscale WC powder, and nanoscale WC powder was prepared by reduction carbonization of the nanoscale WO_3 powder [2-6]. Applications of nano-related technology in W-Ni-Fe heavy alloys and W-Cu alloys were also reported [7-8].

At present, micrometer tungsten powder was used for the production and research of tungsten materials. This type of tungsten powder is sintered at a temperature higher than 2000°C in order to be densified. Thereafter, it can be further processed. However, tungsten grain size increases quickly during the sintering, and may be up to several hundreds micrometers. These coarse tungsten grains lower the mechanical and physical properties as well as rolling characteristic. Nanoscale powder has more surface energy and can be densified more easily than micrometer powder. Vashi *et al.* studied the consolidation of nanoscale tungsten powder under a high pressure of 1 GPa at a lower temperature to get tungsten material with superfine grains [9]. But so high pressure is hardly applied into industrial production. In this paper, nanoscale tungsten powder was prepared and its compacting and sintering were investigated according to a procedure similar to the conventional process.

2 Experimental

First, nanoscale WO_3 powder was prepared from a APT (ammonium paratungstate) solution by a ultrasonic spray thermo-conversion process, and was then reduced in hydrogen. The reduction was carried out in two steps. WO_3 was first reduced to the blue tungsten oxide $WO_{2.90}$, and then $WO_{2.90}$ was reduced to tungsten. In the above process, nanoscale WO_3, $WO_{2.90}$ and tungsten powders were milled by an high energy shear miller. The specific surface area of these nanoscale powders was measured by an ST-03 specific surface area tester, by which an average particle size was calculated. The powder shape was observed with an H-800 TEM (transmission electron microscopy). Nanoscale tungsten powder was formed with a rubber die

Corresponding author: Tao Lin, **E-mail:** lintao@mater.ustb.edu.cn

and a steel die respectively. The compact density was measured based on the Archimedes method. Nanoscale tungsten compact was sintered in hydrogen at a temperature elevating rate of 10°C/min with a high temperature dilatometer. Furthermore, conventional tungsten powder with an average particle size of 2.5 μm was compacted and sintered to compare with the nanoscale tungsten powder.

3 Results and discussion

3.1 Preparation of nanoscale tungsten powder

Blue tungsten oxide $WO_{2.90}$ was prepared by reduction of nanosclae WO_3 at 500°C for 40 min in hydrogen. Subsequently, the resulted blue tungsten oxide was reduced at a series of temperatures for 60 min to get tungsten powders. **Table 1** shows the powder characteristics of the resulted tungsten powders.

As shown in table 1, the average particle size of tungsten powder reduced at 720°C is 19 nm, which is much less than that of conventional tungsten powder. The particle size of tungsten powder increases with increasing the reduction temperature. In addition, the tungsten powder reduced at 680°C is so fine that it self-ignited after taken out from the reduction furnace. Nanoscale tungsten powders reduced at 720°C and 780°C keep stable in the air. Therefore, 680°C can not be applied as a reduction temperature. The nanoscale tungsten powder should be stored in vacuum bags or bags filled with inert gas.

Table 1 Effects of reduction temperature on characteristics of nanoscale tungsten powder

Reduction temperature /°C	Specific surface area / $(m^2.g^{-1})$	Average particle size / nm
680	—	Self-ignited
720	16.3	19
780	5.2	59

Figure 1 shows the X-ray diffraction spectrum of nanoscale tungsten powder reduced at 720°C. As shown in this figure, there is no other phases besides tungsten in the resulted powder, which illustrates that blue tungsten oxide can be completely reduced into tungsten at 720°C. This temperature is lower than that of conventional tungsten powder.

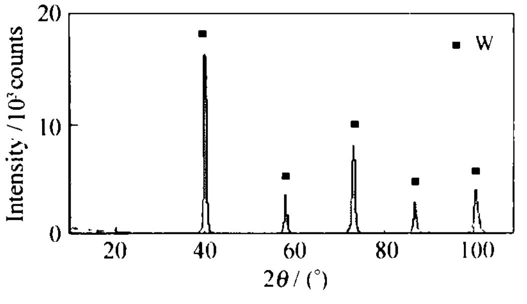

Figure 1 X-ray diffraction spectrum of nanoscale tungsten powder.

Figure 2 is a TEM photo of nanoscale tungsten powder. As shown in figure 2, the shape of tungsten particles is approximately spherical. Tungsten particles agglomerate together, and it is very difficult to separate the agglomerated particles into a single particle by ultrasonic dispersion during sample preparation.

3.2 Compaction of nanoscale tungsten powder

Nanoscale tungsten powders were compacted with a steel die and a rubber die respectively. In the case of compaction with a steel die, the relative density of the resulted compact is 28.3% when the unit compacting pressure is 200 MPa. When the compacting pressure was higher than 200 MPa, some defects such as delamination and fracture were observed in the compacts.

The compacting pressure for a rubber die can be up to 300 MPa, resulting in a compact free of defects with a relative density of 46.2%. Even with a compacting pressure of 200 MPa, the relative density of the compact can also be up to 44.0%, which is remarkably more than that obtained by compacting with a steel die. It shows that the green density of nanoscale tungsten powder can be greatly improved by compacting with a rubber die.

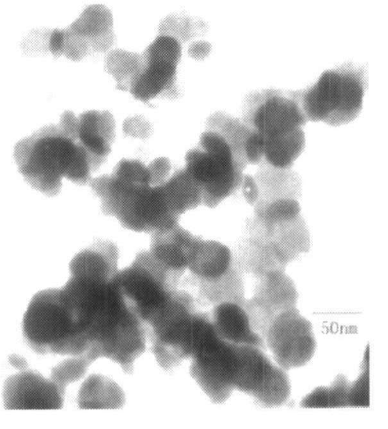

Figure 2 TEM photo of nanoscale tungsten powder.

In the case of conventional tungsten powder (average particle size of 2.5 μm), the relative density of the compact formed under 300 MPa is 64.3%, which is higher than that of a nanoscale tungsten compact.

In general, compared with compacting with a steel die, compacting with a rubber die is advantageous for nanoscale powder.

3.3 Sintering of nanoscale tungsten powder

Nanoscale tungsten compacts and conventional tungsten compacts were sintered in hydrogen in a high temperature dilatometer. **Figure 3** shows the sintering shrinkage kinetic curves. As shown in figure 3, conventional tungsten powder barely shrunk below 1600°C, while nanoscale tungsten powder almost completed its shrinkage below 1600°C. This illustrated that nanoscale tungsten powder has high activity in sintering.

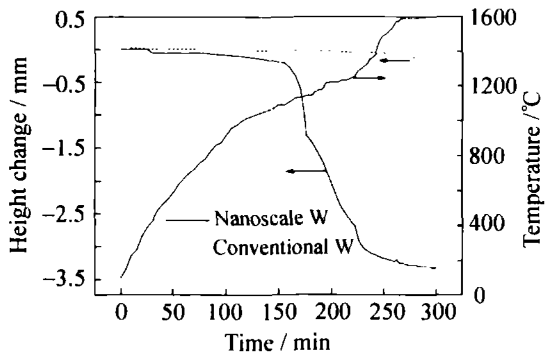

Figure 3 Sintering shrinkage kinetic curves of nanoscale W powder and conventional W powder.

Figure 4 shows the height change of a nanoscale tungsten compact with increasing temperature. As shown in figure 4, the nanoscale tungsten compact starts shrinkage at 1050°C, and shrink speedily at 1130°C. The shrinkage rate achieves the maximum value at 1210°C, and shrinkage almost ends at 1500°C. Based on this result, the sintering temperature of nanoscale tungsten powder can be determined at 1500°C, which is greatly lower than that of conventional tungsten powder.

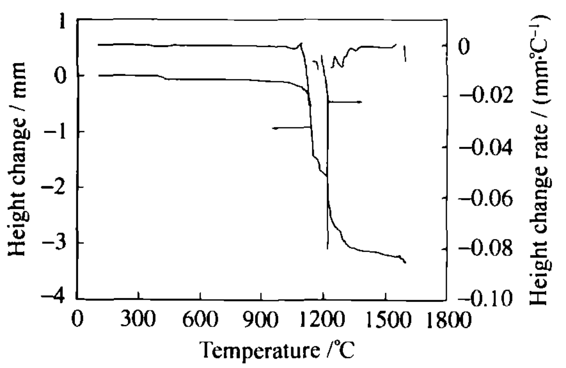

Figure 4 Height change of the nanoscale W compact with increasing temperature.

The relative density of sintered nanoscale tungsten is 96.4%, which increased by 50.2% compared with that before sintering. In the case of conventional tungsten, the relative density after sintered is 68.2%, which only increased by 3.9%. Nanoscale tungsten powder has more surface energy because it has a specific surface area much higher than micrometer tungsten powder. This will greatly promote nanoscale tungsten powder to be densified at a lower temperature.

Figure 5 shows the microstructure of a sintered tungsten sample, in which the black circular areas are pores. Pores become spherical, and uniformly distribute on grain boundaries of tungsten. The grain size of tungsten is about 5.8 μm. This grain size is greatly less than that of conventional sintered tungsten products.

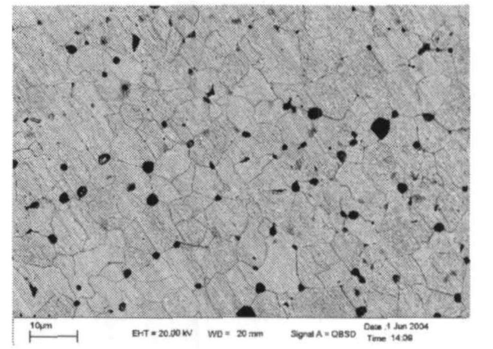

Figure 5 SEM image of sintered nanoscale tungsten powders.

The grains are still grown to about 5.8 μm although nanoscale tungsten powder is used as a starting material. Vashi *et al.* studied the consolidation of nanoscale tungsten powder at 920°C under a high pressure of 1GPa, resulting in a sample with a grain size of 0.17μm and a relative density of 95% [9]. These results show that nanoscale tungsten powder has a high activity, and is very prone to growth.

4 Conclusions

(1) The nanoscale tungsten powder with an average particle size of 19 nm was obtained by gradually reducing WO_3, which was prepared by ultrasonic spray and thermochemical conversion process, into $WO_{2.90}$ and W.

(2) Compacting with a rubber die is a preferred method for making a tungsten green compact with the nanoscale powder, whereby a relative density of 46.2% was achieved.

(3) The compact made from the nanoscale tungsten powder starts shrinkage at 1050°C, and the shrinkage rate is maximum at 1210°C. The shrinkage almost ends at 1500°C. In the case of the traditional tungsten powders, however, the compacts barely shrinks.

(4) After sintered in hydrogen at 1500°C, tungsten samples with a relative density of 96.4% and a particle size of 5.8 μm were prepared. As for the traditional tungsten powder, the relative density is only 68.2% after sintering.

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