Journal of University of Science and Technology Beijing
Volume 12, Number 4, August 2005, Page 360

Materials

Synthesis of nanosized tungsten powder

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(Received 2004-11-09)

Abstract: Nanosized tungsten powder was synthesized by means of different methods and under different conditions with nanosized WO_3 powder. The powder and the intermediate products were characterized using XRD, SEM, TEM, BET (Brunauer Emmett Teller Procedure) and SAXS (X-ray diffracto-spectrometer/Kratky small angle scattering goniometer). The results show that nanosized WO_3 can be completely reduced to WO_2 at 600°C after 40 min, and WO_2 can be reduced to W at 700°C after 90 min, moreover, the mean size of W particles is less than 40 nm. Furthermore, the process of $WO_3 \rightarrow WO_2 \rightarrow W$ excelled that of $WO_3 \rightarrow W$ in getting stable nanosized tungsten powder with less grain size.

Key words: Nano-tungsten powder; reduce; SAXS

[*This work was financially supported by the National Science Funds of Beijing (No.2052015).*]

1 Introduction

The refractory metal tungalloy, which has a series of excellent physical and mechanical properties, has been widely used in the fields of national defense and military industry, avigation and spaceflight, electron and information industry, energy source, metallurgy and machinery industry *etc.*, and occupies the important position in national economy [1-2]. The WC-Co cemented carbide, that has high hardness, strength and good wearability, is a kind of ultra hardness material which is only next to diamond. It is used extensively as cutting tools known as the tooth of modern industry, furthermore, the arising of nanostructured materials will give this kind of alloy a more extensive use. The supreme bending strength of a nanostructured WC hard alloy can reach 5000 MPa and the hardness reaches HRA 93 so that it has very wide application prospect and can meet the market demand used as micro-bits in integrated circuit of electronics industry and printer's needle in computer. Other applications of tungalloys include: W-Ni-Fe high-density alloys used as the bundling shell, penetration shell, frangibility shell and armor piercing shell; W-Cu(Mo-Cu) alloys served as the electric contact materials, microelectron encapsulation materials, heat sink materials for its good heat conductivity, electric conductivity and little thermal expansion coefficient [3-4]; nanostructured W-Cu materials widely used as the electronic package of ample power microwave devices, such as various integrate circuits, thyristors [5].

The mean grain size of the primitive tungsten powder is 2-6 μm, which is used as heavy alloys all over the world. The crystal grains grow up 10-15 times after alloy sintering, as a result, all round mechanical properties of heavy alloys are reduced obviously [6]. So experts and scholars at home and abroad pay much attention to the research of nanosized tungsten powder ($\leq$ 100 nm). In the research of nanosized tungsten alloy materials, the preparation technology of nanosized powder is a very key step. At present, the typical method of making tungsten powder is to reduce WO_3 (yellow tungsten) or $WO_{2.90}$ (blue tungsten) under the atmosphere of H_2. The studied results for years show that it is the nanosized tungsten oxide powder that must be utilized through controlling reducing craft in order to obtain nanosized tungsten powder [7-8]. The process of nanosized WO_3 powder being reduced under the atmosphere of H_2 is studied and the industrialized preparation method of nanosized tungsten powder is discussed in this paper.

2 Experiment

In the experiment, the raw material was the nanosized WO_3 powder made by chemical precipitation. It

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was dried at 200°C in vacuum for 4 h, the moisture content<0.1wt%, BET 54 m^2/g, and the mean grain size<30 nm (SAXS), moreover, its particle size distribution is narrow. **Figure 1** shows the TEM micrograph of nanosized WO_3 powder and **figure 2** shows the histogram of WO_3 particle size distribution. Its chemical composition (wt%) is: Fe, 0.25-0.6; Al, 0.05-0.11; Si, 0.12-0.3; Mn, <0.05; Mg, 0.07-0.17: Ni, <0.05; Ti, <0.05; V, <0.05; Co, <0.05; As, <0.1.

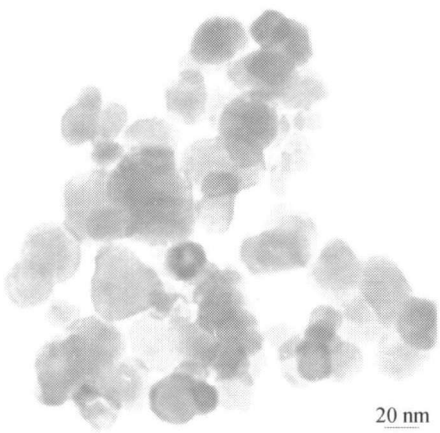

Figure 1 TEM micrograph of nanosized WO_3 powder.

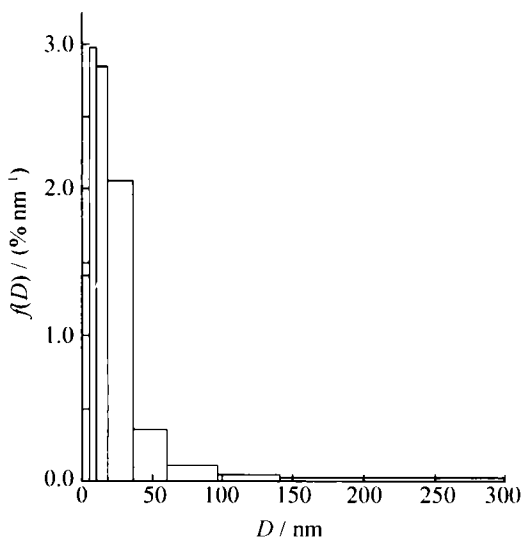

Figure 2 Histogram of WO_3 particle size distribution (SAXS).

The main instruments and equipment used in the experiment are: tubular type reducing furnace, model Dmax-RB X-ray diffractometer, model 2000XCX transmission electron microscope, model S-250MK2 scanning electron microscope, model Bs100 analytical balance, external specific surface apparatus, *etc.* The surface area was measured by the single point BET adsorption.

2.1 Reduction from nanosized WO_3 powder to nanosized W powder

Table 1 shows the reducing technology. The phase and particle shape of the reaction products were tested and analyzed by X-ray diffraction analyzer, TEM and external specific surface apparatus *etc.* under the condition of a certain temperature and a certain flux of hydrogen.

Table 1 Condition of nanosized WO_3 reducing to nanosized W

Serial number	Temperature/ °C	Holding time/ min	Flux of Hydrogen / ($mL \cdot min^{-1}$)
A1	600	150	400
A2	650	150	400
B1	700	60	400
B2	750	60	400
C	700	90	600

2.2. Reduction from nanosized WO_2 powder to nanosized W powder

The experiments include the reduction from nanosized WO_3 to nanosized WO_2 powder (the first stage) and the reduction from nanosized WO_2 to nanosized W powder (the second stage). In the first stage, it was tested whether the phase had been changed from WO_3 to WO_2 using an XRD analyzer under the condition of a certain temperature and a certain flux of hydrogen in different reaction time. In the second stage, the phase change from WO_2 to W was tested with an XRD analyzer under the condition of a certain temperature and a certain flux of hydrogen in different reaction time, and the specific surface and particle shape of W powder were determined. **Table 2** gives the reducing craft.

Table 2 Conditions of nanosized WO_3 reducing to nanosized WO_2

Serial number	Temperature/ °C	Holding time/ min	Flux of Hydrogen / ($mL \cdot min^{-1}$)
a	510	60	400
b	550	40	400
c	590	40	400
d	600	40	400

Conditions of the reducing process from nanosized WO_2 powder to nanosized W powder were: the reducing temperature, 700°C; the holding time, 90 min; the flux of hydrogen, 600 $mL \cdot min^{-1}$.

3 Results and discussion

3.1 Reduction from nanosized WO_3 powder to nanosized W powder directly

Figure 3 shows that nanosized W powder can not be wholly obtained under the condition of A1 and A2 at the stage of reduction from nanosized WO_3 powder

to nanosized W powder. The product still contains WO_2 and a little of β-W; with the change of process conditions, especially rising the temperature, under the conditions of B2 and C, pure nanosized W powder was obtained. It is similar to the rule of reducing conventional WO_3. Because reducing reaction is an endothermic reaction, the reaction temperature is higher and the reducing reaction is easier to carry out [9].

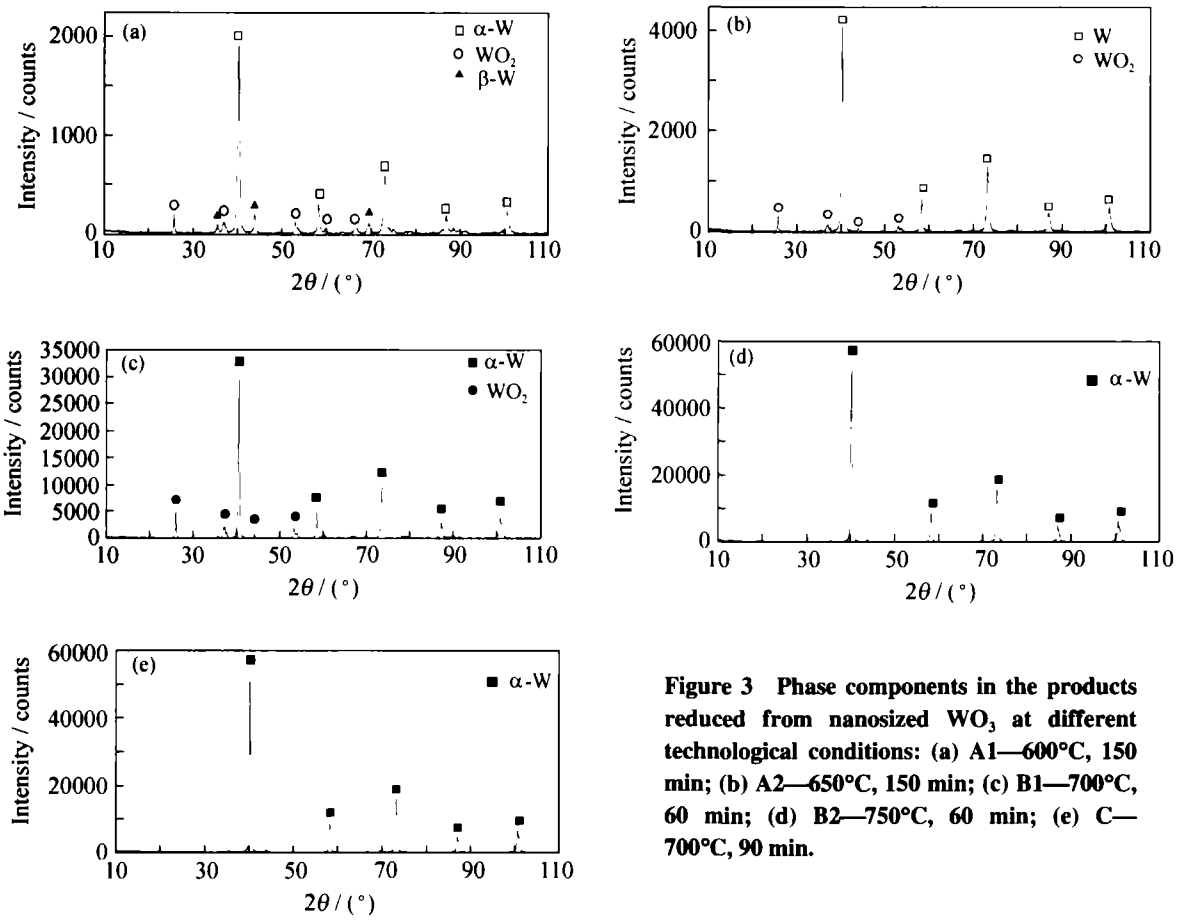

Figure 3 Phase components in the products reduced from nanosized WO_3 at different technological conditions: (a) A1—600°C, 150 min; (b) A2—650°C, 150 min; (c) B1—700°C, 60 min; (d) B2—750°C, 60 min; (e) C—700°C, 90 min.

When the reducing temperature is certain, the reaction of $WO_3 \rightarrow W$ progresses more adequately along with the holding time. Compared with the reducing temperature (about 800°C) of conventional WO_3 powder, the reducing temperature of nanosized WO_3 powder is lower by 100°C or so. Since nanosized WO_3 powder has great specific surface area and specific surface energy, solidoid WO_3 absorbing hydrogen is strengthened, and the contact area of hydrogen and solidoid WO_3 is enlarged at the same time, which promotes the reaction and accelerates the reaction rate [10].

Nanosized W powder, that is subsphaeroidal, can be achieved with nanosized WO_3 powder at a suitable reducing temperature (700°C-750°C) in a certain holding time (60-90 min).

With the reducing temperature rising, the time that WO_3 is fully reduced is shortened while the specific surface area of nanosized W powder is diminished and its particle size is enlarged. **Figure 4** and **table 3** point to the conclusion that the evaporability of nanosized WO_3 is augmented, the smoke of them deposits on the surface of low valence tungsten oxide or tungsten powder being reduced and W powder particles are grown up when the WO_3 powder are reduced afresh.

3.2 Reduction from nanosized WO_2 powder to nanosized W powder

Figure 5 shows that nanosized WO_3 can be reduced to nanosized WO_2 under the condition of 600°C holding for 40 min. **Figure 6** shows that nanosized WO_2 powder can be fully reduced to nanosized W powder.

Figure 7 shows the particle shape of nanosized W powder through the two stages of reducing. The SEM micrograph is blurring which indicates that the powder particles are extremely small so that the SEM is unable to show clearly. The TEM photo shows that the particle size of nanosized W powder is about 40 nm, the particle size distribution is narrower (**figure 8**) and the particles are subsphaeroidal which accords with the BET particle size of W powder given in **table 4**.

Table 4 shows that the particle size of nanosized W powder reduced through nanosized WO_2 has little change compared with nanosized WO_2 powder. This indicates that the course of reaction can be controlled effectively, and the growing behavior of W powder can be restrained and nanosized W powder, which has tiny and steady particle size, can be obtained finally by means of grading reduction.

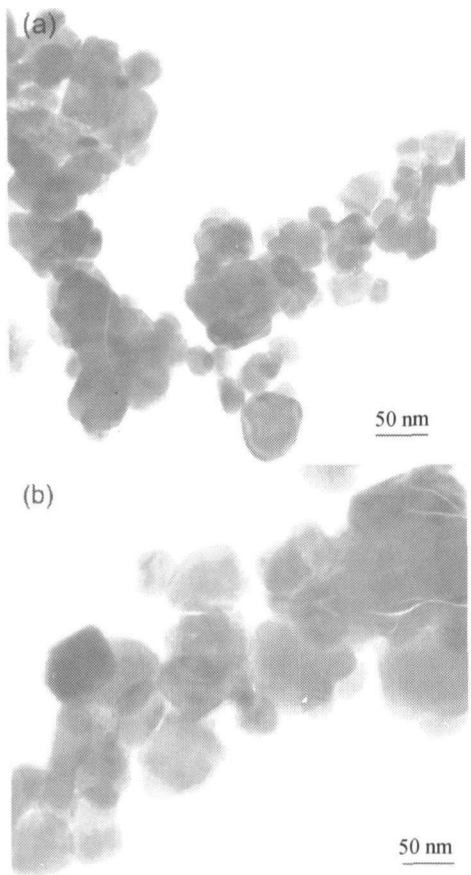

Figure 4 TEM micrographs of the W powders under double process conditions: (a) C—700°C, 90 min; (b) B2—750°C, 60 min.

Table 3 Contrast of W particle size reduced from WO_3 in different technological conditions

Serial number	Technological conditions	Surface area / ($m^2 \cdot g^{-1}$)	Particle size from BET/ nm
B2	750°C, 60 min	5.967	52.1
C	700°C, 90 min	6.386	48.7

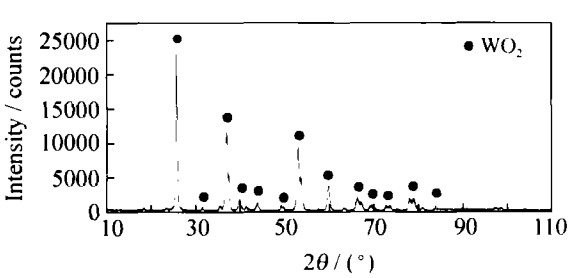

Figure 5 XRD pattern of WO_3's reducing products at 600°C after 40 min.

3.3 Growth mechanism of nanosized tungsten powder

Nanosized WO_3 powder has great specific surface and their particle size is very small which means that they are much easier to volatilize than conventional WO_3 powders at a certain temperature. So the particle size of the tungsten powder reduced at 750°C is larger than that of the tungsten powder reduced at 700°C in the process of $WO_3 \rightarrow W$ (see figure 3). This accords with the growth mechanism "oxidation-reduction" of tungsten powder [10]. The grading reduction process of nanosized tungsten powder can lower the reduction temperature to decrease the volatility of WO_3 in order to get finer particle size.

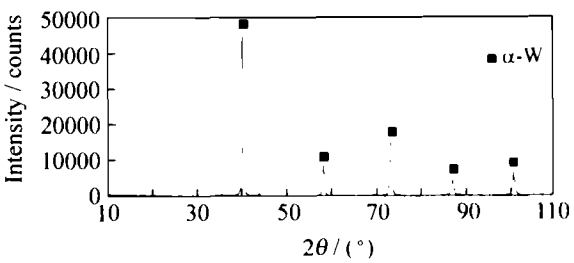

Figure 6 XRD pattern of WO_2's reducing products at 700°C after 90 min.

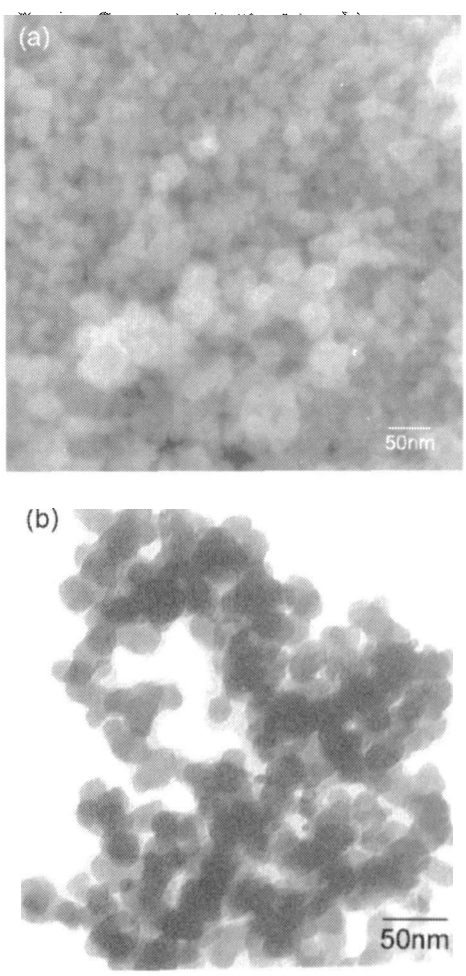

Figure 7 SEM (a) and TEM (b) micrographs of nanosized W powder.

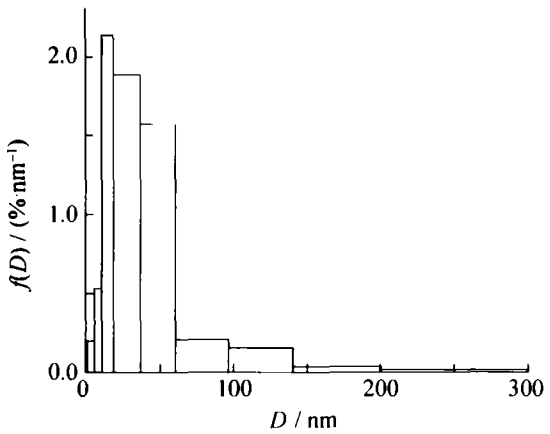

Figure 8 Histogram of nano-W particle size distribution (SAXS).

Table 4 Particle sizes of nano-WO_3 powder and nano-W powder

Powder category	Technological conditions	Surface area/ ($m^2 \cdot g^{-1}$)	Particle size from BET / nm
WO_2	600°C, 40 min	15.627	35.0
W	700°C, 90 min	8.510	36.5

4 Conclusions

1) The reduction course of $WO_3 \rightarrow W$ shows that the nanosized W powder with a shape of subsphaeroidal can be achieved with nanosized WO_3 powder at a suitable reducing temperature (700-750°C) in a certain holding time (60-90 min). The time that WO_3 is fully reduced is shortened while the specific surface area is minished and the particle size is augmented.

(2) In the reduction course of $WO_3 \rightarrow WO_2 \rightarrow W$, nanosized WO_3 can be reduced to nanosized WO_2 under the condition of 600°C holding for 40 min, and nanosized WO_2 powder can be fully reduced to nanosized W powder at 700°C after 90 min.

(3) Comparing the grading reduction of $WO_3 \rightarrow WO_2 \rightarrow W$ with the reduction of $WO_3 \rightarrow W$, the former can obtain the nanosized W powder with tiny and steady particle size and subsphaeroidal particles.

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