



Effects of various rare earth oxides on morphology and size of oxide dispersion strengthening (ODS)-W and ODS-Mo alloy powders

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Received 12 July 2021; accepted 17 February 2022

Abstract: Ultrafine oxide dispersion strengthening (ODS)-Mo and ODS-W alloy powders containing different types of oxide nanoparticles were successfully synthesized by spraying method (solid–liquid mixing method) combined with the reductions with carbon black and hydrogen in sequence. It is concluded that the solution concentration and type of rare earth oxide have no effect on the grain size of ODS-Mo alloy powder, but have obvious effect on that of ODS-W alloy powder. The higher the concentration of rare earth solution is, the smaller the average grain size of ODS-W alloy powder is. Furthermore, compared with doping with CeO₂, the grain sizes of reduction products of La₂O₃ and Y₂O₃ doped WO₃ are relatively larger. Compared with the undoped case, there is almost no change for grain size of ODS-Mo alloy powder, while the grain size of ODS-W alloy powder becomes much larger. This is probably due to the appearance of the composite oxide (such as La₂WO₆) formed by the reaction between tungsten oxide and rare earth oxides, which promotes the heterogeneous nucleation and growth of tungsten grains during the reduction process of ODS-W, while there is no complex oxide composed of molybdenum and rare earth oxides in the reduction process of ODS-Mo.

Key words: grain size; rare earth oxide; oxide dispersion strengthened alloy; W; Mo

1 Introduction

Tungsten (W) and molybdenum (Mo) are important refractory metals with high melting point, high density and high hardness [1–5]. Furthermore, owing to their high temperature strength, good corrosion resistance, good thermal conductivity, good electrical conductivity, low thermal expansion coefficient, they have great potential applications in military weapons, nuclear reactor protection materials and aerospace flight equipments [6–11]. Especially, lower sputtering rate makes them promising candidates for plasma facing materials (PFM) in future fusion power reactors [11–17].

However, as PFM materials, W and Mo also face serious problems of low temperature brittleness, high temperature or recrystallization brittleness and radiation-induced brittleness, due to their high ductile-to-brittle transition temperature (DBTT) [11,13–16].

In order to solve these problems, it is necessary to improve the properties and optimize the microstructure of conventional Mo/W materials. At present, the optimization methods are mainly focused on the second phase dispersion strengthening and fine grain strengthening [1–4,6,10–13]. The secondary phase dispersion strengthening can not only refine the grain size, but also reduce the concentration of impurities and optimize their

distribution state at the grain boundary [10–16]. The added materials for secondary phase dispersion strengthening can be divided into oxides (La_2O_3 [1,3,4,12], Y_2O_3 [11,13,15,16], and ZrO_2 [2,5,10,14]), and carbides (TiC [9], and ZrC [7]). Among them, thermally stabilized rare earth oxides (La_2O_3 , Y_2O_3 , etc) are important additives for oxide dispersion strengthening of W or Mo [1,3,4,11–13,15,16]. Dispersed rare earth oxide particles inhibit recrystallization and grain growth by preventing grain boundary sliding. Besides, they also reduce ductile-to-brittle transition temperature (DBTT) [1,4,11–13,15] and increase grain boundary density [1,4,11–13,16].

As is known to all, ultra-fine/nano powder has a high sintering activity, and fine-grained Mo-based or W-based alloy can be obtained by low-temperature sintering [1,18–26]. Therefore, the preparation of ultrafine/nano oxide dispersion strengthened molybdenum (tungsten) (ODS-Mo (W)) alloy powder is the key to obtain ODS-W (Mo) alloy with excellent properties [1,4,11,16]. Up to now, various methods have been developed to prepare the pre-cursor of ODS-W (Mo) composite powder, which can be divided into three categories: solid–solid mixing between solid Mo (W) source and solid oxide powder (S–S mixing), solid–liquid mixing between solid Mo (W) source and liquid solution of oxide (S–L mixing) [2–4,10,12–17], as well as liquid–liquid mixture between liquid Mo (W) source and liquid solution of oxide (L–L mixing) [1,14,19]. S–S mixing method mainly uses high energy ball milling to mix solid raw materials. S–L mixing method is mainly the direct mixing of solid W (Mo) oxide and rare earth oxide solution, while L–L mixing methods include freeze drying, sol–gel method, hydrothermal method and spray drying method [1,14,19,27]. Nowadays, both S–S and S–L mixing methods are suitable for industrial production, and S–L mixing has better effect than S–S mixing. However, it is difficult to stably prepare ultra-fine/nano ODS-Mo (W) alloy powders by the traditional solid–liquid method combined with hydrogen reduction [1,19]. In this study, through the simple and effective spraying method [1], oxide nanoparticles can be introduced into the surface of molybdenum trioxide (MoO_3) or tungsten trioxide (WO_3), and then ultrafine ODS-Mo or ODS-W alloy powder can be obtained by reducing MoO_3 or WO_3 with carbon black and

hydrogen in sequence. This method has the advantages of low cost, high efficiency and industrialized preparation, which has high application potential. Furthermore, the effects of rare earth oxide type and solution concentration on the grain size of ODS-W (Mo) alloy are also studied.

2 Experimental

2.1 Materials

Commercial MoO_3 powder (99.9% in purity) from Jinduicheng Molybdenum Co., Ltd., Xi'an, China, with an average particle size of 1.422 μm , was used as the molybdenum source. Yellow WO_3 powder (>99 wt.%, Sinopharm Chemical Reagent Co., Ltd.) was used as the W source. Carbon black (MA100, Mitsubishi Chemical Corporation) with an average particle size of 50 nm was used as the main reducing agent. Lanthanum nitrate hexahydrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), cerium nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), yttrium nitrate hexahydrate ($\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) (99% in purity, Shanghai Aladdin Biochemical Technology Co., Ltd.) were used as dopers.

2.2 Procedures

The preparation process of ultrafine ODS-W (Mo) alloy powder is shown in Fig. 1. Appropriate amount of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ or $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ or $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was weighed and dissolved in deionized water to prepare solutions with different concentrations, as shown in Table 1. Then, rare earth salt solution with various concentrations was sprayed into the MoO_3 or WO_3 powder. The total addition amount of salt was 1 wt.%. After that, the sprayed powders were dried at 100 $^\circ\text{C}$ for 4 h in the oven. The dried MoO_3 or WO_3 powders doped with rare earth oxide were homogeneously mixed with carbon black in agate mortar. According to our previous research [18,21,23,25,26], in order to prepare high-purity and ultra-fine ODS-Mo or ODS-W alloy powder, the optimal molar ratio of carbon black to MoO_3 was 1.9:1, while the optimal molar ratio of carbon black to WO_3 was 2.3:1. In the carbothermal reduction experiment, after the alumina crucible containing the sample was put into the furnace, the sample was heated from room temperature to the specified reduction temperature at a heating rate of 5 $^\circ\text{C}/\text{min}$ under the protection of

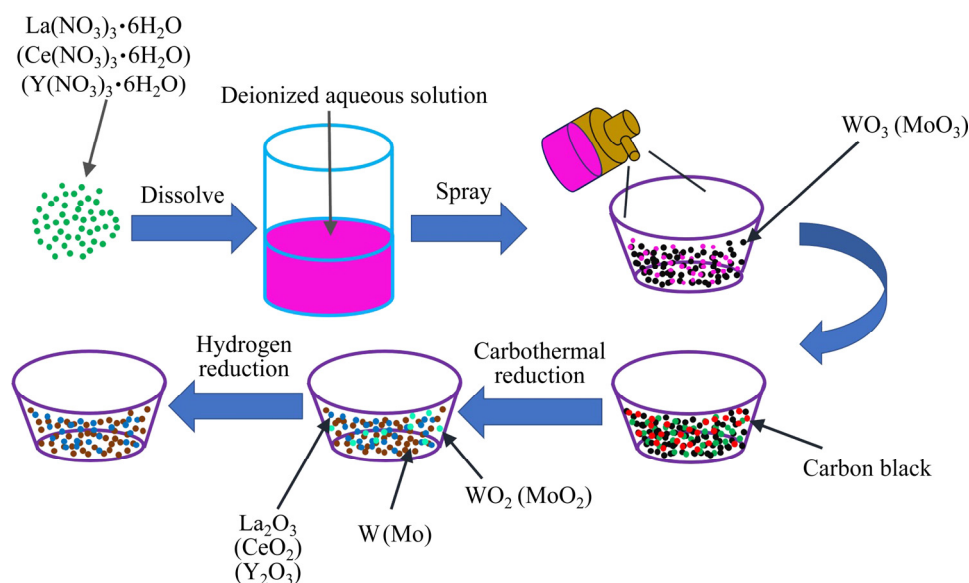


Fig. 1 Preparation process of ultrafine ODS-W (Mo) alloy powder

Table 1 Different concentrations of rare earth oxide solution

Solution	Concentration/(g·mL ⁻¹)
La(NO ₃) ₃ ·6H ₂ O	0.4, 0.2, 0.02
Ce(NO ₃) ₃ ·6H ₂ O	0.4, 0.2, 0.02
Y(NO ₃) ₃ ·6H ₂ O	0.4, 0.2, 0.02

flowing argon (400 mL/min). The carbothermal reduction reaction of molybdenum oxide was carried out first at 600 °C for 1.5 h, and then at 1050 °C for 2 h. However, the carbothermal reduction reaction for tungsten oxide was carried out at 1150 °C for 2 h. Then, all pre-reduced powders after carbothermal reduction reaction were deeply reduced by hydrogen at 800 °C for 2 h. Moreover, pure WO₃ and MoO₃ without doping were also reduced following the same program. As a comparison, the doped precursor materials were also reduced by pure hydrogen at 1050 and 1150 °C for 2 h, respectively.

The morphology and particle size of the products were detected by the FE-SEM (ZEISS Gemini 500, Oberkochen, Germany) and TEM equipped with EDX detector (JEM-2100F, JEOL, Japan). The XRD (SMARTLAB (9), TTR III, Rigaku Corporation, Japan) using Cu K_α radiation in the 2θ range of 10°–90° with a scanning rate of 10 (°)/min was used to determine the phase composition of products. The working voltage and working current were 20–45 kV and 10–200 mA, respectively. The residual carbon content was

measured using the infrared carbon–sulfur analyzer (EMIA-920 V2, HORIBA, Japan). Each sample was measured twice and the average value was taken.

3 Results and discussion

3.1 Preparation of ultrafine/nano W (Mo) powders

The XRD patterns of the products of the undoped MoO₃ and WO₃ after carbothermal reduction and deep hydrogen reduction are shown in Figs. 2(a, b). It can be seen that the products after carbothermal reduction are composed of Mo or W and a small amount of dioxide (molybdenum dioxide (MoO₂) or tungsten dioxide (WO₂)). The main purpose of keeping a small amount of dioxide is to reduce the residual carbon content in the final powder [25]. To convert the minor amounts of MoO₂/WO₂ to Mo/W, the pre-reduced powder after carbothermal reduction is then subjected to hydrogen reduction, with the XRD patterns of products shown in Figs. 2(a, b). The FE-SEM image of the carbothermal reduction products of pure MoO₃ is shown in Fig. 2(c), from which it can be seen that the grain size of the pre-reduced products maintains at 200–300 nm. However, after deep reduction by hydrogen, as shown in Fig. 2(d), the grain size of products is almost the same as that of pre-reduced products. Figures 2(e, f) show the FE-SEM micrographs of the reduced products of pure WO₃. It is shown that there is also no significant difference in the grain size (about 100 nm)

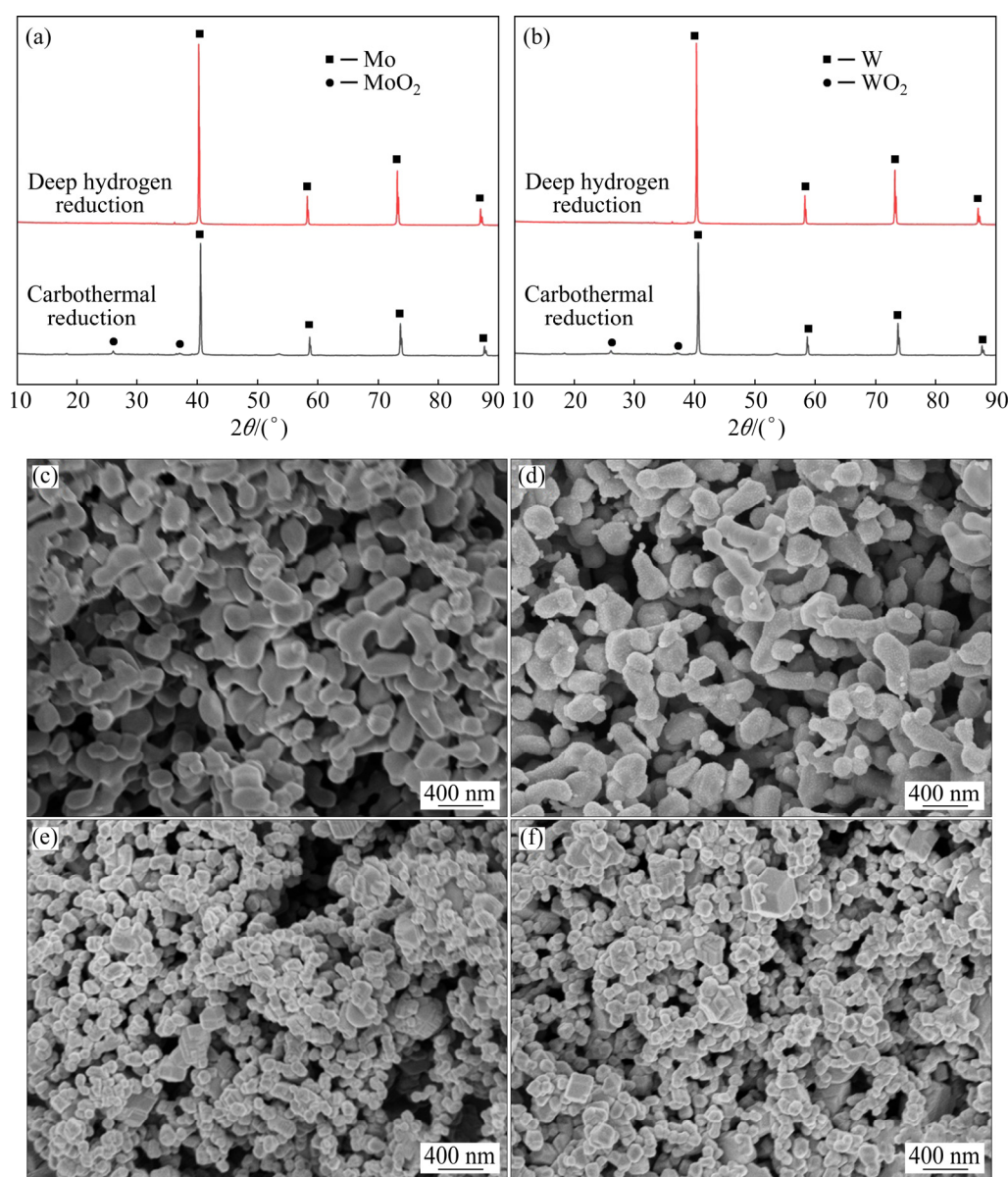


Fig. 2 XRD patterns (a, b) and FE-SEM images of carbothermic pre-reduction products (c, e) and final products after hydrogen reduction (d, f): (a, c, d) MoO₃; (b, e, f) WO₃

of the two reduction products before and after hydrogen reduction.

For the preparation of ultrafine Mo (W), the advantage of using carbon black as a reducing agent is its nano size. A large number of small particles can provide a considerable number of nucleation sites, and form a great number of dispersed MoO₂(WO₂)/Mo (W) nuclei [18,21,23,25,26]. At the same time, there is no gaseous transportation phase, such as MoO₂(OH)₂ or WO₂(OH)₂, during the reduction processes of MoO₃ (WO₃) by carbon black. Thus, the migration of Mo (W) atoms is very difficult, and only the atoms close to the formed Mo (W) nuclei can be used for their growth. But, when

the reaction interface is far away from the formed Mo (W) particles, Mo (W) particles are difficult to grow due to the limited number of free Mo (W) atoms near the Mo (W) particles. Therefore, it is feasible to prepare ultrafine Mo (W) powder by carbothermal reduction method.

3.2 Preparation of ultra/nano rare earth oxides doped W (Mo) powders

The XRD patterns of the finally prepared products by reducing rare earth oxides doped MoO₃ or WO₃ with the above process are shown in Fig. 3, from which it can be seen that Mo or W powders containing different rare earth oxides are prepared.

However, since the addition amount of rare earth oxide is only 1 wt.%, the diffraction peak of rare earth oxide cannot be detected in the XRD patterns.

Figure 4 and Table 2 show FE-SEM images and average powder size of carbothermal pre-

reduction product of ODS-Mo, respectively. Table 2 shows that the grain sizes of pre-reduced products are all in the range of 172–183 nm. Furthermore, by changing the type and solution concentration of rare earth oxide, the grain size of the products does

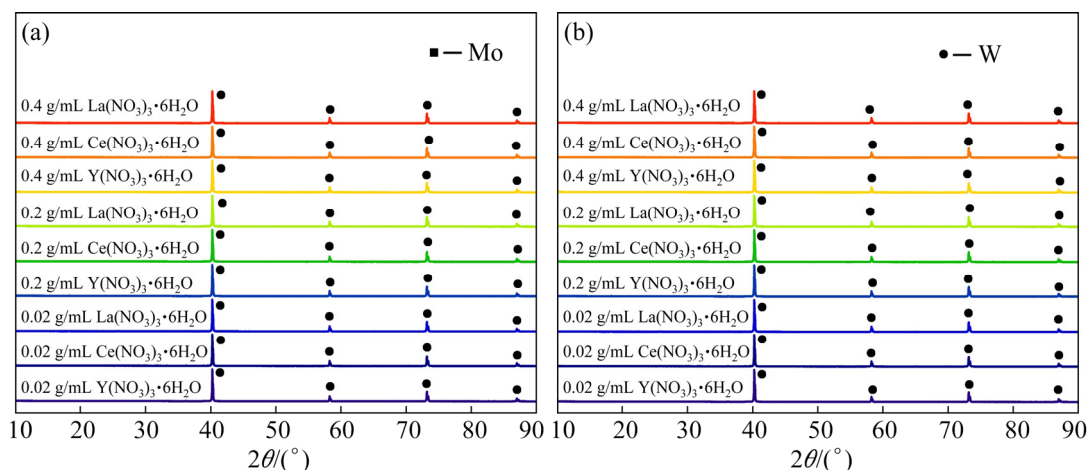


Fig. 3 XRD patterns of final products obtained by deep hydrogen reduction with different solution concentrations of rare earth oxides: (a) ODS-Mo; (b) ODS-W

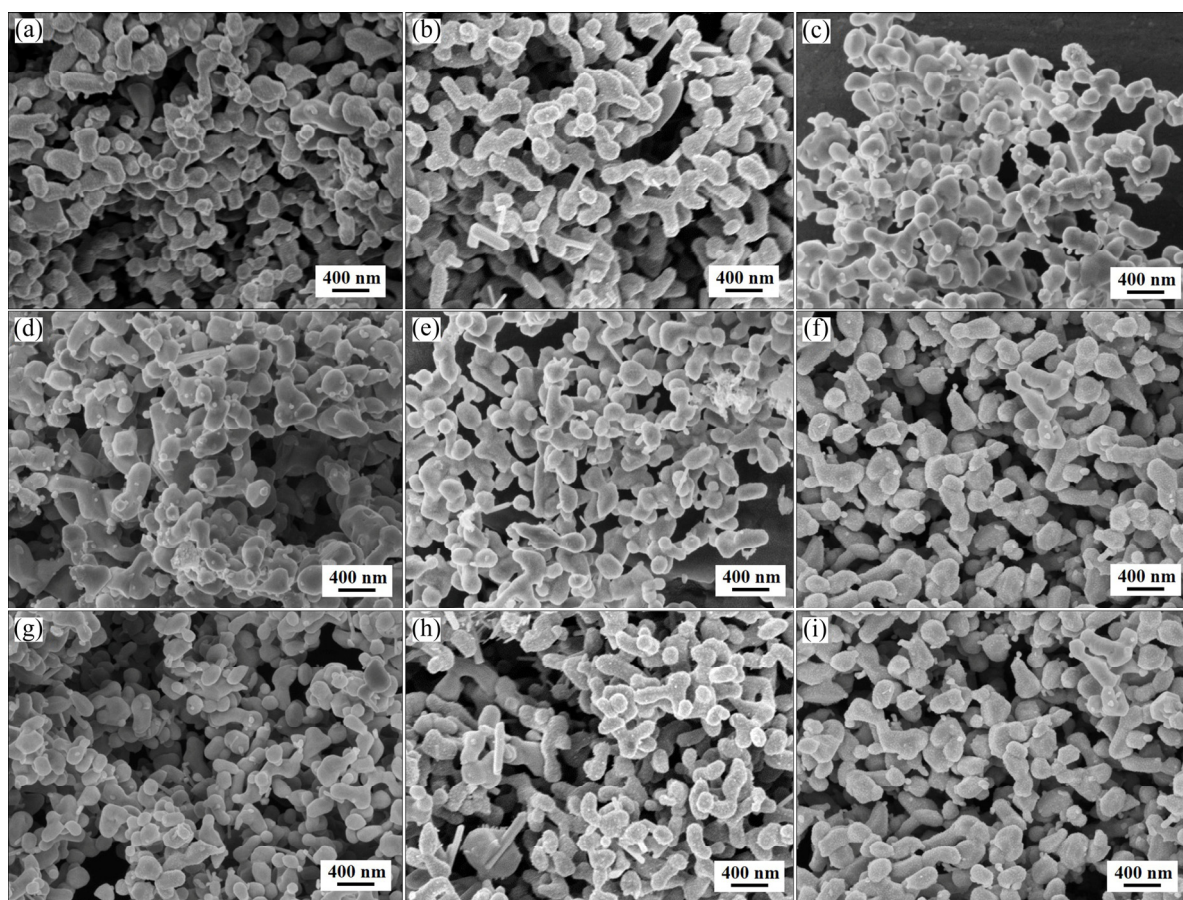


Fig. 4 FE-SEM images of carbothermal reduction products of ODS-Mo composite powders: (a) Mo–La₂O₃, 0.4 g/mL; (b) Mo–CeO₂, 0.4 g/mL; (c) Mo–Y₂O₃, 0.4 g/mL; (d) Mo–La₂O₃, 0.2 g/mL; (e) Mo–CeO₂, 0.2 g/mL; (f) Mo–Y₂O₃, 0.2 g/mL; (g) Mo–La₂O₃, 0.02 g/mL; (h) Mo–CeO₂, 0.02 g/mL; (i) Mo–Y₂O₃, 0.02 g/mL

Table 2 Average powder size of carbothermal reduction products of ODS-Mo under different conditions

Alloy composition	Solution concentration/(g·mL ⁻¹)	Average powder size/nm
Mo	–	172
Mo–La ₂ O ₃	0.4	177
Mo–La ₂ O ₃	0.2	175
Mo–La ₂ O ₃	0.02	179
Mo–CeO ₂	0.4	180
Mo–CeO ₂	0.2	178
Mo–CeO ₂	0.02	183
Mo–Y ₂ O ₃	0.4	178
Mo–Y ₂ O ₃	0.2	181
Mo–Y ₂ O ₃	0.02	174

not change significantly. The FE-SEM images and average grain size of final products obtained by deep hydrogen reduction of ODS-Mo composite powders are shown in Fig. 5 and Table 3, respectively. From Table 3, it can be seen that the

grain sizes of the products are still between 173 and 185 nm, and there is no obvious change in the morphology compared with the carbothermal pre-reduction products shown in Fig. 4. Compared with the reduction products of pure MoO₃ without doping, the grain size and morphology of the reduction products also have no obvious change. Therefore, the existence of rare earth oxides does not affect the nucleation and growth of products in the carbothermal reduction process of MoO₃ [1].

The FE-SEM images and average grain size of carbothermal reduction products of ODS-W composite powders are shown in Fig. 6 and Table 4, respectively, from which it can be seen that with the decrease of solution concentration, the grain size of pre-reduced product of ODS-W gradually increases from 111 to 1017 nm. At the same solution concentration, the different types of rare earth oxides have different effects on the grain size of the reduction products, and the grain size of W–La₂O₃ alloy powder is the largest, followed by W–Y₂O₃, while W–CeO₂ alloy powder is the smallest. When

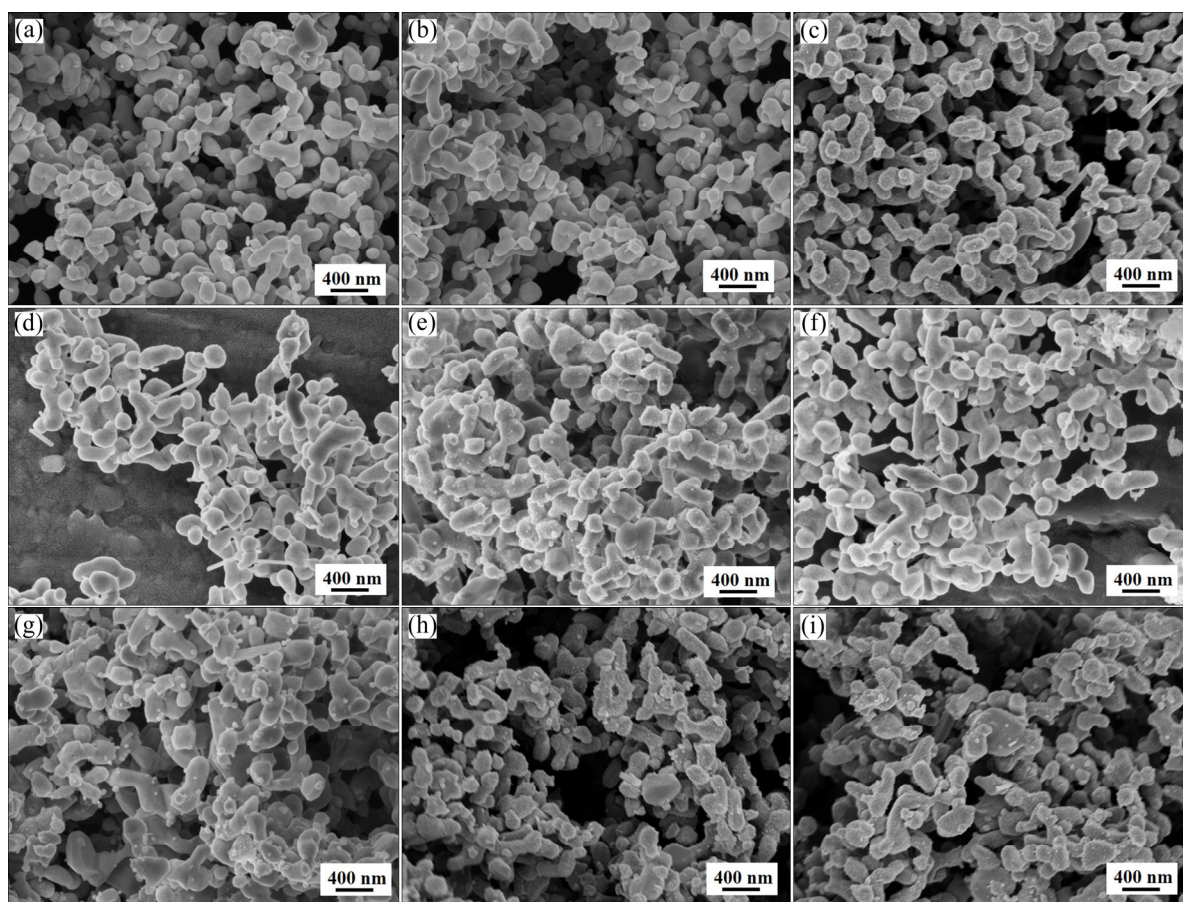


Fig. 5 FE-SEM images of final products obtained by deep hydrogen reduction of ODS-Mo composite powders: (a) Mo–La₂O₃, 0.4 g/mL; (b) Mo–CeO₂, 0.4 g/mL; (c) Mo–Y₂O₃, 0.4 g/mL; (d) Mo–La₂O₃, 0.2 g/mL; (e) Mo–CeO₂, 0.2 g/mL; (f) Mo–Y₂O₃, 0.2 g/mL; (g) Mo–La₂O₃, 0.02 g/mL; (h) Mo–CeO₂, 0.02 g/mL; (i) Mo–Y₂O₃, 0.02 g/mL

Table 3 Average powder size of deep hydrogen reduction products of ODS-Mo under different conditions

Alloy composition	Solution concentration/(g·mL ⁻¹)	Average powder size/nm
Mo	–	173
Mo–La ₂ O ₃	0.4	178
Mo–La ₂ O ₃	0.2	177
Mo–La ₂ O ₃	0.02	181
Mo–CeO ₂	0.4	182
Mo–CeO ₂	0.2	180
Mo–CeO ₂	0.02	184
Mo–Y ₂ O ₃	0.4	183
Mo–Y ₂ O ₃	0.2	185
Mo–Y ₂ O ₃	0.02	179

the solution concentration is 0.02 g/mL, the grain sizes of the carbothermal reduction products doped with La₂O₃, CeO₂ and Y₂O₃ can be increased to about 1017, 599 and 801 nm, respectively.

Compared with the products of carbothermal reduction of WO₃ without doping, it can be found that the addition of rare earth oxides can promote the grain growth of the reduction products. Especially, when the solution concentration decreases, the grain size increases more obviously. When rare earth oxide doped WO₃ is subjected to carbothermal reduction, tungsten oxide first reacts with rare earth oxide to form the composite oxide before it is reduced by carbon black due to its high reduction temperature (≥ 953 °C) [25], and the composite oxide can be used as the core for the heterogeneous nucleation and growth of W.

The FE-SEM images and average grain size of the product obtained by deep hydrogen reduction of ODS-W composite powders are shown in Fig. 7 and Table 5, respectively. Table 5 displays that the grain size of finally reduced product of ODS-W composite powder increases gradually with the decrease of solution concentration, and Fig. 7 shows that the number of larger particles in the

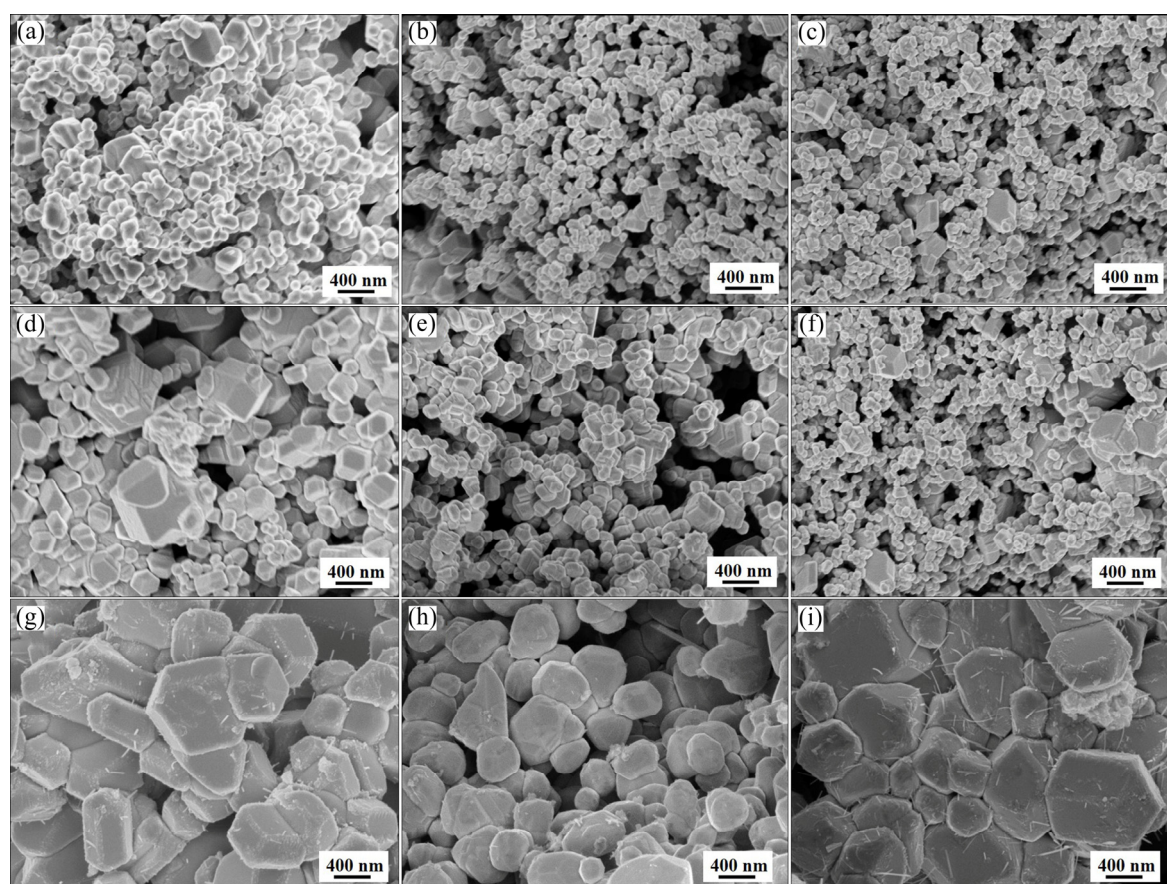


Fig. 6 FE-SEM images of carbothermal reduction products of ODS-W composite powders: (a) W–La₂O₃, 0.4 g/mL; (b) W–CeO₂, 0.4 g/mL; (c) W–Y₂O₃, 0.4 g/mL; (d) W–La₂O₃, 0.2 g/mL; (e) W–CeO₂, 0.2 g/mL; (f) W–Y₂O₃, 0.2 g/mL; (g) W–La₂O₃, 0.02 g/mL; (h) W–CeO₂, 0.02 g/mL; (i) W–Y₂O₃, 0.02 g/mL

Table 4 Average powder size of carbothermal reduction products of ODS-W under different conditions

Alloy composition	Solution concentration/(g·mL ⁻¹)	Average powder size/nm
W	–	108
W–La ₂ O ₃	0.4	144
W–La ₂ O ₃	0.2	232
W–La ₂ O ₃	0.02	1017
W–CeO ₂	0.4	111
W–CeO ₂	0.2	195
W–CeO ₂	0.02	599
W–Y ₂ O ₃	0.4	120
W–Y ₂ O ₃	0.2	211
W–Y ₂ O ₃	0.02	801

product also increases gradually. When the solution concentration is high (0.4 g/mL), the grain size distribution of the product is relatively uniform, and there are only a few large grains in the product; when the solution concentration is medium

(0.2 g/mL), the grain size distribution of the product becomes more inhomogeneous, and the number of large grains begins to increase; when the concentration is low (0.02 g/mL), there are many large particles in the reduction product, and the overall grain size becomes large. The possible reason may be that as the concentration of solution is lower, the number of composite oxide core is larger, and thus more large grains are produced. It can also be seen that the grain growth of La₂O₃ doped WO₃ is more obvious than that doped with CeO₂ and Y₂O₃ at the same solution concentration. At the same time, there is almost no change in the grain size of products before and after hydrogen reduction.

Tables 6 and 7 show the residual carbon content of products obtained by deep hydrogen reduction of ODS-Mo and ODS-W under different conditions, respectively. The results indicate that the residual carbon contents of final products are all controlled at 0.023–0.026 and 0.022–0.027 wt.%, respectively. Therefore, the residual carbon contents

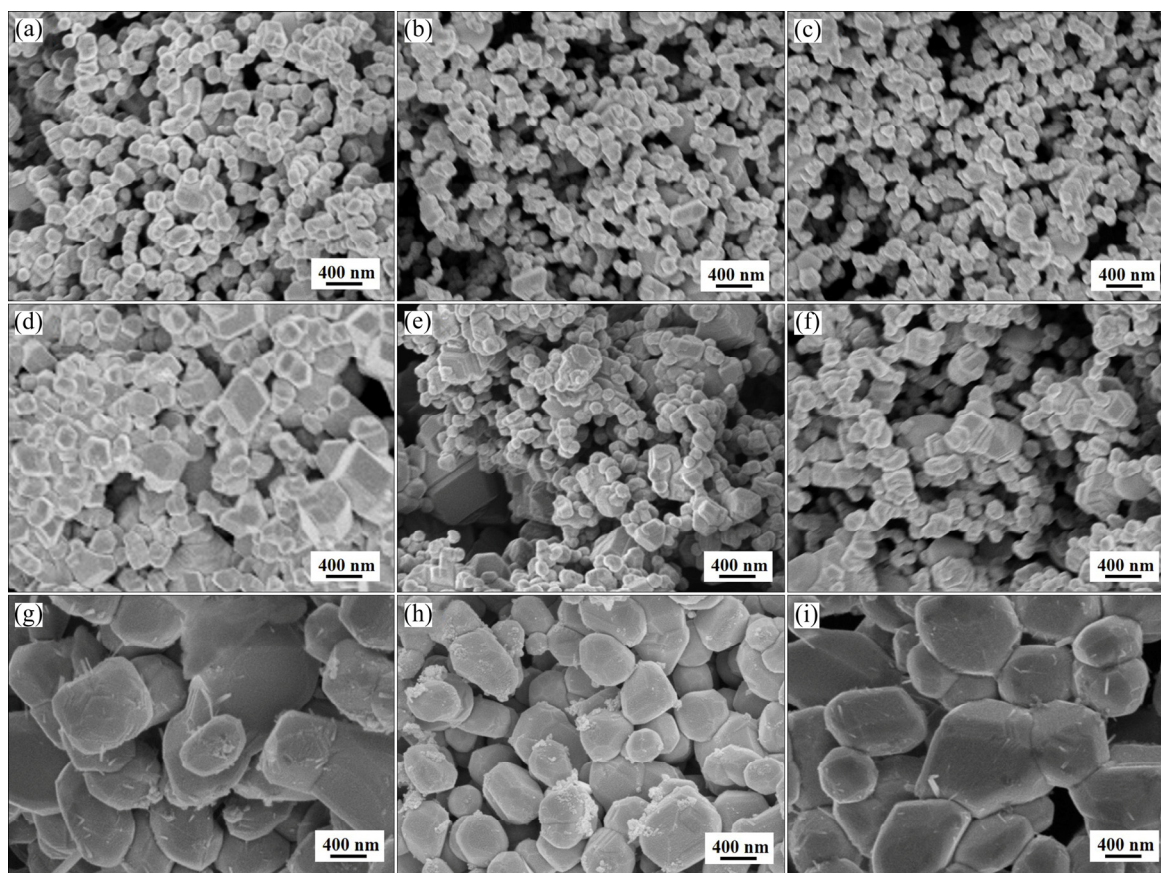


Fig. 7 FE-SEM images of final products obtained by deep hydrogen reduction of ODS-W composite powders: (a) W–La₂O₃, 0.4 g/mL; (b) W–CeO₂, 0.4 g/mL; (c) W–Y₂O₃, 0.4 g/mL; (d) W–La₂O₃, 0.2 g/mL; (e) W–CeO₂, 0.2 g/mL; (f) W–Y₂O₃, 0.2 g/mL; (g) W–La₂O₃, 0.02 g/mL; (h) W–CeO₂, 0.02 g/mL; (i) W–Y₂O₃, 0.02 g/mL

Table 5 Average powder size of deep hydrogen reduction products of ODS-W under different conditions

Alloy composition	Solution concentration/(g·mL ⁻¹)	Average powder size/nm
W	–	110
W–La ₂ O ₃	0.4	146
W–La ₂ O ₃	0.2	235
W–La ₂ O ₃	0.02	1023
W–CeO ₂	0.4	112
W–CeO ₂	0.2	199
W–CeO ₂	0.02	608
W–Y ₂ O ₃	0.4	122
W–Y ₂ O ₃	0.2	214
W–Y ₂ O ₃	0.02	807

Table 6 Residual carbon content of products obtained by deep hydrogen reduction of ODS-Mo under different conditions

Alloy composition	Solution concentration/(g·mL ⁻¹)	Residual C content/wt. %
Mo–La ₂ O ₃	0.4	0.023
Mo–La ₂ O ₃	0.2	0.024
Mo–La ₂ O ₃	0.02	0.023
Mo–CeO ₂	0.4	0.025
Mo–CeO ₂	0.2	0.023
Mo–CeO ₂	0.02	0.024
Mo–Y ₂ O ₃	0.4	0.023
Mo–Y ₂ O ₃	0.2	0.026
Mo–Y ₂ O ₃	0.02	0.025

Table 7 Residual carbon content of products obtained by deep hydrogen reduction of ODS-W under different conditions

Alloy composition	Solution concentration/(g·mL ⁻¹)	Residual C content/wt. %
W–La ₂ O ₃	0.4	0.022
W–La ₂ O ₃	0.2	0.025
W–La ₂ O ₃	0.02	0.026
W–CeO ₂	0.4	0.026
W–CeO ₂	0.2	0.024
W–CeO ₂	0.02	0.025
W–Y ₂ O ₃	0.4	0.027
W–Y ₂ O ₃	0.2	0.023
W–Y ₂ O ₃	0.02	0.026

of ODS-Mo and ODS-W powders are almost unchanged with the types of rare earth oxides and solution concentration, which maintain at a relatively low level. In addition, the residual carbon content of ODS-Mo powder is basically consistent with that of ODS-W powder.

3.3 TEM image analysis of ultra/nano rare earth oxides doped W (Mo) powders

The TEM images of the products obtained by carbothermal reduction of La₂O₃ doped WO₃ and their EDS mapping results are shown in Figs. 8(a–d). It can be seen that elements W, La and O are concentrated in different regions. Meanwhile, it is also shown that the distribution of W element is uniform in the area enriched in lanthanum oxide, which indicates the product may be the W–La–O ternary compounds. Subsequently, further EDS results of three different points in TEM images are shown in Figs. 8(e–g). From Fig. 8(g), it can be seen that Point C is mainly W grain. However, as shown in Figs. 8(e, f), Points A and B mainly include elements La, O and W, indicating the possibility of the existence of W–La–O ternary compounds. Since La–W–O phase includes La₂W₃O₁₂, La₆WO₁₂, La₆W₂O₁₅, La₄W₃O₁₅ etc, it is necessary to further verify the specific phase composition of La–W–O ternary compounds. The HRTEM image analysis and SAED pattern in different points of the products obtained by carbothermal reduction of La₂O₃ doped WO₃ are shown in Fig. 9, from which the distribution states of W and La₂O₃ can be seen, and meanwhile, the existence of La₂WO₆ is also proven. The SAED pattern and HRTEM image of Point C (Fig. 8(a)) are presented in Figs. 9(b, d), respectively, where the lattice spacing corresponds to (110) plane of W. Moreover, Figs. 9(a, c) show the SAED pattern and HRTEM image of Point B (Fig. 8(a)), respectively, and the lattice spacing corresponds to (431) plane of La₂O₃. Furthermore, the spacing lattice of SAED pattern and HRTEM image of Point A (Fig. 8(a)) corresponds to (220) and (004) planes of La₂WO₆, as shown in Fig. 9(e). Through the HRTEM image in Fig. 9(e), we also find the existence of La₂WO₆ near W, which is consistent with the energy spectrum analysis results, as shown in Figs. 8(a–d). The previous investigations also indicated that ternary compounds of La₂WO₆, Ce₂WO₆ and Y₂WO₆ could be formed at 1000–1400 °C [26–33]. HE et al [30]

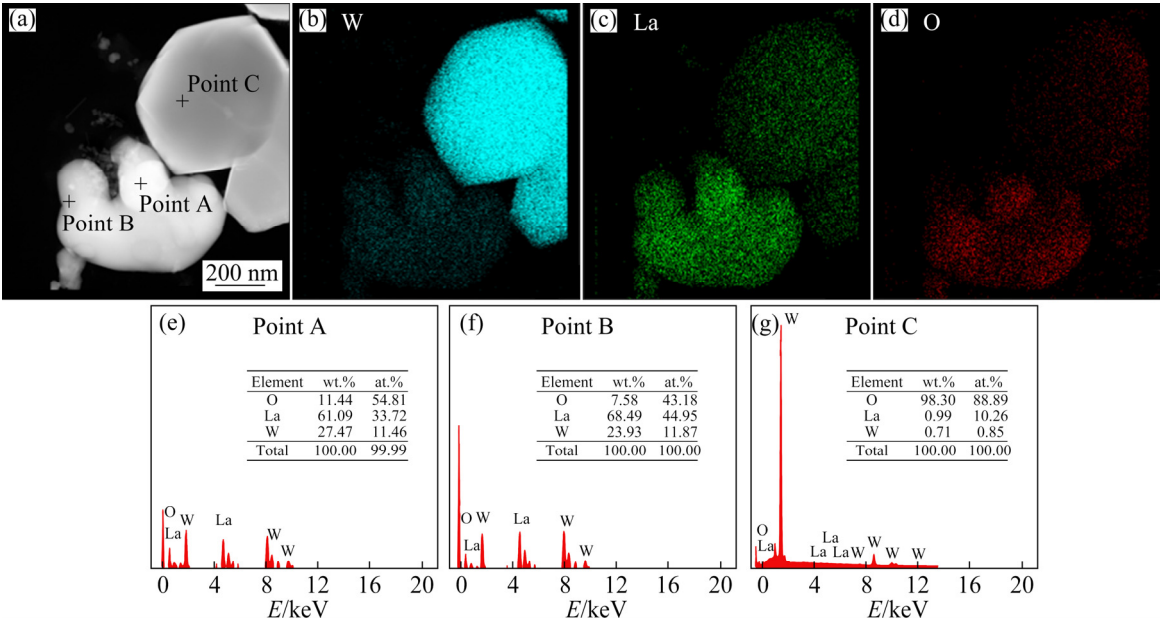


Fig. 8 TEM image (a) of products obtained by carbothermal reduction of La_2O_3 doped WO_3 , EDS mapping results (b–d), and EDS spectra of three Points A (e), B (f) and C (g)

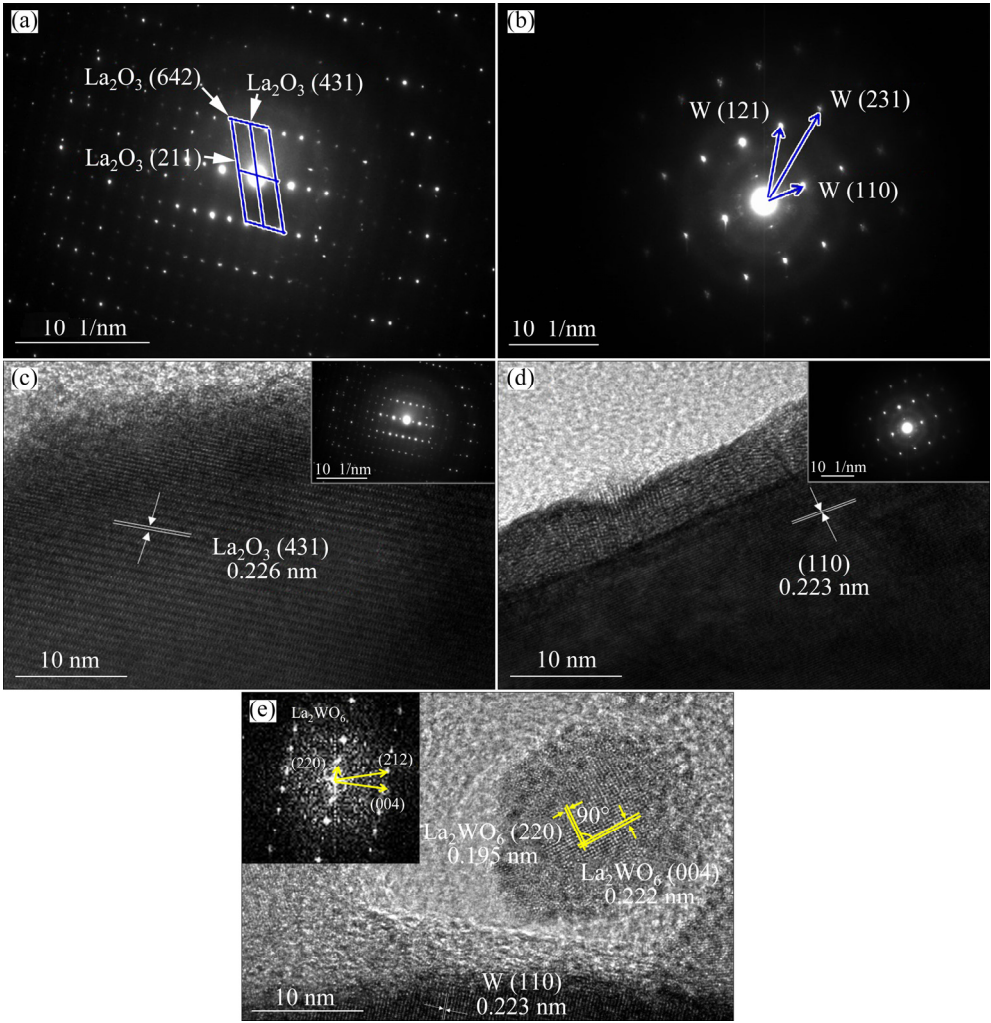


Fig. 9 HRTEM image and SAED pattern of different points in Fig. 8(a): (a) SAED pattern of Point B; (b) SAED pattern of Point C; (c) HRTEM image of Point B; (d) HRTEM image of Point C; (e) HRTEM image and SAED pattern of Point A

reported that WO_3 and Y_2O_3 could react to form Y_2WO_6 at 800 °C in hydrogen atmosphere. HUANG et al [31] found that Y_2WO_6 could be also formed at the temperatures as low as 750 °C. WANG et al [32] showed the possibility of the formation of different Y-tungstates during chemical synthesis at room temperatures. Hence, through the above analyses, we can infer that these ternary compounds can be formed under the current experimental conditions.

The TEM images and corresponding EDS results of the products obtained by carbothermal reduction of La_2O_3 doped MoO_3 are shown in Figs. 10(a–f). It is shown that the products are mainly Mo particles, but it is difficult to find the existence of ternary compound composed of Mo,

La and O. Furthermore, SAED pattern and HRTEM image of the product are presented in Figs. 10(g, h), where the lattice spacing corresponds to $(21\bar{1})$ plane of Mo. Therefore, the existence of a substance similar to La_2MoO_6 in Mo– La_2O_3 powder is not found, which proves that the formation of La_2MoO_6 is almost impossible under the current experimental condition. This is mainly because MoO_3 reacts with carbon black at 600 °C to generate MoO_2 [22], while MoO_2 and La_2O_3 can not react to form La_2MoO_6 at a lower temperature [27].

Under the standard condition ($1.01 \times 10^5 \text{ Pa}$), the required reaction temperature between La_2WO_6 and carbon black is 1280 °C which is higher than the experimental temperature. Meanwhile, relative to the reduction of La_2WO_6 (as shown in Eq. (1)), it

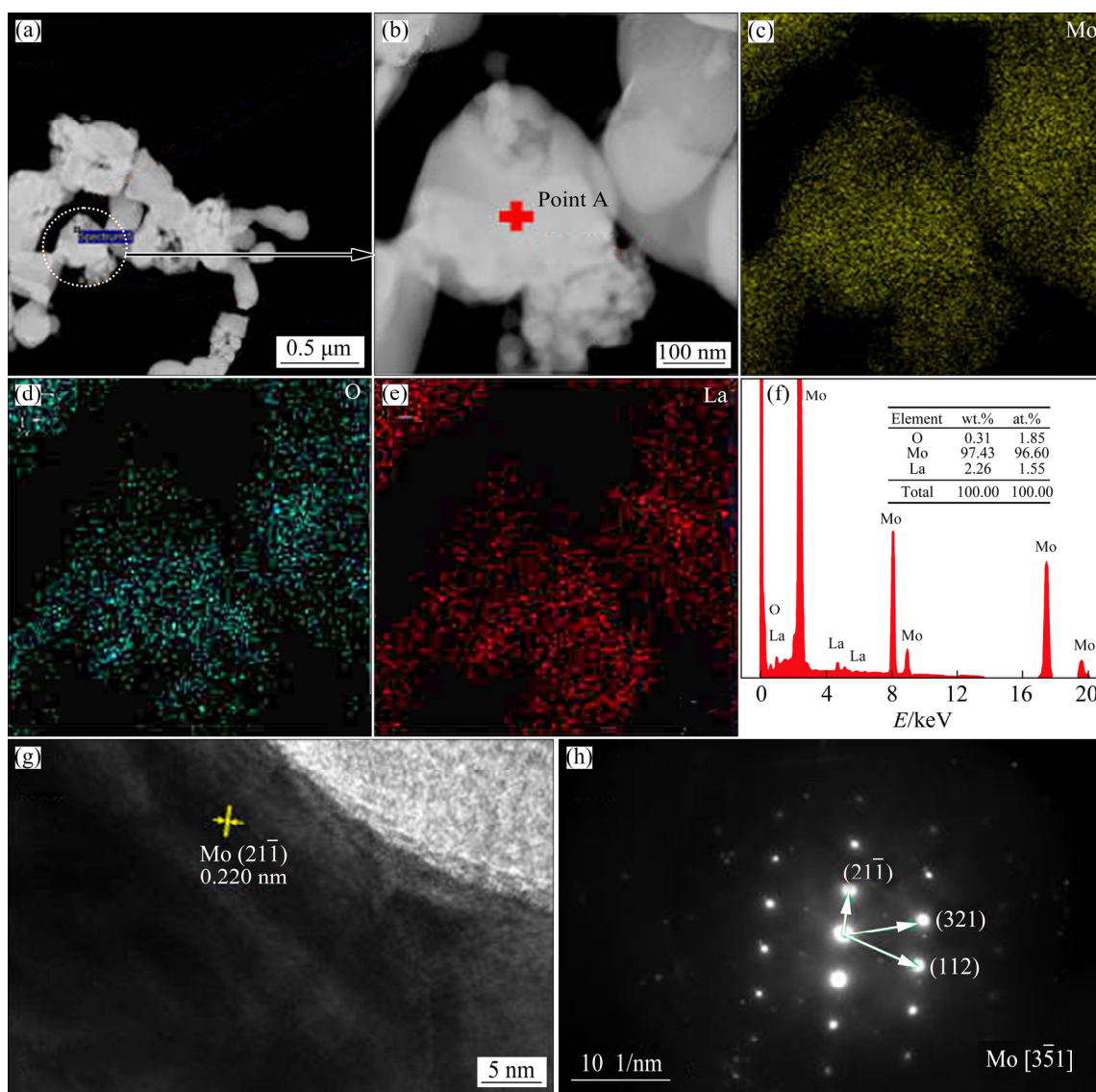
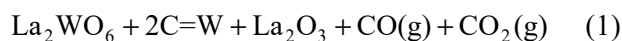


Fig. 10 TEM images of products obtained by carbothermal reduction of La_2O_3 doped MoO_3 (a, b); EDS mapping results (c–e) of (b); EDS spectrum of Point A (f); HRTEM image (g) and corresponding SAED pattern (h)

is easier to reduce WO_3 to form W, owing to the deficient addition of carbon black. Therefore, a certain number of La_2WO_6 can still be found in the final reduction products.



According to the equation (as given by Eq. (2)) of lattice mismatch degree proposed by BRAMFITT [33], the related two-dimensional lattice mismatch degree between W and La_2WO_6 , W and Ce_2WO_6 , W and Y_2WO_6 are calculated, respectively. In this study, the required lattice parameters are from W (PDF #04-0806, BCC, $Im\bar{3}m$ [229], $a=3.164 \text{ \AA}$), La_2WO_6 (PDF #27-0265, Tetragonal, $a=b=5.512 \text{ \AA}$, $c=8.88 \text{ \AA}$), Ce_2WO_6 (PDF #30-0313, Tetragonal, $a=b=5.469 \text{ \AA}$, $c=8.79 \text{ \AA}$), Y_2WO_6 (PDF #23-1489, Orthorhombic, $a=8.591 \text{ \AA}$, $b=20.84 \text{ \AA}$, $c=5.233 \text{ \AA}$), respectively. The lattice mismatch degree between the low exponential crystal planes (100), (110) and (111) of $\text{La}_2\text{WO}_6/\text{W}$ interfaces, (100), (110) and (111) of $\text{Ce}_2\text{WO}_6/\text{W}$ interfaces as well as (100), (121) and (012) of $\text{Y}_2\text{WO}_6/\text{W}$ interfaces can be calculated. The mismatch degrees of $\text{La}_2\text{WO}_6/\text{W}$, $\text{Ce}_2\text{WO}_6/\text{W}$ and $\text{Y}_2\text{WO}_6/\text{W}$ interfaces are 8.94%, 12.15% and 9.63%, respectively, which are all less than 13%. The misfit between the La_2WO_6 and W planes (8.94%) is the smallest. A smaller misfit leads to a weaker misfit strain around the particles, and thus, the resistance of W grains growing along a specific interface direction is reduced, which makes the grain larger. In addition, from Figs. 8 and 9, the La_2WO_6 particles are uniformly distributed in the W matrix, and semi-coherent with W lattice. In addition, YAR et al [29] found the appearance of Ce_2WO_6 around tungsten and tungsten oxide whose crystal structure was similar to that of La_2WO_6 . Recently, HE et al [30] also observed the Y_2WO_6 was evenly distributed around tungsten powder. Therefore, La_2WO_6 (Ce_2WO_6 or Y_2WO_6) particles can be regarded as heterogeneous nucleating cores for W, which can promote its nucleation and growth. At the same time, the smaller the mismatch degree between composite oxides and W lattice is, the more obvious the promotion effect on W crystal growth is [33]. Therefore, at the same solution concentration, the grain size of W- La_2O_3 alloy powder is the largest, followed by W- Y_2O_3 , while W- CeO_2 alloy powder is the smallest. With the decrease of solution concentration, the number of

composite oxide cores is larger, and thus more large W grains are produced.

$$\delta_{(hkl)_s}^{(hkl)_n} = \sum_{i=1}^3 \frac{|(d[uvw]_s^{\cos\theta}) - d[uvw]_n^i|}{d[uvw]_n^i} \bigg/ 3 \times 100\% \quad (2)$$

where δ is the lattice mismatch between two crystal planes; $(hkl)_s$ and $(hkl)_n$ are low-index planes of the substrate and nucleated solid, respectively; $[uvw]_s$ and $[uvw]_n$ are low-index directions in $(hkl)_s$ and $(hkl)_n$, respectively; d is the interatomic spacing; θ is the angle between $[uvw]_s$ and $[uvw]_n$.

In Refs. [15,34,35], the preparation process of W- Y_2O_3 composite powder with nano grain size was mainly composed of two stages: precursor powder preparation and two-stage low-temperature hydrogen reduction. The precursor powders were mainly prepared by freeze-drying [34,35] or sol-gel methods [15] with the raw materials of ammonium metatungstate (AMT) and yttrium nitrate hexahydrate ($\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$). Then, the two-stage low-temperature hydrogen reduction process was carried out at 600 and 800 °C. Within this low temperature range, W oxide and Y_2O_3 did not react, and the uniformly distributed Y_2O_3 particles isolated W grains well, which made the growth of W grains more difficult [15,34,35]. However, in this study, ODS-W powder is mainly prepared by the combination of carbothermal reduction and hydrogen reduction. Especially, in the carbothermal reduction stage, due to the high temperature of 1050–1150 °C, tungsten oxide and rare earth oxides may react to form composite oxides which can be used as the heterogeneous nucleation of W. Therefore, it is considered that the presence of rare earth composite oxides promotes the growth of W grains.

3.4 Comparative analysis of reduction process between ultrafine ODS-Mo and ODS-W alloy powders

In the overall carbothermal reduction process of ODS-Mo composite powder, due to the lower reduction temperature from MoO_3 to MoO_2 (500–600 °C), it is difficult for MoO_3 to form composite oxides by reacting with the rare earth oxides before being reduced [1]. Meanwhile, the MoO_2 formed by reduction is unable to form composite oxides with rare earth oxides, so rare earth oxides do not participate in the carbothermal reduction process of MoO_3 , and only carbon black

plays the role of dispersed nucleation [1]. Therefore, there are no obvious changes in the morphology and grain size after carbothermal reduction products of doped or undoped MoO_3 . However, for WO_3 doped with rare earth oxide, WO_3 reacts with rare earth oxide to form composite oxide (La_2WO_6) before it is reduced by carbon black due to its high reduction temperature (953–1076 °C) [26]. After that, the composite oxide can not be reduced by carbon black at the temperature lower than 1280 °C, which can be used as the cores for the heterogeneous nucleation and growth of W [36]. The experimental results also show that when the concentration is low, the grain growth is more obvious. This may be because in the case of a lower solution concentration, the number of oxide core becomes larger, which makes more product particles grow [37].

3.5 Obtained ODS-Mo and ODS-W prepared by pure hydrogen reduction

The FE-SEM images of ODS-Mo powders

obtained by pure hydrogen reduction are shown in Fig. 11, from which it can be seen that the products have polyhedral shape and their grain sizes maintain at 3–4 μm . Meanwhile, it is shown that the average grain sizes of the products almost do not change with the change of rare earth oxide type and solution concentration. In addition, Fig. 12 displays the FE-SEM images of ODS-W powders obtained by pure hydrogen reduction. It is shown that the average sizes of product all maintain at about 4 μm .

Overall, the average grain sizes of ODS-Mo and ODS-W powders obtained by pure hydrogen reduction are relatively large. However, the particle sizes of the powders obtained by the combination of carbothermal reduction and hydrogen reduction are relatively small and have good dispersion. During the carbothermal reduction (carbon deficient) process, fine carbon black is wrapped around the oxide to provide a large number of nucleation points, and results in the formation of a large number of dispersed MoO_2 (WO_2)/Mo (W) nuclei [18,21,23,25,26]. Compared with pure

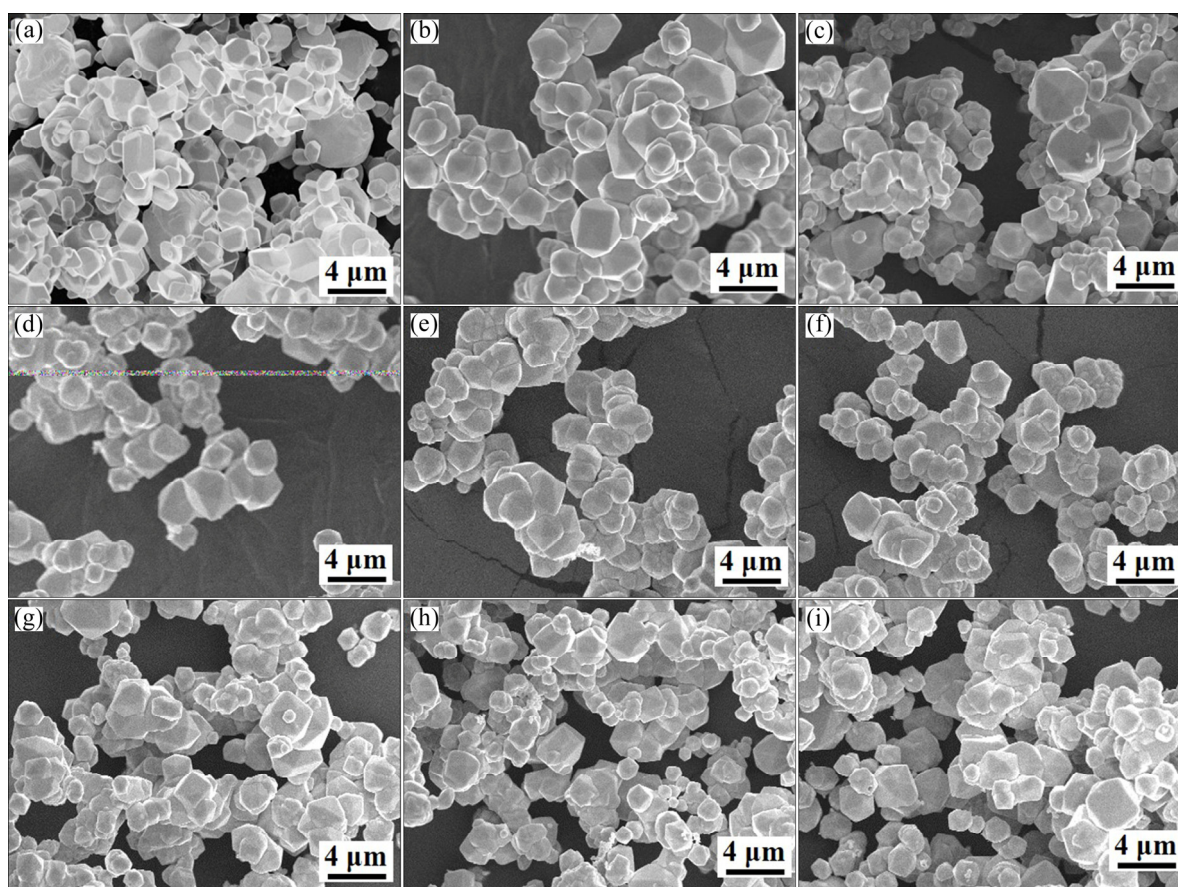


Fig. 11 FE-SEM images of final products obtained by deep hydrogen reduction of ODS-Mo composite powders: (a) Mo- La_2O_3 , 0.4 g/mL; (b) Mo- La_2O_3 , 0.2 g/mL; (c) Mo- La_2O_3 , 0.02 g/mL; (d) Mo- CeO_2 , 0.4 g/mL; (e) Mo- CeO_2 , 0.2 g/mL; (f) Mo- CeO_2 , 0.02 g/mL; (g) Mo- Y_2O_3 , 0.4 g/mL; (h) Mo- Y_2O_3 , 0.2 g/mL; (i) Mo- Y_2O_3 , 0.02 g/mL

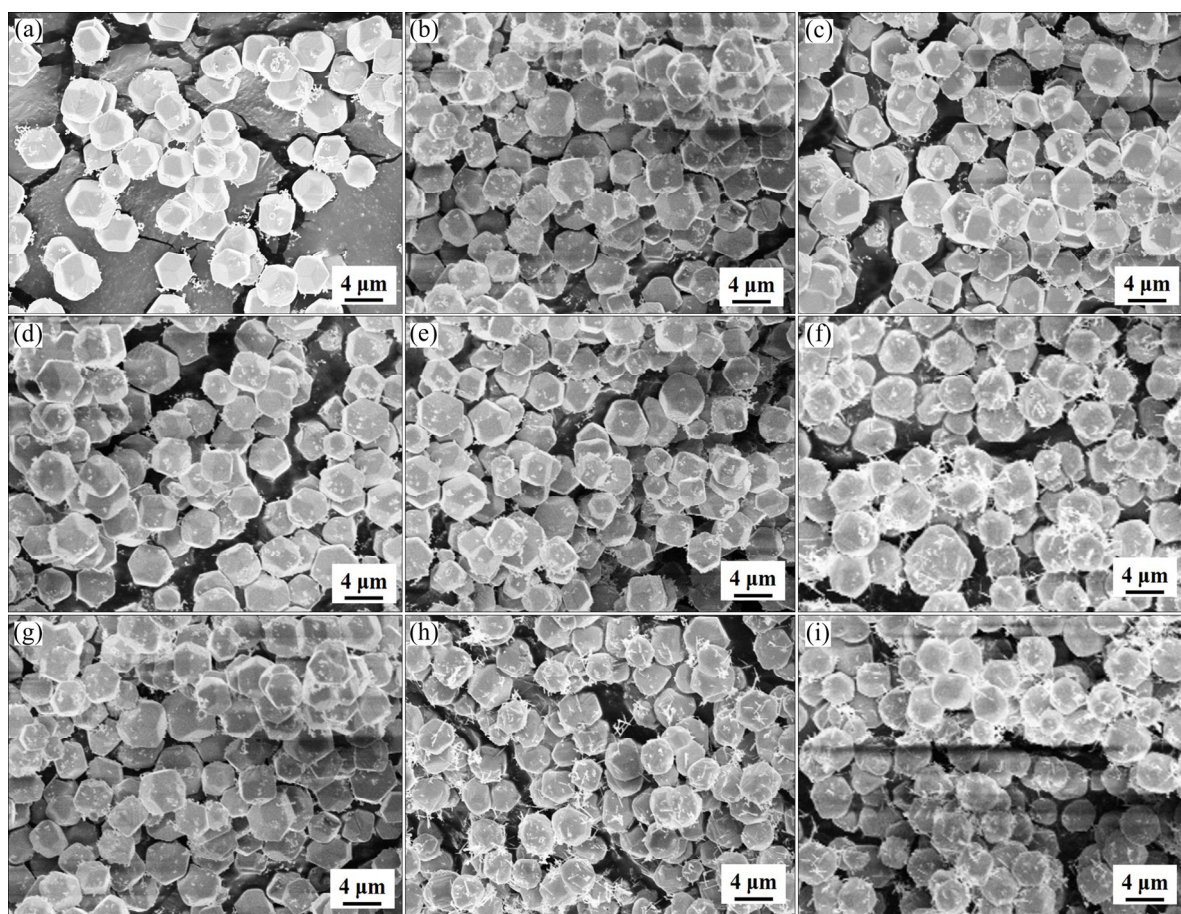


Fig. 12 FE-SEM images of ODS-W powder obtained by pure hydrogen reduction: (a) W-La₂O₃, 0.4 g/mL; (b) W-La₂O₃, 0.2 g/mL; (c) W-La₂O₃, 0.02 g/mL; (d) W-CeO₂, 0.4 g/mL; (e) W-CeO₂, 0.2 g/mL; (f) W-CeO₂, 0.02 g/mL; (g) W-Y₂O₃, 0.4 g/mL; (h) W-Y₂O₃, 0.2 g/mL; (i) W-Y₂O₃, 0.02 g/mL

hydrogen reduction, there is no gaseous transport phase such as MoO₂(OH)₂ or WO₂(OH)₂ in the carbothermal reduction process, which avoids the growth of products through chemical vapor transport (CVT) mechanism. Subsequently, during the deep hydrogen reduction process, the remaining oxygen atoms in the pre-reduction product is removed by hydrogen. At the same time, due to the weak CVT mechanism resulting from the small content of remaining MoO₂(WO₂), the grain size of final product hardly grows.

4 Conclusions

(1) The rare earth oxide type and solution concentration of additive have different effects on the grain size of ODS-Mo and ODS-W alloy powders.

(2) For preparing ODS-W alloy powder, the concentration of rare-earth-containing solution and the types of rare earth oxide affect the grain size of

the reduction product.

(3) The higher the solution concentration is, the smaller the grain size of the product after carbothermal reduction and hydrogen reduction is.

(4) In the same solution concentration, the grain sizes of the reduction products doped with La₂O₃ and Y₂O₃ are larger, while the grain size of the reduction products doped with CeO₂ is smaller.

Acknowledgments

The authors gratefully acknowledge financial support from the National Natural Science Foundation of China (No. 51734002).

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不同稀土氧化物对 ODS-W 和 ODS-Mo 合金粉末形貌和尺寸的影响

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摘 要: 采用喷雾法(固液混合法)结合炭黑和氢气还原, 成功合成含有不同类型纳米氧化物粒子的超细 Mo(ODS-Mo)和 W(ODS-W)粉末。结果表明, 溶液浓度和稀土氧化物种类对 ODS-Mo 合金粉末的晶粒尺寸没有影响, 但对 ODS-W 合金粉末的晶粒尺寸有明显的影响。所用稀土溶液浓度越高, ODS-W 合金粉末的平均晶粒尺寸越小。此外, 与掺杂 CeO₂ 相比, 掺杂 La₂O₃ 和 Y₂O₃ 的 WO₃ 的还原产物晶粒尺寸相对较大。与未掺杂情况相比, ODS-Mo 合金粉末的晶粒尺寸几乎没有变化, 而 ODS-W 合金粉末的晶粒尺寸变大。这可能是由于钨氧化物与稀土氧化物反应形成的复合氧化物(如 La₂WO₆)的出现, 促进 ODS-W 还原过程中钨晶粒的异相成核和长大; 而在 ODS-Mo 的还原过程中, 不存在由钼和稀土氧化物组成的复合氧化物。

关键词: 粒度; 稀土氧化物; 氧化物弥散强化合金; 钨; 钼

(Edited by Bing YANG)