Influence of Yttrium Addition on the Reduction Property of Tungsten Oxide Prepared via Wet Chemical Method

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Abstract

W–Y₂O₃ composite nanopowders prepared via wet chemical method exhibit unique morphologies and microstructures. The yttrium addition during chemical reaction process affects not only the composition of tungsten acid hydrate precursors, but also the reduction property of tungsten oxide transformed from precursors. In this study, the morphology evolution of the samples with and without yttrium during reduction process has been studied, and it is found that the addition of yttrium can exert a strong influence on the reduction route of tungsten oxide and the final morphology of tungsten particles. The cause of the difference of reduction route and tungsten particle morphology is also analyzed. It is suggested that the composition of the samples with yttrium at the beginning of reduction is pure cubic system WO₃(c-WO₃), and the c-WO₃ particles have c-WO₃ whiskers attached to the surface. This kind of whiskers is essential for c-WO₃ to be reduced directly to tungsten and also helpful to obtain W–Y₂O₃ powders with small size and good uniformity.

Keywords W–Y₂O₃ nanopowders · Wet chemical method · Reduction property

1 Introduction

Tungsten is a common refractory metal, which has many extraordinary properties, and has been used in various industrial fields, such as machining, heating and imaging [1–10]. Tungsten-based materials are usually produced by powder metallurgy technology due to their high melting temperature [11]; however, the product obtained after sintering process always has a series of vital defect, such as low density, large tungsten grain size and poor mechanical properties, which limits the use of tungsten material [12–17]. The second-phase dispersion strengthening technology developed these years provides a feasible method to improve the properties of

sintered tungsten-based material through increasing sintering density and refining grains and broadens its application field [18–27]. According to previous researchers, Y₂O₃ has been considered to be the best oxide dispersion phase which could significantly improve the sintering density and refine the grain size of tungsten [2, 3]. Thus, the preparation of W–Y₂O₃ composite powders becomes essential.

W–Y₂O₃ composite powders could be obtained through various methods. Wet chemical method has been used by many researchers recently in preparation of various composite high-temperature alloy materials [28–37] and is an effective method for preparation of nanosized W–Y₂O₃ powders. Since the samples synthesized by this method are produced by bottom-up process, the tungsten particles possess nanometer-scale grain size, high purity and excellent uniformity. In the meantime, nanosized Y₂O₃ particles also uniformly disperse around tungsten particles theoretically. An effective chemical method to prepare W–Y₂O₃ composite nanopowders has been introduced recently [38–44] and been used as reference in our previous research. In this method, tungsten oxide hydrate precursor with yttrium was fabricated firstly and then the precursor was reduced to W–Y₂O₃ nanopowders under hydrogen atmosphere. The minimal grain size of the reduced tungsten powders could be dozens of

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nanometers, while Y_2O_3 particles distributed evenly around tungsten powders.

In our previous study, we have found that the addition of yttrium could change the composition of the precursor, leading to the formation of white tungsten acid under specific reaction conditions [42–46]. This kind of precursor with yttrium could be reduced to $W-Y_2O_3$ composite nanopowders with small particle size, good uniformity and no bimodal structures. However, the formation mechanism of $W-Y_2O_3$ with good morphology still needs to be investigated, while the reduction process of the precursor also needs to be studied.

In this study, pure tungsten nanopowders and $W-Y_2O_3$ composite nanopowders were prepared by wet chemical method under same conditions. The morphology transformation of the two kinds of samples during reduction process was studied with aim of figuring out whether yttrium could affect the reduction route of tungsten oxide which was transformed from precursors. On top of that, a proper mechanism was also proposed to explain how the reduction property of the samples was affected by yttrium.

2 Experimental

The specific experimental details of chemical reaction were described in our previous work [42–46]. After chemical reaction, the collected precursors were reduced through a two-step process. The precursors were firstly heated at 500 °C under argon atmosphere for 1 h and then heated at 600 °C under pure hydrogen atmosphere. The samples were heated for different times at this temperature and then cooled down under a flow of pure argon gas. The heating rate and flow rate of argon and hydrogen gas during the reduction progress were also the same as our previous work [42–46].

Field emission scanning electron microscope (Hitachi, S4800), transmission electron microscope (JEOL, JEM-2100f) and X-ray powder diffractometer (Bruker D8 Advance) were used to analyze the morphology, crystal structures and phase composition of the powder samples, respectively.

3 Results and Discussion

Figure 1 shows the phase evolution of two kinds of powder precursors with and without yttrium during reduction process. It can be indicated from XRD results that the two samples seem to follow different reduction route during this process. The samples were all pure cubic system WO_3 (c- WO_3) at the first time (Fig. 1a). Then, after beginning the reduction process, the samples with yttrium transformed from c- WO_3 into α -W and β -W simultaneously and then the ratio of β -W decreased, which indicates the conversion into α -W under hydrogen atmosphere. As for samples without yttrium (Fig. 1b), the crystal system of the tungsten oxide before reduction was various. After 10 min of reduction, the phases of the samples had been changed completely into WO_2 , α -W and β -W. The ratio of both WO_2 and β -W decreased gradually with reduction lasting and turned into almost zero after 2-h reduction.

The morphology evolution during hydrogen reduction process of the samples with yttrium is shown in Fig. 2. Figure 2a shows the initial morphology of the sample at the beginning of hydrogen reduction after roasting at 500 °C for 1 h. It can be seen that there are some small cuboid particles with size less than 10 nm emerge from the surface of WO_3 matrix with relatively large size (Fig. 2a), and it could also be indicated from XRD result that the phase composition of the sample is only cubic system WO_3 (Fig. 1a). After the

Fig. 1 XRD patterns of phase change during hydrogen reduction of the samples **a** with yttrium, **b** without yttrium

Fig. 2 Morphology evolvement during hydrogen reduction process of the samples with yttrium

hydrogen reduction begins, the WO_3 matrix starts to contract which leads to the exposure of cuboid particles out of the surface (Fig. 2b). When the reduction process continues, the cuboid particles will also contract and finally disappear at 40 min after the start of reduction process (Fig. 2c, d). Then, it could be observed that the matrix decomposes into nanoparticles with an average size less than 10 nm, as shown in Fig. 1e. As reduction prolongs, the shape of the nanoparticles gets explicit with their size increasing gradually (Fig. 2f). The growth rate of nanoparticles tends to slow down after reduction for 2 h (Fig. 2g), and it could be observed that there will be no obvious change in size of the nanoparticles after reduction for 5 h (Fig. 2h).

As for samples without yttrium, the morphology evolution during reduction process is totally different. At the very beginning of reduction, the tungsten oxide particles have un-modified shape and the average size of approximately

50 nm (Fig. 3a). Then, some particles turn into square with relatively small size attached to their surface (Fig. 3b). The size of the square particles grows gradually, and the proportion of small particles reduces when the reduction proceeds (Fig. 3c, d). Subsequently, the square particles start to transform into un-modified particles with the increasing size, while the small particles vanish gradually (Fig. 3e–g). The growth of tungsten particles shows no sign of retardation even after 5 h of reduction (Fig. 3h).

The changes in average grain sizes of the two kinds of samples calculated by Scherrer's equation are shown in Fig. 4. It can be indicated that the average grain size of the samples with yttrium shows an asymmetrical U-shaped distribution over reduction time. With the increasing time of reduction, the average grain size decreases sharply at first and then increases slowly. As for the samples without yttrium, their average grain sizes keep increasing in general

Fig. 3 Morphology evolvement during hydrogen reduction process of the samples without yttrium

Fig. 4 Variation of the average grain size with reducing time of the two kinds of the samples calculated by Scherrer's equation

since the start of reduction, which differs a lot from the samples with yttrium.

Basing on the data and results above, it can be inferred that the difference of morphology evolution between two kinds of samples is caused by the existence of yttrium; thus, we further studied the evolution of the morphology at nanoscale in order to clarify the mechanism leading to this difference. Figure 5 shows the micromorphology evolution of the samples with yttrium obtained at different times after reduction began. At the beginning of reduction (Fig. 5a), the tungsten oxide particles have pretty large in size and quite a large quantity of columnar particles attached to their surface,

which is corresponding to Fig. 2a. This kind of columnar particle is proposed to be $c\text{-WO}_3$ whisker based on results of crystal phase analysis. As reduction proceeds, the $c\text{-WO}_3$ whiskers are reduced to tungsten which is prior to the reduction of $c\text{-WO}_3$ particles.

Figure 5b shows a whisker obtained at 30 min after reduction started, which is partly reduced. Then, large $c\text{-WO}_3$ particles are also reduced to tungsten particles with small sizes, as shown in Fig. 5c. In order to figure out whether there is any influence of hydrogen on the formation of $c\text{-WO}_3$ whiskers, the samples were heated in the same heating route under Ar atmosphere, and the result is shown in Fig. 5d. It can be seen that after heating at 600 °C for 4 h in Ar, the small cuboid particles, which are $c\text{-WO}_3$ whiskers, get more exposed out of the surface like the sample as shown in Fig. 2a, but there seems to be little change to the size of WO_3 matrix at all. Thus, it can be indicated that the formation of $c\text{-WO}_3$ whiskers in the samples with yttrium is only relevant to the temperature.

The schematic diagram in Fig. 6 illustrates the morphology evolution process of the samples with yttrium during reduction. For this kind of samples, their phase composition is $c\text{-WO}_3$ after heating for 1 h in argon atmosphere before hydrogen reduction. The $c\text{-WO}_3$ particles transformed from tungsten acid hydrate have $c\text{-WO}_3$ whiskers attached to their surface. During reduction process, the $c\text{-WO}_3$ whiskers are reduced firstly. The reason is that they have large specific surface area and more surface contacting with hydrogen. This causes a large amount of crevices in $c\text{-WO}_3$ particles, making them

Fig. 5 TEM images of the samples with yttrium obtained at different times: **a** 0 min, **b** 30 min, **c** 50 min after reduction started, **d** SEM image of sample with yttrium obtained at 4 h after heating at 600 °C under Ar atmosphere

Fig. 6 Diagrammatic sketch of transformation process of the samples with yttrium during reduction

easier to be reduced to tungsten directly. Also the crevices let tungsten oxide molecules on the surface of particles and inside the particles reduce almost simultaneously, retarding the growth and fusion of tungsten nanoparticles. The growth of newly formed tungsten nanoparticles is also inhibited by Y_2O_3 nanoparticles distributing uniformly around them, leading to small particle size and good uniformity of the reduced tungsten particles, which was discussed in our previous work [45]. Thus, it can be summarized that during preparation process of tungsten powders through wet chemical method, the influence of yttrium takes place in both chemical reaction process and hydrogen reduction process.

As for the samples without yttrium, their phase composition after heating in argon atmosphere is orthorhombic WO_3 rather than $c-WO_3$. Owing to the small specific surface area of large WO_3 particles, the reduction of tungsten oxide is less sufficient than the samples with yttrium. Consequently, WO_3 particles are reduced to WO_2 firstly, and then, WO_2 particles are reduced to tungsten. Meanwhile, the reduction of tungsten oxide molecules on the surface of the particles starts before the molecules inside the particles, and the growth and fusion of tungsten particles could not get restrained by Y_2O_3 nanoparticles during hydrogen reduction process, which leads to relatively larger particle size and worse uniformity.

Therefore, it can be deduced that the difference between the reduction routes of two kinds of the samples should be caused by the formation of $c-WO_3$ whisker that attached to the surface of $c-WO_3$ particles. The formation of this kind of whisker may be due to the effect of yttrium or the natural property of $c-WO_3$ formed under the effect of yttrium, which could still need to be researched. Yet, it is certain that the addition of yttrium can definitely influence a lot on the reduction property of tungsten oxide prepared via wet chemical method.

4 Conclusion

During the preparation process of tungsten nanoparticles via wet chemical method, the addition of yttrium can exert a strong influence on the reduction route of tungsten oxide and the ultimate morphology of tungsten particles. The phase composition of the samples with yttrium before reduction is cubic system WO_3 , and the $c-WO_3$ particles have $c-WO_3$ whiskers attached to their surface. During reduction process, these whiskers are reduced to tungsten firstly leaving many crevices in $c-WO_3$ particles, which increases their specific surface area and makes $c-WO_3$ reduce to tungsten directly. Also, the tungsten oxide molecules inside and on the surface of the particles could be reduced simultaneously, and the growth and fusion of tungsten particles could be inhibited by Y_2O_3 nanoparticles, leading to small particle size and good uniformity of the reduced tungsten particles. As for samples without yttrium, their phase composition is orthorhombic WO_3 rather than $c-WO_3$. During reduction process, because of the smaller specific surface area of WO_3 particles, their reduction is insufficient. Therefore, they are firstly reduced to WO_2 and then reduced to pure tungsten. Meanwhile, the reduction of tungsten oxide molecules occurs from the surface of particles to the interior, and the growth and fusion of tungsten particles could not get restrained by Y_2O_3 nanoparticles, which leads to relatively larger particle size and worse uniformity. The results in the present work are significantly helpful for the synthesis of various oxide-doping nanosized refractory metal powders.

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