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Recycling high density tungsten alloy powder by oxidation-reduction process①

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[Abstract] The processes of directly recycling high density tungsten alloy by oxidation-reduction technique were investigated. The particle size of recycled powder is fine, and the shape of powder particle is regular when the final reduction temperature is 850 ℃, in which the average size of the tungsten alloy particles reduced is about 1.5 μm. The average size of the alloy particles increase to 6 μm and 9 μm when increasing the reduction temperature to 900 ℃ and 950 ℃, respectively. However, if the reduction temperature is higher than 900 ℃, the surface feature of powder is complicated. Increasing reduction temperature from 900 ℃ to 950 ℃, the content of oxygen of recycled powder decreases from 0.2314% to 0.1700%, and powder particles grow slightly. It has been also found that the chemical composition of the recycled alloy powder is the same as the initial powder.

[Key words] tungsten alloy; oxidation-reduction process; recycle; saving environment
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1 INTRODUCTION

High density tungsten alloy is not only of high strength, good plasticity, machinability and weldability but also of good corrosion-resistance, oxidation-resistance, electric and heat conduction, good ability to being electroplated and absorb radioactive ray. It has been widely used in national defense and civil industry. However, the high density tungsten alloy produced by powder metallurgy method is mainly semi-finished product. It needs to be machined by 30%～50% allowance when used for parts making, which results in many machining scales and wastes of expensive tungsten alloy. Therefore, how to recycle the valuable machining scale of high density tungsten alloy becomes one of important problems of environmental protection and resource reutilization[1～3]. To date there have been a number of methods for recycling the high density tungsten alloy waste, such as melt-bath[4,5], hydrometallurgy[6], and electro-lytic[7] processes, etc. The materials recycled showed usable properties[8,9]. Unfortunately, no method could recycle the alloy waste without bringing about a second dust pollution. A simple method, direct oxidation-reduction method, is proposed to recycle the high density tungsten alloy waste.

2 EXPERIMENTAL

The test material used is scale of cutting W-Ni-Fe high density tungsten alloy. Its chemical composition tested by chemical solubilization method is listed in Table 1. Firstly, the alloy scale was washed by 5% NaOH and HCl solution, respectively, in order to clear away the greasy dirt and impurity on the alloy surface. And then, it was washed again with water. After dried, the alloy was ground and mixed homogeneously in a bifilar helix mixer. It became pure oxide by the static air oxidation process at 850, 900 and 950 ℃, respectively for 2 h in a well-shape furnace. Afterward, the oxidized powder was ground to 74 μm in a cylinder ball mill and finally hydrogenated at 850, 900 and 950 ℃, respectively for 2 h. The phase analyses of both oxidized and reduced powders were carried out on a D/MAX-RA X-ray diffractmeter. The microscopic characteristics of the reduced powder were examined by a JSM-5600LV scanning electron microscopy. A Micro-plus laser diffraction size gauge and TC-436 oxygen-nitrogen analyzer were used to measure the size and oxygen content of the powder, respectively.

Table 1 Chemical compositions of high density tungsten alloy (%)

W	Ni	Fe	Co	Mn
93.442	4.040	2.310	0.200	0.028

3 RESULTS AND DISCUSSION

3.1 Oxidation procedure

After oxidation, the dense high density tungsten alloy becomes loose fragile scale oxide and is lightly yellow in color. Fig. 1 shows the X-ray diffraction analysis result of the oxide formed by the high density tungsten alloy scale at oxidation temperature of 900 ℃ for 2 h. It is found that the oxide mainly consists of WO_3 and $(Ni, Fe)WO_4$ phases. Since $FeWO_4$ can dissolve in $NiWO_4$, only the peak of $NiWO_4$ appears in Fig. 1. There is no peak of $CoWO_4$ in Fig. 1 because the content of Co in the alloy is

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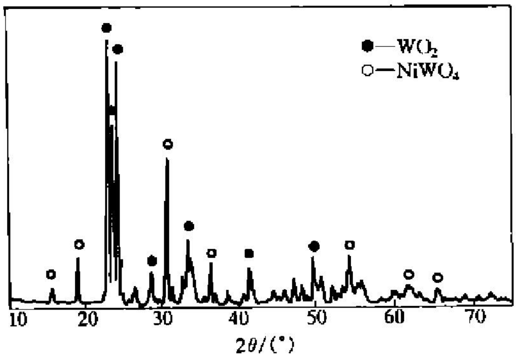

Fig. 1 XRD pattern of oxide of high density tungsten alloy scale fromed at 900 ℃ for 2 h

small in this test and it can not be found as previous article[10]. In addition, no single element phase of Fe_2O_3 or NiO exists, which means Fe and Ni elements in the high density tungsten alloy react chemically with firstly oxidized WO_3 to become to $FeWO_4$ and $NiWO_4$, rather than difficultly oxidized Fe_2O_3 and NiO. Furthermore, there is no any single elemental phase of metal, indicating that the tested alloy can be completely oxidized under this condition of oxidation, i. e. the temperature is 900 ℃ and the duration is 2 h.

The high density tungsten alloy can be also completely oxidized at different oxidation temperatures if temperatures are above 850 ℃ and the phases of formed oxides are the same, as shown in Fig. 2.

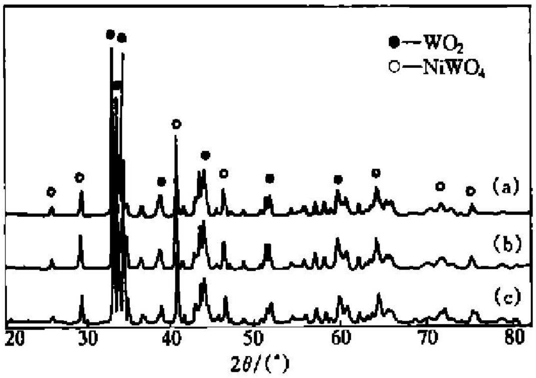

Fig. 2 XRD patterns of oxide formed by high density tungsten alloy scale at different temperatures
(a) —850 ℃; (b) —900 ℃; (c) —950 ℃

3. 2 Ball milling

The dry milling is adopted for ball milling. The ball material is high-strength hard alloy and its diameter is about 10 mm. The mass ratio of ball to powder is 10 to 1. After ball milling for 2 h, the oxide formed by the high density tungsten alloy scale can easily pass through the sifter hole of 74 μm in diameter. Obviously, it is of good fragility.

3. 3 Reduction

After hydrogenation, the oxide formed on the high density tungsten alloy scale is comprised of single substances of W, Ni and Fe, as shown in Fig. 3. Since the oxide of alloying powders is used for direct reduction, Fe phase solid dissolved with Ni can be formed as the joining phase of high dense alloy. Therefore, there are only the X-ray diffraction peaks of W and Fe appearing in Fig. 3. During the reduction of the oxide, the phase transition of WO_3 is $WO_3 \rightarrow WO_{2.90} \rightarrow WO_{2.72} \rightarrow WO_2 \rightarrow W$[11]. Accordingly, the phase transition of (Ni, Fe) WO_4 is that: (Ni, Fe) WO_4 is decomposed to Ni and $FeWO_4$ at the stage of $WO_{2.72} \rightarrow WO_2$; and $FeWO_4$ is reduced to be Fe and Ni at the stage of $WO_2 \rightarrow W$[5]. Fe and Ni forms solid solution phase distributing on the grain boundary of tungsten. Table 2 shows the chemical composition of the powder reduced at 900 ℃ for 2 h by the oxide of high density alloy. Compared with Table 1, it can be seen that the chemical compositions of reduced powder is almost consistent with the initial powder. From Fig. 4 it is found that the reduced alloy powders have the same phase composition at different temperatures of reduction. But their oxygen contents are different. For example, the oxygen content is 0.2314% after reducing at 900 ℃, while it decreases

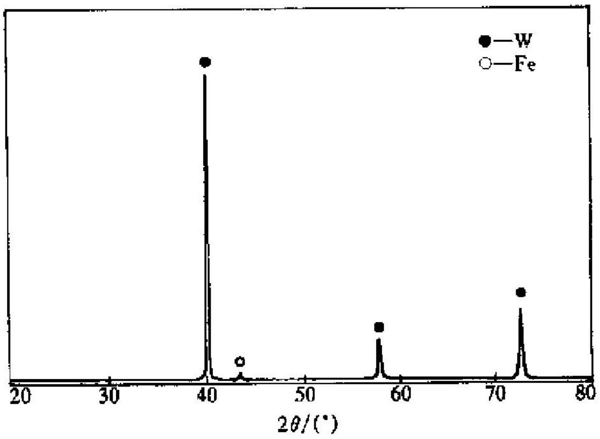

Fig. 3 XRD pattern of alloy powder hydrogenated by oxide of high density tungsten alloy scale at 900 ℃ for 2 h

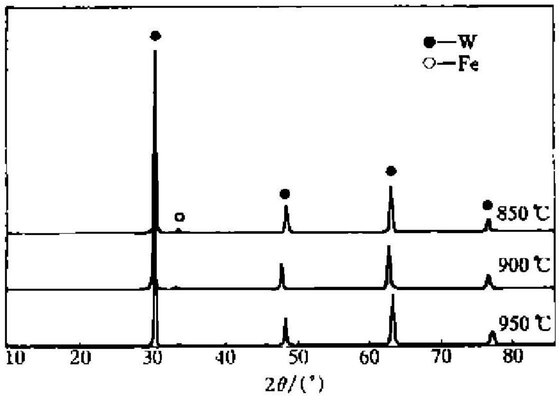

Fig. 4 XRD patterns of alloy powder hydrogenated by oxide of high density tungsten alloy scale at different reduction temperatures

Table 2 Compositions of reduced powder (%)

W	Ni	Fe	Co	Mn
93.071	4.110	2.520	0.270	0.029

to 0.1700% at 950 ℃. Thus the oxygen content of alloy powder can be decreased with increasing the reduction temperature. Fig. 5 shows the particle size of the hydrogenated alloy powder at 900 ℃, 950 ℃. Fig. 6 is the SEM micrographs of the alloy powder

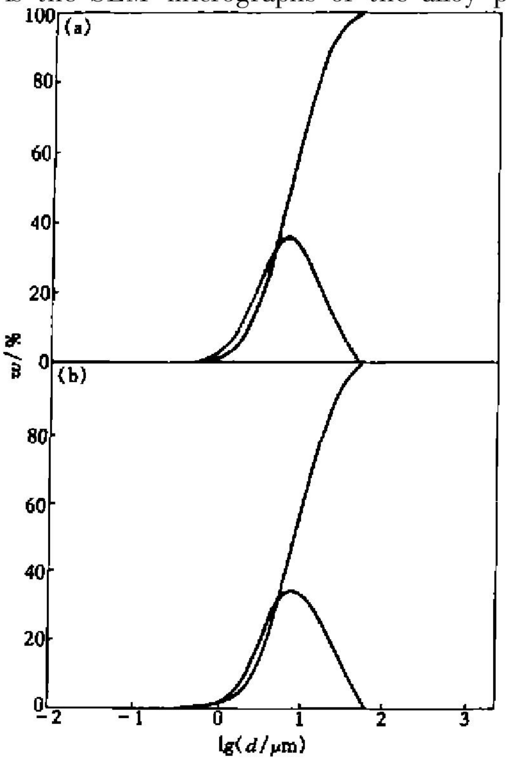

Fig. 5 Particle size distributions of hydrogenated alloy powder at 900 ℃ (a) and 950 ℃ (b)

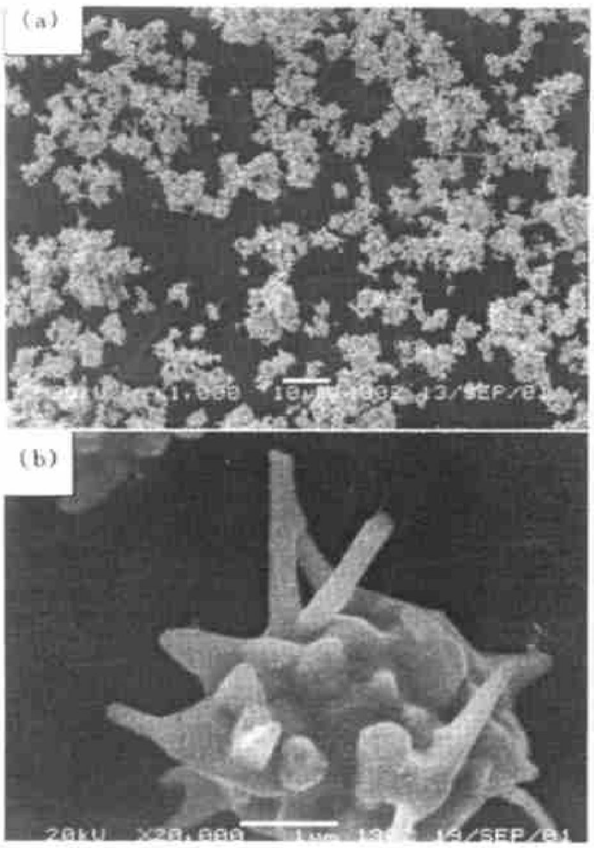

Fig. 6 SEM micrographs of alloy powder hydrogenated by oxide of high density tungsten alloy scale at 900 ℃ (a) and 950 ℃ (b) for 2 h

hydrogenated by the oxide of the high density tungsten alloy scale at 950 ℃ for 2 h. Obviously, the alloy powders are very fine. Comparison of Fig. 5(a) with Fig. 5(b) indicates that the particle size increases with the increase of the reduction temperature. In general, it is due to vaporization-deposition mechanism when the oxide is reduced[12]. The principle of this mechanism is that, since WO_3 is of easy volatilitzation at high temperature (> 400 ℃), the volatile WO_3 is reduced from vapor to solid and then deposed on the surface of the tungsten powder obtained by first reduction of the low valence WO_3, which leads to the growth of the tungsten powder.

Fig. 7 shows that the higher the reduction temperature, the larger the size of powder particle and

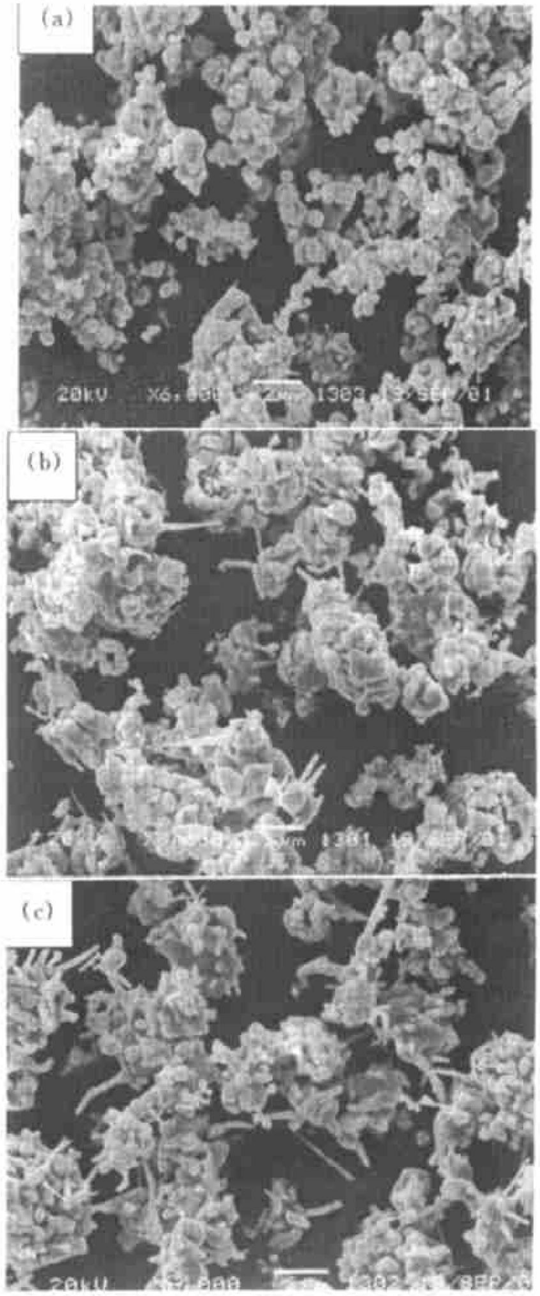

Fig. 7 SEM micrographs of alloy powder hydrogenated by oxide of high density tungsten alloy scale at 850 ℃ (a), 900 ℃ (b) and 950 ℃ for 2 h (c)

the more and thicker the root hairs However, after reduction at 850 ℃ for 2 h, the powder particle is regular ball or polyhedron and its size is about 1 μm, as shown in Fig. 7(a). It is seen that the powder particle is irregular in shape. Many root hairs directionally appear on the surface of powder particle and make the surface shape more complicated. In this case the particles loosely accumulate together. It is also found that the surface of powder particle is very smooth without any root hair formed by reduction at the higher temperature.

Fig. 8 shows the EDX spectra of the surface of powder particle and root hairs hydrogenated by the oxide of the high density tungsten alloy scale at 900 ℃ for 2 h, respectively. It can be seen that the powder particle has almost the same chemical composition as the root hairs, i. e., both of them are composed of W, Ni and Fe element. That means after reduction the Fe-Ni solid solution phase formed by joining phase homogeneously distributes on the grain boundary of tungsten. Therefore, the reduced powder particle has advantage over the element powder alloy in press shaping, sintering and mechanical.

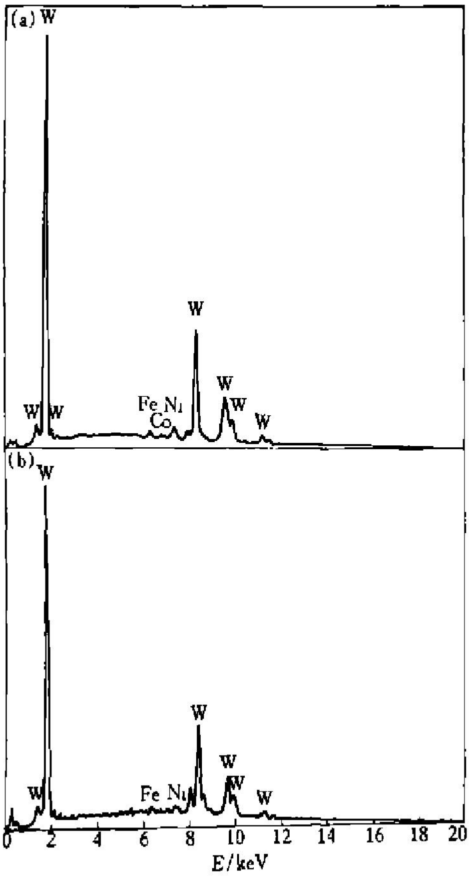

Fig. 8 EDX spectra of surface of powder particle (a) and root hairs (b) hydrogenated by oxide of high density tungsten alloy scale at 900 ℃ for 2 h

In addition, if the chemical composition of recycling tungsten powder need to be changed, $FeWO_4$, $NiWO_4$ or $CoWO_4$ may be added by wet or dry milling in the process of reduction.

4 CONCLUSIONS

1) The oxide formed by the high density tungsten alloy consists of WO_3, $(Fe, Ni)WO_4$, Fe and Ni without any refractory oxide.

2) The reduced powder particle consists of W, Ni and Fe. After reduction Fe and Ni forms the Fe-Ni solid solution phase which homogeneously distributes on the grain boundary of tungsten.

3) The surface shape of the reduced powder particle is irregular and complicated at high temperature. As the reduction temperature increases, the powder particle becomes larger and more and thicker root hairs directionally grow, resulting in more complicated surface shape of the powder particle.

4) Fine and regular shape powder alloy can be produced by decreasing the temperature of reduction.

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