

Review on the Effect of Alloying Elements on Hydrogen Reduction Process of Tungsten Oxides and Microstructures and Properties of Tungsten Related Materials

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Abstract: In the hydrogen reduction process of tungsten oxides, it is difficult to avoid some impurity elements (the characteristic alloying elements of Fe, Cr, Co and Ni, *etc.* from the reduction boats or furnace tubes) entering the powder. In addition, in order to improve the properties of tungsten related materials (W powder, WC powder, W-based alloys, and WC-based alloys, *etc.*), some alloying elements will also be pre-doped into ammonium paratungstate (APT) or tungsten oxides powders. It is obvious that the above alloying elements will affect the reduction process of tungsten oxides, and further affect the properties of tungsten related materials. In this paper, effects of alloying elements (including start state, content, existence state, distribution, *etc.*) on the hydrogen reduction process of tungsten oxides and the quality of tungsten powder have been summarized. The growth mechanisms of tungsten particles (grains) are classified by analyzing the chemical reaction evolution between alloying elements and tungsten oxides in the hydrogen reduction process, including forming $WO_x \cdot nMe_2O$ or Me_2O , non-volatile tungstates, volatile alloy oxides, and tungsten solid solution, *etc.*, and reduction effect of alloying elements to tungsten oxides. Effects of alloying elements on microstructures and properties of final powder metallurgical tungsten related materials are also proposed by analyzing strengthening, phase-transition, grain growth, and interface structure forming mechanisms, *etc.* It is expected that some theoretical assistance can be guided to the actual production of tungsten related materials and products.

Key words: alloying elements; tungsten oxides; hydrogen reduction; tungsten powders; grain morphology; tungsten related materials

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合金元素对氧化钨氢还原过程和钨相关材料的组织与性能影响研究综述

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摘要: 在氧化钨氢还原过程中, 很难避免一些杂质元素(例如还原舟皿或炉管中的 Fe, Cr, Co 和 Ni 等特征合金元素)进入粉末中; 另外, 为了改善钨相关材料(例如 W 粉末、WC 粉末、W 基合金及 WC 基合金等)的性能, 也会在仲钨酸铵(ammonium paratungstate, APT)或氧化钨粉末中预掺杂合金元素, 很明显这些合金元素会影响氧化钨的氢还原过程, 进一步也会影响钨相关材料的性能。详细综述了合金元素(包括其初始状态、含量、存在状态、分布等)对氧化钨氢还原过程和还原钨粉末性能的影响。通过分析氢还原过程中合金元素与氧化钨的化学反应过程(包括形成 $WO_x \cdot nMe_2O$ 或 Me_2O 、难挥发性钨酸盐、挥发性合金氧化物及钨固溶体等, 以及合金元素对氧化钨的

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还原),对钨颗粒(晶粒)的生长机制进行了分类。通过分析合金元素的作用机理(包括:强化机理、相变机理、晶粒生长机理及界面结构形成机理等),详细总结了合金元素对最终粉末冶金钨相关材料组织与性能的影响。期望能对钨相关材料产品的实际生产起到理论指导作用。

关键词: 合金元素; 氧化钨; 氢还原; 钨粉末; 晶粒形貌; 钨相关材料

1 Introduction

Tungsten powder used in the powder metallurgy industry is usually prepared in a multi-tube reduction furnace by the following two techniques: ① directly hydrogen reducing ammonium paratungstate (APT)^[1,2], as the decomposition and reduction process are carried out simultaneously, it is relatively difficult to accurately control the quality of tungsten powder; ② the usual or easier control technique: APT is firstly calcined to obtain tungsten oxides powder, and then which is reduced by reducing gases (hydrogen or carbon monoxide or alkane, the first is commonly used) to obtain tungsten powder. In the second technique, the decomposition and reduction process are separated, to a certain extent, which is beneficial to control the quality of tungsten powder. But in fact, the composition and crystal structure of tungsten oxides obtained by calcining APT are very complex. Usually, it is a mixture of yellow tungsten oxide (WO_3 , YTO), blue tungsten oxide ($\text{WO}_{2.9}$, BTO), and violet tungsten oxide ($\text{WO}_{2.72}$, VTO). Therefore, effects of phase composition^[3,4], crystal structure^[5,6], morphology^[7,8], and particle or grain size^[7-9] of tungsten oxide powder, and reduction process^[10-12] on the quality of tungsten powder have been studied sequentially. In addition, the ineluctable impurity elements during the manufacturing process from tungsten ore to tungsten oxides or the pre-doped alloying elements will also affect the reduction process of tungsten oxides. In this paper, based on the manufacture and application experience of tungsten powder and published literatures, effect of alloying elements on the hydrogen reduction process of tungsten oxides and the properties of tungsten related materials are summarized and analyzed, and some future research directions are also suggested.

2 Tungsten oxides hydrogen reduction process and mechanisms

There are two main mechanisms^[13] for the growth of tungsten particles (grains) during the hydrogen reduction process of tungsten oxides.

2.1 Chemical vapor migration growth mechanism

In general, the hydrogen reduction phase transition

process of WO_3 is $\text{WO}_3 \rightarrow \text{WO}_{2.9} \rightarrow \text{WO}_{2.72} \rightarrow \text{WO}_2 \rightarrow \text{W}$. The effects of process factors on the mechanisms can be ultimately attributed to the reducing temperature and pressure of water vapor, then the isothermal equation of the above four phase transitions can be expressed uniformly as equation (1):

$$\Delta G_n = \Delta G_n^0 + RT \ln \left(\frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2}} \right) = \Delta G_n^0 + RT \ln (K_p) \quad (1)$$

where, $\Delta G_n^0 (n = 1, \dots, 4)$ are the Gibbs free energy of the above four phase transitions at room temperature, respectively; R is the gas constant; T is the reduction temperature (K); K_p is the equilibrium constant, $K_p = p_{\text{H}_2\text{O}}/p_{\text{H}_2}$. Fig. 1 shows the hydrogen reduction equilibrium curves of WO_3 ^[14]. Though, the phase transition process of different raw materials of tungsten oxides is greatly different at various reduction temperature, the following gas-solid phase transition process is inevitable.

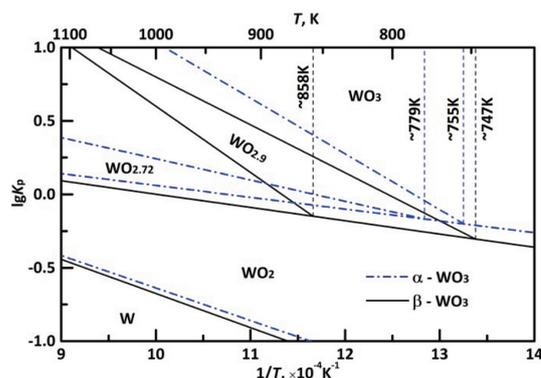


Fig. 1 The hydrogen reduction equilibrium curves of WO_3 ^[14]

WO_x reacts with water vapor to form the volatile $\text{WO}_x \cdot n\text{H}_2\text{O} (x \leq 3)$, which is reduced in a gas phase, then the reduced tungsten atoms deposit on low valence tungsten oxides grains or the formed tungsten grains. The “volatilization-deposition” process is called as the chemical vapor migration mechanism. The volatilization temperature of $\text{WO}_x \cdot n\text{H}_2\text{O} (x \leq 3)$ increases with x value decreases, and the gas-phase migration rate of $\text{WO}_x \cdot n\text{H}_2\text{O} (x \leq 3)$ decreases. Therefore, this is also one of the reasons why VTO is more suitable for preparing ultrafine tungsten powder.

Similar to the effects of alloy elements on austenitic phase region in Fe-C phase diagram, the addition of alloying elements can also change the “volatilization-deposition” phase

transition during the hydrogen reduction process of WO_x , and in further affects the characterization of the final tungsten powder^[15, 16]. When the reducing temperature is lower than 700 °C, alloying elements strongly inhibit the hydrogen reduction process of WO_x , and the inhibition effect decreases with the temperature increases; when the reduction temperature is raised to 700~800 °C, the reduction rate for WO_x without alloying elements is faster than that for WO_x with alloying elements, when the completion ratio of the reduction reaction is less than 60%, but there is an opposite result when the completion ratio is more than 60%; when the reduction temperature is higher than 800 °C, the reduction rate for WO_x without alloying elements is slower than that for WO_x with alloying elements^[16].

The alloying elements can also react with WO_x to form various compounds, which are usually deposited on the surface of particles as the nucleation cores to promote the nucleation of tungsten grains and to inhibit the “volatilization-deposition” process.

2.2 Short-range order growth mechanism

Oxygen atoms in WO_x are *in-situ* taken away by H_2 remaining tungsten atoms, which leads to ordered short-range rearrange according to the crystal structure of tungsten, finally growing into tungsten grains. The alloying elements will be partially solid-dissolved in tungsten lattice to change the short-range order diffusion energy, and in further to change the surface morphology and size of tungsten grains.

3 Alloying elements' effects

3.1 Alkali metal elements (Li, Na and K)

Alkali metal elements can act as carriers of oxygen atoms (by forming $WO_x \cdot nMe_2O$ or Me_2O ($Me=Li, Na, \text{ or } K$)) to prolong the retention time of oxygen in the powder layer, so the chemical vapor migration reaction^[17-25] between $WO_x \cdot nMe_2O$ and H_2 is promoted to lead to the growth of tungsten grains (particles). The volatilization temperature of $WO_x \cdot nMe_2O$ or Me_2O increases with the increase of the atomic number of Me element, and the order for promoting the growth of tungsten grains (particles) in a descending manner is $Li > Na > K$ ^[21].

$WO_x \cdot nMe_2O$ is deposited on the crystal surface of tungsten nucleus, then tungsten grains grow up. $WO_x \cdot nMe_2O$ is deposited on the region between the adjacent tungsten grains will form a sintered neck^[22], then these tungsten grains merge and grow into polycrystalline particles.

The study of Walter *et al.*^[23] showed that tungsten grains

nucleate firstly in the concentration region of K atoms, which are easily buried or absorbed in tungsten particles during the subsequent deposition and growth. A bimodal size distribution of tungsten powder is also easily caused because of the inhomogeneous distribution of K atoms. The research results of Lux *et al.*^[25] showed that the residual amount of K atoms in tungsten powder increases because the existence of Si or Al elements causes a decrease of the volatilization rate of K atom, but Si or Al elements do not affect the coarsening effect of K on tungsten grains. However, the research results of Lake *et al.*^[24] showed that Na plays a role of refining tungsten grains because of the existence of Si element, but the authors did not give a clear explanation.

It needs to be pointed out that alkali metal elements will cause a strength decrease of sintered tungsten related materials (pure tungsten, tungsten alloys and cemented carbides, *etc.*)^[26], so the holding time should be prolonged as much as possible before liquid-phase sintering or closed pores formation during solid state sintering, in order to decrease their residue.

3.2 Mg and Ca

Many studies^[17, 27] have shown that Mg and Ca have a slight refining effect on the reduced tungsten grains. After calcining APT, Ca with a form of $CaWO_4$ is remained in tungsten oxides powder, then after hydrogen reduction, is remained in tungsten powder with the forms of $CaWO_4$ and $Ca_{4.26}W_{10}O_{30}$ ^[27], which can probably pin on the migration of tungsten grain boundary.

Ca can deteriorate the properties of WC-Co cemented carbide due to the non-uniform growth of WC grains^[27] and the formation of Ca aggregation pores^[27, 28].

3.3 B

B can slow down the reduction rate of $WO_2 \rightarrow W$ process. When the doping content of B is higher than 1000 ppm, B has a refining effect on tungsten grains, but the reduced tungsten particles are aggregates of nanoparticles, no distinct single crystals can be detected, even if the reduction temperature is higher than 900 °C^[24]. When K and B are co-doped, B can inhibit the volatilization of K due to the formation of potassium borate during calcining APT and hydrogen reduction of tungsten oxides^[29]. However, the evolution of B during hydrogen reduction of tungsten oxides is still not very clear.

B can inhibit the growth of tungsten grains in an arc-melted dilute W-B alloy due to the grain boundary pinning effect of tungsten boride phase^[30].

B can improve the distribution uniformity of cobalt phase, the strength and hardness of WC-Co cemented carbides, due to the formation of $\text{Co}_x\text{W}_y\text{B}_z$ phase, the optimum B adding content is about 0.01wt%^[31]. Based on the principle of B diffusion into cemented carbide during liquid phase sintering, the boron gradient cemented carbide with boronized wear resistance in the surface and high toughness in the core can be prepared^[32].

3.4 Al

Many studies^[22, 33, 34] have shown that Al has a refining effect on the reduced tungsten grains, and there are three refining mechanisms: ① when the doping content of Al is less than 80 ppm, it can be completely solid-dissolved in tungsten lattice, which changes tungsten's lattice constant during reduction, and then inhibits the growth of tungsten grains by changing the formation of the growth steps on the surface of tungsten grains^[22]; in addition, Al also inhibits the aggregation and coalescence growth of tungsten grains due to the change of their surface morphologies, and the inhibition effect is not affected even if the alkali metal element exists; ② when the doping content of Al is higher than 80 ppm, the growth of tungsten grains are inhibited due to the formation of a thin layer of oxide with high stability on their surfaces, and the change process of the morphology of tungsten grain is as follows: cube with a rough surface \rightarrow polyhedron \rightarrow sphere^[33]; ③ the "volatilization-deposition" process of tungsten atoms has been inhibited due to the formation of AlWO_4 and $\text{Al}_2(\text{WO}_4)_3$ phases^[34].

Al atoms exist in the Co binder phase and the collection region of small WC grains, resulting in the decrease of density, hardness and fracture toughness of WC-Co cemented carbide^[34]. Al has the effect of solution strengthening and precipitation hardening on the binder due to the formation of Ni_3Al in the WC-Ni(Co)-Al cemented carbides^[35, 36]. Al can also improve corrosion and high temperature oxidation resistance of WC-Co cemented carbide due to the formation of Co-Al intermetallic compounds^[37].

3.5 C

The pressure of water vapor in the reduction system with C impurity will decrease because C can react with H_2O (gas) to form CO and H_2 , thus the "volatilization-deposition" process of tungsten atoms is inhibited. So C can strongly inhibit the growth of tungsten grains, do help to obtain ultrafine or even nanometer tungsten powder, and the growth mechanism is dominated by solid-state diffusion mechanism^[38].

Spherical tungsten powder with a grain size of 56.4 nm can be obtained when C and W mole ratio is 2.6^[39]. The research results of Mizukami *et al.*^[40] showed that WC powder with a grain size less than 100 nm can be obtained when WO_3 is reduced and carbonized directly by carbon, and the evolution process is $\text{WO}_3 \rightarrow \text{WO}_{2.72} \rightarrow \text{WO}_2 \rightarrow \text{W} \rightarrow \text{W}_2\text{C} \rightarrow \text{WC}$, and the key process to control the size of final WC grains is $\text{WO}_{2.72} \rightarrow \text{WO}_2$.

It needs to be pointed out that the temperature must be higher than 900 °C for WO_3 being reduced and carbonized directly to prepare WC powder by solid-carbon+hydrogen^[39], or methane+hydrogen^[41], or methane^[42], although WO_3 reacts with C at higher than 750 °C^[43]. The complete reduction-carbonization temperature (1215 °C) for the milled WO_3 and graphite mixture powders is about 150 °C lower than that for un-milled mixture powders^[44].

3.6 Si

In 750~1000 °C, Si has no significant influence on the reduction process of tungsten oxides and the morphology of tungsten grains, and the morphology of tungsten grain mainly presents the shape of tetrahedron or cube^[45]. But the study of Ge *et al.*^[46] showed that Si has a slight coarsening effect on tungsten grains because the volatilization rate of water vapor is affected due to the formation of $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ gel.

The solid-solution strengthening of the nickel binder by Si will significantly improve the mechanical properties of the WC-Ni-Si cemented carbides in comparison with WC-Ni cemented carbides, and the strength and toughness of WC-Ni-Si cemented carbides is also higher than those observed in similar WC-Co cemented carbides, without sacrificing the hardness significantly^[47].

3.7 P

To some extent, P can refine the tungsten grain because the reduction rate of $\text{WO}_{2.72} \rightarrow \text{WO}_2$ is increased therefore promoting nucleation of WO_2 grains, and these ultrafine WO_2 grains easily aggregate to form small flower like (starlets) aggregates^[45, 48, 49], the size of which depends on the water vapor content of the hydrogen atmosphere, and the formation of starlet shaped WO_2 can be a controlling factor in determining the final grain size of tungsten powder^[49]. Normally, P is basically evaporated before WO_2 is formed during the hydrogen reduction process, but if P is remained in WO_2 powder, it will be retained in the final tungsten powder^[48].

P can play a role in activated sintering for WC-Co cemen-

ted carbides by decreasing sintering temperature^[50, 51], and the research results of Kobylanshi *et al.*^[52] and Pan *et al.*^[53] showed that the segregation of P at the grain boundary during sintering causes brittle fracture of sintered tungsten related materials. So it is suggested that the doping content of P in tungsten related materials should not be more than 0.3wt%.

3.8 S and halogens

Usually, S remains in APT during the tungsten ore smelting process to APT. In the process of hydrogen reduction of tungsten oxides, S can be removed by volatilizing itself or by transforming to highly volatile hydrogen sulfide, it is very important to extend the reduction time appropriately, avoiding to affect the size of tungsten particles (grains)^[22]. Because S remained in WC-Co cemented carbides can deteriorate alloy strength due to the formation of S aggregation pores^[27], S must be removed as far as possible.

3.9 As

During calcining APT, part of As atoms or the gaseous As₂O₃ can be volatilized causing the formation of the porous WO₃ particles, which is beneficial to the entry of hydrogen and the discharge of water vapor during the hydrogen reduction. In addition, the “volatilization-deposition” process of tungsten atoms can also be inhibited because the pressure of water vapor in the reduction system is decreased by the volatile As and As₂O₃. The formation of WAs₂ phase on the surface of tungsten grains during the reduction can provide more nucleation cores for tungsten grains, and can also inhibit the migration of tungsten grain boundary. So As plays a role of refining tungsten grains^[54] in the hydrogen reduction process of tungsten oxides. The decomposition rate of APT is accelerated by co-doped As and P, and the porous tungsten oxide particles (which is beneficial to the hydrogen reduction process) are formed due to the release of large amount of As₂O₃ and P₂O₃ gas. The release of P₂O₃ gas can further lower the water pressure during the hydrogen reduction of tungsten oxide. Thus, compared with only doping As into APT, a finer tungsten powder with an average particle size of 79 nm can be obtained by co-doping 0.3wt%As and 0.3wt%P^[55].

As has a positive effect on improving the sinterability, grain refinement, strengthening and toughening of WC-Co cemented carbide^[54].

3.10 Ti

When nanometer WO₃-TiH₂ mixed powders obtained by co-ball-milling TiH₂ and WO₃ powders is reduced by H₂ atmos-

phere, the reduction process is changed to WO₃→WO₂→W at 800 °C, and WO₃ was deoxidized to W at 850 °C. The formation of a small amount of nanoscale TiO₂ can pin tungsten grain boundary, which is beneficial to refine the size of tungsten grains^[56]. The diffusion of Ti into W matrix was suppressed due to nanoscale TiO₂ in grain boundaries during sintering of W-Ti alloys^[56]. The research results of Kang *et al.*^[57] showed that a WO₃-TiH₂ powder mixture can be reduced by hydrogen to W at 800 °C and a TiW alloy phase was also formed.

3.11 V and Cr

The formation of V_{0.3}W_{0.7}O₂ (V-O-W bonze) on the surface of WO₂ grains can provide more nucleation cores for tungsten grains, and could also lead to the decrease of reduction rate with the V content increases^[58].

Cr usually exists in tungsten oxides powder as the form of Cr₂O₃ (the reduction temperature of Cr₂O₃ to Cr by hydrogen should be at least more than 1000 °C^[59]), which is distributed on the surface of tungsten grains during the hydrogen reduction, then inhibits the “volatilization-deposition” process of tungsten atoms^[60]. The research results of Wu *et al.*^[39] showed that the maximum effective addition of Cr₂O₃ is about 0.9wt%.

In the WC-Co cemented carbides, V and Cr are widely used as WC grain growth inhibitor^[61], and there are three main inhibiting mechanisms: ① dissolving into liquid phase Co to inhibit the dissolution-precipitation of WC; ② forming a W-V(Cr)-C solid-solution thin layer with a thickness of about 30~50 nm on the WC grains surface to lower the surface energy; ③ precipitating on the WC grain boundaries to play a pinning role. The formation of W-V(Cr)-C solid-solution can also increase the shear modulus of WC^[62].

Cr can also improve the corrosion resistance of WC-Co (Ni) cemented carbides due to the formation of more protective chromium containing oxide on the binder phase^[63].

3.12 Mn

Similar to Al element, during the hydrogen reduction process of WO₃, Mn can be partly solid-dissolved in tungsten lattice to change tungsten's lattice constant, which causes edge passivation of tungsten grain, namely the shape of tungsten grain transforms from polyhedron to sphere. In fact, most of Mn atoms by the form of MnWO₄ are distributed on the surface of tungsten grains, inhibiting the “volatilization-deposition” process of tungsten atoms^[64]. In the ongoing reduction process, MnWO₄ is easily incorporated into the tungsten grains, which

will form a significant open porosity in the final particles^[65].

In tungsten heavy alloys, Mn can purify grain boundaries by reacting with oxygen and sulfur to form oxides and sulfides, and can also play a role in activated sintering and grain refining^[66]. The optimum content is about 0.25wt% for W-Ni-Fe alloys^[67].

In WC-Co cemented carbides, Mn can improve the strength and hardness by refining WC grains and solid-solution strengthening Co binder^[68].

3.13 Fe

When the mass content of Fe is 200 ppm, the clear growth steps structure is formed on the surface of tungsten grain (particle). When the content of Fe is higher than 200 ppm, Fe easily reacts with WO_3 to form FeWO_4 during the early stage of reduction, which inhibits the “volatilization-deposition” process, and eventually is reduced to W and Fe_7W_6 ^[69].

The friction coefficient of WC-Co-Ni-Fe cemented carbide can be reduced by adding appropriate Fe, and the optimum addition content is $m_{\text{Fe}} : m_{\text{Co}} = 1 : 1$ ^[70]. Fe plays a role in refining WC grains for WC-Co cemented carbide used for rock-drilling, but results in the decrease of the transverse rupture strength (TRS) due to the increase of porosity, and it is suggested that Fe content should not be more than 0.3wt%^[71].

3.14 Co

Co plays a role of the catalyst to improve the reduction rate of tungsten oxides^[65]. Co can also promote the formation of needle-like $\text{WO}_{2.72}$ grains with a larger length-diameter ratio^[72]. To some extent, Co improves the nucleation rate of tungsten grains to form ultrafine or even nano-grains. In turn, Co can also easily lead to the agglomeration of tungsten grains into a large polycrystalline particle^[73]. The study of French *et al.*^[74] showed that Co_3W (which disappears at above 900 °C) and Co_7W_6 phase are formed during hydrogen reduction. The final Co_7W_6 phase, which is formed by the decomposition of CoWO_4 in the early stage of reduction, is easily incorporated into the tungsten grains^[65]. Co can also improve the carburizing rate of tungsten powder, and the complete carburization temperature of W-Co mixed powders is 800~900 °C^[75].

3.15 Ni

Ni can slightly decrease the reduction temperature to inhibit the growth of tungsten grains, and the formation of NiWO_4 can also inhibit the “volatilization-deposition” process^[76]. Nickel oxides can be rapidly reduced into Ni during the early stage of reduction, then tungsten grains are nucleated with Ni as nucleation cores^[69]. W-Ni powder with an

average particle size of about 100 nm can be obtained by hydrogen reducing ball-milled WO_3 -NiO powder at 800 °C for 1 h^[77]. At a higher reduction temperature (>900 °C), Ni can easily lead to tungsten grains growing into whiskers with an octahedral tip^[69] along to <110> crystal direction^[78, 79], but the preferential growth mechanism is not very clear.

Ni plays a role of activated sintering for sintered tungsten related materials, but the plasticity of W-Ni alloys decreases due to the formation of W-Ni brittle phase on grain boundary^[80]. Ni can also improve the high temperature oxidation resistance of WC-Co-Ni cemented carbide, and the optimum mass ratio of Co and Ni is 1:1^[81].

3.16 Cu

Cu can provide the nucleation cores for tungsten grains, which is beneficial to refine the size of tungsten grains^[82]. In addition, the hydrogen-reduction temperature of WO_2 for WO_3 -CuO mixtures is lower than that for WO_3 powders, which promotes the “volatilization-deposition” process of tungsten grains on the surface of Cu^[83].

Cu plays a definite role in inhibiting the growth of WC grain and stabilizing fcc-Co, and retards the morphology evolution of WC grains from round shape to faceted shape for the ultra-coarse grained WC-6Co cemented carbide, but results in the decrease of wear resistance^[84]. However, Huang's study^[85] have yielded the opposite result: Cu can improve hardness and wear resistance of the sub-micro grain WC-6Co cemented carbide fabricated by spark plasma sintering (SPS). The insufficient diffusion of Cu and the poor wetting between WC and Cu are disadvantageous to the density and mechanical strength, leading to a decrease in density and fracture toughness. The above different results are probably due to the different roles of Cu in the two alloys. The low wear resistance of the ultra-coarse WC-6Co-1.2Cu is due to the poor oxidation resistance of Cu and low interface bonding strength of WC/Co(Cu), while the high wear resistance of the submicro WC-6Co with Cu is due to the obvious refinement of WC grains by Cu.

3.17 Zn

Zn can increase the reduction rate of tungsten oxides, thus promoting the formation of plate-like $\text{WO}_{2.92}$ crystals and needle-like $\text{WO}_{2.72}$ crystals, which is beneficial to improve the nucleation rate of tungsten grains and also determines the final particle size of tungsten powder^[86].

Zn plays a role of strengthening WC-10(Co,Zn) cemen-

ted carbide, and the strengthening effect decreases with the increasing mean grain size of WC. The strength of WC-10 (Co, Zn) is insensitive to sintering conditions of 1360 ~ 1440 °C and holding time of 1 ~ 5 h^[87].

3.18 Zr

Similar to Ni element, Zr can slightly decrease the reduction temperature to inhibit the growth of tungsten grains, the formation of $Zr(WO_4)_2$ can also inhibit the “volatilization-deposition” process^[76].

Zr can improve hot-hardness, oxidation resistance, and wear resistance of cemented carbides^[88] and ultimate tensile strength (UTS) of solid solute tungsten alloys^[89].

3.19 Mo

Many studies^[64, 90] have shown that Mo has a refining effect on the reduced tungsten grains, there are two refining mechanisms: ① similar to Al and Mn elements, Mo can be partly solid-dissolved in tungsten lattice to change the formation and growth steps on tungsten grains, which causes edge passivation of tungsten grain, namely the shape of tungsten grain transforms from polyhedron with sharp edges to near-sphere with smooth edges; ② Mo can react with WO_3 to form MoO_2 , which can provide more nucleation cores for WO_2 grains.

In addition, Mo has a great influence on the crystallization process and particle morphology of APT^[91]. Mo has no obvious effect on the morphology of WC particles during the preparation of WC powder by carbonization of tungsten powder^[64]. Mo can also improve hardness and strength of WC-Co (Fe, Ni) cemented carbide by refining WC grains and solid-solution strengthening for the binder, but decrease fracture toughness, and the best comprehensive performance can be obtained when the content of Mo is 5wt%^[92, 93]. Other results indicate that: although Mo can refine WC grain for a WC-6.5Co cemented carbide, maybe due to the increase of porosity with increasing of Mo content, the strength decreases slightly, and the fracture toughness of WC-6.5Co with 2.4wt% Mo reaches a maximum of about $11.8 \text{ MPa} \cdot \text{m}^{1/2}$ ^[94].

3.20 Pd

Similar to Co element, Pd plays a role of the catalyst to improve the reduction rate (especially the start reduction rate) of tungsten oxides^[95].

3.21 Pt

Pt plays a role of catalysis for the hydrogen reduction process of WO_3 by accelerating the dissociation of molecular

hydrogen. Therefore, it can reduce the reduction temperature and improve the hydrogen reduction rate of WO_3 ^[96].

3.22 Rare-earth elements

Rare-earth (RE) elements have a refining effect on the reduced tungsten grains, there are three refining mechanisms: ① RE can improve the reduction rate of tungsten oxides by decreasing the reduction temperature^[97], and some studies^[98] showed that WO_2 is not found during the reduction process, but to form W_5O_{14} and W_3O_5 ; ② grain boundaries are pinned by RE distributed at grain boundaries of tungsten oxides or tungsten grains^[99]; ③ RE elements by the form of tungstate are deposited on the surface of tungsten grains to inhibit the “volatilization-deposition” process^[100]. RE elements can also accelerate the crystallization of tungsten grains (particles) to make them more regular (from spherical to polyhedral)^[101].

RE can purify grain boundaries or interfaces of cemented carbides by reacting with the harmful impurity elements (e. g. S, Ca, *etc.*) to form the second phase hard particles, therefore improving cemented carbides mechanical properties^[102]. It needs to be emphasized that RE metals should be added instead of RE oxides, otherwise it may have some uncertainty negative effects^[88].

4 Summary and prospect

Based on above analysis, effects of alloying elements on the size of reduced tungsten particles (grains) can be roughly summed up in the following seven categories:

(1) The formation of $WO_x \cdot nMe_2O$ or Me_2O ($Me = Li, Na, \text{ or } K$) similar to $WO_x \cdot nH_2O$ or H_2O during reduction can prolong the retention time of oxygen in the powder layer, then the chemical vapor migration reaction between $WO_x \cdot nMe_2O$ and H_2 is promoted to lead to the growth of tungsten grains (or particles).

(2) Fe, Ni, Mn, Al, Zr, V, Ti, and RE, *etc.* can react with WO_x to form non-volatile tungstates, which are deposited on the surface of particles as the nucleation cores to promote the nucleation of tungsten grains and to inhibit the “volatilization-deposition” process.

(3) Cr, V, Mo, and RE, *etc.* can react with WO_x to form stable oxides which are deposited on the surface of tungsten grains to inhibit the “volatilization-deposition” process.

(4) Al, Mo, Mn, Cu, Ni, Nb, and Ta, *etc.* can be partially solid-dissolved in tungsten lattice to change tungsten's lattice constant, then inhibits the growth of tungsten

grains by changing the formation of the growth steps on the surface of tungsten grains.

(5) As, P, and B, *etc.* can react with WO_x to form volatile oxides to decrease the pressure of water vapor, they can also react with W to form compounds, which can provide more nucleation cores for tungsten grains.

(6) Strong reductive elements, C and Zn, *etc.* can decrease the pressure of water vapor, to inhibit the “volatilization-deposition” process.

(7) The effect of Ca, Mg, and Si, *etc.* on the reduced tungsten grain size is not obvious, more detailed research is needed.

In fact, the combined influence of multiple alloying elements makes the hydrogen reduction process more complicated, this is also one of the focuses of future research. In addition, in order to prepare nano grained cemented carbides with high strength and toughness and ultra-coarse grained cemented carbide for mining, the preparation of nano and spherical single crystalline ultra-coarse tungsten powder by doping is also a future research hotspot.

Alloying elements can improve the performances of WC-Co(Ni, Fe) cemented carbides mainly by the following five ways: ① strengthening (solid-solution or precipitation) the binder; ② suppressing fcc \rightarrow hcp phase transition of the Co binder; ③ modifying the morphology and size of WC grains; ④ optimizing the WC/binder interface structure; ⑤ forming a ternary (W, Me)C solid-solution phase.

With the development of advanced specimen preparing and microstructure detection technologies, such as SEM, electron-probe microanalysis (EPMA), electron backscattered scattering detection (EBSD), focused ion beam (FIB), TEM, *et al.*, the internal microstructure (pore, boundary, sub-boundary, texture^[1] and composition, *etc.*) in a particle can be analyzed accurately instead of originally qualitative analysis, so it is of great help for understanding hydrogen reduction mechanisms and controlling the quality of tungsten powder. Besides, the hydrogen reduction characteristics of tungsten oxide are studied in depth by using some new theories^[103] or research methods^[104], and the aided computer simulation of tungsten grain growth in the hydrogen reduction process^[105] is also helpful.

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