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Influences of sub-micrometer Ta and Co dopants on microstructure and properties of tungsten heavy alloys①

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Abstract: Tungsten heavy alloys are aggregates of particles of tungsten bonded with Ni/Fe or Ni/Cu via liquid-phase sintering. The sub-micrometer Ta Co powder was added to this aggregate to strengthen the bonding phase. It is found that the main fracture pattern of the alloys is cleavage of tungsten grains and ductile rupture of bond phase, leading to improved tensile strength and elongation. Dopant Ta can act as grain size inhibitor in tungsten heavy alloys.

Key words: tungsten heavy alloys; sub-micrometer; Co powder; Ta powder; cleavage fracture

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1 INTRODUCTION

Tungsten heavy alloys have high density and high strength, they are extensively used in military area, such as penetrators instead of DU. Tungsten heavy alloys have excellent radiation resistance, they are used as nuclear and medical shields. They have small coefficient of expansion and large modulus of elasticity, so they are also used as balance weights, aircraft components.

Tungsten heavy alloys are aggregates of particles of tungsten bonded with Ni/Fe or Ni/Cu binder via liquid-phase sintering, so the mechanical properties of the alloys depend on the strength of the ductile binder and the cohesion between binder and particles of tungsten. Fig. 1 presents the main fracture modes of this bi-phase alloy, in which A_1 is a mode of ductile rupture of Fe/Ni binder, A_2 is a mode of cleavage across W grains, A_3 is a mode of fracture along W/binder interface and A_4 is the W/W grain boundary de-cohesion respectively. A weak cohesion between W grains and the binder will lead to fracture along W/binder (Fe/Ni) interface, while poor "wetting" results in W/W grain boundaries de-cohesion fracture mode. Both cases result in lower tensile strength and poor elongation[1].

By improving the strength of the binder and the cohesion between the binder and W grains, it is possible to increase the tensile strength and elongation of tungsten heavy alloys, whose fracture mode is ductile rupture of Fe/Ni binder, even cleavage across W grains. Element Co and Mn can improve the wetting of binder to W grains[1, 4]. On the other hand, Ta, Mo, Re and La can decrease the amount of W dissolved in the binder and purify the boundary, leading to improved plasticity of the binder[4, 14]. Here we choose dopants Ta and Co to strengthen the alloy. To improve the activity of the Ta and Co powders and the distribution of dopants, the sub-micrometer Ta, Co powders were used. The influences of sub-micrometer Ta and Co dopants on the microstructure, properties and fracture mode of tungsten heavy alloys were studied in this paper.

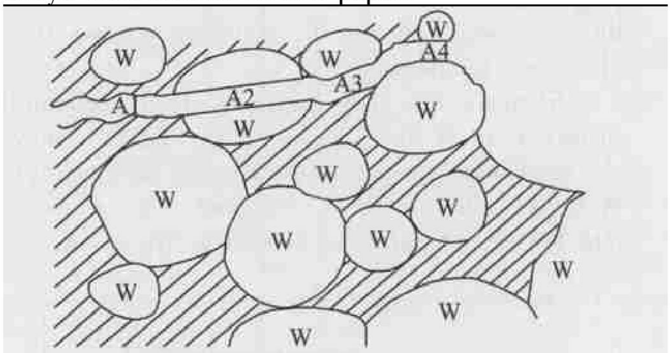

Fig. 1 Main fracture modes of heavy alloys
A_1 —Rupture of ductile binder;
A_2 —Cleavage of W grains;
A_3 —Fracture along W/binder interface;
A_4 —W/W grain boundary de-cohesion

2 EXPERIMENTAL

2.1 Specimen preparation

The average particle size of Ta, Co powders was less than 0.5 μm, while the average particle size of

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Fe, Ni and W powder was around 2 μm. The content of the alloy (mass fraction) was: 92% W, 6.5%−8% (Fe-Ni), with dopant elements Ta, Co as the balance. The powders were ball milled, vacuum dried, and cold isostatic pressed at 200 MPa. The green compacts were then vacuum sintered at elevated temperatures.

2.2 Characterization

The density of sintered samples was measured by Archimedes method. A standard 5 mm diameter specimen was adopted to measure the tensile strength and elongation with the DLY-10A type equipment. An AMRAY 1845FE type field emission scanning electron microscope (SEM) and its accessory EDS were used to analyze the fracture pattern and contents of binder.

3 RESULTS AND DISCUSSION

3.1 Influences of Co dopant

Samples of W-Fe-Ni-Co and W-Fe-Ni are sintered at elevated temperatures with same soaking time (50 min) in vacuum. The density increases with increasing the sintering temperature. When the relative density is over 98% (≥17.3 g/cm^3), the sintering temperature range for W-Fe-Ni-Co is from 1 460 ℃ to 1 490 ℃, and for W-Fe-Ni is from 1 480 ℃ to 1 490 ℃, as shown in Fig. 2. The addition of Co powder widens the sintering temperature range. This may result from the fact that by doping element Co, the melting point of Fe-Ni alloy drops[2], which makes the sintering process start at a lower temperature.

Element Co also improves the mechanical properties of W-Fe-Ni heavy alloys. Table 1 shows the mechanical properties of different heavy alloys. W-Fe-Ni alloy with Co dopant shows excellent tensile strength and plasticity, the σ_b, $\sigma_{0.2}$, δ and Ψ reach 950 MPa, 580 MPa, 25% and 22% respectively. It is quite possible that the Co dopant improves the cohesion between the W grains and the bonding phase[2], and also changes the fracture mode of the heavy alloy, leading to improved mechanical properties.

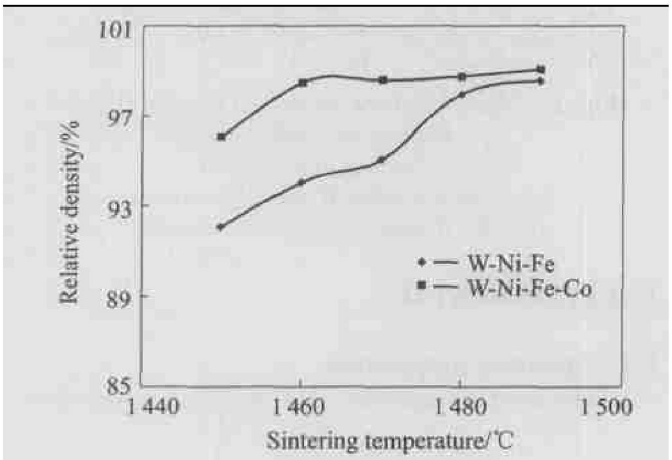

Fig. 2 Relation between sintering temperature and relative density

Table 1 Mechanical properties of heavy alloys

Alloy	σ_b/MPa	$\sigma_{0.2}$/MPa	δ/%	Ψ/%	E/GPa
W-Fe-Ni-Co	950	580	25	22	350
W-Fe-Ni-Co-Ta	1 000	600	20	19	320
W-Fe-Ni	900	570	10	12	320

The SEM observation of fractured specimen proves the role of Co too. The W-Fe-Ni heavy alloy shows mainly the fracture mode of rupture of the ductile binder and partially W-W grain boundary de-cohesion fracture mode, as shown in Figs. 3(a), (b) respectively. On the other hand, the W-Fe-Ni heavy alloy with Co dopant presents mainly the fracture mode of cleavage across W grains, and the cleavage area accounts for over 40% of the total cross section, as shown in Fig. 4. The fracture mode of cleavage across W grains shows improved strength of binder phase and improved cohesion between the W grains and the binder.

How does dopant Co improve the cohesion between the W grains and the bonding phase? As the wetting angle (δ) decreases, the wetting ability of the binder is improved. When δ comes to near 0,

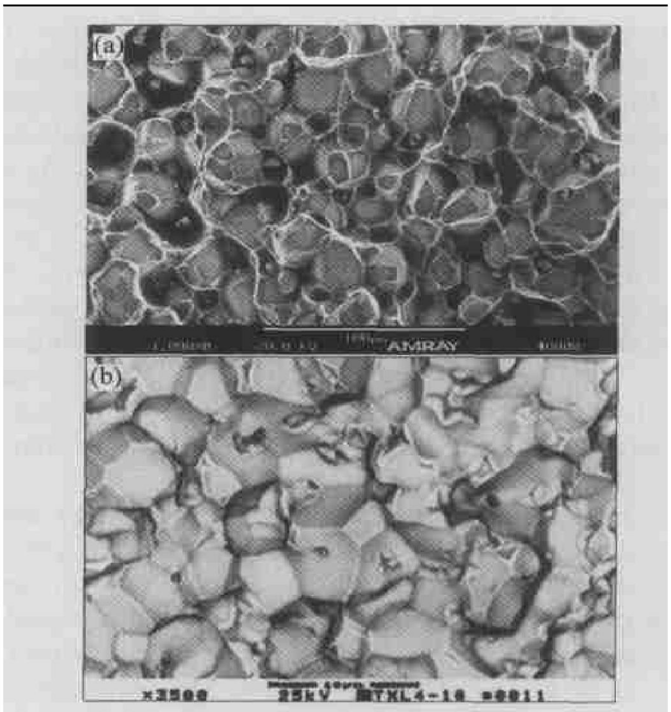

Fig. 3 SEM images of W-Fe-Ni fracture
(a) —Rupture of tensile binder;
(b) —De-cohesion of W-W grains

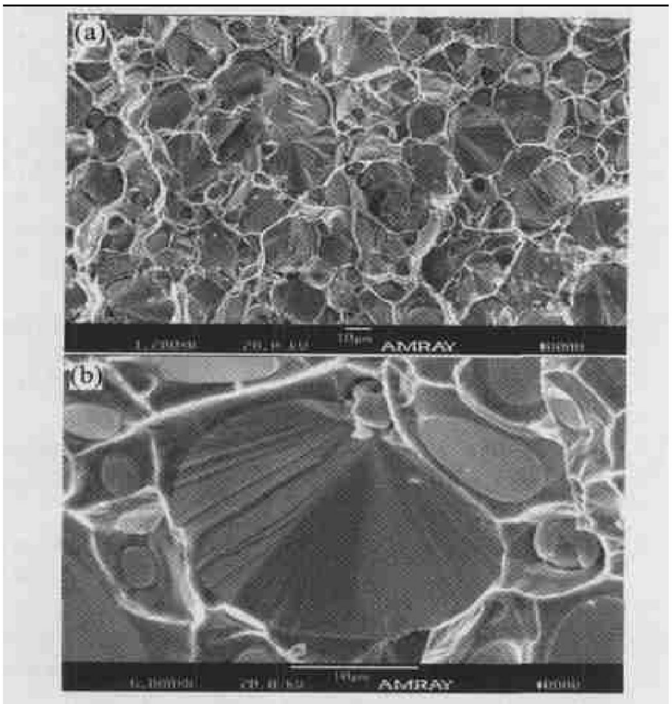

Fig. 4 SEM images of W-Fe-Ni-Co fracture
(a) —Mainly cleavage of W grains;
(b) —Typical cleavage of W grain

the bonding phase can wet W grains completely, thus greatly improving the cohesion between the W grains and the bonding phase, as shown in Fig. 5. Zhou et al[2] proved that the dopant Co can decrease the wetting angle δ, for example, δ of 70Ni-30Fe at 1 440 ℃ in H_2 is 24°, while δ of 70Ni-30Fe+ Co under the same condition drops to 4°. This will certainly improve the cohesion.

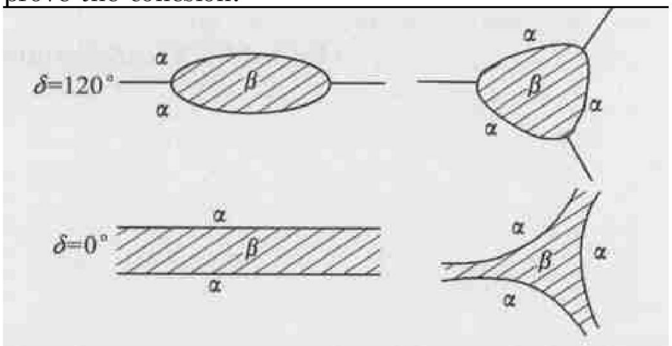

Fig. 5 Relationship between wetting angle(δ) and wettability to W grains

Fig. 6 shows the EDS pattern of the bonding phase. The main contents of the binder are Fe, Ni, Co and W. Co exists in the binder, which improves the cohesion of two phase.

The excellent elongation(δ and Ψ reach 25% and 22% respectively) mainly relies on the axial elongation and radial shrinkage of ductile binder, because W grains are difficult to deform under present stress condition. This is verified by SEM image of W-Fe-Ni-Co alloy along elongation direction(the arrow direction in Fig. 7).

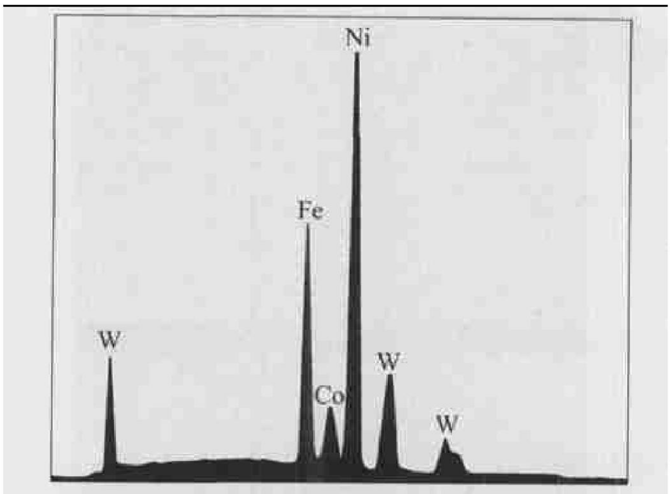

Fig. 6 EDS pattern of binder

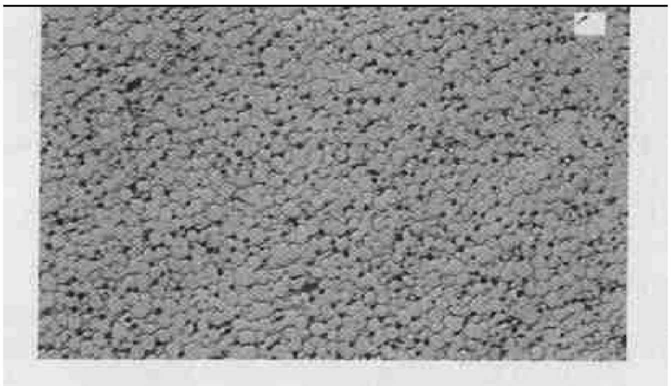

Fig. 7 SEM image of W-Fe-Ni-Co along elongation direction

3.2 Influences of Ta dopant

Element Ta is added to the alloy system together with element Co. From Table 1, it can be seen that the tensile strength of W-Fe-Ni-Co-Ta is higher than that of W-Fe-Ni-Co, and the elongation is a little lower than that of W-Fe-Ni-Co. The role of dopant Ta is that it can decrease the amount of W dissolved in the binder, inhibiting the diffusion of W atoms, leading to finer W grain size. Fig. 8(a) and (b) show the SEM images of W-Fe-Ni-Co and W-Fe-Ni-Co-Ta respectively. The average W grain size of W-Fe-Ni-Co is around 25 μm, while that of W-Fe-Ni-Co-Ta is around 20 μm. The strengthening effect may result from the decreasing of grain size and solution(W-Ta) strengthening.

4 CONCLUSIONS

1) The fracture mode of W-Fe-Ni heavy alloys with Co dopant is mainly cleavage across W grains and ductile rupture of bonding phase.

2) W-Fe-Ni heavy alloys with Co dopant have excellent mechanical properties.

3) Dopant Ta can act as grain size inhibitor element.

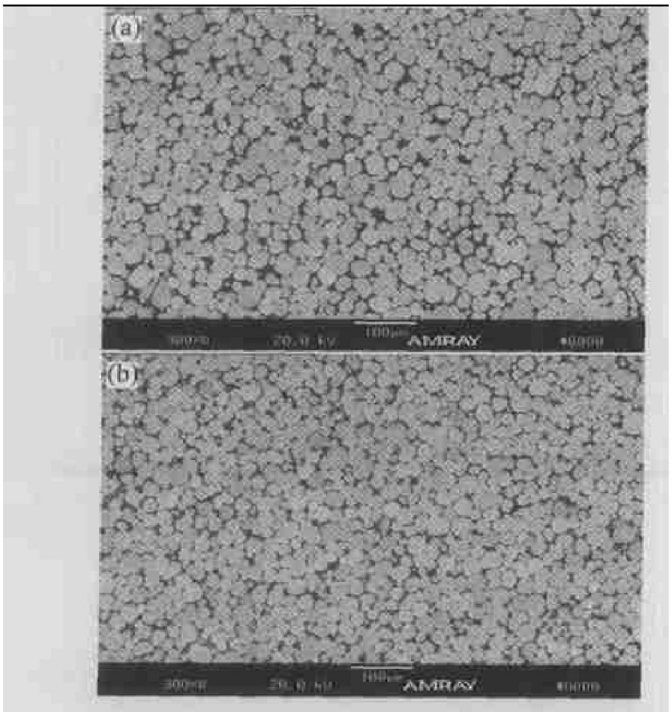

Fig. 8 SEM images of W-Fe-Ni-Co(a) and W-Fe-Ni-Co-Ta(b)

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