Article ID: 1003 - 6326(2004) 02 - 0241 - 05

Grain refinement of W-Ni-Fe heavy alloys by tantalum element adding ①

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Abstract: 90W-7Ni-3Fe and (90 - x) W-xTa-7Ni-3Fe (x = 1, 3, 5, 7, 10) specimens were attained by liquid phase sintering. A model describing the process of liquid forming and spreading was proposed to point out the differences between alloys doped with tantalum and traditional tungsten heavy alloys. Tantalum priority of entering matrix and a relative high solubility in liquid matrix depress tungsten solubility in liquid matrix, which decreases kinetic rate constant K and consequently results in the reduction of W grain size. The grain refinement is influenced by Ta content and becomes more obvious when Ta content is over 5%. The sample with less than 3% Ta has dominant W and matrix phases. While besides W and matrix phases, intermetallic phases emerge in 85W-5Ta-7Ni-3Fe sample. Ta is superfluous and forms a new tantalum phase when more than 7% Ta is added into alloys.

Key words: tungsten heavy alloys; alloying element addition; grain refinement; tantalum
CLC number: TF 125.2; TG 146.4 **Document code:** A

1 INTRODUCTION

Tungsten based heavy alloys are two-phase composites produced by liquid phase sintering mixed elemental tungsten, nickel and iron powders[1, 2]. Typical compositions have 90% tungsten with the balance of iron and nickel, usually in the ratio of 7∶3. After sintering the matrix has a face-centered cubic structure with an approximate composition of 20% - 24% W, 23% - 25% Fe and 52% - 55% Ni[3, 4].

According to Hall-Petch formula, coarsening of grains results in a decrease of alloys' strength, which implies that reducing grain size is an effective method to improve alloys' performance. W-Ni-Fe heavy alloys fabricated by powder metallurgy(P/M) process usually have 20 - 60 μm size of tungsten grains which are studded in matrix[5, 6]. The presence of liquid phase Ni-Fe-W ternary system aids rapid densification of alloys, but leads to microstructural coarsening[7-9]. This is due to the relatively high solubility of tungsten in the matrix phase during sintering and W atoms sufficiently dissolving into and reprecipitating from the liquid matrix during soaking, solution-reprecipitation mechanism induces growth[10-12].

Alloying element addition offers an approach to reduce grain size in the system of tungsten based heavy alloys[13]. Reports reveal that Mo element exhibits evidently positive effect on the reduction of tungsten grain size just because Mo atoms take part of W atoms in matrix and consequently depress the solubility of W atom in the liquid[3, 14, 15]. Also, V and Cr elements that belong to body-centered cubic refractory metals have the same influence on the microstructure of tungsten heavy alloys[14]. Tantalum has solubility in W and matrix phases simultaneously, however, to date, there isn't a systematic study on the effect of Ta on the microstructure of heavy alloys. This paper describes the phenomenon of grain refinement and changes of phase constituent in tungsten heavy alloys with Ta alloying element addition.

2 EXPERIMENTAL

The characteristics of the starting powders are listed in Table 1. Ta has a high solubility in W and matrix phases, and its operating mechanism is different from that of doped trace element, so the addition of high content Ta is permitted. The chemical composition of the alloys prepared in this experiment is given in Table 2. Elemental powders were mixed in the medium of alcohol for 12 h, and 1.5% stearine was used to improve mixture's compacting ability. Dog-boned tensile specimens were compacted at 300 MPa, and the resulting green density was approximately 75% of the theoretical density. Thermal heating cycle consists of pre-sintering at 800 ℃ for 1 h, heating to 1 480 ℃ for W-Ni-Fe green and to 1 440 ℃ for greens added with Ta for 1 h. The final compacts were cooled to room temperature in furnace. The whole cycle was conducted in a vacuum of about 10 Pa. The microstruc-

① **Received date:** 2003 - 05 - 23; **Accepted date:** 2003 - 10 - 15
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Table 1 Characteristics and content of major impurities of powders

Powder	Fisher subsieve size/μm	Apparent density/ (g·cm⁻³)	Processing routine	Purity/ %	Major impurities/ %				
					O	C	N	Mo	Si
W	1.98	–	Oxide reduction	> 99.5	0.053	–	–	0.0015	–
Ni	2.3	0.6	Carbonyl decomposition	> 99.5	< 0.20	< 0.30	–	–	–
Fe	2.3	3.2	Carbonyl decomposition	> 99.0	< 0.30	< 0.30	< 0.20	–	–
Ta	0.4	0.62	–	> 99.0	0.604	0.0045	0.0067	–	0.0222

Table 2 Designed composition of alloys (mass fraction, %)

Sample No.	W	Ta	Ni	Fe
1	90	–	7	3
2	89	1	7	3
3	87	3	7	3
4	85	5	7	3
5	83	7	7	3
6	80	10	7	3

ture was observed with Polvar– MET wide-version optical microscope, and the phase constitute of as-sintered alloys was analyzed with D/Max-rA X-ray diffractometry (XRD). The phase composition was measured with energy dispersive analysis (EDS).

3 RESULTS AND DISCUSSION

3.1 Sintering model of specimens added with Ta

The liquid phase appears at 1 435 ℃ or so in the system of binary Fe-Ni alloy[16]. So the liquid phase sintering of W-Ni-Fe greens actually starts as the Ni-Fe liquid firstly appears. The sintering is promoted by the emergence and diffusion of liquid Ni-Fe substance. Specimens doped with tantalum alloying element have a new mechanism of sintering promotion which is different from W-Ni-Fe sintering course. The emergence of liquid phase occurs at about 1 322 ℃ and 1 342 ℃ in Ni-Ta, Fe-Ta systems according to their binary phase diagrams respectively[17]. As temperature rises in the course of sintering cycle, the liquid phase firstly emerges between Ni, Ta particles in contact rather than Ni, Fe particles, as shown in Fig. 1(b), consequently fills in the interspaces among tungsten particles because of the capillary force from the wetting liquid. Meanwhile Ta particles having no contact with Ni particles are still in the state of solid, begin to integrate with Fe powder and to melt at higher temperature (Fig. 1(c)). Excellent wetting ability between solid and liquid aids the quick spread of melting phase. The liquid phases of both Ni-Ta and Fe-Ta gradually converge along with the opening of channels caused by W particles just because protruding edges and small size particles of W dissolve into liquid and further tungsten particles rearrange (Fig. 1 (d)). The convergence of liquid phase greatly accelerates matrix uniformity and the present liquid consists of four elements Ni, Fe, Ta and W. The steep chemical gradient of tungsten between solid and liquid greatly enhances the diffusion of W atoms, which undoubtedly increases the volume fraction of liquid until liquid is saturated. Atom's rapid diffusing ability in liquid advances the dissolving progress of Ni, Fe and Ta solid, in fact, their particles dissolve completely into liquid in a very short time.

3.2 Refinement of microstructure of sintered alloys

Microstructural coarsening is a common phenomenon in the production of liquid phase sintered W-Ni-Fe alloys[7–9]. Solution and reprecipitation is a dominant mechanism that controls coarsening process of the grains[11, 12]. A certain degree of solid solubility in liquid matrix ensures the success of sintering, and alternatively the solubility of tungsten in the matrix is the key to grain growth. Generally, the grain size will vary linearly with soaking time[18, 19]:

$$G^n = G_0^n + Kt \qquad (1)$$

where t is the soaking time at sintering temperature, G is the tungsten grain size at t, G_0 is the initial tungsten particle size, and K is the kinetic rate constant. Most models of solution-reprecipitation controlled grain growth during liquid phase sinte-

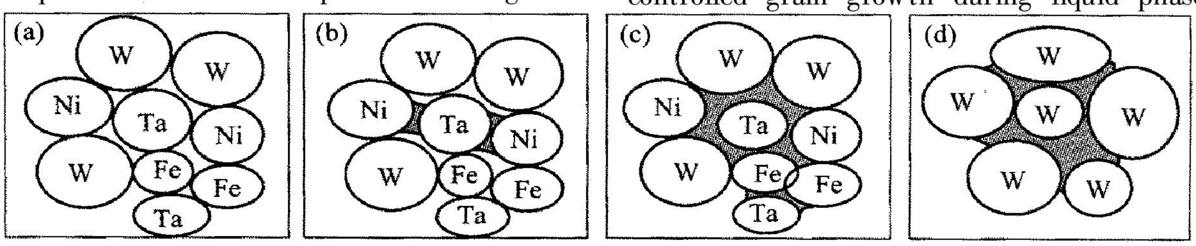

Fig. 1 Conceptual stages during liquid phase sintering for mixture of W, Ta, Ni, Fe powders
(a) —Initial stage; (b) —Emergence of liquid; (c) —Intermediate stage of liquid diffusion; (d) —Completion of liquid form

ring predict the exponent n to be 3. The tungsten based heavy alloys give the exponent as 2.8 after analyzing grain growth. The kinetic rate constant K is dependent on the material constant and can be expressed in the following equation:

$$K = gDC\Omega\tau/[kT(1-\varphi^{1/3}]\qquad(2)$$

where g is a numerical constant, D is the diffusivity of solute tungsten in the liquid matrix, C is the solubility of solute in the liquid, Ω is the atomic volume, τ is the interfacial energy, k is Boltzmann constant, T is the absolute temperature and φ is the volume fraction of solid.

Theoretically, the reduction of the concentration of solute tungsten in the liquid will result in the decrease of rate constant K, therefore grain's refinement. The mode of Ta entering matrix is greatly different from that of W, i.e. the former enters matrix through eutectic reaction with Ni and Fe (discussed in pervious section), which determines the priority of Ta entering matrix material, while the latter does by diffusing into the liquid. The body-centered cubic metal tantalum exhibits a high solubility in matrix phase of the W-Ni-Fe alloys (EDS results of 85W-5Ta-7Ni-3Fe alloy are given in Table 3), thus Ta alloying addition will reduce the solubility of W atoms in the matrix material, further begets grain refinement. This study brings forth a direct manifestation of this theory in the aspect of experiment, as shown in Fig. 2. The degree of grain refinement is gradually enhanced as higher content Ta is added to W-Ni-Fe

Table 3 Phase's composition of 85W-5Ta-7Ni-3Fe and 90W-7Ni-3Fe alloys(mass fraction, %)

Sample	W phase				Matrix phase			
	W	Ta	Ni	Fe	W	Ta	Ni	Fe
90W-7Ni-3Fe	97.8	–	1.4	0.8	23.0	–	52.3	24.7
85W-5Ta-7Ni-3Fe	85.7	13.0	0.72	0.67	14.7	16.1	45.2	22.2
80W-10Ta-7Ni-3Fe	90.7	8.2	1.1	0	15.9	18.7	49.1	16.2

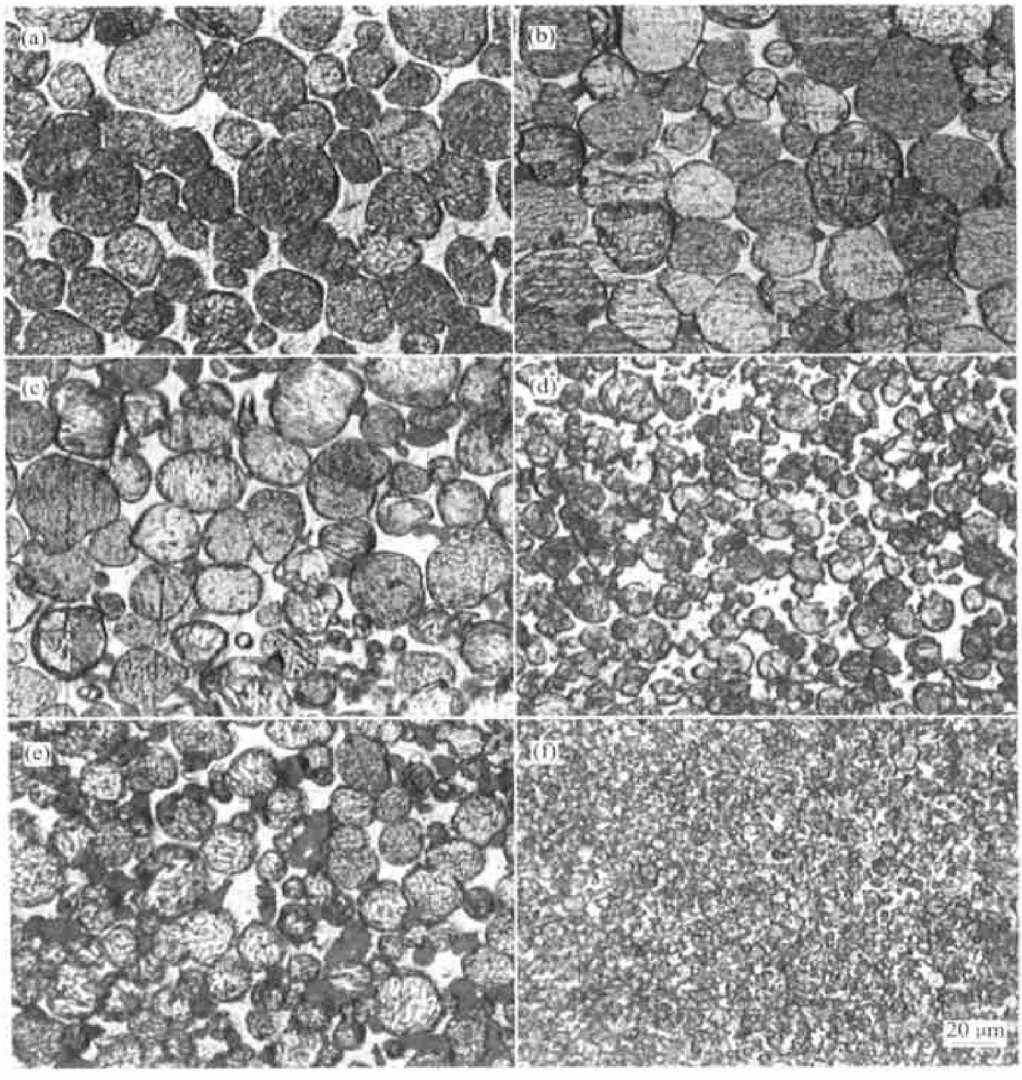

Fig. 2 Optical micrographs showing change of microstructure
(a) —90W-7Ni-3Fe; (b) —89W-1Ta-7Ni-3Fe; (c) —87W-3Ta-7Ni-3Fe;
(d) —85W-5Ta-7Ni-3Fe; (e) —83W-7Ta-7Ni-3Fe; (f) —80W-10Ta-7Ni-3Fe

alloy. Obviously, the reducing extent of tungsten grains in these alloys containing 1% and 3% Ta is not enough, and yet changes are very notable in alloys added with more than 5% Ta. As the content of Ta added is increased to 10%, the microstructural refinement is very visible and the grain size is about 5 μm. Theoretically, there is a solution limit of tantalum in Ni-Fe material at the given sintering temperature. As Ta addition is less than a critical value (between 3% and 5%), the effect of Ta reducing the solubility of W atoms in the matrix liquid is not saliently enough even though all Ta particles are dissolved completely. The amount of W atoms in the liquid phase is sufficient for the proceeding of solution-reprecipitation, and W particles grow at an almost unaffected rate. Ta content over the critical value can remarkably retard the process of W solution-reprecipitation at large, and so displays great effect on the microstructural refinement.

3.3 Phase analysis of sintered specimens

W and matrix phases are dominant in alloys doped with tantalum. According to the binary phase diagram of Ni-Ta and Fe-Ta, several kinds of intermetallic phases exist at certain temperatures and compositions[17]. So it's interesting to check phase constituent of alloys containing Ta element, and the results are shown in Fig. 3. The XRD patterns show that 87W-3Ta-7Ni-3Fe sample is composed of W,

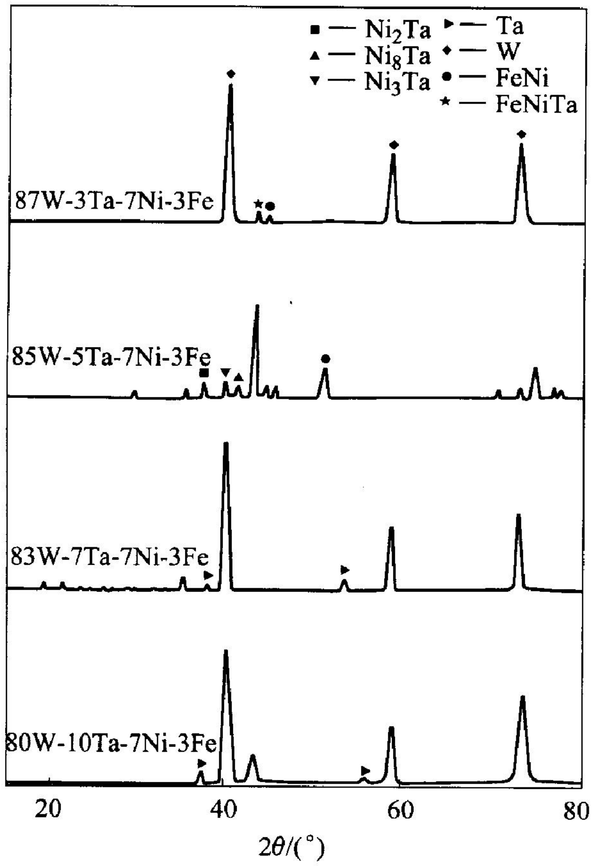

Fig. 3 XRD patterns of sintered alloys

FeNi and FeNiTa phases, and apart from them, three intermetallic phases are found in 85W-5Ta-7Ni-3Fe alloy: Ni_8Ta, Ni_3Ta and Ni_2Ta, and alloys with Ta content up to 7% have a different phase constituent from the above for a new phase Ta is present. The difference among the patterns is probably related with tantalum solubility in liquid matrix, reprecipitation and preferable reaction with Ni and Fe atoms. The existence of FeNi phase reflects the strong ability of reactivity between Ni and Fe.

4 CONCLUSION

Tantalum alloying additions have a profound effect on the microstructure of tungsten based heavy alloys. Because of the lower eutectic temperature in Ni-Ta and Fe-Ta than in Ni-Fe binary system, the liquid phase firstly emerges because of the uppermost integration between Ni and Ta, followed by liquid produced between Fe and Ta, which is greatly different from liquid emerging mechanism in traditional W-Ni-Fe system. Tantalum priority of entering matrix takes up a fraction of places in matrix that is usually occupied by W atoms, therefore the tungsten solubility in liquid is decreased, further the kinetic rate constant K is decreased too and so W grain size is reduced. The degree of microstructural refinement varies as Ta is added in different content. W and matrix are dominant phases in Ta doped alloys, and the intermetallic phases appear in microstructure. The superfluous Ta as a new phase exists in alloys containing more than 7% Ta.

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(Edited by YUAN Sai-qian)