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Influence of minor elements additions on microstructure and properties of 93W–4·9Ni–2·1Fe alloys

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Abstract. Effects of elements rhenium and chromium additions on properties and microstructure of 93W–4·9Ni–2·1Fe alloys were investigated. Optical microscope (OM), scanning electron microscope (SEM) and EDAX energy spectrometer were used to characterize the microstructure and compositions of the alloys, respectively. The tensile strength and elongation of alloys were evaluated using the quasi-static tensile testing machine, and the relative densities of the alloys were evaluated using the Archimedes water immersion method. The experimental results indicated that when elements Re and Cr were in the range of 0–1·0 wt.%, relative density, elongation, tensile strength of 93W–4·9Ni–2·1Fe alloys varied from 99·4%, 26·4%, 997·2 MPa without Re additions to 99·5%, 8·6%, 1161·2 MPa with 1·0 wt.% Re addition, respectively. Rhenium generated solid-solution strengthening, grain refinement, reducing ductile tearing and increasing transcrystalline fracture, which resulted in the ductility reduction and the strength increase of the heavy alloys. With the increase of Cr content from 0–1·0 wt.%, the tensile strength, relative density and elongation of 93W–Ni–Fe alloy reduced from 997·2 MPa, 99·3%, 15% to 844·4 MPa, 95·2%, 5·7%, respectively. Element Cr formed interphases with elements W, Ni, Fe and O and gathered along the interface of the alloys, which induced interfacial cohesion and resulted in lower mechanical properties of 93W–Ni–Fe alloys.

Keywords. 93W–Ni–Fe alloys; microstructure; mechanical properties; element chromium; element rhenium.

1. Introduction

Tungsten heavy alloys have been used for kinetic energy penetrators since the early fifties. The first alloys to be used were tungsten–nickel–copper. Later, tungsten–nickel–iron alloys were used because of their higher strength and ductility (German 1985; Hogwood and Bentley 1995). The design of tungsten heavy alloys has been the subject of many studies. According to some studies (Edmonds and Jones 1979; Muddle 1984), the toughness of liquid phase sintered tungsten heavy alloys is controlled mainly by the strength of the tungsten particle–matrix interface. Furnace cooling of W–Ni–Fe alloys results in increased brittleness due to precipitation of an intermetallic compound at the tungsten–matrix interface (Edmonds and Jones 1979). Another study of a commercial W–4·5Ni–4·5Fe alloy found the precipitate phase along the grain boundary under furnace cooling conditions. Moreover, a heat treatment profile subsequent to the isothermal hold at the sintering temperature, which consisted of solution treatment at 1350°C, water quenching, and isothermal aging in the temperature range from 600–900°C, caused W–7·2Ni–2·4Cu alloy to induce the precipitation of a continuous interphase boundary film, WNi4, worsening the mechanical properties.

Addition of Mo to W–Ni–Fe alloys was first reported by Bose and coworkers (Bose *et al* 1988; German *et al* 1989). They believed that the dissolution of W and Mo into the matrix was competitive such that addition of Mo reduced the concentration of W in the liquid matrix phase during sintering, and, consequently, refined microstructure. Subsequently, the effect of Mo addition on the mechanical properties (Bose and German 1990; Kemp and German 1995), and the microstructural evolution (Bose and German 1988; Kemp and German 1991; Park *et al* 1996) of the alloys were reported. These prior reports indicated the liability of forming a precipitated phase with the addition of high concentration of Mo, which led to the brittleness of the alloys.

Researchers have used lanthanum additions to improve microstructure of alloys. They found the reduction of the interfacial segregation of phosphorous, sulfur and its embrittlement effect by lanthanum additions in a W–Ni–Fe heavy alloy (Hong *et al* 1991; Wu *et al* 1999). But the influence of minor additions of Cr and Re elements on microstructure and properties of 93W–4·9Ni–2·1Fe alloys was not reported. The effects of minor Cr and Re elements additions on the microstructure and mechanical properties of 93W–4·9Ni–2·1Fe alloys are the aim of this study.

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Table 1. Properties of raw materials.

Elements/ Properties	W (reduced)	Ni (carbonyl)	Fe (carbonyl)	Re	Cr
Fsss (μm)	2.0	5~8	5~8	0~3	0~3
Content (wt.%)	99·8	99·5	99·5	99·8	99·8
Manufacturer	601 factory	Co. Ltd. of Jiangyou	Co. Ltd. of Jiangyou		

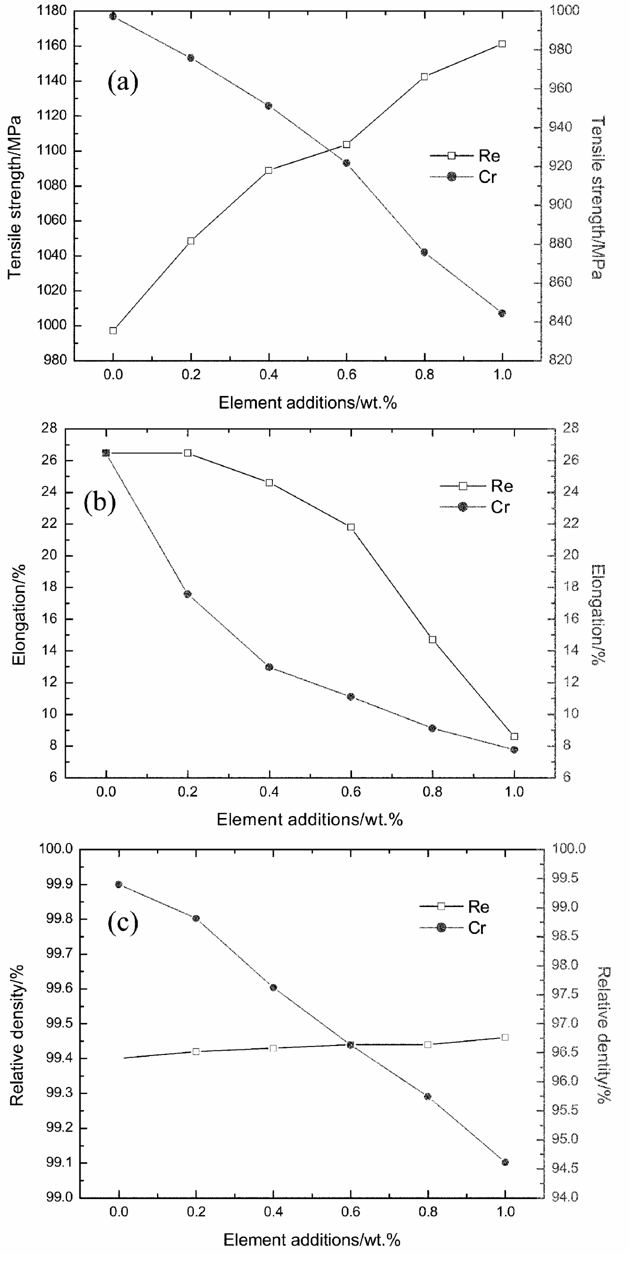

Figure 1. Properties of samples with element additions: (**a**) tensile strength, (**b**) elongation and (**c**) relative density.

2. Experimental

The raw materials in this experiment included the reduced tungsten powder, carbonyl nickel, carbonyl iron powder, chromium and rhenium powder (table 1). Tungsten, nickel and iron powders were mixed with a composition ratio of 93 wt.%W–4·9 wt.%Ni–2·1 wt.%Fe. Ethanol, which was analytically pure, was used as a medium in ball milling process. Element chromium or rhenium was added with 0·2, 0·4, 0·6, 0·8, 1·0 wt.% additions before ball milling. Particle sizes of BET and crystal sizes of mixed powder after ball milling for 50 h was 0·30 μm and 25·5 nm, respectively.

1·0 wt.% paraffin wax was mixed with milling powder as binder before press moulding, and the mixed powder was pressed with 25 ton YH41-25C type oil press machine. The compact was debinded at 850°C for 2 h in hydrogen atmosphere.

The sintering condition was 1490°C for 90 min in this experiment. The densities of the sintered specimens were measured with the Archimedes water immersion method. The tensile properties of specimens were tested on LJ-3000A type mechanical tensile machine with 2 mm·min^{-1} strain-rate. Samples were cut from testing machine and polished to observe the microstructure with PMG3 type optical microscope. Fracture surfaces of the tensile tested specimens were examined under JEOL JSM-5600LV scanning electron microscopy. The W-grain size was estimated by average diameter of all W-grains along two diagonal lines in optical micrograph.

3. Results and discussion

3.1 *Influence of minor element additions on mechanical properties of 93W–4·9Ni–2·1Fe alloys*

Figure 1 shows curves between relative density, tensile strength, elongation of specimens and different Re, Cr additions. As seen from figures 1(a) and (b), with the increase of Re additions from 0–1·0 wt%, tensile strength of sintered specimens increased from 997·2 MPa to 1161·2 MPa, but elongation of specimens reduced abruptly from 26·4–8·6%. With the increase of Cr additions from 0–1·0 wt.%, tensile strength of alloys reduced from 997·2–844·4 MPa, and elongation of specimens reduced quickly from 26·4–7·7%. From figure 1(c), relative densities of sintered specimens were maintained at 99·4–99·5% when Re content was in the range of 0–1·0 wt% but reduced from 99·4–94·6% with 1·0 wt% Cr, which resulted in reduction of mechanical properties of 93W–Ni–Fe alloys.

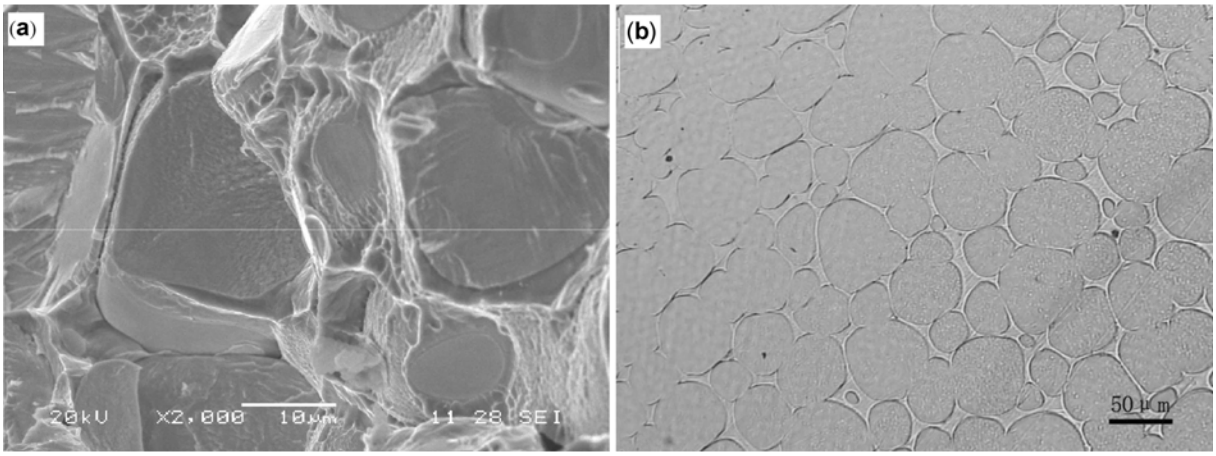

Figure 2. Tensile fracture features and optical micrograph of samples without element additions: (**a**) SEM and (**b**) OM.

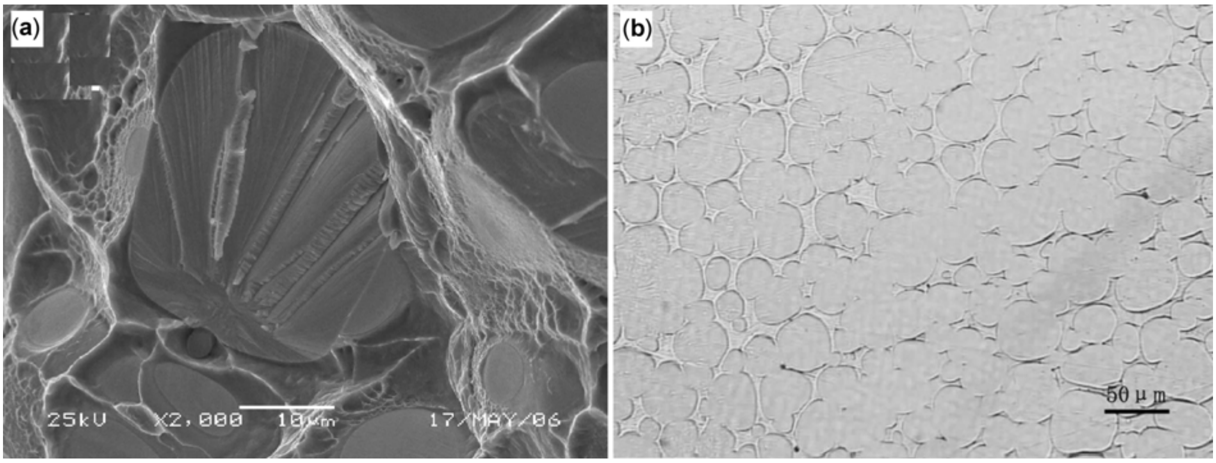

Figure 3. Tensile fracture features and optical micrograph of samples with 0·4 wt.% Re additions: (**a**) SEM and (**b**) OM.

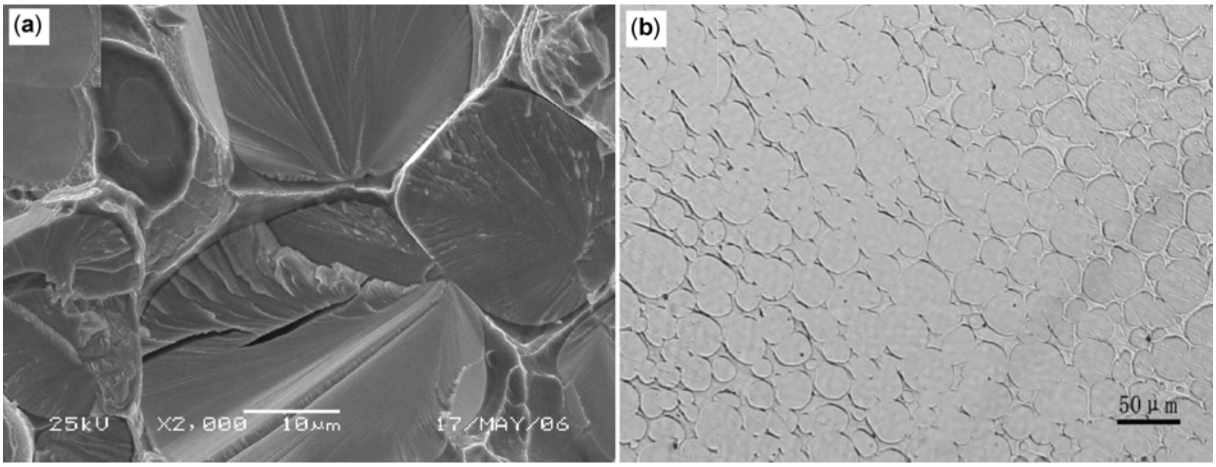

Figure 4. Tensile fracture features and optical micrograph of samples with 0·8 wt.% Re addition: (**a**) SEM and (**b**) OM.

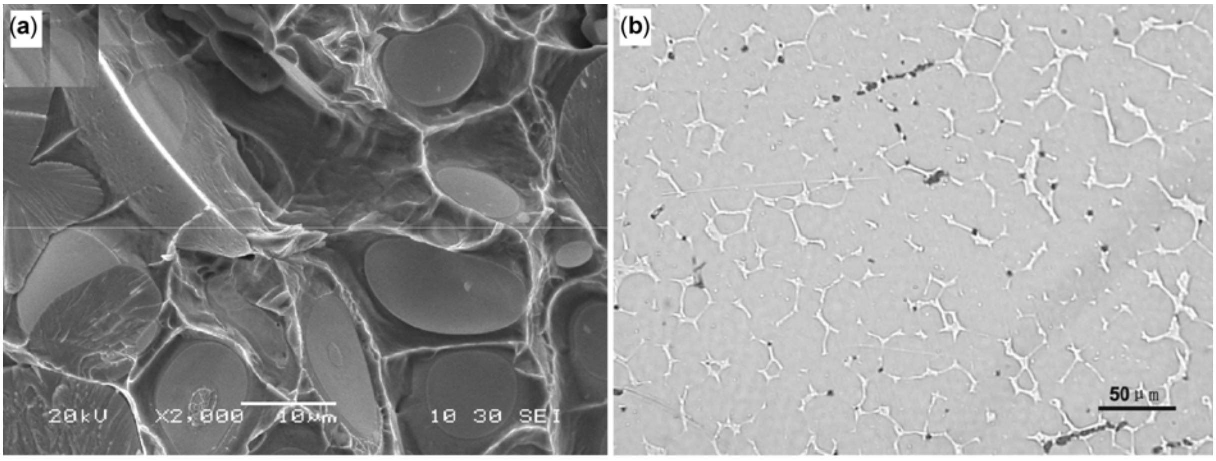

Figure 5. Tensile fracture features and optical micrograph of samples with 0·4 wt.% Cr additions: (**a**) SEM and (**b**) OM.

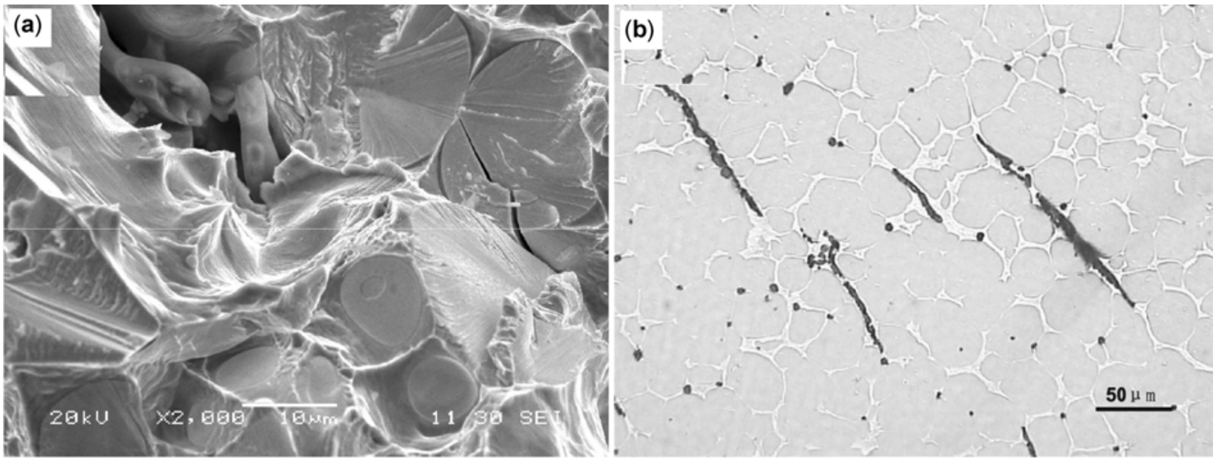

Figure 6. Tensile fracture features and optical micrograph of samples with 0·8 wt.% Cr additions: (**a**) SEM and (**b**) OM.

3.2 *Influence of minor element additions on microstructure of 93W–4·9Ni–2·1Fe alloys*

3.2a *Influence of Re additions on microstructure of specimens*: Figure 2 shows the fracture morphology and optical micrograph of alloys without Cr and Re. As seen from figure 2, ductile tearing of matrix and little transgranular cleavage fracture of W-grains are the main fracture mechanisms in 93W–4·9Ni–2·1Fe alloys. W-grain sizes of 93W–4·9Ni–2·1Fe alloys are 40–45 μm without element additions because the alloys are liquid sintering materials and W-grains grow from W atoms solution-precipitation through matrix.

Figure 3 shows tensile fracture morphology and optical micrograph of alloys with 0·4 wt% Re addition. As seen in figure 3, the ductile tearing and transcrystalline are main fracture models in 93W–4·9Ni–2·1Fe alloys. Matrix surrounded the W-grains homogeneously. As compared to figure 2(b), figure 3(b) shows W-grains sizes to reduce obviously. It was obvious that some Re additions could inhibit W-grains from growth and refined microstructure.

Figure 4 shows tensile fracture morphology and optical micrograph of alloys with 0·8 wt.% Re additions. As seen in figure 4, W-grains sizes of 93W–4·9Ni–2·1Fe alloys reduced from 40–45 μm without element additions to 20–25 μm with 0·8 wt.% Re additions. Matrix and W-grains distributed homogeneously. Transgranular cleavage fracture of W-grains were main fracture models in 93W–4·9Ni–2·1Fe alloys, but ductile fracture was found to be very little in the alloys. It showed that, with the increase in Re additions, elongation of alloys reduced and W-grains were refined effectively.

On the other hand, element Re was a solid solution in the matrix and after adding Re, it was found to improve structure and interface of alloys, enhancing tensile strength and reducing elongation.

Solid solution alloy was produced with some Re additions containing alloys due to element Re possessing high melting point, good strength and toughness and high solu-

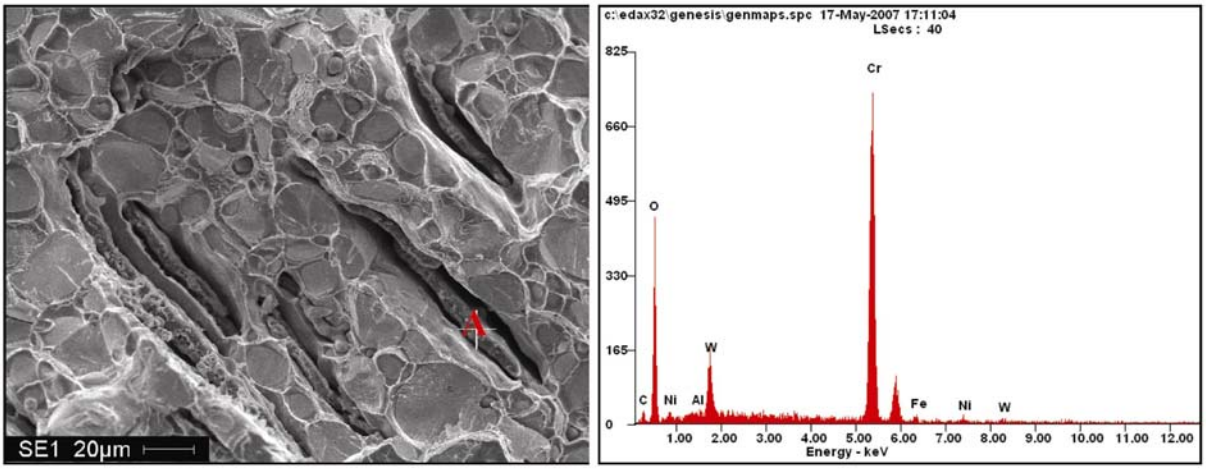

Figure 7. EDAX pattern of tensile fracture of samples with 1 wt.% Cr additions.

tion in *bcc* or *fcc* crystal structure, which resulted in solid-solution strengthening of alloys. Meanwhile, adding Re prevented W-atoms from solution-diffusion and inhibited W-grains from precipitation-growth because of solid solution alloy produced at interface of alloys and element Re owning high solution in matrix. It was grain refinement strengthening because of refining W-grain sizes.

3.2b *Effect of Cr additions on microstructure of specimens*: Figure 5 shows tensile fracture morphology and optical micrograph of alloys with 0·4 wt.% Cr additions. As seen in figure 5, interfacial fracture of alloys (W/W, W/M) and part transcrystalline cleavage fracture of W-grains were main fracture models in 93W–4·9Ni–2·1Fe alloys with 0·4 wt.% Cr additions. As compared to figure 2(b), figure 5(b) shows reduced W-grains sizes. It was obvious that some Cr additions could inhibit W-grains from growth.

Figure 6 shows tensile fracture morphology and optical micrograph of alloys with 0·8 wt.% Cr additions. As seen from figure 6, matrix and W-grains distributed inhomogeneously. 93W–Ni–Fe alloys owned high tungsten–tungsten contiguity. Element Cr formed aggregation in alloys, which led to lower density and mechanical properties of alloys.

Figure 7 shows EDAX pattern of aggregation in alloys with 1 wt.% Cr additions. As seen in figure 7, the higher the Cr contents were, the larger the aggregations were. Element Cr formed interphases with elements W, Ni, Fe and O when some Cr were added. Aggregations distributed along interface of alloys, inducing innerstress concentration and crack nucleating or extending, which reduced greatly mechanical properties of alloys.

4. Conclusions

(I) When element Re was in the range of 0–1 wt.%, relative density, elongation and tensile strength of 93W–4·9Ni–2·1Fe alloys varied from 99·4%, 26·4%, 997·2 MPa without Re additions to 99·5%, 8·6%, 1161·2 MPa with 1 wt.% Re additions, respectively. Solid solution alloy was produced with some Re additions containing alloys, which generated solid-solution strengthening of alloys. Meanwhile, adding Re prevented W atoms from solution-diffusion and inhibited W-grains from precipitation-growth, which generated grain refinement strengthening.

(II) With the increase of Cr content from 0–1 wt.%, the tensile strength, relative density and elongation of 93W–Ni–Fe alloy reduced from 997·2 MPa, 99·3%, 15% to 844·4 MPa, 95·2%, 5·7%, respectively. Element Cr formed interphases with elements W, Ni, Fe and O and gathered along interface of the alloys, which induced interfacial cohesion and resulted in lower mechanical properties of 93W–Ni–Fe alloys.

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