

## Fabrication of nano-crystalline W-Ni-Fe pre-alloyed powders by mechanical alloying technique

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Received 10 August 2009; accepted 15 September 2009

**Abstract:** Nano-crystalline pre-alloyed powders of W-Ni-Fe were fabricated by high energy ball milling mechanical alloying (MA) technique. The change of appearances and the crystallite sizes of powders before and after high energy ball milling were investigated by XRD, TOPAS P software, SEM and EDS. The results show that the nano-crystalline pre-alloyed powders can be fabricated by 5 h high energy ball milling. During the MA process, the diffusion of W, Ni and Fe happens in the process of repeated welding and fracturing. As a result, nano-crystalline supersaturated solid solutions are formed. The crystallite sizes won't be refined after 10 h ball milling. The crystallite sizes of different compositions are almost the same under the same MA condition. Due to the toughening mechanism of rare earth element, the powders of 90W-4Ni-2Fe-3.8Mo-0.2RE alloy are seriously agglomerated after ball milling compared with the other alloys. It can be concluded that the optimal sintering temperature of 90W-4Ni-2Fe-3.8Mo-0.2RE pre-alloyed powders after 15 h mechanical alloying is 1300–1350 °C.

**Key words:** tungsten based high-density alloy; mechanical alloying; high energy ball milling; nano-crystalline; low temperature sintering

### 1 Introduction

With the development of technique and science, tungsten based high-density alloy plays an important role in conventional fields of national defense, war industry, aviation and spaceflight, and its consumption as a refractory material is largely increased in such fields as electronic information, energy and dynamical mechanism[1–5]. Due to the particular properties of nano-materials, nano-crystalline tungsten based high density alloys will be used widely not only as structural material, but also as functional material. Nano-crystalline tungsten-based alloys possess its good properties of high melting point, high temperature strength, erosion resistance and so on, moreover, its integrated room temperature mechanical properties are improved greatly[6–10].

Nano-crystalline alloy powders can be obtained by high energy ball milling technique, which is the most widely used way to produce pre-alloyed powders

because it is simple and effective[11–12]. The elemental powder mixture of 90W-7Ni-3Fe was mechanically alloyed in the QM-2SP16 planetary high energy ball mill. The optimal MA process was investigated by FAN et al[13]. CAI et al[14] investigated the mechanical properties of high energy ball milled and sintered 93W-4.9Ni-2.1Fe alloys, LIU et al[15] investigated the sintering characteristics of ultrafine 93W-4.9Ni-2.1Fe pre-alloyed powder prepared by MA. The results show that ultrafine 93W-4.9Ni-2.1Fe pre-alloyed powder has BET particle sizes of 25.5 nm, and the element area distribution of the powder is homogeneous after milling 50 h. W crystal morphology of the alloy sintered at 1480 °C for 90 min is spherical or nearly spherical.

At present, the study of high melting point nano-crystalline tungsten based high-density alloys fabricated by MA technique focuses on the following three aspects: reactivity[16], agglomeration[17] and grain growth in sintering[16–17]. In recent years, the technique and mechanism of MA have been studied, however, the result

of MA study are far from utilization[18].

In this work, the technique and mechanism of high energy MA and sintering technology of nano-crystalline W-Ni-Fe alloy powders were researched. The sintering characteristics of W-Ni-Fe pre-alloyed powder prepared by MA were studied in order to explore the sintering properties of W-Ni-Fe alloys.

## 2 Experimental

In this experiment, deoxidization tungsten(W) powders, hydroxy iron(Fe) powders, high pure molybdenum(Mo) and RE (rare earth element  $\text{La}_2\text{O}_3 + \text{Y}_2\text{O}_3$ ) powders were used as raw materials. They were then ball milled in protective argon gas, which was introduced into the ball mill after it was vacuumized. The ball mill used in this experiment was QM-ISP2-CL type gear ball mill with high energy equipped with stainless steel balls and pots, the mass ratio of balls to raw powders was 5:1 and the rotation rate was 400 r/min. The prepared 90W-4Ni-2Fe-4Mo, 90W-4Ni-2Fe-3.8Mo-0.2RE and 86W-7Ni-3Fe-4Mo pre-alloyed powders were analyzed with X-ray diffraction diffractometer (XRD, D8 ADVANCE), in order to study the change of crystallite sizes. The test conditions are as follows: radiation target is Cu  $\text{K}_{\alpha 1}$ , tube voltage is 40 V, and tube electricity is 40 mA; radiation slot receives slot, and solon slot is  $1^\circ$ ,  $0.1^\circ$  and  $2.3^\circ$ , respectively. Scan angle ranges from  $30^\circ$  to  $90^\circ$ , scan step is  $0.02^\circ$ , scan speed is  $0.5^\circ/\text{s}$ . Phase identification and linearity analysis were conducted by EVA (Search/Match) software and TOPAS P software, respectively.

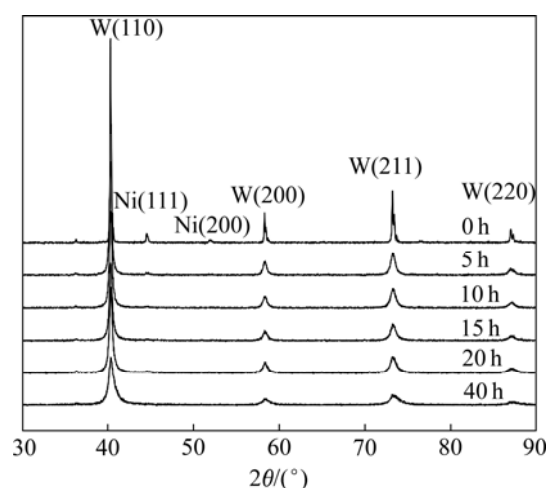
The sintering experiments were performed in high purity argon atmosphere. Sheet specimens with size of  $d14 \text{ mm} \times 3 \text{ mm}$  were obtained after pre-alloyed powders were pressed at pressure of 500 MPa and sintered in vacuum furnace (1 300  $^\circ\text{C}$ , 75 min; 1 350  $^\circ\text{C}$ , 60 min; 1 400  $^\circ\text{C}$ , 80 min). The morphologies of nanosized grains powders and the crystalline size and microstructures of tungsten grains after sintering were observed by scanning electron microscopy (SEM, FEI Quanta200), and elements analyses were accomplished with INCA energy dispersive spectroscopy (EDS).

## 3 Results and discussion

### 3.1 XRD patterns of 90W- 4Ni-2Fe-3.8Mo-0.2RE powders with different ball milling times

Fig.1 shows the XRD patterns of 90W-4Ni-2Fe-3.8Mo-0.2RE powders prepared after the ball milling time of 0, 5, 10, 20, and 40 h, respectively. W, Ni, Fe and Mo powders mixture underwent deformation and cold

welding caused by continuous collision and split between balls and powders, and their crystal lattice were also aberration. As can be seen in Fig.1, ball milling makes diffraction peaks become wide and the peaks intensities decrease. For original powders, the diffraction peaks of W powders are very strong and Ni has two preferred orientations of (111), (200), while Fe and Mo have no diffraction peak. The reason is that W content is very high and Fe and Mo contents are low, as a result, the Fe, Mo diffraction lines are so weak that they can't be detected. After 5 h ball milling, Ni peaks obviously decrease and W peaks broaden, the strongest peak also decreases. When the ball milling time increases to 10 h, the Ni peaks disappear, only the diffraction peaks of W occur. In the further ball milling process, diffraction peaks of W widen and the intensities decrease.



**Fig.1** XRD patterns of 90W-4Ni-2Fe-3.8Mo-0.2RE powders prepared with ball milling time of 0, 5, 10, 20 and 40 h, respectively

The broadening of diffraction peaks reflects that the crystallite size is refined and microcosmic stress increases. On the one hand, when the crystallite size is refined to some extent, the number of crystal faces to participate in reflection toward a particular Prague direction becomes less, so when the incidence angle deviates a little from Prague angle, there remains some non-Prague angle diffraction strength after X-ray is reflected and synthesized which make the diffraction line wider. On the other hand, the crystal lattices continuously deform in the process of high energy ball milling and Ni atoms move into W crystal lattice to form solid solution, accordingly there is microcosmic strain in powders. Different crystallite sizes have different crystal constants. When the interval between crystal faces is a little more than that of normal ones, the Prague angle becomes a little decrease so the reflection lines are a sum

of the total displaced reflection lines which make the diffraction lines broaden as well.

### 3.2 Nano-crystallization of 90W-4Ni-2Fe-3.8Mo-0.2RE prealloy powders in process of MA

Crystallite size determination is one of the most important applications in powder diffractometry for materials characterization. Powders size can be summarized as follows: particle or grain size, crystal size, crystallite size and domain size. The particle size and grain size are not accessible by powder diffraction. Typical methods used for particle size determination are light microscopy, laser size analysis, sieving and others. Complications may arise due to the fact that particles can agglomerate.

X-ray diffraction patterns can be used to calculate crystallite sizes (the sizes of micro-crystallite with the same crystal lattice orientation) by linear-analysis-method. X-ray diffraction lines can be broadened because of the lessening of crystallite size in the MA process. So the crystallite sizes of powders can be calculated with the full width at half maximum of Ni (111) peak.

In the past researches[17–18], there are two factors resulting in the broadening of X-ray diffraction lines: Physic broadening and geometry broadening. Physic broadening is due to the lessening of crystallite size and lattice aberration. Geometry broadening (instrument broadening) is due to the test conditions. In order to know the crystallite size nicely, the influences of lattice aberration and geometry broadening must be eliminated. The crystallite size influence function is nearly tally with Cauchy Function, and the lattice aberration influence function is nearly tally with Gaussian function. Thus the analysis of X-ray diffraction line broadening can adopt the rolling integration:

$$I(x) = \int I_c(u) I_g(x-u) du \quad (1)$$

where  $I(x)$  is Voigt function. TOPAS P software is based on foundation parameter method. The radius of goniometer, slot widths and wavelength of X-ray were imported to eliminate the influences of geometry broadening. Based on Scherre formula, the X-ray diffraction lines broadening was calculated,  $B_c = 0.9\lambda/(L_{hkl}\cos\theta)$  and  $B_g = 4\epsilon\tan\theta$ , thus the crystallite size of Ni(111) (it is the main peak) was obtained.

Table 1 shows the crystallite sizes of W with different ball milling time. In order to investigate the influences of lattice aberration, the crystallite size of powders in different ball milling times was calculated with Scherre formula again. In this way, pseudo-voige function was used to calculate full width at half

maximum of Ni(111) peak, which doesn't eliminate the influences of lattice aberration.

Scherre formula is

$$D = 0.94\lambda/(\beta\cos\theta) \quad (2)$$

where  $D$  is crystallite size;  $\lambda$  is X-ray wavelength;  $\beta$  is full width at half maximum;  $\theta$  is Prague angle.

In this work, the anode target is made of copper, and the X-ray wavelength  $\lambda$  is 0.154 06 nm; W grain (110) diffraction peak is used to calculate W grains sizes. The results are listed in Table 2.

**Table 1** Tungsten crystallite sizes of 90W-4Ni-2Fe-3.8Mo-0.2RE powders (calculated by (110) peaks)

| Ball milling time/h | W crystallite size/nm |
|---------------------|-----------------------|
| 0                   | 254.7                 |
| 5                   | 38.0                  |
| 10                  | 34.7                  |
| 20                  | 29.5                  |
| 40                  | 18.6                  |

**Table 2** W crystallite sizes calculated by Eqn.(1)

| Ball milling time/h | $\lambda/\text{nm}$ | $\beta/(\circ)$ | $2\theta/(\circ)$ | W crystallite size/nm |
|---------------------|---------------------|-----------------|-------------------|-----------------------|
| 0                   | 0.154 06            | 0.047 846 14    | 40.302 12         | 184.725               |
| 5                   |                     | 0.292 953 10    | 40.302 85         | 30.170                |
| 10                  |                     | 0.312 933 20    | 40.315 38         | 28.245                |
| 20                  |                     | 0.360 317 00    | 40.323 40         | 24.531                |
| 40                  |                     | 0.710 670 90    | 40.354 45         | 12.439                |

As can be seen from Tables 1 and 2, the datum of the crystallite size is smaller when the influence of lattice aberration is neglected. That is to say, the lattice aberration has influence on X-ray diffraction lines broadening. The results is well accordance with the broadening of tungsten diffraction shown in Fig.1.

In the process of ball milling, repeated welding and fracturing among powders make them lose original shape and form composite microstructure. With the prolonged ball milling time, W crystallite sizes become further refined. The crystallite sizes reach 38 nm after 5 h ball milling. W crystallite sizes keep stable basically from 10 h to 20 h and only reach 18 nm after 40 h ball milling. Because the speed of W crystallite refining and distortion becomes slower and the nano-crystallite powders are very active and agglomeration occurs easily. In the further milling process, the refining of powders and reversion tend to become balanceable. The energy offered by stainless steel balls can only make W

crystallite sizes refine to 20 nm.

$$\sigma=(2ER/D)1/2^{[11]} \tag{3}$$

where  $\sigma$  is the impact force in the process of ball milling,  $E$  is plastic modulus,  $R$  is the radius of crack peak,  $D$  is the grain size.

The impact force of grain refining is proportional to the square root of crystallite size. The more refined the grains, the stronger the impact force. So the bigger balls, the higher rotate speed and higher ratio of balls to raw material were used.

Fig.2 shows the secondary electron image of powders. The original powders disperse well. After 5 h ball milling, the refining of crystallite size happens. After 20 h ball milling, powders show floc shape and the chromatic aberration isn't distinct. The mass of floc becomes bigger after 40 h ball milling because of agglomeration. Cold melting and collision in the high energy ball milling make dispersion of powders become difficult.

3.3 W crystallite sizes, morphologies and compositions of powders after 15 h ball milling

XRD patterns of three different compositional powders after 15 h ball-milling were analyzed and W crystallite size were then calculated by TOPAS P software as shown in Table 3. The mixture states of elemental powders in different compositions are the same after the same milling time.

Table 3 W crystallite sizes with different compositions after 15 h ball milling

| Composition             | W crystallite sizes/nm |
|-------------------------|------------------------|
| 90W-4Ni-2Fe-4Mo         | 28.20                  |
| 90W-4Ni-2Fe-3.8Mo-0.2RE | 28.50                  |
| 86W-7Ni-3Fe-4Mo         | 27.75                  |

Fig.3 shows the morphologies and compositions of three compositional powders after 15 h ball milling. Figs.3(a'), 3(b'), 3(c') and Tables 4, 5 and 6 show the

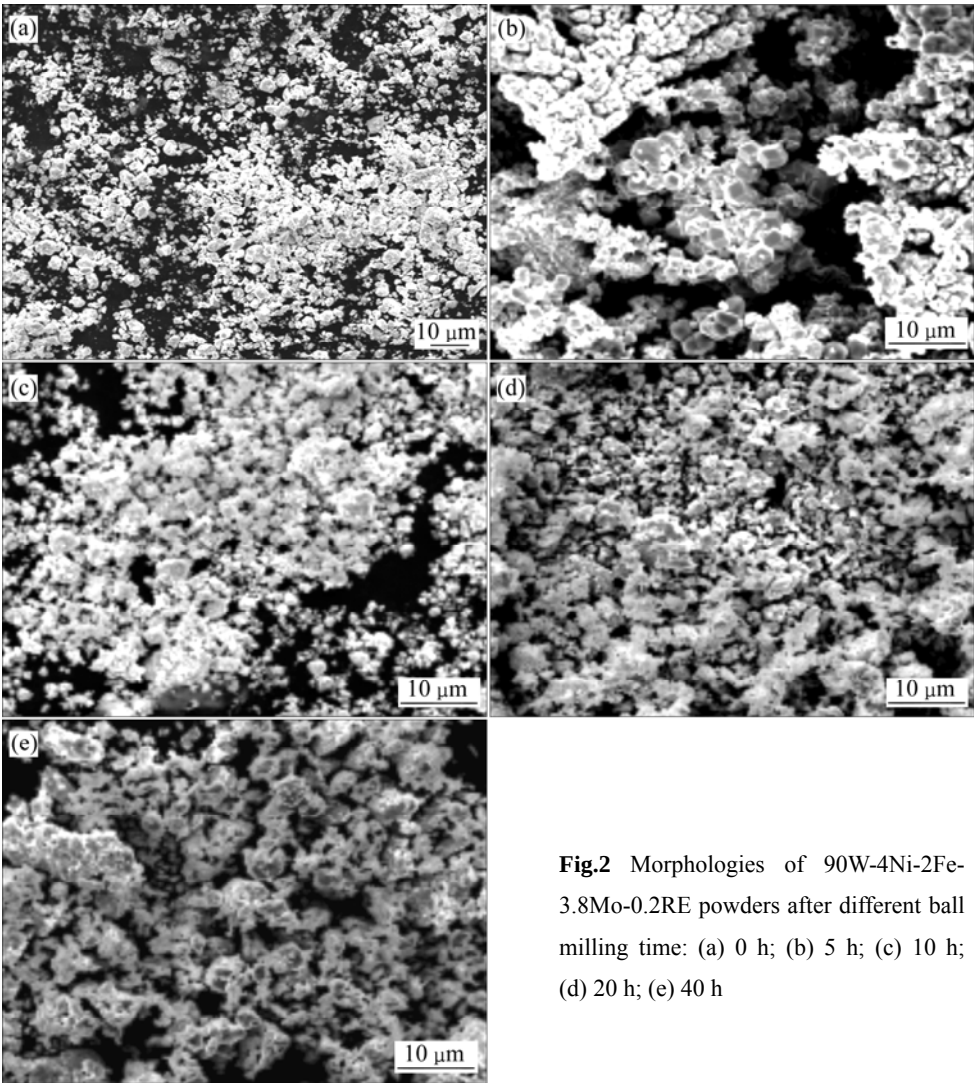
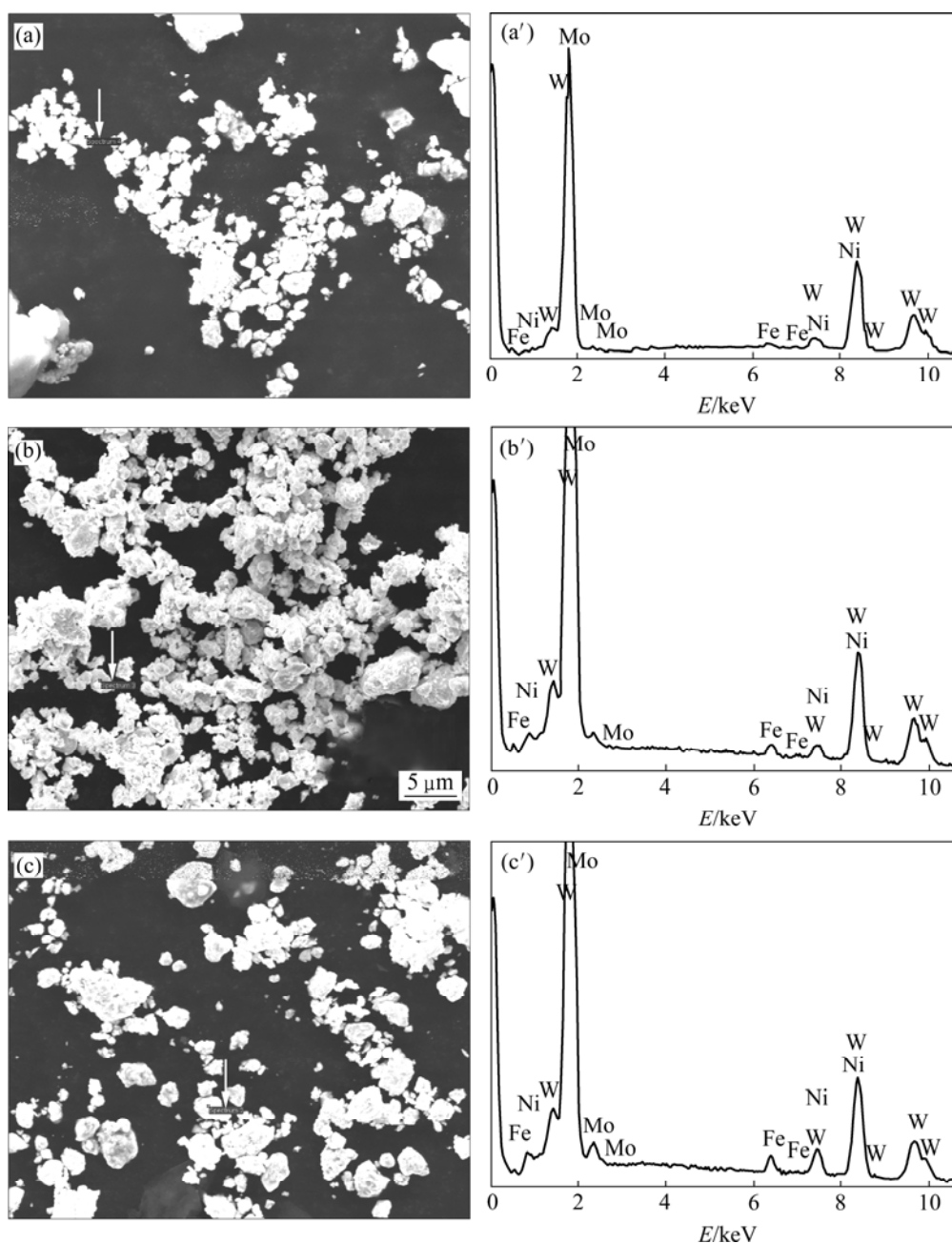


Fig.2 Morphologies of 90W-4Ni-2Fe-3.8Mo-0.2RE powders after different ball milling time: (a) 0 h; (b) 5 h; (c) 10 h; (d) 20 h; (e) 40 h



**Fig.3** Morphologies and compositions of three compositional powders after 15 h ball milling: (a), (a') 90W-4Ni-2Fe-4Mo; (b), (b') 90W-4Ni-2Fe-3.8Mo-0.2RE; (c), (c') 86W-7Ni-3Fe-4Mo

EDS spectra and chemical element contents of particles in Figs.3(a)–(c) tested by EDS point-scan.

As can be seen from Tables 4–6, the mixture states of elemental powders in different compositional powders are the same after the same milling time. The total trend is that W content increases and Ni, Fe, Mo content decrease correspondingly. This is because W content is high, cold welding occurs frequently and the opportunities to contact with other grains are high in the process of ball milling. As a result, W based powders mixture is formed. In addition, from Fig.1, the diffraction peaks continuously move to higher angle, which means

the crystal lattices of W crystallites get bigger than those of W crystallites in original powders. That is to say, solid solution forms, the binder phase is soluted in W and W supersaturated solid solutions forms. From the results

**Table 4** Element contents of 90W-4Ni-2Fe-4Mo

| Element | Mass fraction/% | Mole fraction/% |
|---------|-----------------|-----------------|
| Fe      | 1.36            | 4.03            |
| Ni      | 3.21            | 9.05            |
| Mo      | 1.06            | 1.84            |
| W       | 94.37           | 85.08           |

**Table 5** Element contents of 90W-4Ni-2Fe-3.8Mo-0.2RE

| Element | Mass fraction/% | Mole fraction/% |
|---------|-----------------|-----------------|
| Fe      | 1.81            | 5.38            |
| Ni      | 2.28            | 6.45            |
| Mo      | 1.70            | 2.95            |
| W       | 94.21           | 85.22           |

**Table 6** Element contents of 86W-7Ni-3Fe-4Mo

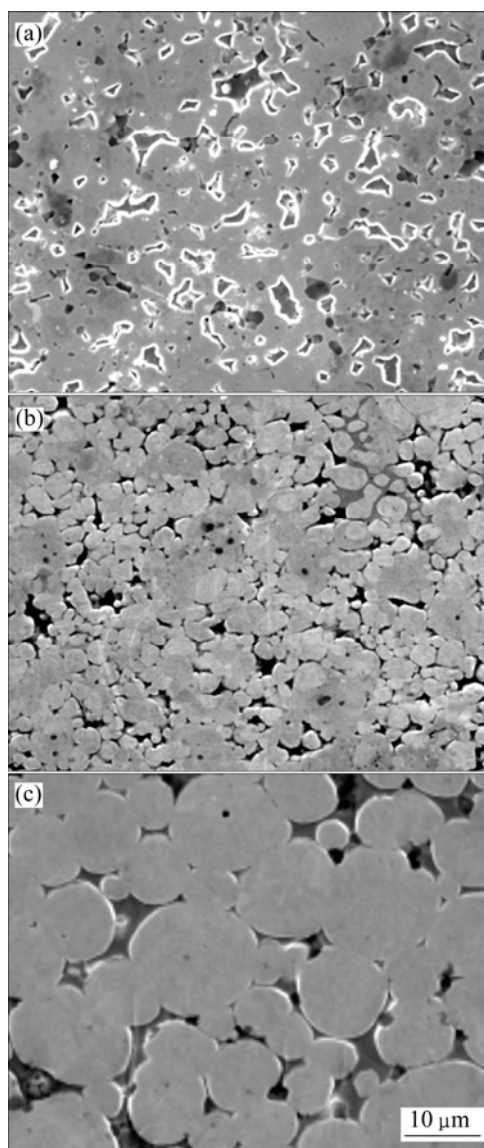
| Element | Mass fraction/% | Mole fraction/% |
|---------|-----------------|-----------------|
| Fe      | 2.30            | 6.37            |
| Ni      | 4.64            | 12.21           |
| Mo      | 4.20            | 6.76            |
| W       | 88.86           | 74.66           |

of EDS analysis, the compositions of powders are no longer single composition. This means that after 5 h high energy ball milling, the diffusion of Ni, Fe, Mo atoms into W atoms occurs.

From the morphology of powders, the particle sizes of 90W-4Ni-2Fe-4Mo and 86W-7Ni-3Fe-4Mo powders are very small and agglomeration phenomenon is not distinct. But 90W-4Ni-2Fe-3.8Mo-0.2RE powders agglomerate seriously, and the powders show floc shape. The conceivable reason is that rare earth elements dissolve in W crystal lattice in the high energy ball milling process, and the plasticity of W powder is improved, as a result, the repeated welding of W powder particle is more serious and fracturing is more difficult. Thus agglomeration is rather serious compared with that of the other two kinds of compositions.

### 3.4 Microstructures of sintered specimens

Fig.4 shows the microstructures of the tungsten based high-density alloys under different sintering conditions. It can be seen from Fig.4 that with the increase of sintering temperature from 1 300 °C to 1 400 °C, tungsten phase gets gradually spherical and tungsten grain sizes slightly enlarge. It also can be seen that the grains remain nano-crystalline at 1 300 °C and grow gradually at 1 350 °C and 1 400 °C. It can be concluded that high-energy ball milling can prepare nanocrystalline pre-alloyed powders and can reduce the sintering temperature. When the sintering temperature increases from 1 300 °C to 1 400 °C, tungsten phase (the lighter colored phase in pictures) in the same composition specimens gradually change from irregular to spherical shape and the grain sizes become bigger.



**Fig.4** Microstructures of 90W-4Ni-2Fe-3.8Mo-0.2RE specimen: (a) 1 300 °C, 75 min; (b) 1 350 °C, 60 min; (c) 1 400 °C, 80 min

## 4 Conclusions

1) Uniform nano-crystalline powders can be fabricated by high energy ball milling. Nano-crystalline powders can be gotten after 5 h ball milling.

2) At the beginning of ball milling, powders are crashed, grains are increasingly refined and deformed. During the MA process, the diffusions of W, Ni and Fe happen in the process of repeated welding and fracturing. As a result, nano-crystalline supersaturated solid solutions are formed.

3) With the further prolonged ball milling time, crystallite size is further refined and after 10 h ball milling, the effect of refining isn't distinct gradually.

4) Due to the toughening mechanism of rare earth

elements, the agglomeration phenomenon of 90W-4Ni-2Fe-3.8Mo-0.2RE powders is very serious compared with the other two kinds of compositions.

5) High-energy ball milling mechanical alloying technique can increase sintering driving force greatly. Compared with conventional technique, the vacuum sintering temperature of 90W-4Ni-2Fe-3.8Mo-0.2RE alloys can be 1 300 °C to 1 350 °C when high-energy ball milling mechanical alloying technique is adopted.

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(Edited by CHEN Can-hua)