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Synthesis and characteristics of W-Ni-Fe nano-composite powders prepared by mechanical alloying①

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Abstract: The mixture of 90 W-7 Ni-3 Fe(mass fraction, %) powders was milled in a planetary ball mill. Its structure changed during milling, the surface characteristics and thermal stability of the milled powders were studied with X-ray diffraction(XRD), Brunaure-Emmett-Teller(BET) nitrogen adsorption technique and differential thermal analysis(DTA). The results show that high-energy ball milling leads to the formation of composite powders with amorphous binder phase and supersaturated W(Ni, Fe) nano-crystalline grains in which great lattice distortion exists. The crystallization temperature of the amorphous binder phase during heating decreases with milling time. The specific surface area and the pore size of the powder mixtures decreases with milling time due to agglomeration and welding between particles.

Key words: tungsten-based heavy alloy; mechanical alloying; nano-crystalline powder **Document code:** A

1 INTRODUCTION

Tungsten-based heavy alloy is a unique material due to the combination of its high density, high strength, high ductility, high conductivity and good machinability[1,2]. It is widely used for radioactive shielding, inertial and military penetrating applications. Fully dense W-Ni-Fe heavy alloys are typically processed via liquid-phase sintering of compacts from elemental W powder blended with Ni and Fe powders[3]. However the relatively high processing temperature and long-term exposure usually result in a coarse final microstructure and progressive compact slumping and distortion[4,5]. It is known that finer and more uniform microstructure is beneficial to the strength and hardness of tungsten-based heavy alloys, and the problem of distortion during liquid-phase sintering can be effectively reduced through solid state sintering[1,6]. However, the compacts of elemental powder mixture are very difficult to be fully consolidated through solid state sintering due to lack of enough driving force for sintering[6,7]. In this study, mechanical alloying technique was applied to the W-Ni-Fe system to get finer and more uniform raw powders and the characteristics of the milled powders were evaluated.

2 EXPERIMENTAL

The mixture of 90 % W, 7 % Ni and 3 % Fe powders were subjected to mechanical alloying. The as-received elemental powders are reduced tungsten, carbonyl nickel and carbonyl iron powders respectively[5]. The ball milling process was conducted in a QM-1 planetary ball mill with 100 ml jars. The mass ratio of ball to powder was 5∶1. The rotation speed of the sun disk and the jar was 200 r/min. The experiments were carried out in a high purity argon atmosphere to avoid oxidation.

After various time of milling, a small amount of milled powder was taken out from the jar and glued onto a silica plate for X-ray diffraction analysis. Cu K_α radiation ($\lambda = 0.1540598$ nm) was used at a scanning speed of 0.1°/s. The peaks of W(110) and W(321) were selected for calculating the grain size (D) and lattice distortion ($\varepsilon = \Delta d/d$) according to the Cauchy-Gauss approximate function[8]:

$$B\cos\theta = 0.94\lambda/D + 2\varepsilon\sin\theta \quad (1)$$

where B, θ and λ are the integral width, diffraction angle and radiation wave length respectively. The relative intensity of W and Ni was determined in terms of $R = I_{W(110)}/I_{Ni(111)}$. The surface characteristics of the milled composite powders, including specific surface area, meso pore area, micro pore area and average pore radius were determined by means of Brunaure-Emmett-Teller(BET) nitrogen adsorption technique. DTA was carried out with a Perkin Elmer 7 series thermal analysis system. About 30 mg of the powder was used for each DTA test and a fixed heating rate of 10 ℃/min was selected from 30 ℃ up to 1 470 ℃.

3 RESULTS AND DISCUSSION

3.1 Structural evolution

Fig.1 shows the X-ray diffraction patterns of the powder mixtures milled for different times. Milling

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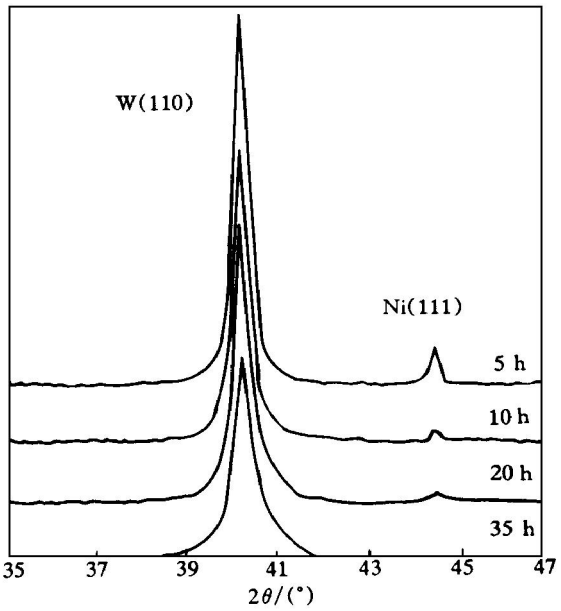

Fig.1 X-ray patterns of powder mixtures milled for different times

causes broadening of the line profiles. The Bragg peaks of γ-Ni phase decrease in intensity with milling time and even become almost invisible for powders milled for over 35 h. The relative intensity value(R) increases with milling time as shown in Fig.2. Fig.3 shows the morphology of the powder mixture milled for 20 h. From the results of X-ray diffraction and EDX of SEM, it was determined that the lattice constant of W phase decreased with milling time and alloying happened during milling[9]. Therefore it can be concluded from the above results that the amorphous (Ni, Fe) phase and W(Ni,Fe) supersaturated solid solution are produced by milling. Fig.4 shows the crystalline grain size and lattice distortion of

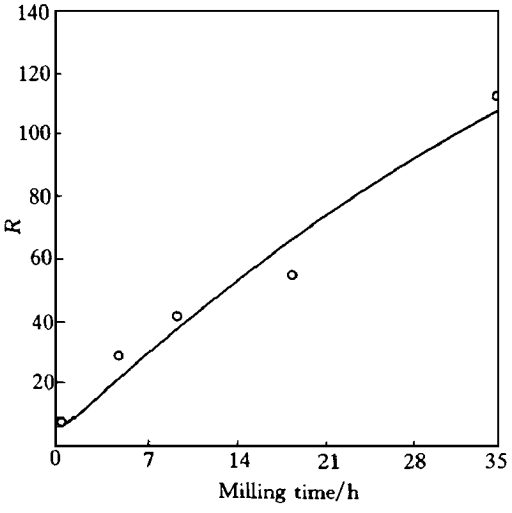

Fig.2 Variation of relative intensity value with milling time

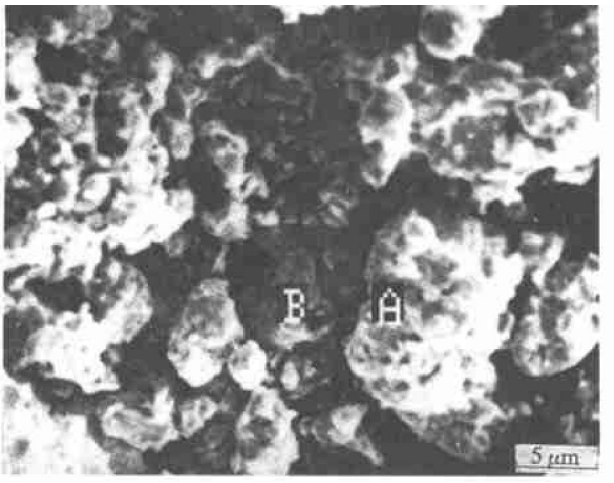

Fig.3 Morphology of powder mixture milled for 20 h

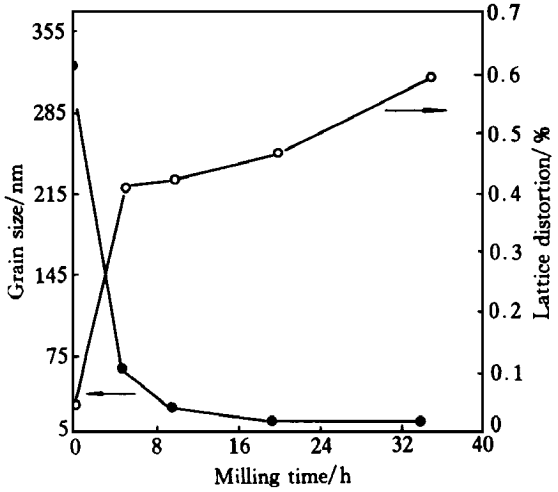

Fig.4 Crystalline grain size and lattice distortion versus milling time

W(Ni, Fe) phase versus milling time. A rapid decrease in grain size and a rapid increase in lattice distortion occurred during the first 10 h of milling due to high-energy impact of the balls and the resultant work hardening. After 10 h of milling, the rate of comminution decreases and the crystalline grain size reaches a constant value, while the lattice distortion continues increasing slowly. The slow-down of comminution process is believed to be due to the recovery of powders and welding between particles. When the equilibrium between recovery and comminution is approaching, the grain size tends to be a constant value.

3.2 Surface characteristics

Fig.5 is a plot showing the relationship between the specific surface area of the powder and milling time. It can be seen that the specific surface area decreases with milling time, which suggests that high agglomeration of powders and atom diffusion be-

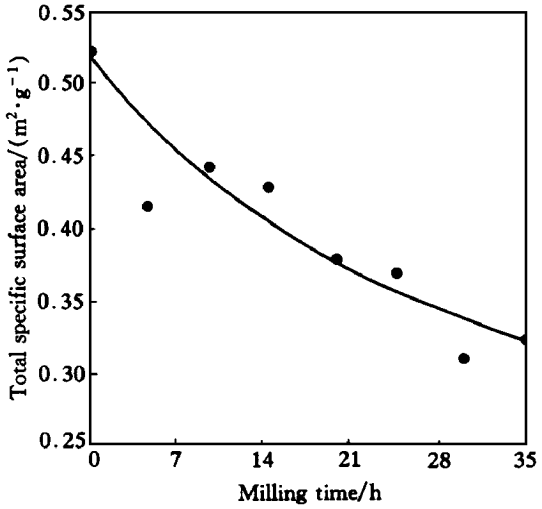

Fig.5 Specific surface area of powder mixtures versus milling time

tween particles happened during milling. The meso pore (2 ~ 50 nm) area also decreases with milling time as shown in Fig.6. However the micro pore (< 2 nm) area increases rapidly during the first 10 h of milling and then decreases as shown in Fig.7. At the beginning of milling the area of micro pores is almost zero, and only macro pores and meso pores coexist. During milling, the agglomerated bodies are compressed by repeated impacting, the pores become smaller and even are compressed into cracks which performs as micro pores when tested with BET technique, therefore, the total specific surface area and meso pore area decrease while the micro pore area increases at the initial milling stage. Afterwards, cold welding and diffusion between powders make the cracks healed up and the powders become more and more dense with milling time longer. Therefore the micro pore area decreases with milling time when the powder mixture continues to be milled. Thus it is easy to understand that the average pore size decreases with milling time as demonstrated in Fig.8.

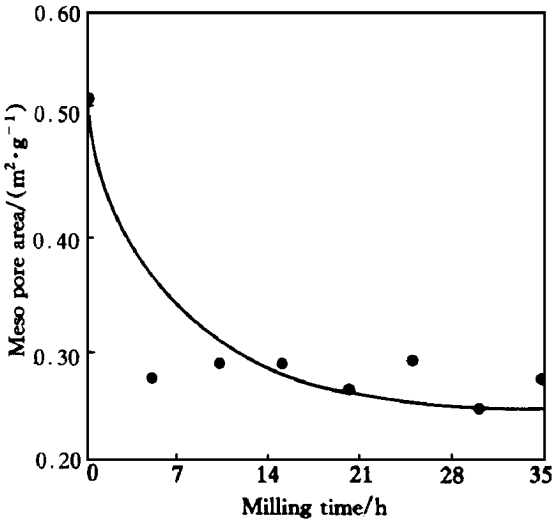

Fig.6 Meso pore area versus milling time

3.3 Thermal stability

Fig.9 shows the DTA curves of the powders milled for different times. For the milled powder compacts, there are two exothermic peaks and one endothermic peak during the heating process. The first exothermic peak are relatively broad and flat lasting from 200 ℃ to 750 ℃. This is contributed mainly to the overlapping of the precipitation of the supersaturated W(Ni, Fe) solid solution, the stress relaxation, and nano grain growth. However, the second exothermic peak is narrow and steep, which is corresponding to the crystallization of the amorphous binder phase, as showing with XRD method by heating powder up to the temperatures around the peak. Because no amorphous phase exists in the un-milled powder compact, the second exothermic peak does not appear on the curve. It is interesting to see that

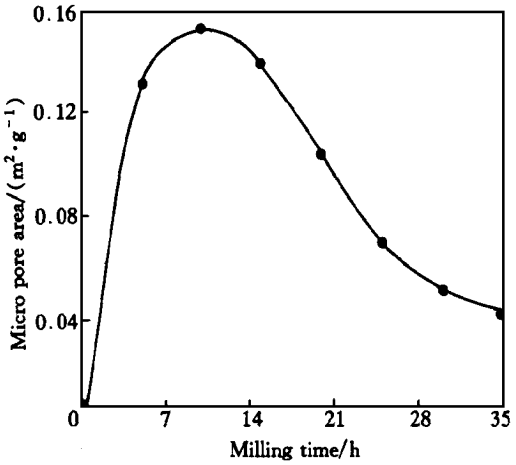

Fig.7 Micro pore area versus milling time

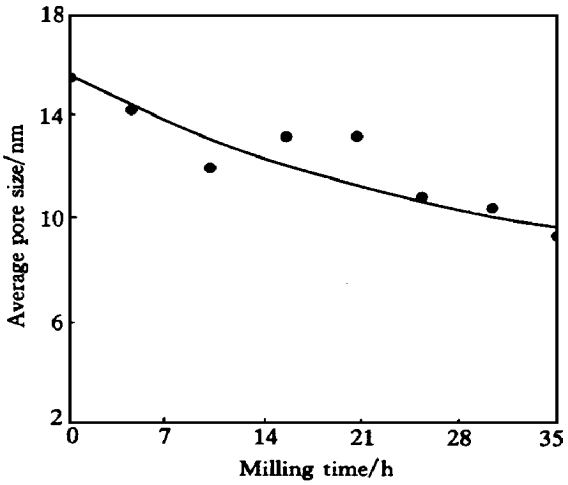

Fig.8 Average pore size versus milling time

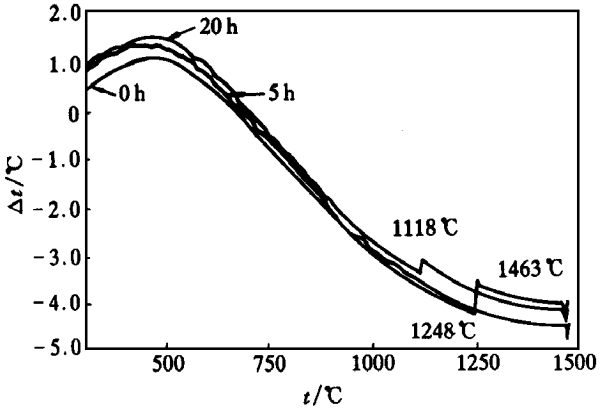

Fig.9 DTA curves of powder mixtures milled for different times

the crystallization temperature decreases with increase of milling time. The endothermic peak at about 1 463 ℃ in the DTA curve corresponds to the melting of γ (Ni, Fe, W) binder phase. It is seemed that the melting point is not influenced by milling. This result is different from that of other mechanically alloyed systems. For W-Ni-Fe system, although the melting point of the binder phase should decrease with milling time because a large amount of defects and nano-structure grains are produced by milling, the extension of solubility of W into γ-(Ni, Fe) binder phase due to milling will increase the melting point of the binder phase at the same time. The balance effect of these two factors results in the relatively stable melting point.

4 CONCLUSIONS

1) The X-ray diffraction analysis reveals that nano-crystalline W-Ni-Fe composite powders which consist of supersaturated solid solution and amorphous phase have been developed by mechanical alloying. With increasing milling time, the grain size of the supersaturated solid solution phase decreases and its lattice distortion rapidly increases.

2) BET results show that the specific surface area and meso pore area of the powders are reduced by mechanical alloying, and the average pore size becomes smaller with milling time.

3) Milling decreases the crystallization temperature of the milling-resultant amorphous binder phase but does not influence its melting point.

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