

Microstructure and properties of ultra-fine tungsten heavy alloys prepared by mechanical alloying and electric current activated sintering

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Abstract: The microstructure and properties of the 93W-4Ni-2Co-1Fe (mass fraction, %) tungsten heavy alloys prepared by mechanical alloying and electric current activated sintering from mixed elemental powders were investigated. After 15 h milling, the average W grain size in the powders is decreased to 120 nm. For the powders milled for 15 h, the density, hardness and transverse rupture strength of the alloys sintered only by an intensive pulse electric current are the maximum. When the total sintering time keeps constant, the properties of the sintered alloys can be obviously improved by optimizing the sintering time of pulse- and constant-currents. A bulk ultrafine alloy with an average W grain size of about 340 nm can be obtained by sintering 15 h-milled powders in a total sintering time of 6 min. The corresponding sintered density, hardness and transverse rupture strength reach 16.78 g/cm³, HRA84.3 and 968 MPa, respectively.

Key words: 93W-4Ni-2Co-1Fe alloy; mechanical alloying; electric current activated sintering

1 Introduction

Tungsten heavy alloy has been widely used as kinetic energy penetrators, counter-weights, radiation shields, vibration damping devices and electrical contacts because of its larger density, higher strength at elevated temperature, more excellent ductility and lower cost compared with other refractory metals[1–3]. Moreover, tungsten alloy can get rid of health hazard that is found in depleted uranium alloy used as kinetic energy penetrators[4–5]. In the past decades, numerous investigations have been carried out to improve the mechanical properties of tungsten heavy alloys by adjusting Ni-to-Fe ratio, adding refractory elements such as Co and Mo, mechanical alloying (MA) treatment, intensive pulse electric current sintering, and deformation strengthening, etc[6–9]. Among these ways, MA technique developed by BENJAMIN[10] is an advanced fabrication process that can cheaply produce powders with ultra-fine grains and homogeneous microstructure[11–12]. It has also been used to fabricate ultra-fine grained tungsten powders and consequently to

enhance the properties of sintered materials. Recently, a novel electric current activated sintering (ECAS) technique, also known as spark plasma sintering, was quickly developed, which is in essence an intensive pulse electric current sintering. ECAS is seen as an ideal route to sinter ultrafine and even nanocrystalline powders, because of its unique characteristics of rapid self-heat sintering, relatively low sintering temperature and plasma activation effect. It has been proved that ECAS mainly associated with particle surface activation, was obviously superior in preparation of ultra-fine and nanocrystalline bulk materials and parts[13–16]. In order to obtain fine microstructure and resultingly to improve the mechanical properties of sintered tungsten alloys, ECAS technique is used to sinter the powders prepared by MA in this work. The influence of milling time and sintering parameters on the microstructure and properties of sintered alloys is studied.

2 Experimental

2.1 Preparation of ultra-fine tungsten base powders

The commercial W, Ni, Co and Fe elemental

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powders were mixed in the stoichiometric composition of W-4Ni-2Co-1Fe (mass fraction, %). The characteristics of the starting elemental powders are shown in Table 1. The elemental powders were blended for 24 h in a low energy mixer. Then, the mixed powders were moved into a QM-2SP20 high energy attritor and milled in high purity argon atmosphere with cemented carbide milling balls. The mass ratio of ball to powder was 10:1. The milling speed was 226 r/min.

Table 1 Characteristics of starting powders

Starting powder	Purity/%	Average size/ μm
W	99.9	3.0
Ni	99.8	2.6
Fe	99.5	6.0
Co	99.5	3.5

2.2 Sintering processing of powders

In order to consolidate powders, 20 g powders every time were removed into an Al_2O_3 ceramic die with an inside diameter of 20 mm and then sintered in an ECAS device under a pressure of 30 MPa. During the sintering process, an intensive pulse current was applied first, of which the peak current, base current, repetition frequency and duty ratio were 3 000 A, 360 A, 50 Hz and 50%, respectively. Subsequently, a constant current of 1 500 A was applied for sintering except especial statement in the present work. The total sintering time of the pulse and constant currents kept 6 min.

2.3 Characteristic analysis

D/max-1200 X-ray diffraction (XRD) analyzer was used to characterize the mixed or the milled powders. The density of the samples was measured based on the Archimedes' principle. The morphology of the fracture surface of the samples was observed by a LEO 1530 VP scanning electron microscope (SEM). The transverse rupture strength and hardness of the sintered alloys were examined on a Xinsansi-CMT5105 mechanical property test device and a HDI-1875 Rockwell apparatus. A JEM 2010 transmission electron microscope was used to analyze the microstructure and impurity.

3 Results and discussion

3.1 Influence of mechanical alloying

The morphologies of powders milled for different times are shown in Fig.1. Milling obviously refines powders and homogenizes the size distribution of powder particle. After milling of about 15 h, the average particle size approaches the minimum, owing to the role of colliding and rolling of milling balls. With further milling, the powders start to agglomerate instead. The longer the milling time is, the more seriously the

powders agglomerate. As shown in Fig.1(c), after 80 h milling not only the powder particles markedly agglomerate but also the unhomogeneity of particle size aggravates. With the change of the powder appearance, the microstructure also changes, which is proved by the XRD patterns of the powders milled for different times. Because the contents of other elements in the powders are too small to be detected, only diffraction peaks of W phase are observed in the XRD patterns. The diffraction peaks become gradually widened and lower with the increase of milling time, indicating a continuous decrease in the W grain size and the presence of a large amount of defects in W phase. Fig.2 shows the influence of milling time on the W grain size and lattice distortion, calculated from the XRD patterns of milled powders. Here, the starting average W grain size was measured using optical microscopy. After 15 h milling, the W grain dramatically decreases from original 2.3 μm down to 120 nm, and the lattice distortion in W phase increases substantially. Although a longer time milling causes finer grains and larger lattice distortion, the change trends become weaker and weaker. There is no significant shift

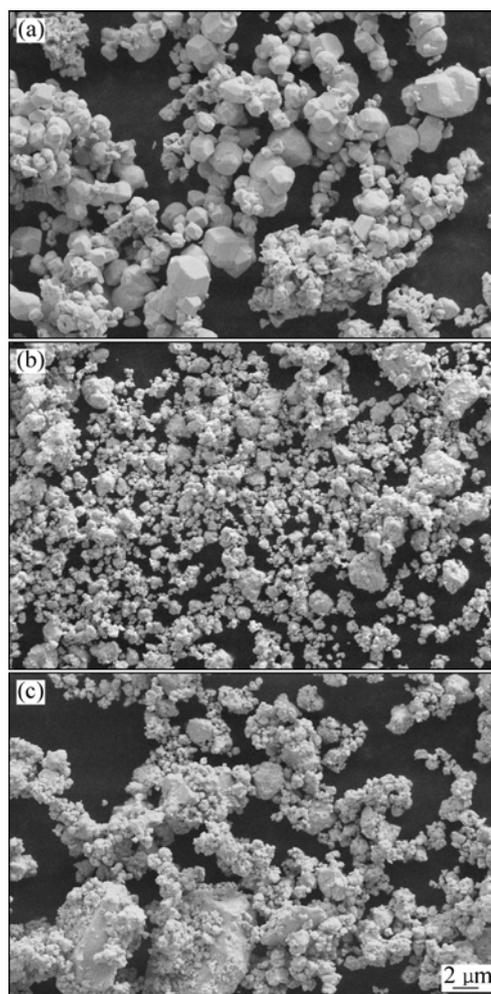


Fig.1 SEM images of powders milled for different times: (a) 0 h; (b) 15 h; (c) 80 h

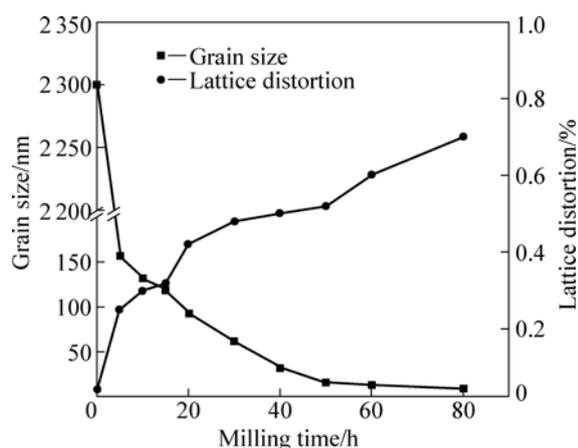


Fig.2 Effect of milling time on grain size and lattice distortion of W phase in milled powders

in the position of the major X-ray peaks as a function of the milling time. Even after the milling time is prolonged to 80 h, no evidence shows the milled powders have completely become amorphous.

In order to study the influence of mechanical alloying on the microstructure and properties of sintered samples, the W based powders milled for various times were sintered for 6 min by the pulse current with a peak of 3 kA. In all the XRD patterns of the samples sintered from milled powders, no diffraction peak of other phase is found except W. This indicates that if there are other phases in the sintered alloys, their amount is too small to detect. That is, even though undesirable brittle phases such as NiW and Ni₄W form in sintering, their contents are so small that the properties of the sintered samples are not extremely devastated. With the increase of milling time, the diffraction intensity of every crystal plane of tungsten phase decreases gradually, and the diffraction peak width becomes broader. The change trend with milling time is similar to that of the milled powders, suggesting milling refines W grains in sintered alloys. However, there are some differences between the diffraction patterns before and after sintering. Sintering causes the diffraction peak intensity to increase and the width to decrease. Obviously, sintering inevitably induces the W grain growth more or less. Fig.3 presents the relationship of milling time and W grain size in sintered alloys, which are obtained by SEM analysis. With milling time increasing, the W grain size decreases continuously. The grain size in sintered alloys of 80 h milling reduces from 4.5 μm of unmilling to 100 nm. Long time milling is helpful to refining the microstructure of sintered samples and even to obtaining bulk nanocrystalline materials.

A proper time milling can improve the sintered density, but overlong milling causes a low sintered density, as plotted in Fig.4. After milling for about 15 h,

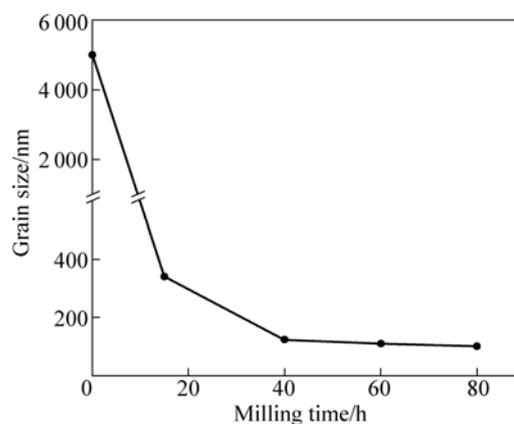


Fig.3 Effect of milling time on W grain size in sintered alloys

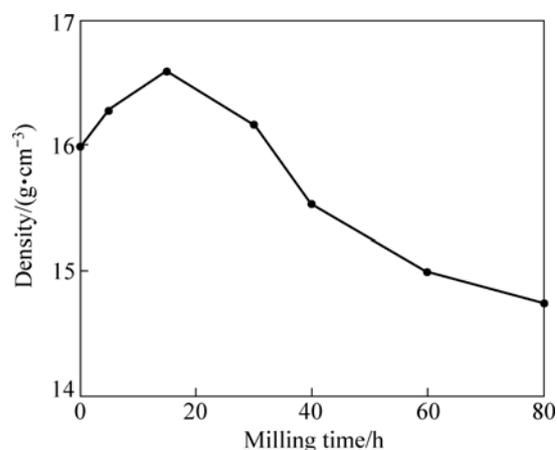


Fig.4 Effect of milling time on sintered density of tungsten heavy alloys

the sintered density reaches the maximum, being 16.58 g/cm^3 . The change of hardness and transverse rupture strength of sintered sample with milling time is similar to that of the sintered density. When the milling time is about 15 h, they are optimal, being HRA83.0 and 860 MPa, respectively, as shown in Fig.5. As mentioned above, mechanical alloying not only refines components, grains and particles but also augments lattice distortion. So, milling effectively activates the powders; and with the same sintering parameters, the atomic diffusions in powder body and especially on the powder surface are enhanced by milling. In addition, the refining of powder particles intensifies spark plasma forming among particles in sintering, because of the more interfaces of particles. Therefore, the sintering of properly milled powders is improved obviously. Consequently, the sintered density and mechanical properties increase. Though overlong milling can further refine W grains, the powder agglomeration becomes more and more terrible as shown in Fig.1. In the agglomerated powders, the small gaps among the particles are frequently enclosed and obstruct mass transfer during sintering; and in such way the spark sputtering phenomenon is restrained by

the bridge conjunction of clean interfaces among particles. Furthermore, the big agglomerating granules reduce the parent density before sintering and depress the total number of possibly forming discharges, owing to the decrease of contacting times among powder granules. All the above factors lead to an insufficient sintering. Therefore, the decrease of the sintered density and properties appears with milling time increasing. It is seen from Fig.4 and Fig.5 that 15 h milling is optimal to obtain high density and good mechanical properties. To further investigate the influence of sintering on microstructure and properties, 15 h-milled powders are chosen as the objects in the following research work.

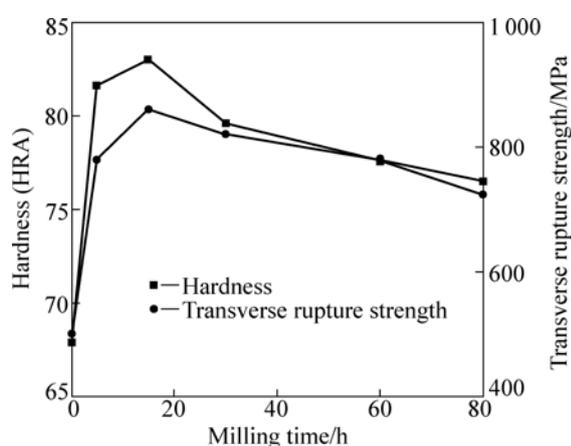


Fig.5 Effect of milling time on hardness and strength of sintered tungsten heavy alloys

3.2 Influence of sintering process

Clarifying the individual contribution of pulse current and constant current to sintering is necessary to optimize sintering parameters. So, in the present study, a pulse current and subsequent constant current were used to sinter 15 h-milled powders with a total sintering time of 6 min. The peak current, base current, repetition frequency and duty ratio of pulse current were set at 3 000 A, 360 A, 50 Hz and 50%, respectively, and the constant current was 1 500 A except special statement.

Fig.6 shows the effect of the pulse current sintering time on the sintered density. It is observed that the sintered density comes to the maximum of 16.78 g/cm^3 , when a 2 min pulse-current and subsequent 4 min constant-current sintering is supplied. With the pulse-current sintering time increasing or decreasing, the sintered density decreases obviously. If only the pulse current is applied to sintering, the sintered density falls down to the minimum, being 16.58 g/cm^3 . This is because the discharge plasma generated by the intensive pulse current among the powder particles has the effects of cleaning and activation on the surfaces of powders. In addition, the discharge shock pressure caused by the pulse current also results in the concentration of local

stress and heat energy. These promote the atomic diffusion on the surfaces of powders. As a result, the application of an intensive pulse current for sintering is favorable to the densification of powders. Nevertheless, the average value of the pulse current used in the present work is so small that the Joule heat produced by it is not enough in unit volume of the powders. A requisite sintering temperature for the tungsten based powders, in turn, is difficult to obtain only by the single pulse current of 6 min. Hence, the milled powders cannot be sufficiently sintered by the pulse current for such a short time. On the other hand, the constant current hardly generates discharge plasma to activate powders, since its value is constant and much less than the peak of the pulse current. But, it leads to a rapid temperature rising, because it has a higher mean value compared with the pulse current. So, a proper combination application of the pulse and constant currents is in favor of sintering, such as the 2 min pulse-current plus 4 min constant-current sintering. This not only takes full of the advantages of spark plasma generated by the intensive pulse current among the powder particles, but also benefits from the rapid heating of the constant current. As a result, the powders are sintered sufficiently.

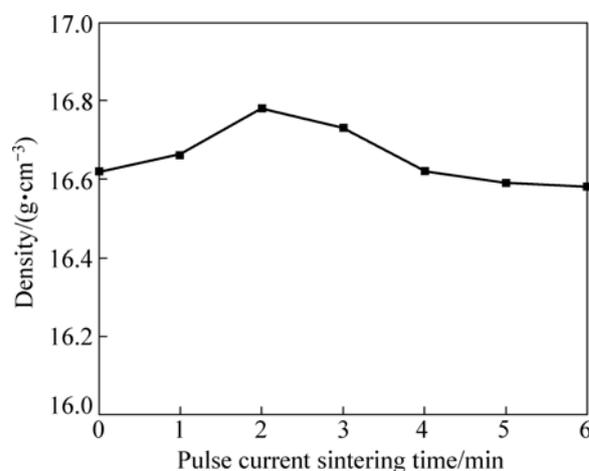


Fig.6 Effect of pulse current sintering time on sintered density of tungsten heavy alloys (Total sintering time: 6 min)

The variations of the hardness and transverse rupture strength of sintered alloys with pulse current sintering time are shown in Fig.7. When a 2 min pulse-current and subsequent 4 min constant-current sintering is supplied, the hardness and strength of the sintered alloys simultaneously reach the maxima, being HRA84.3 and 968 MPa, respectively. Further increasing the pulse-current sintering time tends to bring the decrease of the hardness and strength. This change is in agreement with the sintered density shown in Fig.6. An explanation to it is that sintered density represents porosity in materials, and porosity, in turn, determines

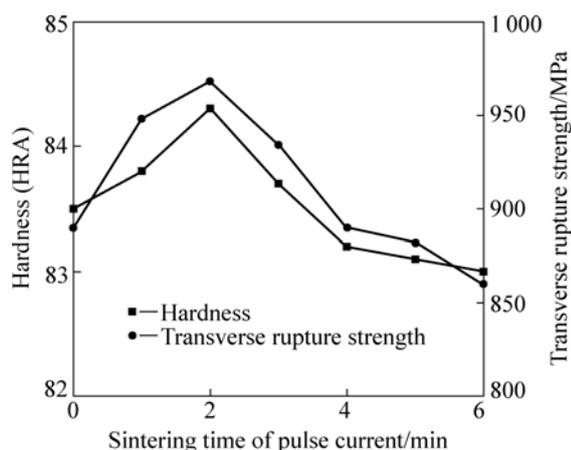


Fig.7 Effect of pulse-current sintering time on hardness and strength of tungsten heavy alloys

mechanical properties. When a 5 min pulse-current and subsequent 1 min constant-current sintering is adopted, the original morphology of the powder particles is even distinguished on the fracture surface, as shown in Fig.8(a), which is attributed to the low sintering temperature caused by the constant current sintering for short time. The final sintering temperature increases with the constant-current sintering time. When the constant-current sintering time is prolonged to 4 min, that is, the pulse-current sintering time is reduced to 2 min correspondingly, the final sintering temperature rises up to 1 200 °C. In comparison with conventional sintering of W based powders, the sintering temperature is still relatively lower. Hence, the grain growth of W is in a

good control. The average W grain size is only about 340 nm after sintering. Meanwhile, the sintered density comes to the peak. Consequently, the hardness and strength of the as-sintered alloys are improved. When the constant-current sintering time is further increased to 6 min, that is, the pulse-current sintering is completely canceled, the sintered density decreases instead and there exist a few small pores in the sintered sample, as shown in Fig.8(c). So, the decrease of mechanical properties happens. Using the constant current to sinter powders for 6 min, the sintered density is 16.62 g/cm³, which is higher than that of the single pulse current sintering, owing to its higher mean value. In case of constant current sintering, a higher sintered density of 16.92 g/cm³ can be achieved by intensifying electric current. In spite of lacking the activation effect of intensive pulse current, the plastic deformability of powders and the diffusion velocity of atom are improved, because of the sintering temperature elevated by the higher current. The sintering temperature is so high and reaches 1 402 °C. So, the W grains rapidly grow up to about 3 μm, as shown in Fig.8(d). Resultingly, the hardness and strength of the sintered alloys inversely become decreased. Obviously, it is too hard to manufacture a promising W alloys only sintered by a constant current.

From Fig.8(b), we can find that the sample prepared by the optimal sintering parameters is relatively dense. However, its density is just 16.78 g/cm³ and 94.32% of the theoretical density. Besides a small quantity of extremely tiny pores still existing in the sample, there are two other possible reasons for the relatively low density.

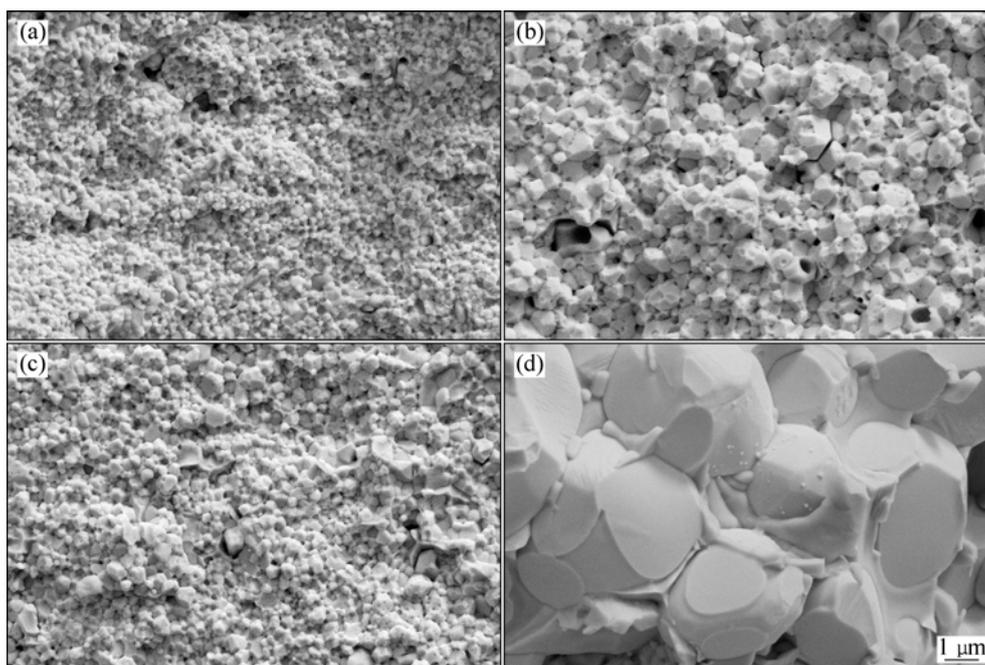


Fig.8 SEM images of tungsten heavy alloys sintered by pulse current for 5 min and subsequent constant current for 1 min (a), pulse current for 2 min and subsequent constant current for 4 min (b), 1 500 A constant current for 6 min (c), and 1 620 A constant current for 6 min (d)

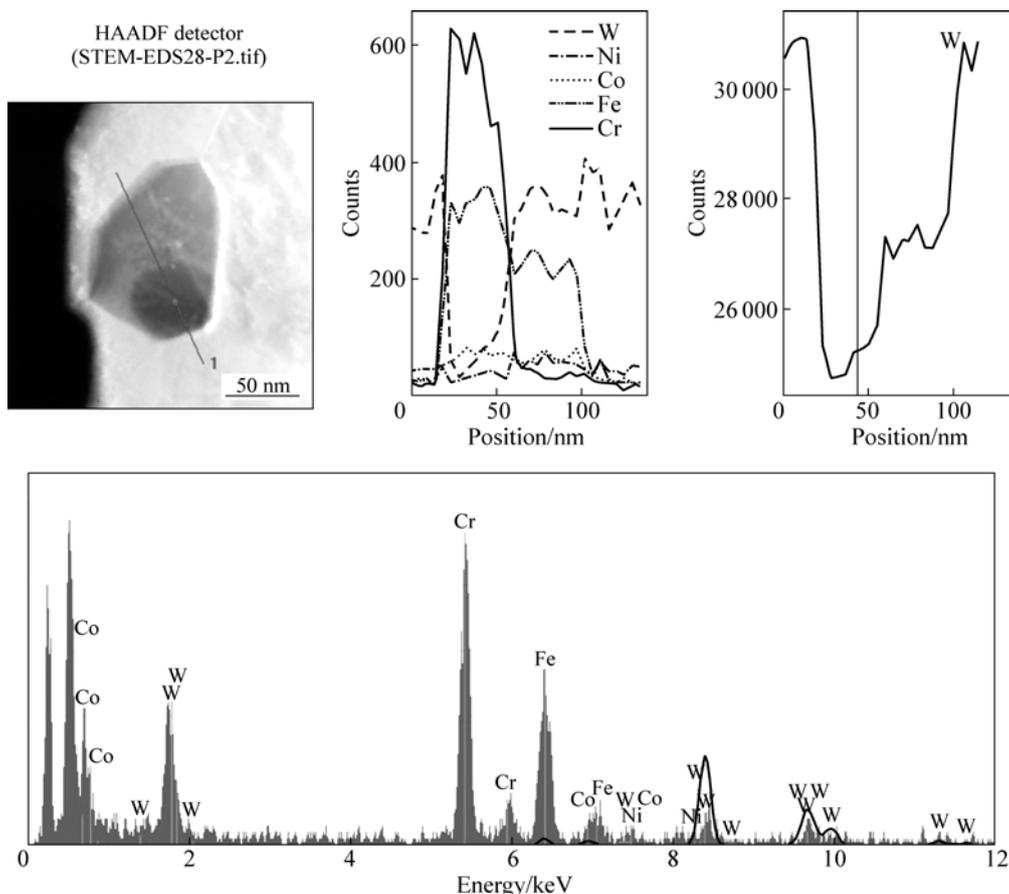


Fig.9 TEM image and energy spectrum analysis result of sintered tungsten heavy alloy

One is that the ultrafine microstructure of the as-sintered sample produces more grain boundaries. The other is there exist serious solid solutions of the binder components in the W phase and even some intermetallic compounds between the binder and W phases. The formation of intermetallic compounds such as NiW, NiW₂ and Ni₄W can be expected according to the binary phase diagram of W and Ni. Despite no direct evidences of these brittle phases are obtained from TEM observes, we believe that it is possible because the sintering temperature is higher than the peritectoid reaction temperatures of the above mentioned phases. As a result, the corresponding strength is still somewhat low. From the TEM analysis, chromium contamination is observed, distributing at the W grain boundaries, as shown in Fig.9. Cr in the sintered alloys is mainly introduced by mechanical alloying from the stainless steel mill wall. The impurity unavoidably weakens the joints among the W grains. Certainly, if the impurity is effectively avoided by choosing a harder or W milling vial, the strength of sintered alloys can be expected to further increase.

4 Conclusions

1) The milled W-4Ni-2Co-1Fe powders can be

sintered at a lower temperature and within a shorter time by an intensive electric current. A proper coupling of pulse current and subsequent constant current sintering facilitates the high relative density and sound mechanical properties of the alloys.

2) 15 h milling prior to sintering is helpful to preparing fine grain and good property bulk W-4Ni-2Co-1Fe alloy. The density, hardness and transverse rupture strength of the sintered alloy reach 16.78 g/cm³, HRA84.3 and 968 MPa, respectively, by optimizing the sintering times of pulse- and constant-currents. Meanwhile, the W grain growth in sintering is effectively inhibited. Reducing of impurity introduced in milling and brittle intermetallic compounds forming in sintering can further improve the mechanical properties of sintered alloys.

References

- [1] YU Y, WANG E D, HU L X. Effect of nanocrystalline tungsten powders on the microstructure and properties of liquid-phase sintered 93W alloys [J]. *Materials Science and Technology*, 2006, 14(4): 385–389.
- [2] HONG S H, RYU H J. Combination of mechanical alloying and two-stage sintering of a 93W-5.6Ni-1.4Fe tungsten heavy alloy [J]. *Materials Science and Engineering A*, 2003, 344(1/2): 253–260.

- [3] ZHU Y B, WANG Y, ZHANG X Y, QIN G W. W-Ni-Fe phase interfacial characteristics of liquid-phase sintered W-Ni-Fe alloy [J]. *International Journal of Refractory Metals and Hard Materials*, 2007, 25(4): 275–279.
- [4] RAVI B, RANDALL M G. Heating rate effects on microstructural properties of liquid phase sintered tungsten heavy alloys [J]. *International Journal of Refractory Metals and Hard Materials*, 2004, 22(2/3): 117–127.
- [5] XU, X P, UPADHYAYA A, GERMAN R M, LACOCOA R G. The effect of porosity on distortion of liquid phase sintered tungsten heavy alloys [J]. *International Journal of Refractory Metals and Hard Materials*, 1999, 17(5): 369–379.
- [6] JANG J S C, FWU J C, CHANG L J, CHEN G J, HSU C T. Study on the solid-phase sintering of the nano-structured heavy tungsten alloy powder [J]. *Journal of Alloys and Compounds*, 2007, 434: 367–370.
- [7] RYU H J, HONG S H, BAEK W H. Microstructure and mechanical properties of mechanically alloyed and solid-stage sintered tungsten heavy alloys [J]. *Materials Science and Engineering A*, 2000, 291(1/2): 91–96.
- [8] LEE K H, CHA S I, RYU H J, HONG S H. Effect of two-stage sintering process on microstructure and mechanical properties of ODS tungsten heavy alloy [J]. *Materials Science and Engineering A*, 2007, 458(1/2): 323–329.
- [9] DE MACEDO H R, DA SILVA A G P, DE MELO D M A. The spreading of cobalt, nickel and iron on tungsten carbide and the first stage of hard metal sintering [J]. *Materials Letters*, 2003, 57(24/25): 3924–3932.
- [10] BENJAMIN J S. Mechanical alloying [J]. *Scientific American*, 1976, 234(5): 108–116.
- [11] LI X Q, HU L X, WANG E D, HE W X, LIU Z Y. Microstructure of TiAl alloy prepared by intense plastic deformation and subsequent reaction sintering [J]. *Transactions of Nonferrous Metals Society of China*, 2002, 12(4): 621–624.
- [12] LI YY, LI XQ, LONG Y, SHAO M, XIA W. Pulse electric current sintering of iron-base powders prepared by high energy milling [J]. *Key Engineering Materials*, 2006, 315/316: 445–449.
- [13] MAMORU O. Sintering, consolidation, reaction and crystal growth by the spark plasma system (SPS) [J]. *Materials Science and Engineering A*, 2000, 287(2): 183–188.
- [14] VANMEENSEL K, HUANG S G, LAPTEV A, SALEHI S A, SWAMAKAR A K, VAN DER BIEST O, VLEUGELS J. Pulsed electric current sintering of electrically conductive ceramics [J]. *Journal of Materials Science*, 2008, 43(19): 6435–6440.
- [15] YAMAN B, MANDAL H. Spark plasma sintering of Co-WC cubic boron nitride composites [J]. *Materials Letters*, 2009, 63(12): 1041–1043.
- [16] RRU R, LICHERI R, LOCCI A M, CINCOTTI A, CAO G. Consolidation/synthesis of materials by electric current activated/assisted sintering [J]. *Materials Science and Engineering R*, 2009, 63(4/6): 127–287.

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