The synthesis of nonmagnetic Ni(W) solid solution derived from highly reactive ammonium paratungstate as the tungsten source

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Abstract. An effective technique for making nonmagnetic Ni(W) solid solution using Ni and ammonium paratungstate (APT) as the starting materials was developed. It was found that powder particles using APT as the W source have larger contact area between W and Ni and higher activity, which is conducive to the mutual diffusion between Ni and W, leading to a faster solid phase reaction and higher content of W diffused into Ni. The value of magnetic saturation (Ms) of Ni(W) solid solution powders using APT as the tungsten source is nearly zero under the suitable diffusion condition (550 °C×2 h +800 °C×2 h in hydrogen), much lower than that when using W powder.

1. Introduction
Utilization of forming die and cutting tool which is nonmagnetic and has good wear resistance, the forming resistance and cutting resistance of magnetic components can be reduced, and consistency of the electromagnetic characteristics and processing quality and efficiency of magnetic components can be guaranteed [1-3]. The magnetism of hard tool materials is mainly due to the magnetism of Co, Ni and Fe, which is usually used as binder material. In order to realize no magnetization of the hard tool materials, nickel based nonmagnetic solid solution powder is worthy of serious thought for binder of hard tool materials. When the metal alloying of binder phase is promoted by each metal atoms including W, the interfacial energy between the alloy and the ceramics can be reduced and the wettability between ceramic and binder phase can be improved. The solid solution strengthening of binder phase plays the important rule in the utility of tool materials including WC base cemented carbide. The pre-solution treatment of the binder phase can not only improve the effect of solid solution strengthening, but also inhibit grain growth by elimination of dissolution and precipitation of hard phase [3]. And from Ni-W binary diagram, it can be seen that the maximum solubility content of W in Ni is 31 wt.%, and when the W solubility content in Ni is more than 18 wt.%, the magnetic transition temperature of nickel is reduced to room temperature and the Ni-W solid solution becomes non-magnetic [3]. Owing to their superior mechanical, electrical and corrosion resistance properties compared to Ni, Ni-W alloys are attractive as potential candidates for quite a number of industrial applications such as environmentally friendly substitutes for hard chrome plating, substrate for high temperature superconductors and catalysts for hydrogen evolution from alkaline solutions [4], but
there is only a few information on the study of nonmagnetic Ni-W alloy. Ni-W alloys are usually fabricated using electro-deposition [5], mechanical alloying (MA) [6-9] and hydrogen reduction of nickel oxide-tungsten oxide [10-11]. For the conventional mechanical alloying process, nickel and tungsten powders were normally used as the starting materials, and comparatively high temperature is needed for the formation of solid solutions, resulting in aggregation of the solid solution powders. In the present work, we used nickel powder and ammonium paratungstate (APT) as the starting materials of the mechanical alloying method. APT is the basic raw material for preparation of tungsten powders, and by controlling the decomposition condition of APT, ultrafine tungsten powder can be produced [12]. The decomposition of APT should be conducive to the mutual diffusion between Ni and W. From this point of view, nonmagnetic Ni(W) solid solution powders were manufactured by mechanical alloying and diffusion of Ni and APT powders.

2. Experimental procedure

The Ni(W) solid solutions were prepared by using APT and pure tungsten powder as the tungsten source, respectively. Nickel (99.9%, 36 μm) and APT (99% purity, 0.8 μm) powders were mixed to constitute powder blends with APT contents of 30.0 wt.% (convert to 20 wt.% W). Blended mixtures were mechanically alloyed (MA’d) for 48 h using a XQM series planetary ball mill (Changsha Tianchuang Powder Technology Co., Ltd., China) with a speed of 360 rpm with WC-Co balls and the ball-to-powder weight ratio was 7:1. Diffusion of Ni-APT powders were conducted at 550 °C for 2 h and then 800 °C for 2 h under H₂ atmosphere. For the sample without using APT, nickel (99.9%, 36 μm) and W (99.9%, 18 μm) powders were mixed to constitute powder blends with the composition of 80 wt.% Ni and 20 wt.% W. The condition of mechanical alloying of the Ni-W powder blend is the same as that of the Ni-APT powders. Diffusion of the powder was conducted at 800 °C for 2 h under H₂ atmosphere. The shapes and sizes of the diffused powders were conducted using a JSM-7001F Thermal Field Emission Scanning Electron Microscope (SEM). The phases of the as-MA’d and diffused powders were examined by Smartlab Polycrystalline X-ray diffractometer (XRD) (Cu Kα radiation). W solubility amounts in the Ni lattice of Ni(W) solid solution were calculated by using the formula (1) of Vegard’s law [13] with XRD peak (111) diffraction angle of the Ni(W) phase.

\[
X_W = -7.5208 + 2.13429A_{Ni-W} \quad (1)
\]

where \(X_W\) is the atomic fraction of W in Ni, and \(A_{Ni-W}\) is the lattice parameter.

Magnetic saturation of the diffused powders were determined using Lake Shore (VSM). The system was calibrated using pure nickel references. The test piece of the powder was weighed and inserted into a non-magnetic holder. The external magnetic field intensity was 4000 G. Each measurement was repeated twice to check consistency of results.

3. Results and discussion

The variation of W solubility amounts in Ni and the magnetic saturation (Ms) of the Ni-30 wt.% APT diffused powders and the Ni-20 wt.% W diffused powders were illustrated in Table 1.

| The kinds of powder | Amount of W in Ni (wt.%) | Ms (emu/g) |
|---------------------|--------------------------|------------|
| Ni-30 wt.% APT      | 19.47                    | 0.003      |
| (550°C×2h→800°C×2h) |                          |            |
| Ni-20 wt.% W        | 16.30                    | 3.92       |
| (800°C×2 h)         |                          |            |

As seen in Table 1, when using APT as the tungsten source, the W dissolved in Ni is higher than
that by using pure W at the same reduction temperature. From the above results, the magnetic saturation (Ms) of diffused Ni-APT powders is lower than that of the diffused Ni-W powders. Fig. 1 shows XRD patterns of the Ni-30 wt.% APT diffused powders and the Ni-20 wt.% W diffused powders. It can be seen that XRD peaks of the diffused powders belong to the Ni(W) solid solution phase. Shifts of XRD peaks of the powders from the Ni peaks were observed as a result of W dissolution in Ni lattice, and the peak shift of the Ni-APT diffused powders was more than that of the Ni-W diffused powders.

![XRD patterns of the diffused powders](image)

Fig. 1. X-ray diffraction (XRD) patterns of the diffused powders. (a) Ni-20 wt.% W (800°C×2h), (b) Ni-30 wt.% APT (550°C×2h→800°C×2h), (c) Standard PDF card information of nickel (JCPDS 04-0850). (■) Ni solid solution phase.

Fig. 2 shows SEM images of the Ni-30 wt.% APT diffused powders and the Ni-20 wt.% W diffused powders. It can be seen that the Ni-APT diffused powder is finer than the Ni-W diffused powder.

![SEM graphics of the diffused powders](image)

Fig. 2. SEM graphics of the diffused powders. (a) Ni-30 wt.% APT diffused powder; (b) Ni-20 wt.% W diffused powder.

According to the decomposition conditions of APT, three different kinds of tungsten oxide i.e. yellow tungsten oxide, blue tungsten oxide and purple tungsten oxide can be prepared, especially purple tungsten oxide is good for the preparation of homogeneous ultrafine tungsten powder [12]. It has fine acicular structure, with high activity and can be reduced quickly in hydrogen. Thus, ultrafine tungsten powder can be produced using purple tungsten oxide by hydrogen reduction. Under the diffusion condition (firstly 550 °C for 2 h, followed by at 800 °C for 2 h under H₂ atmosphere) of Ni-APT MA'd powders which was selected in this study, purple tungsten oxide and finally ultrafine tungsten powder can be obtained from APT [13]. The decomposition and reduction of MA'd powder of Ni and APT can be expressed by Equation (2), (3) and (4) [14, 15], i.e. the decomposition and reduction reaction of APT take place first, followed by the diffusion of the W into Ni. The diffusion of W into Ni is a volume diffusion, as shown by Equation (5) [16].

\[
3[5(NH₄)₂O \cdot 12WO₃ \cdot 5H₂O] \rightarrow 2W₁₈O₄₉ + 40H₂O + 35H₂ + 15N₂ \quad (2)
\]

\[
W₁₈O₄₉ \rightarrow WO₁₂ + H₂O \quad (3)
\]

\[
\frac{25}{18}WO₂_{1,72} + H₂ = \frac{25}{18}WO₂ + H₂O \quad (3),
\]
\[
\frac{1}{2} \text{WO}_2 + 2\text{H}_2 = \frac{1}{2} \text{W} + \text{H}_2\text{O} \quad (4)
\]

\[
d = 2\sqrt{Dt} \quad (5)
\]

Where \(d\) is the penetration distance, \(D\) is the volume diffusion coefficient of \(W\) into \(Ni\), and \(t\) is diffusion time.

The tungsten powders prepared by decomposition of APT as the tungsten source (550 °C for 2 h, followed by 800 °C for 2 h under H2 atmosphere) are even finer than the pure tungsten powders used in this study. Thus, in the diffusion process the powder particles derived from APT have larger contact area between \(W\) and \(Ni\) and higher activity, which is conducive to the mutual diffusion between \(Ni\) and \(W\), leading to a faster solid phase reaction and higher content of \(W\) diffused into \(Ni\). It is clear that mechanical alloying and diffusing using \(Ni\) and APT as the raw materials is an effective technique for manufacturing nonmagnetic \(Ni(W)\) solid solution powder. The appropriate diffusion condition for manufacturing nonmagnetic \(Ni(W)\) solid solution powder is 550 °C for 2 h, followed by 800 °C for 2 h under H2 atmosphere.

### 4. Conclusion

Nonmagnetic \(Ni(W)\) solid solution powders were fabricated using \(Ni\) and ammonium paratungstate (APT) powders via mechanical alloying and diffusion. For comparison, mechanical alloying and diffusion using \(Ni\) and \(W\) powders were also studied. Independent of manufacture conditions, the magnetic saturations (Ms) of \(Ni(W)\) solid solution powders derived from APT as the tungsten source were lower than that from \(W\) powder. The powders prepared using APT as the tungsten source have higher activity and finer particle size, which is conducive to the mutual diffusion between \(Ni\) and \(W\), resulting in a faster solid phase reaction and the amount of \(W\) dissolved in \(Ni\) is higher. The more the amount of \(W\) in \(Ni\), the lower the magnetic saturation of \(Ni(W)\) solid solution is. Thus, the mechanical alloying and diffusion of \(Ni\) and APT is an effective way for manufacturing nonmagnetic \(Ni(W)\) solid solution powders. The suitable condition for manufacturing the nonmagnetic \(Ni(W)\) solid solution powder using \(Ni\) and APT is 550 °C×2 h + 800 °C×2 h in hydrogen, and the amount of \(W\) in \(Ni\) is more than 19wt.% (\(Ni\)-30wt.%APT powder, converting to 20 wt.% \(W\)). The obtained \(Ni(W)\) solid solution powders are nearly zero magnetization.

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