The characteristics of WC based cemented carbide using nonmagnetic Ni(W) solid solution derived from ammonium paratungstate as the binder

Myongson Hong¹,², Xudong Sun¹,²*, Zhimeng Xiu¹,² and Donggil Kim¹,²

¹Key Laboratory for Anisotropy and Texture of Materials (Ministry of Education), Northeastern University, Shenyang, Liaoning 110819, China
²Institute of Ceramics and Powder Metallurgy, School of Materials Science and Engineering, Northeastern University, Shenyang, Liaoning 110819, China
*Corresponding author’s e-mail: xdsun@mail.neu.edu.cn

Abstract. An effective technique for making nonmagnetic WC based cemented carbide by using Ni(W) solid solution manufactured from ammonium paratungstate (APT) as the binder was developed. It was found that powder particles using APT as the W source had larger contact area between W and Ni and higher activity, which was conducive to the mutual diffusion between Ni and W, leading to a faster solid phase reaction and higher content of W diffused into Ni. And the mechanical and nonmagnetic properties of WC based cemented carbide derived from nonmagnetic Ni(W) solid solution as the binder are much better than those derived from pure Ni as the binder.

1. Introduction
With the 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 [1-2]. 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 non-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 atom 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 role in the utility of tool materials including WC based 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 [2]. 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 [2]. In the present work, nickel powder and ammonium paratungstate (APT) as the starting materials of the mechanical alloying method was used. 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 [3]. The decomposition of APT should be conducive to the
mutual diffusion between Ni and W. And the characteristics of the WC based cemented carbide using this nonmagnetic Ni(W) solid solution as the binder were also studied.

2. Materials and Methods

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 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 H\textsubscript{2} 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 was the same as that of the Ni-APT powders. Diffusion of the powder was conducted at 800 °C for 2 h under H\textsubscript{2} 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 SmartlabPolycrystalline X-ray diffractometer (XRD) (Cu Kα radiation). W solubility amounts in the Ni lattice of Ni(W) solid solution were calculated by using the equation (1) of Vegard’s law [4] with XRD peak (111) diffraction angle of the Ni(W) phase.

\[ X_W = -7.5208 + 2.13429A_{Ni-W} \]  

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 was 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.

Ni(W) solid solution powders which were made from Ni-30 wt.% APT (convert to 20 wt.% W) powder and Ni-20 wt.% W powder were sintered in a hot-press sintering furnace at 1200 °C under inert Ar gas for 15 min (hereafter referred to be as Ni-APT alloy and Ni-W alloy, respectively). And WC-20 wt.% Ni(W) and WC-20 wt.% Ni cemented carbides using nonmagnetic Ni(W) solid solution and pure Ni as the binder were sintered in a hot-press sintering furnace at 1420 °C under inert Ar gas for 15 min (hereafter referred to be as WC-Ni(W) alloy and WC-Ni alloy, respectively).

Microstructural characterizations of sintered samples were carried out using a Smartlab Polycrystalline X-ray Diffractometer (XRD) (Cu Kα radiation) and a JSM-7001F Thermal Field Emission Scanning Electron Microscope (SEM). The sintered densities of WC-Ni(W) and WC-Ni alloy were measured using the Archimedes’ method. Vickers microhardness of WC-Ni(W) and WC-Ni alloy were conducted using a HMV2000 Digital Microhardness Tester under a load of 196N for 15 seconds, respectively. Samples for magnetic measurement were cylinders 3 mm in diameter and 3 mm in height made by electrical discharge wire cutting of the as-sintered samples. Magnetic saturation of the sintered samples was determined using Lake Shore VSM. The system was calibrated using pure nickel references. 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-APT alloy        |                          |            |
| WC-Ni(W) alloy      |                          |            |
| Ni-W alloy          |                          |            |
| WC-Ni alloy         |                          |            |

Table 1. The amount of W in Ni and magnetic saturation (Ms) of the powders.
As seen in Table 1, when using APT as the tungsten source, the W dissolved in Ni was 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 was lower than that of the diffused Ni-W powders. Figure 1 shows XRD patterns of the Ni-30 wt.% APT diffused powders and the Ni-20 wt.% W diffused powders. It could be seen that XRD peaks of the diffused powders belonged 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. Figure 2 shows SEM images of the Ni-30 wt.% APT diffused powders and the Ni-20 wt.% W diffused powders. It could be seen that the Ni-APT diffused powder was finer than the Ni-W diffused powder.

| Material            | Ms    | Ms
diffused Ni-APT powders was lower than that of the diffused Ni-W powders. |
|---------------------|-------|--------------------------------------------------------------------------|
| Ni-30 wt.% APT      | 19.47 | 0.003                                                                    |
| (550℃×2h→800℃×2h)  |       |                                                                           |
| Ni-20 wt.% W        | 16.30 | 3.920                                                                    |
| (800℃×2 h)         |       |                                                                           |

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

Figure 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 [3]. 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 [4]. The decomposition and reduction of MA’d powder of Ni and APT can be expressed by Equation (2), (3) and (4) [5,6], 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) [7].

\[
\begin{align*}
3[5(\text{NH}_4)_2\text{O} \cdot 12\text{WO}_3 \cdot 5\text{H}_2\text{O}] & \rightarrow 2\text{W}_{18}\text{O}_{49} + 40\text{H}_2\text{O} + 35\text{H}_2 + 15\text{N}_2 \\
\text{W}_{18}\text{O}_{49} & \rightarrow \text{WO}_{2.72} \\
\frac{25}{18} \text{WO}_{2.72} + \text{H}_2 & = \frac{25}{18} \text{WO}_2 + \text{H}_2\text{O} \\
\frac{1}{2} \text{WO}_2 + 2\text{H}_2 & = \frac{1}{2} \text{W} + \text{H}_2\text{O} \\
\end{align*}
\]

\[d = 2\sqrt{D}t\]

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.

XRD patterns of the sintered samples (hereafter referred as Ni-W sample and Ni-APT sample, respectively) made from the Ni(W) solid solution powders (Ni-20 wt.% W powder and Ni-30 wt.% APT powder converting to 20 wt.% W) showed that both samples were composed of Ni (W) solid solution phase (Figure 3). The Ni (W) phase had a greater \(d\) value than the pure Ni phase, as indicated by the shift of peaks to the left of Ni (W) compared with the peaks of Ni. The shift of peaks of Ni-APT alloy was bigger than that of the Ni-W alloy.
Figure 3. X-ray diffraction (XRD) patterns of the sintered samples. (a) Ni-W alloy, (b) Ni-APT alloy, (c) Standard PDF card information of nickel (JCPDS 04-0850). (■) Ni solid solution phase.

Microstructural observation (SEM) showed that the sintered samples were consist of only one particular phase, i.e. the Ni(W) solid solution phase (Figure 4). Relative density values of WC-Ni(W) and WC-Ni alloy measured using the Archimedes’s method were also presented in Table 2, indicating that the value of relative density of the WC-Ni(W) alloy (98.89%) was slightly higher than that of the WC-Ni alloy (97.35%). This is due to better sinterability of the WC-Ni(W) powder than those of the WC-Ni powder. Vickers hardness value of the WC-Ni(W) alloy (1320 MPa) was higher than that of the WC-Ni alloy (1287 MPa), owing to a stronger solid solution strengthening and higher density for the WC-Ni(W) alloy. Meanwhile, the magnetic saturation of the WC-Ni(W) alloy was lower than that of the WC-Ni alloy due to the higher amount of W dissolved in Ni lattice for the WC-Ni(W) alloy. The solid solution of non-magnetic W particles with 0μTm³kg⁻¹ decreased the proportion of Ni magnetic atoms, thereby reducing the density of the magnetic atom interactions. According to Miracle [8], this reduction would lead to lower exchange interaction between Ni atoms and the suppression of the Ni metal moment by the charge transfer to the d-band and by the d–d hybridization which decreases the number of polarization d-states. Thus, the utilization of nonmagnetic Ni(W) solid solution as the binder is effective way for manufacturing nonmagnetic hard tool materials.

Figure 4. Microstructure of the sintered samples (SEM).

(a) Ni-W alloy; (b) Ni-APT alloy.

| Specimen | Amount of W in Ni lattice (wt.% | Relative density (%) | Vickers hardness (GPa) | Magnetic saturation (emu/g) |
|----------|---------------------------------|---------------------|-----------------------|-----------------------------|
| WC-Ni(W) |                                 |                     |                       |                             |
| WC-Ni    |                                 |                     |                       |                             |
4. CONCLUSIONS
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 had higher activity and finer particle size, which was conducive to the mutual diffusion between Ni and W, resulting in a faster solid phase reaction and the amount of W dissolved in Ni was higher. The mechanical and nonmagnetic properties of WC based cemented carbide derived from nonmagnetic Ni(W) solid solution as the binder are much better than those derived from pure Ni as the binder. Thus, the utilization of nonmagnetic Ni(W) solid solution as the binder is an effective way for manufacturing nonmagnetic WC based cemented carbide.

Acknowledgements
This work supported by the Joint Funds of the National Natural Science Foundation of China (U1302272), and the fund of the State Key Laboratory of Advanced Technologies for Comprehensive Utilization of Platinum Metals (SKL-SPM-201506, SKL-SPM-201505 and SKM-SPM-201504).

References
[1] Zhang, M., Yang, Q., Xiong, W. (2015) Effect of Mo and C additions on magnetic properties of TiC-TiN-Ni cerments. Journal of Alloys and Compounds., 650: 700-704.
[2] Gao, H. (2006) Research Progress of Nonmagnetic Carbide. Rare Metals and Cemented Carbide., 34(3): 51-54.
[3] Wan, L. (2010) Tungsten Metallurgy. Zhongnan University Press, Changsha.
[4] Juskenas, R., Valsiunas, I. (2009) On the state of W in electrodeposited Ni–W alloys. Electrochim.Acta., 54: 2616.
[5] Chen, S. (1997) The manufacture of ultrafine tungsten powder and ultrafine tungsten carbide powder by using of W$_{18}$O$_{49}$. Journal of ZhongNan University of Technology., 28(5): 456-460.
[6] Kalpakli, A., Arabaci, A., Kahruman, C. (2013) Thermal decomposition of ammonium paratungstate hydrate in air and inert gas atmosphere. Refractory Metals and Hard Materials., 37: 06-116.
[7] Zhang, Q. (2005) Molybdenum Tungsten Metallurgy. Metallurgical Industry Press, Beijing.
[8] Miracle, DB. (2003) The influence of efficient atomic packing on the constitution of metallic glasses. Sanders WS. Philos Mag., 83: 2409.