Materials Research Express

PAPER

Ni-coated graphene nanoplatelets and their application as reinforcements for WC-Co cemented carbides

Yigao Yuan, Xingxing Xu and Jianguo Zhang

College of Mechanical Engineering, Donghua University, Shanghai, People’s Republic of China

E-mail: fnzjg@dhu.edu.cn

Keywords: graphene nanoplatelets, Ni plating, WC-Co, reinforcement properties

Abstract

In the current research, Ni-coated graphene nanoplatelets (Ni-GNPs) were fabricated by electroless Ni plating process. The Co-cemented tungsten carbides (WC-Co) samples doped with Ni-GNPs were obtained by vacuum hot pressing sintering. The effect of various content of Ni-GNPs on the mechanical and frictional properties of as-sintered WC-Co samples was investigated. Vickers hardness of WC-Co samples decreased from 1896 MPa to 1743 MPa with the content of Ni-GNPs varied from 0.0 wt% to 0.4 wt%. The fracture toughness reached to the highest value of 10.85 MPa · m$^{1/2}$ with 0.05 wt% Ni-GNPs. The friction coefficient dropped from 0.43 of the sample with 0.0 wt% Ni-GNPs to 0.21 of the sample with 0.4 wt% Ni-GNPs. The results revealed that the Ni-GNPs have considerable effect on improving the combination properties of WC-Co cemented carbides. Within the mentioned content range, the optimal content of the Ni-GNPs in WC-Co sample was 0.05 wt%.

1. Introduction

Due to their high hardness and wear resistance, Co-cemented tungsten carbides (WC-Co) are widely used in machining tools, dies and wear-resistant parts in the manufacturing industry [1–4]. They are fabricated from tungsten carbide (WC) and metal cobalt (Co) powders by liquid phase sintering at approximately 1400 °C, in which the WC as hard phase supports the high hardness and wear resistant, while the Co as binder phase is in charge of the fracture toughness and strength [5]. Typically, as the Co content decreases at fixed WC particle size, the wear resistance of the alloy increases and the fracture toughness decreases. This shortcoming limits the applications of WC-Co composites in industrial fields. For this reason, the researches for improving mechanical properties of WC-Co materials, especially equilibrating the contradictory performances between hardness and fracture toughness have drawn considerable attention in the hardmetal industry [6–10].

Graphene nanoplatelets (GNPs), composing of a few graphene layers, have been attracting great attention due to their unique properties [11]. Owing to the excellent combination mechanical and physical properties such as low density, high tensile strength, high Young’s modulus and favourable thermal conductivity, the GNPs are considered potential high-performance material to be used as the reinforcement for metal matrix composite and ceramics [12–17]. Numerous studies have demonstrated that addition of GNPs to various ceramics, such as SiC, Al$_2$O$_3$ and B$_4$C, can simultaneously improve the fracture toughness and wear resistance of composites, even at relatively low GNPs content [18–21]. Other researchers have investigated the effect of GNPs reinforcement on the metal matrix composite. Wang et al used graphene nanosheets (GNSs) as the raw material to fabricate the GNSs/Al matrix composites. The tensile strength has enhanced by 62% than that of the Al matrix composite, when the GNSs content reaches only 0.3 wt% [22]. Yue et al investigated the effect of graphene contents on the mechanical properties and fracture mechanisms of GNSs-Cu matrix composites, they concluded that the fracture mechanism of the composites changes from ductile to brittle with increasing the GNSs content [23].

As a promising reinforcement, the GNPs have attracted significant interest for improving the mechanical properties of WC-Co cemented carbides. However, there are two challenging issues need to be solved in terms of...
reinforcing WC-Co cemented carbide with GNPs. One is the large density difference between GNPs and WC-Co matrix, which makes GNPs difficult to disperse homogeneously in WC-Co powders. The other is the GNPs easily corroded with metal Co during liquid phase sintering process. Previous studies have showed that surface modification of carbon materials is beneficial to improve their dispersion in WC-Co powder, and to avoid their corrosion during the liquid phase sintering. Morisada et al adopted multi-walled carbon nanotubes (MWCNTs) with SiC coating to reinforce WC-10 wt%Co cemented carbide. The results showed that the hardness of the composite increase by 14% than that of WC-10 wt%Co [24]. Shi et al deposited WC layers on the surfaces of MWCNTs and prepared the MWCNTs/WC-10 wt%Co composites. They found that the transverse rupture strength and fracture toughness of the MWCNTs/WC-10 wt%Co composite doped with 0.4 wt% WC-coated MWCNTs were enhanced by 32.8% and 1.2%, respectively [25].

Electroless deposition method is widely applied in the aerospace, automobile and electronic industries to modify the surface of various materials, such as non-conductors, semiconductors and metals, due to its low cost and its suitability for any profile of metallic or electrically non-conductive materials [26]. Considering that metal nickel (Ni) is also a common binder phase of cemented carbide, and the solubility of carbon atoms in Ni is much lower than that of Co during the liquid phase sintering, the electroless Ni plating was selected to modify the surfaces of GNPs. And the preparation of Ni-coated GNPs (Ni-GNPs) reinforcing WC-Co composites (WC-Co/Ni-GNPs) was conducted by vacuum hot pressing sintering. The mechanical and frictional properties of as-sintered WC-Co/Ni-GNPs samples were investigated.

2. Experimental

2.1. Materials

The WC-10 wt%Co and GNPs powders in this investigation were used as the matrix material and reinforcement, respectively. The WC-10 wt%Co powders, with average grain size of 0.8 μm and cobalt content of 10 wt%, were provided by Shanghai Materials Research Institute, and the GNPs were purchased from Nanjing XFNANO Materials Tech Co., Ltd, having average thickness and particle size of 3–10 nm and 5–10 μm, respectively. Electroless deposition of Ni on GNPs was established by using H2SO4, HNO3, SnCl2, HCl, PdCl2, Na3C6H5O7, C6H5OH, H2O, Na2CO3, NiSO4 · 6H2O, NaOH and hydrazine hydrate. All chemicals were supplied from Sinopharm Chemical Reagent Co., Ltd

2.2. Fabrication of the Ni-coated GNPs

The electroless Ni depositing process was used to precipitate Ni on the surfaces of GNPs, which are accomplished sequentially by the following steps:

(1) Oxidation. The GNPs powders (2.5 g) were added into 250 ml solution of HNO3 and H2SO4 (1:1 in volume), and then the mixture was stirred by magnetic stirrer at 80 °C for 2 h. After that, the powders were filtered and washed with distilled water followed by drying in an electric furnace. The oxidation of GNPs surface can improve the hydrophilia of the graphene and insert acid functional groups at the edge of the graphene, which provided attachment points for chemical nickel plating process.

(2) Sensitization. The oxidized GNPs were added into the sensitizing solution of 4 ml hydrochloric acid, 2 g SnCl2 and 100 ml distilled water. And the mixture was stirred by magnetic stirrer at 45 °C for 1 h. After that, the mixture were filtered and washed with distilled water followed by drying in an electric furnace.

(3) Activation. The sensitized GNPs were added into the activating solution of 2 ml hydrochloric acid, 0.05 g PdCl2, and 98 ml distilled water, and then was stirred by magnetic stirrer at 45 °C for 1 h. After that, the mixture were filtered and washed with distilled water followed by drying in an electric furnace.

(4) Metal deposition. The activated GNPs were added into the nickel plating solution of 3 g Na2C2O4 · 2H2O, 2.1 g Na2CO3, 4 g NiSO4 · 6H2O, and 200 ml distilled water at 80 °C under magnetic stirring. The pH value of the nickel plating solution was adjusted to 11 by sodium hydrate, and then 5 ml hydrazine hydrate was added into the mixture. After 2 h, the mixture was filtered and washed with distilled water followed by drying in an electric furnace to obtain Ni-coated GNPs.

2.3. Preparation of the WC-Co/Ni-GNPs composites

The Ni-GNPs powders were added to the WC-Co powders, and they were stirred in alcohol by magnetic stirrer at a rotation of speed of 450 rpm for 1 h. The content of the Ni-GNPs in the composites were 0.0 wt%, 0.05 wt%, 0.1 wt%, 0.2 wt% and 0.4 wt%, respectively. After that, alcohol was removed and the powders were dried in the vacuum rotary dryer at 95 °C for 1 h. The dried powders were then pressed in a cold pressing mold at 200 MPa
into green compacts of $\Phi 12 \text{ mm} \times 20 \text{ mm}$ in dimensions. Finally, the green compacts were sintered in vacuum at $1380 ^\circ \text{C}$ for 1 h with a uniaxial pressure of 40 MPa to fabricate the Ni-GNPs reinforced WC-Co composites.

2.4. Characterization of properties
The properties of the GNPs were elaborated by thermogravimetric analysis (TGA, NETZSCH STA 449), atomic force microscope (AFM, MFP-3D) morphology and Fourier transform infrared spectroscopy (FT-IR, Nicolet iN10 MX). The crystal structures of the GNPs before and after Ni-plating were assessed by Raman spectroscopy (Renishaw, InVia-Reflex). The light source was an argon ion laser with a wavelength of 532 nm. The phase composition of the Ni-GNPs powders and sintered samples were identified by x-ray diffractometer (XRD, D/max-2550PC type, Rigaku, Japan). Field Emission Scanning Electron Microscope (FE-SEM, S-4800, Hitachi, Japan) was used to analyze the morphologies of GNPs and Ni-GNPs, indentation crack, fracture and worn surfaces of the sintered samples. The densities of sintered samples were determined using the Archimedes method, and the theoretical density was estimated from rule of mixtures. The average grain size of WC in the sintered specimens was measured using the backscattered electron (BSE) images and image analysis software.

Microhardness testing was conducted on polished surfaces of the sintered samples using a Vickers hardness tester (HVS-30Z, Shanghai Taiming Optical Instrument Co., Ltd). The load was 30 Kg and the dwell time was 15 s. The hardness measurements were repeated five times on each sample to obtain the mean value. Due to the brittle properties of WC-Co material, the damage created on surfaces by solid particle contact is related to the elastic/plastic indentation regimes. The tensile stresses are parallel to the surface, and create lateral cracks. The formation of the cracks is determined by the flaw properties of the test material as defined by the fracture toughness [27]. The fracture toughness of the samples were calculated according to the equation: $K_{IC} = 0.15(\text{HV}_{30}/L)^{1/2}$, where $K_{IC}$ is fracture toughness, MPa $\cdot$ m$^{1/2}$; HV is Vickers hardness, Kg mm$^{-2}$; L is total crack length, mm.

The tribological studies were carried out on the ball-on-disk tribometer (HSR-2M, Zhong Ke Kai Hua Corporation, China). The WC-Co balls with 3 mm radius were used as the counterpart of rubbing. The tribological test parameters were: room temperature, reciprocating distance of 5 mm, frequency of 4.2 Hz, applied constant load of 50 N. The friction coefficient was automatically measured and recorded in real time by the system of tribometer. The wear rate was calculated by dividing the mass loss of the sintered WC-Co samples with the testing time.

3. Results and discussion
Figure 1 presents the TGA curve for GNPs indicating the weight loss through varying temperatures. When the temperature reaches to 700 $^\circ \text{C}$, the weight reduces about 30%. The 2D nanocomposite of GNPs is shown in figure 2. In figure 3, the spectrum shows a peak around 3434 cm$^{-1}$ representing O-H stretching vibrations. The peak related the C-C vibrations from the graphene domains is observed at 1632 cm$^{-1}$. Figure 4 shows the SEM morphologies of the GNPs before and after Ni-plating. The surfaces of Ni-GNPs are covered with continuity and uniformity of Ni layer as shown in figure 4(b). The Raman spectra were performed to characterize the structural integrity of GNPs and Ni-GNPs in figure 5. Three prominent features of D-band ($\sim$1350 cm$^{-1}$), G-band
(~1580 cm\(^{-1}\)) and 2D-band (~2710 cm\(^{-1}\)) are observed for the GNPs. The peak of D-band disappears in the Ni-GNPs, while the peaks of G-band and 2D-band become weak.

It is attributed to the tight confinement on vibration in the radial direction owing to the interfacial bonding between Ni layer and GNPs. To further confirm the structures, XRD was used to characterize crystalline structure of the GNPs before and after Ni-plating. Figure 6 shows the XRD patterns of the raw GNPs and Ni-GNPs. In the diffraction pattern (2θ) of Ni-GNPs, the three peaks are observed at 44.5°, 52.1° and 76.5° correspond to the (111), (200) and (220) crystal planes of Ni layer. While for the raw GNPs, there is a sharp peak at 25° corresponding to (002) crystal plane of graphene. The peaks with low intensity at 45° and 55° are related to (101) and (004) crystal plane of graphene\[28, 29\]. And the related peaks of the Ni-GNPs become weaker, which are attribute to the coverage of the Ni layer.

Figure 7 shows the XRD patterns of sintered monolithic WC-Co and WC-Co doped with different contents of Ni-GNPs. As shown in figure 7, there are only WC phase in the Ni-GNPs doped WC-Co cemented carbide, and the phases related to graphene are not be detected by XRD. It suggests that the carbon atoms did not spread from the GNPs to the cemented carbide matrix during the sintering process, proving the integrity of GNPs structure. The nine crystal planes imply the fine crystallinity of WC grains.

The relative density of the sintered samples is plotted in figure 8, it shows that all the values get more than 97.5%, suggesting the processing route is suitable for the preparation of Ni-GNPs reinforced WC-Co composites. Figure 9 shows the comparison of mechanical properties for the sintered WC-Co samples with
different contents of Ni-GNPs. The Vickers hardness of WC-Co samples has a slight decrease from ∼1896 MPa to ∼1863 MPa when the content of Ni-GNPs increases to 0.05%. As the content of Ni-GNPs further increasing, the hardness first decreases to ∼1833 MPa, and then it increases to ∼1857 MPa according to the content varied from 0.1 wt% to 0.2 wt%. The variation of hardness value is within the measurement error range. When the content of Ni-GNPs increases to 0.4 wt%, the value of hardness decreases to ∼1743 MPa. It suggests that the

Figure 4. SEM micrographs of GNPs (a) before and (b) after Ni-plating.

Figure 5. Raman spectroscopy of GNPs and Ni-GNPs.
Figure 6. X-ray diffraction patterns of GNPs and Ni-GNPs.

Figure 7. X-ray diffraction patterns of sintered monolithic and Ni-GNPs reinforced WC-Co samples.

Figure 8. Relative density of WC-Co samples with different content of Ni-GNPs.
hardness has an obvious decrease with relatively high content of Ni-GNPs. Due to the existence of element Ni, the solubility of WC in Ni is higher than that in metal Co, the recrystallization effect was reinforced during the sintering process. It leads to the enlargement of grain particle, causing to the reduction of hardness. The average particle size of WC in the WC-Co samples varies from $\sim 0.8 \mu m$ to $\sim 1.0 \mu m$ according to the content of Ni-GNPs changing from 0.0 wt% to 0.4 wt%. When the content reaches to 0.4 wt%, the agglomeration of Ni-GNPs leading to the weak bonding force of WC-Co composite could also reduce the hardness.

Nevertheless, compared with the monolithic WC-Co composites, the Ni-GNPs doped WC-Co samples have higher fracture toughness. The fracture toughness of WC-Co/Ni-GNPs is 28% higher than that of the monolithic WC-Co, when the content of Ni-GNPs is 0.05 wt%. Then the values of fracture toughness decrease with the content of Ni-GNPs increasing. Figure 10 shows the fracture surface of the WC-Co/0.05 wt% Ni-GNPs sample, in which the Ni coated GNPs (the yellow circle) are visible between the WC particles. During the liquid sintering process, the solubility of carbon in element Ni is much less than that in the element Co, the Ni could prevent the corrosion effect on graphene by Co. The exist of Ni-GNPs is further testified by the XPS spectra shown in figure 11. In the extension path of WC-Co/0.05 wt% Ni-GNPs sample, a deflected crack path and crack bridging are shown in figure 12. It is attribute to plastic deformation and bridging ligament of the coated GNPs, which is conducive to the enhancement in fracture toughness of WC-Co [30].

The frictional coefficient and wear rate of the WC-Co samples were tested to study the influence of Ni-GNPs on the tribological properties. As indicated in figure 13, most of the curves present similar evolution, which could be characterized by two stages: initial and dynamic steady-state. At the second stage, the friction coefficient of WC-Co/Ni-GNPs samples is remarkably lower than that of the monolithic WC-Co sample. The average friction coefficient decreased from 0.43 of monolithic WC-Co sample to 0.21 of WC-Co/0.4 wt% Ni-GNPs sample.
indicating the addition of Ni-GNPs can improve the antifriction performance of the WC-Co material, which is attributed to the lubricating effect of Ni-GNPs. The wear rate of all the samples is shown in figure 14. It can be seen that the wear rate of WC-Co without Ni-GNPs ($25.94 \times 10^{-5} \text{ g \cdot min}^{-1}$) is higher than the that of the sample with 0.05 wt% Ni-GNPs ($22.12 \times 10^{-5} \text{ g \cdot min}^{-1}$). That is because the dispersed Ni-GNPs in the WC-Co sample can improve the wear resistant by preventing the crack diffusion. While the content of Ni-GNPs reaches to 0.4 wt%, the wear rate of the WC-Co/Ni-GNPs slightly increases to $24.20 \times 10^{-5} \text{ g \cdot min}^{-1}$.

Figure 15 presents the SEM micrographs of the worn surfaces of WC-Co samples. It can be seen from figure 15(a) that the WC-Co without Ni-GNPs has a rough worn surface relating to the adhesive wear and delamination wear, suggesting that micro-cracks are generated during the friction process, which is consistent with the high wear rate of the WC-Co with 0.0 wt% Ni-GNPs shown in figure 14. The morphologies of WC-Co/Ni-GNPs exhibit smooth tribofilm on the worn surfaces as shown in figures 15(b)–(e). The smooth tribofilm decreases the friction between the sample and the counterpart ball. It is attributed to the great effect of Ni-GNPs on lubrication during friction tests. The area of tribofilm becomes gradually larger with the content of Ni-GNPs increasing. Adhesive wear and abrasive wear dominate the main wear pattern during the friction process for the WC-Co/Ni-GNPs composites. However, it is noted that the WC-Co sample with 0.4 wt% Ni-GNPs possesses the higher wear rate, which is related to the lower hardness of WC-Co/0.4 wt% Ni-GNPs sample.
4. Conclusions

In the present work, Ni-coated GNPs were obtained by electroless Ni plating process. Then the Ni-GNPs were adopted as reinforcement to fabricate the WC-Co/Ni-GNPs composites. The microstructure, mechanical and frictional properties of the sintered samples were investigated. The relative density of the all samples is more than 97.5%. The Vickers hardness and the fracture toughness values of the WC-Co, WC-Co/0.05 wt%
Ni-GNPs, WC–Co/0.1 wt% Ni-GNPs, WC–Co/0.2 wt% Ni-GNPs and WC–Co/0.4 wt% Ni-GNPs samples were 1896 MPa, 9.49 MPa · m$^{1/2}$ and 1863 MPa, 10.85 MPa · m$^{1/2}$ and 1833 MPa, 10.42 MPa · m$^{1/2}$ and 1856 MPa, 10.14 MPa · m$^{1/2}$ and 1743 MPa, 9.91 MPa · m$^{1/2}$, respectively. The addition of Ni-GNPs can slight affect the Vickers hardness when the content is lower than 0.4 wt%. While the fracture toughness of WC–Co materials can be improved with the increase of the Ni-GNPs content. The Ni-GNPs in the WC–Co composites had a remarkable antifriction property, which could supply the low friction coefficient of ∼0.21 when the content reached to 0.4 wt%. Those results implied that the Ni-coated GNPs can be an effective reinforcing agent for improved mechanical properties of WC-Co cemented carbides. Considering the comprehensive properties of WC-Co/Ni-GNPs composites, the optimal content of the GNPs as reinforcement for WC-Co is 0.05 wt%.

**Acknowledgments**

This work was supported by the Fundamental Research Funds for the Central Universities (No. 2232019D3-35) and Natural Science Foundation of Shanghai (No. 18ZR1401100).
ORCID iDs

Jianguo Zhang  https://orcid.org/0000-0003-1943-8793

References

[1] Zhu E T, Zhang J X, Guo S D, Yang X Y, Zhang X and Yang J G 2019 Mater. Res. Express 6 086522
[2] Sun Y, Su W, Yang H and Ruan J 2015 Ceram. Int. 41 14482–91
[3] Feng Q, Song X, Xie H, Wang H, Liu X and Yin F 2017 Mater. Des. 120 193–203
[4] Sun J, Zhao J, Gong F, Li Z and Ni X 2018 J. Alloy. Compd. 750 972–9
[5] Kumar A, Singh K and Pandey O P 2011 Ceram. Int. 37 1415–22
[6] Zhang K, Zhang Z, Lu X, Li K, Du Y, Long J, Xu T, Zhang H, Chen L and Kong Y 2014 Int. J. Refract. Met. H 44 88–93
[7] Ou X Q, Song M and Shen T T 2011 Int. J. Refract. Met. H 29 260–7
[8] Bounhoure V, Lay S, Charlot F, Antoni-Zdzibek A and Pauty E 2014 Int. J. Refract. Met. H 44 27–34
[9] Chang S H, Chang M H and Huang K T 2015 J. Alloy. Compd. 69 89–95
[10] Xiong J, Guo Z, Yang M, Wan W and Dong G 2013 Ceram. Int. 39 337–46
[11] Huo Q, Jin J, Wang X, Li S, Zhang Y, Ma J and Wang S 2019 Mater. Res. Express 6 075613
[12] Huang L, Zhang D, Zhang F H, Huang Y D, Yang M and Gan Y 2019 Mater. Res. Express 6 085604
[13] Kun P, Tapaszto O, Weber F and Balazsi C 2012 Ceram. Int. 38 211–6
[14] Bódis E, Cora L, Balázi C, Németh P, Károly Z, Kébler S, Fazekas P, Keszler A M and Szépovölgyi J 2017 Ceram. Int. 43 9005–11
[15] Lu Z, Hou D, Meng L, Sun G and Li Z 2015 RSC Adv. 5 100598–605
[16] Nieto A, Huang L, Han Y H and Schoenung J M 2015 Ceram. Int. 41 5926–36
[17] Sun J and Zhao J 2018 Mat. Sci. Eng. A 723 1–7
[18] Huang Y, Jiang D, Zhang X, Liao Z and Huang Z 2018 J. Eur. Ceram. Soc. 38 4329–37
[19] Meng X, Xu C, Xiao G, Yi M and Zhang Y 2016 Ceram. Int. 42 16090–5
[20] Kim W, Oh H S and Shon J J 2015 Int. J. Refract. Met. H 48 378–81
[21] Chen M, Yin Z, Yuan J, Xue W, Ye J and Yan S 2018 Ceram. Int. 44 15370–7
[22] Wang J, Li Z, Fan G, Pan H, Chen Z and Zhang D 2012 Scripta Mat. 66 594–7
[23] Yue H, Yao L, Gao X, Zhang S, Guo E, Zhang H, Lin X and Wang B 2017 J. Alloy. Compd. 69 755–62
[24] Morisada Y and Miyamoto Y 2004 Mat. Sci. Eng. A 381 57–61
[25] Shi X L, Huang H, Wang S, Shao G and Duan X 2008 Mat. Sci. Eng. A 486 489–95
[26] Luo L, Yu J, Luo J and Jan I 2010 Ceram. Int. 36 1989–92
[27] Evans A G and Wildhaw T R 1977 J. Mater. Sci. 12 97–116
[28] Wang G, Yang J, Park J, Gou X, Wang B, Liu H and Yao J 2008 J. Phys. Chem. C 112 8192–5
[29] Yang B, Yu Y, Zhang J, Yuan L, Qiao J and Hu X 2019 Appl. Surf. Sci. 471 263–72
[30] Porwali H, Tatarko P, Grasso S, Khaliqi J, Dlouhy J and Reece M J 2013 Carbon 64 359–69