Rare Metal Materials and Engineering
Volume 54, Issue 7, July 2025
Available online at www.rmme.ac.cn

Science Press

Cite this article as: Li Meng, Wei Dong, Hu Huixuan, et al. Effect of GPLs on Grain Size of WC in WC-Co-GPLs Cemented Carbides: Refinement Mechanism[J]. Rare Metal Materials and Engineering, 2025, 54(07): 1727-1732. DOI: https://doi.org/10.12442/j.issn.1002-185X.20240318.

ARTICLE

Effect of GPLs on Grain Size of WC in WC-Co-GPLs Cemented Carbides: Refinement Mechanism

Li Meng[1,2], Wei Dong[1,2], Hu Huixuan[1], Wu Weiguo[1], Zhong Sisi[1], Gong Manfeng[1], Zhang Chengyu[2]

[1] School of Mechanical and Electrical Engineering, Lingnan Normal University, Zhanjiang 524048, China; [2] School of Materials and Engineering, Northwestern Polytechnical University, Xi'an 710072, China

Abstract: The influence of graphene platelets (GPLs) on the WC grain size of WC-Co-GPLs cemented carbide prepared by low-pressure sintering was investigated. The role of GPLs in refining WC grains was explored by characterizing grain size and phase distribution. Results show that the addition of GPLs leads to significant grain refinement of WC and the more uniform distribution of WC grain size. When the content of GPLs is 0.10wt%, the average WC grain size in the cemented carbide is 0.39 μm, which is 32% lower than that in WC-Co. However, the shape of WC grains is almost unaffected, while the mean free path of Co decreases. The grain refinement of WC is attributed to the homogeneous distribution of GPLs between WC/WC and WC/Co grain boundaries, which hinders the solution and precipitation process of WC in liquid phase Co, as well as the migration and growth of WC grains. Additionally, GPLs can serve as heat transfer plates in materials to improve cooling efficiency, thus inhibiting the growth of WC grain.

Key words: WC-Co cemented carbide; GPLs; WC grain size

1 Introduction

WC-Co cemented carbides have the advantages of high strength, high hardness, and good wear resistance, which are widely used in cutting, drilling, and impact fields[1–2]. In general, the finer the grain size of WC in WC-Co, the lower the Co content of the bonding phase, and the shorter the mean free path of Co, resulting in higher hardness and strength, better wear resistance, thermal shock resistance, and oxidation resistance of the WC-Co cemented carbides[3–4]. Therefore, refining WC grains is an effective method to improve the properties of WC-Co cemented carbides[5–7].

As reinforcing phases, graphene platelets (GPLs) are often distributed at grain boundaries of the matrix material, which can provide the pinning effect[8–11]. The migration of grain boundaries and grain growth are hindered due to the distribution position of GPLs. Therefore, GPLs are the effective inhibitor of grain growth. Meanwhile, the layered structure of GPLs enables them to improve the fracture toughness of composites through toughening mechanisms such as pull-out, crack bridging, and crack deflection[10]. Therefore, GPLs are used as reinforcing phases to improve the mechanical properties of different types of cemented carbides. The addition of GPLs shows great potential in refining WC grain size and improving the fracture toughness of cemented carbides[12–17]. However, due to different types of cemented carbide and sintering processes, the optimal content of GPLs varies greatly among the research results, and the impact of GPLs content on the grain size and hardness of WC in cemented carbide is also varied. In our previous study, GPLs were added into ultrafine WC-8Co cemented carbides to enhance the mechanical properties and wear resistance, in which the optimal content of GPLs was 0.1wt%. However, further research is needed to investigate the effect and

Received date: May 29, 2024
Foundation item: National Natural Science Foundation of China (51572224); Guangdong Young Creative Talents (2023KQNCX039); Guangdong Basic and Applied Basic Research Foundation (2023A1515110551); Innovative Team in Higher Educational Institutions of Guangdong Province (2020KCXTD039); 2023 Lingnan Normal College Students Innovation and Entrepreneurship Training Program (1742)
Corresponding author: Gong Manfeng, Ph.D., Professor, School of Mechanical and Electrical Engineering, Lingnan Normal University, Zhanjiang 524048, P. R. China, Tel: 0086-759-3183869, E-mail: gongmanfeng@163.com

mechanism of GPLs content on WC grain refinement[18].

This work is to reveal the effect of GPLs content on WC grain size of WC-Co-GPLs prepared by low-pressure sintering. The refinement mechanism of GPLs on WC grains was explored by characterizing the microstructure such as WC grain size and phase distribution.

2 Experiment

WC-Co with 8.0wt% Co content was selected as the research object to prepare four groups of WC-Co-*x*GPLs materials (*x*=0, 0.05wt%, 0.10wt%, 0.20wt%), and the composition is shown in Table 1. The prepared mixed powder was cold-pressed and preformed with a tablet press (DY-30, Tianjin Keqi High-tech) at a pressure of 200 MPa and holding time for 3 min. The pressed compact was loaded into the graphite mold and then placed into the sintering furnace to obtain WC-8Co-*x*GPLs cemented carbides for low-pressure sintering at 1380 °C for 60 min. The phases of the as-received WC-8Co-*x*GPLs were characterized using X-ray diffraction (XRD, Rigaku D/max-2400). The morphology of powder mixtures and surfaces of as-received samples were observed by scanning electron microscope (SEM, MIRA3 XMH). The WC grain sizes were determined from SEM images using the Nano Measure software. The electron backscatter diffraction (EBSD) attached with SEM was used to study the phase distribution in WC-8Co-*x*GPLs cemented carbides.

3 Results and Discussion

3.1 Microstructure of WC-Co-GPLs powder mixtures

Fig. 1 shows the morphology of powder mixtures with different components after ball milling. Fig. 1a shows the morphology of mixed powder of WC and Co without GPLs addition, and Fig. 1b – 1d show the morphology of mixed powder with 0.05wt%, 0.10wt%, and 0.20wt% GPLs addition, respectively. It can be seen that the WC and Co particles in all the mixed powders dispersed by ultrasonic and ball milling are uniformly spherical without obvious agglomeration, and the particle size is significantly reduced compared with the initial powder. It is conducive to flow and diffusion of Co during high-temperature liquid-phase sintering, thus promoting the densification during the sintering process. As shown by the arrows in Fig. 1b – 1d, GPLs in WC-Co-GPLs powder mixtures are embedded in fine WC and Co particles, and retain lamellar film characteristics after ball milling dispersion.

Table 1 Composition of powder mixtures for designed WC-Co-*x*GPLs cemented carbides

Material	WC/ wt%	Co/ wt%	GPLs, *x*/ wt%	GPLs/ vol%
WC-Co	92.00	8.00	0	0
WC-Co-0.05GPLs	91.95	8.00	0.05	0.35
WC-Co-0.10GPLs	91.90	8.00	0.10	0.70
WC-Co-0.20GPLs	91.80	8.00	0.20	1.35

The defect structure in the original GPLs powder and the dispersed GPLs powder mixture were further analyzed by Raman spectroscope, as shown in Fig.2. It can be seen that the spectrum of the original GPL powder shows three clear peaks at approximately 1317 cm^{-1} (D band), 1574 cm^{-1} (G band), and 2704 cm^{-1} (2D band), which are typical characteristic peaks of GPLs[19]. No characteristic peaks were detected in the range of 1000–3000 cm^{-1} in the Raman spectrum of WC-Co powder mixture.

In addition, Raman spectral peaks of WC-Co-GPLs powder mixtures with different GPLs doping amounts is similar to

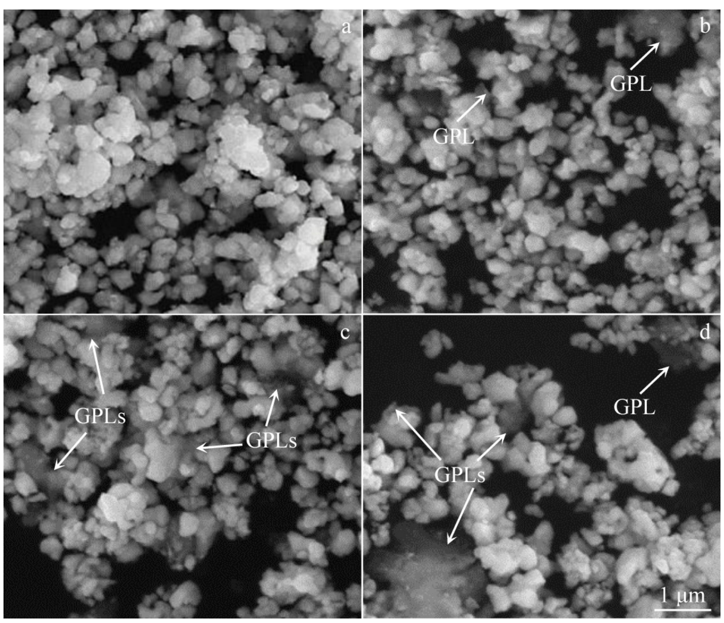

Fig.1 SEM images of powder mixtures of WC-Co-*x*GPLs cemented carbides after ball milling: (a) *x*=0; (b) *x*=0.05wt%; (c) *x*=0.10wt%; (d) *x*=0.20wt%

that of the original GPLs powder, indicating that the structure of GPLs in WC-Co-GPLs powder mixtures is not destroyed after ultrasonic dispersion and ball milling, and GPLs exist in the mixed powders stably. It also shows that the dispersion and ball milling techniques used in this work are feasible. In carbon materials, the strength ratio of D band to G band (I_D/I_G) is usually used to quantify the defect density[20]. It can also be seen from Fig. 2 that the I_D/I_G values of GPLs in the powder mixtures of WC-Co-GPLs are lower than those of original GPLs, and decrease with the increase in GPLs doping amount. It is suggested that the defects of GPLs in the powder mixtures of WC-Co-GPLs are less than those in the original GPL, and GPLs occur to a certain extent during the dispersion process[21].

3.2 Phase composition

Fig. 3 shows XRD patterns of the ultrafine WC-8Co-*x*GPLs cemented carbides. It can be seen that the main phases of all cemented carbides are WC and Co. The peaks of GPLs cannot be observed in XRD patterns of WC-8Co-0.05GPLs and WC-8Co-0.10GPLs. This may be due to the relatively small amount of GPL addition and the fact that dispersion of GPLs in the material is obstructed by WC and Co, which cannot be scanned by X-ray. When x=0.20wt%, only a weak diffraction peak of GPLs is detected at 2θ=26º, as seen in the magnified image of the zone framed by the red box in Fig.3.

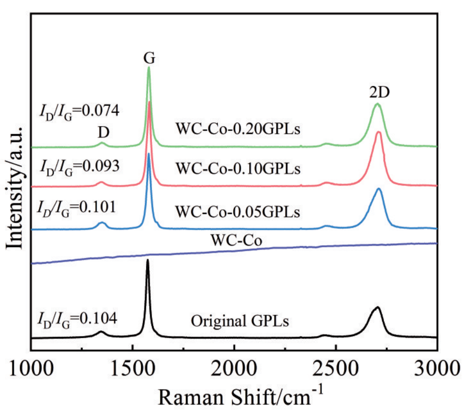

Fig.2 Raman spectra of original GPLs powder and WC-Co-*x*GPLs powder mixtures (x=0.05wt%, 0.10wt%, 0.20wt%)

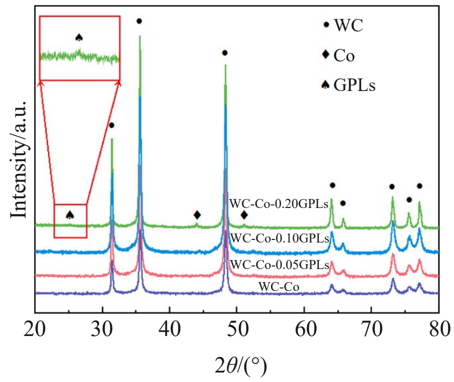

Fig.3 XRD patterns of WC-Co-*x*GPLs cemented carbides

3.3 Surface characteristics

The polished surface morphologies of WC-8Co-*x*GPLs cemented carbides are displayed in Fig. 4. It can be observed that the WC grains are gray white regular polygons, and the Co phase is black or dark gray, which is distributed between the WC grains. As shown in Fig. 4a, there are abnormally grown WC grains in the WC-Co cemented carbide without the addition of GPLs. From Fig. 4b – 4d, it can be found that as GPLs content increases, the proportion of abnormally grown WC grains significantly decreases. Meanwhile, the WC grains gradually become smaller, and Co phase distribution becomes more uniform.

WC grain size is the main factor affecting the mechanical properties of cemented carbide. In order to investigate the

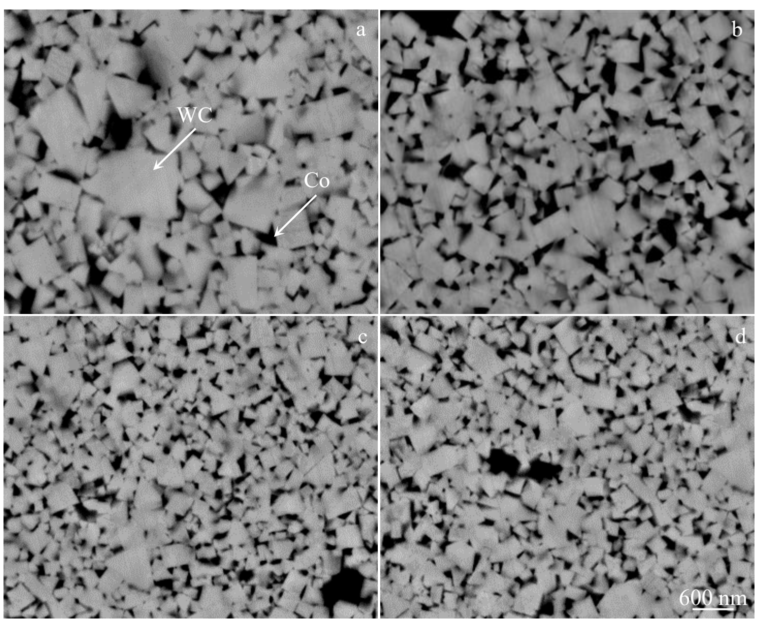

Fig.4 Surface morphologies of WC-8Co-*x*GPLs cemented carbide after polishing: (a) x=0; (b) x=0.05wt%; (c) x=0.10wt%; (d) x=0.20wt%

effect of GPLs addition on the WC grain size, statistics were conducted on the WC grain size and the results are shown in Fig. 5, where μ and σ^2 represent the average values and the dispersion degree of WC grain size, respectively. From Fig.5, it can be seen that μ of WC-Co is 0.57 μm. This indicates that WC-Co cemented carbide belongs to submicron cemented carbide, and its WC grain size is mainly distributed between 0.2–0.9 μm, which is relatively dispersed. Compared with the initial WC powder with a particle size of 0.2 μm, the WC grains in WC-Co significantly grow during the sintering process. This is due to the small particle size and high surface activity of ultrafine WC powder, which has a significant growth driving force during the sintering process, leading to the easy growth of WC grains[22]. As x increases to 0.10wt%, the proportion of grain distribution between 0.6–0.9 μm is significantly reduced, indicating a more uniform distribution of WC grain size in WC-Co-0.10GPLs. It is noted that the μ of WC-Co-0.10GPLs is 0.39 μm, which is decreased by 32% compared with that of WC-Co. Compared with WC-Co-0.10GPLs, the μ of WC-Co-0.20GPLs does not decrease, but its σ^2 value is slightly higher, indicating that when x increases from 0.10wt% to 0.20wt%, the WC grains are not further refined by GPLs. In summary, it can be found that the addition of GPLs has a significant effect on the refinement of WC grains. Meanwhile, according to the grain-size grading standards of hard alloy[23], the grain size of all WC-Co-GPLs cemented carbides has reached the ultra-fine level.

In addition, the WC grain shape and mean free path of Co are observed and the results are proceeded statistics analysis, as shown in Table 2. It can be found that, in all cemented carbides, the WC grains with triangular and hexagonal shapes account for about 33% of the total grain size, and the rest are rectangular-shaped WC grains. This shows that the addition of GPLs has almost no effect on the shape of WC grains when x is in the range of 0–0.20wt%. Moreover, it can be seen that the mean free path of Co reduces when x increases to 0.10wt%. When x increases continuously to 0.20wt%, the mean free path of Co does not decrease further. In general, at a constant Co content, with the decrease in WC grain size, the mean free path of Co binder phase decreases[24]. Combined with Fig. 5 and Table 2, it can be discovered that the variation of GPLs content on WC grain size is consistent with the mean free path of Co.

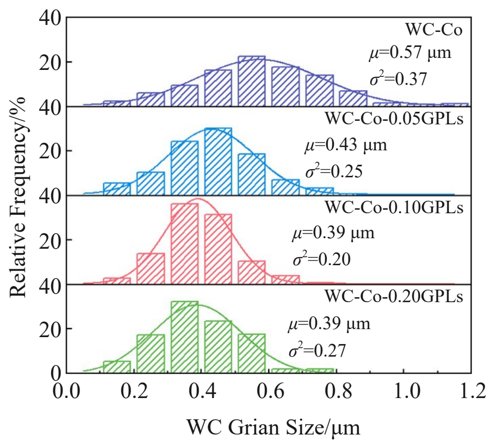

Fig.5 WC grain size distribution in WC-Co-xGPLs cemented carbides

Table 2 WC grain shape and mean free path of Co in WC-Co-xGPLs cemented carbides

x/wt%	WC grain shape/%		Mean free path of Co/μm
	Triangular and hexagonal	Rectangular	
0	33	67	0.163
0.05	35	65	0.128
0.10	31	69	0.119
0.20	32	68	0.121

The phase distribution of WC-Co-xGPLs cemented carbides was analyzed using EBSD, as shown in Fig.6. Fig. 6a shows the phase distribution diagram of WC-Co without GPLs, and Fig.6b–6d show the phase distribution diagrams of WC-Co-xGPLs with x=0.05wt%, x=0.10wt%, and x=0.20wt%, respectively. The blue represents WC grain, yellow represents Co, and red represents GPLs in Fig.6.

From Fig.6a, it can be seen that only WC grain and Co exist in WC-Co cemented carbide, and the distribution of Co plays a bonding role between WC grains. As shown in Fig.6b–6d, the WC grains and Co are finer and more uniform compared with the WC-Co cemented carbide without GPLs. Meanwhile, it can be observed that GPLs are uniformly distributed at the WC/WC and WC/Co interfaces in all WC-Co-GPLs cemented carbides, and the distribution area increases with the increase in GPLs addition.

3.4 Refinement mechanism of GPLs on WC grains

The above results indicate that GPLs can effectively refine WC grains (Fig.5), which is mainly attributed to the following aspects. To begin with, during the liquid-phase sintering process, the main mechanism for WC grain growth is the precipitation of WC on coarse WC particles after supersaturated dissolution in the liquid phase Co, resulting in continuous growth of WC grains[24]. Due to the distribution of GPLs between WC/Co grain boundaries, GPLs can serve as a barrier to block the dissolution and precipitation process of WC in liquid phase Co, thereby inhibiting the growth of WC grains, as shown in Fig.7a. Secondly, the growth of WC grains during the sintering process is mainly controlled by grain boundary migration when the density of WC-Co cemented carbide is greater than 90%[25]. GPLs are uniformly distributed at the WC/WC grain boundaries and WC/Co grain boundaries, which can act as pins to hinder the migration and growth of WC grains, as well as the merging and growth between adjacent WC grains, as shown in Fig.7b[11]. Finally, GPLs with high thermal conductivity of 5000 W/(m·K)[26] can act as thermal conductive plates during the cooling stage of the sintering process. GPLs play a role in heat dissipation, accelerating the cooling rate of the material, and thus preventing the growth of WC grains. In addition, when the

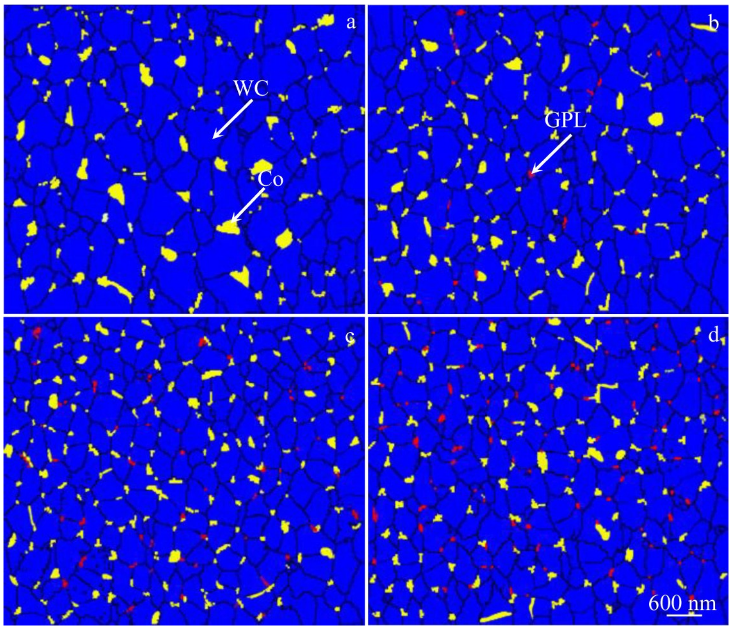

Fig.6 EBSD maps of WC-Co-*x*GPLs cemented carbides: (a) *x*=0; (b) *x*=0.05wt%; (c) *x*=0.10wt%; (d) *x*=0.20wt%

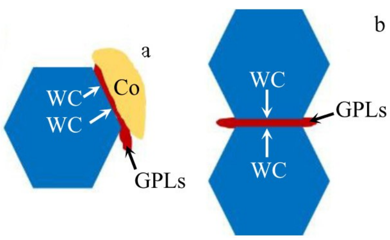

Fig.7 Schematic diagrams of GPLs distributed between WC/Co grain boundaries (a), and WC/WC grain boundaries (b)

content of GPLs is more (0.20wt%), the phenomenon of GPLs wrapping WC grains or overlapping and agglomeration of GPLs will form pores[18]. These pores provide growth space for WC grains, leading to abnormal growth of surrounding WC grains. Therefore, the WC grain size of WC-Co-0.20GPLs cemented carbide is not further refined compared with that of WC-Co-0.10GPLs cemented carbide.

4 Conclusions

1) The WC grain size of WC-Co cemented carbides is refined to ultrafine level by adding GPLs. As the GPLs content increases to 0.10wt%, the distribution of WC grain size is more uniform, and the average grain size of WC is 0.39 μm, which is 32% lower than that of WC-Co. The shape of WC grains is almost unaffected, while the mean free path of Co reduces.

2) The grain refinement of WC is attributed to the homogeneous distribution of GPLs between WC/WC and WC/Co grain boundaries, which results in GPLs hindering the solution and precision process of WC in liquid-phase Co and the migration and growth of WC grains. Additionally, GPLs can serve as heat transfer plates in materials to improve cooling efficiency and prevent WC grain growth.

References

1 Roebuck B, Almond E A. *International Materials Reviews*[J], 1988, 33: 90

2 Gille G, Szesny B, Dreyer K *et al*. *International Journal of Refractory Metals and Hard Materials*[J], 2002, 20(1): 3

3 Makhele-Lekala L, Luyckx S, Nabarro F R N *et al*. *International Journal of Refractory Metals and Hard Materials*[J], 2001, 19(4–6): 245

4 Emani S V, Wang C L, Shaw L L *et al*. *Materials Science and Engineering A*[J], 2015, 628: 98

5 Li Meng, Gong Manfeng, Cheng Zanlin *et al*. *Rare Metal Materials and Engineering*[J], 2023, 52(7): 2653 (in Chinese)

6 Kiuchi M, Hayashi K. *16th International Plansee Seminar 2005: Powder Metallurgical High Performance Materials: Proceedings*[C], Reutte: Plansee AG, 2005

7 Li Yuheng, Liu Xuemei, Liu Chao *et al*. *Rare Metal Materials and Engineering*[J], 2021, 50(6): 2169 (in Chinese)

8 Liu X, Fan Y C, Li J *et al*. *Advanced Engineering Materials*[J], 2015, 17(1): 28

9 Llorente J, Ramírez C, Belmonte M. *Wear*[J], 2019, 430–431: 183

10 Li Z L, Zhao J, Sun J L *et al*. *Ceramics International*[J], 2017, 43(14): 11421

11 Wang X C, Zhao J, Cui E Z *et al*. *Journal of the European Ceramic Society*[J], 2021, 41(2): 1391

12 Sun J L, Zhao J. *Materials Science and Engineering A*[J], 2018, 723: 1

13 Sun J L, Zhao J, Chen M J *et al*. *Material and Design*[J], 2017, 134: 171

14 Su W L, Li S, Sun L. *Ceramics International*[J], 2020, 46(10): 15392

15 Yuan Y G, Xu X X, Zhang J G. *Materials Research Express*[J], 2020, 7(8): 086505
16 Zhang X X, Zhu S G, Ding H *et al*. *International Journal of Refractory Metals and Hard Materials*[J], 2019, 82: 81
17 Hezaveh T, Moazami-Goudarzi M, Kazemi A. *Ceramics International*[J], 2021, 47(13): 18020
18 Li M, Song Z L, Gong M F *et al*. *Ceramics International*[J], 2021, 47(21): 30852
19 Charlier J C, Eklund P C, Zhu J *et al*. *Carbon Nanotubes*[J], 2008, 111: 673
20 Khan U, O'Neill A, Porwal H *et al*. *Carbon*[J], 2012, 50(2): 470
21 Porwal H, Tatarko P, Grasso S *et al*. *Carbon*[J], 2013, 64: 359
22 Fang Z, Maheshwari P, Wang X *et al*. *International Journal of Refractory Metals and Hard Materials*[J], 2005, 23(4–6): 249
23 Xiang Zi. *Cemented Carbide*[J]. 2006, 23(2): 68 (in Chinese)
24 Liu B H, Zhang Y, Ouyang S X. *Materials Chemistry and Physics*[J], 2000, 62(1): 35
25 Fang Z Z, Wang H T, Kumar V. *International Journal of Refractory Metals and Hard Materials*[J], 2017, 62: 110
26 Wang X, Fang Z Z, Sohn H Y. *International Journal of Refractory Metals and Hard Materials*[J], 2008, 26(3): 232
27 Su Y, Li J J, Weng G J. *Carbon*[J], 2018, 137: 222

石墨烯对WC-Co-GPLs硬质合金中WC晶粒尺寸的细化及机理

李　萌[1,2]，魏　栋[1,2]，胡慧璇[1]，吴卫国[1]，钟思思[1]，弓满锋[1]，张程煜[2]

(1. 岭南师范学院 机电工程学院，广东 湛江 524048)

(2. 西北工业大学 材料学院，陕西 西安 710072)

摘　要：研究了石墨烯（GPLs）对低压烧结制备的WC-Co-GPLs硬质合金WC晶粒尺寸的影响。通过表征WC晶粒尺寸和相分布等微观组织，探讨了GPLs对WC晶粒细化的作用。结果表明，GPLs的加入使WC晶粒细化明显且WC晶粒尺寸分布更加均匀。当GPLs含量由0增加到0.10wt%时，WC在硬质合金中的平均晶粒尺寸为0.39 μm，比WC-Co中的WC晶粒的平均晶粒尺寸降低了32%；WC晶粒的形状并未受到影响，而Co的平均自由程随之减小。微结构表征发现GPLs在WC/WC和WC/Co晶界间均匀分布，这阻碍了WC在液相Co中的溶解和析出过程，同时也阻碍了WC晶粒的迁移和生长。此外，GPLs可以作为材料中的传热板，可提高材料的冷却效率从而抑制WC晶粒生长。

关键词：WC-Co硬质合金；石墨烯片；WC晶粒尺寸

作者简介：李　萌，女，1991年生，博士，岭南师范学院，广东 湛江 524048，电话：0759-3183896，E-mail：limeng@lingnan.edu.cn