Effects of multi-layer graphene on the fracture toughness and wear resistance of WC-11Co cemented carbide

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ABSTRACT

The effects of multi-layer graphene (MLG) on the properties of tungsten carbide-11 cobalt (WC-11Co) cemented carbides were studied by transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray diffraction analysis (XRD) and other methods. The results show that when the MLG content is 0.1 wt%, the density, hardness and fracture toughness are 3%, 14.5% and 71.8% higher, respectively, compared with the sample without MLG. Bridging and deflection of cracks by MLG improve the fracture toughness of WC-11Co. In addition, MLG inhibits the transformation of the Co phase into Co₃C during the sintering process and makes Co phase maintain FCC structure at room temperature, thus enhancing the fracture toughness of the matrix. MLG prevent the matrix from generating WC₆Co₃C and Co₃C, thus improving wear resistance. Furthermore, MLG improves the thermal conductivity of cemented carbide and greatly reduces the degree of oxidative wear of the matrix during friction tests. The wear volume of the sample with 0.1 wt% MLG is 98% smaller than that of the sample without MLG, but its mean friction coefficient is 8.8% higher during stable stage. It is because the solid lubricating effect of the wear debris is greater than that of the MLG after 900s.

KEYWORDS

Multi-layer graphene; WC-11Co cemented carbide; fracture toughness; wear resistance

1. Introduction

Tungsten carbide-cobalt (WC-Co) is the most widely used kind of cemented carbide at present. Because of its excellent hardness, fracture toughness and friction properties, it is often used in cutting tools, drilling tools and drawing dies [1-4]. However, cemented carbide workpieces often undergo wear and cracking due to cyclic friction and harsh working environments. Therefore, to reduce industrial costs, improve work efficiency and meet increasingly stringent industrial needs, it is necessary to develop WC-Co cemented carbides with better comprehensive performance [5].

Carbon nanomaterials have attracted much attention due to its unparalleled comprehensive properties. And multilayer graphene is one of the most popular carbon nanomaterials. In recent years, various studies have shown that this material can be used as a reinforcement to strengthen various ceramic materials, e.g. TiC [6,7], Si₃N₄ [8], and Al₂O₃ [9]. Cemented carbide is a typical ceramic matrix composite. A study has shown [10] that MLG can serve as a thermal conductor during liquid phase sintering, increase the volume of liquid phase during the sintering process and uniformly distribute the liquid phase to improve the density and strength of WC-6Co cemented carbides. In addition, MLG can connect WC and Co phase interfaces to improve the thermal conductivity of cemented carbide. Sun et al [11] studied the effect of MLG on nanostructured functionally graded cemented carbides. The results show that MLG hinders the migration of the Co phase and maintains the gradient structure of the matrix, thus improving the bending strength. Zhang et al [12] prepared and characterized graphene platelets (GPLs)/WC-Al₂O₃ composites and showed that GPLs refined the grain size of the matrix, increased the number of crack deflections, and thus enhanced the fracture toughness. Additionally, GPLs had a lubricating effect on friction, thereby improving wear resistance. Li et al [13] sintered WC-Co-GPLs composites in argon atmosphere, and studied the properties of the samples. The results show that GPLs can enhance the thermal conductivity of cemented carbide, increase the sintering cooling rate, and inhibit the grain growth. In addition, they proposed that GPLs could be self-lubricating to protect the substrate during friction process. Sun et al [14] investigated the effect of MLG on the fracture toughness of WC-Co cemented carbides. The results showed that MLG can introduce weak interfaces, which hinder dislocation movement and change the direction of main crack propagation, thus increasing the fracture toughness of cemented carbides. In addition to these studies, other researchers [15] have suggested that graphene can enhance the properties of cemented carbide. In general, most researchers chose to analyze the effects of MLG on the fracture toughness and wear properties of WC-Co cemented carbides from the perspective of interface strengthening and MLG self-lubrication, while ignoring the effects of MLG on these two properties from the perspective of phase composition. Furthermore, little
attention has been paid to the interaction of various properties, such as the influence of relative density on fracture toughness, thermal conductivity on wear properties, etc.

Therefore, in order to have a more comprehensive understanding of the effects of MLG on WC-Co cemented carbide, this paper took WC-11Co as the research object to discuss the effects of MLG on its hardness, fracture toughness and wear properties. The influence of MLG on the phase composition of cemented carbide was analyzed by XRD, TEM and other characterization methods, so as to analyze the influence of MLG on fracture toughness and wear resistance from the perspective of phase composition. Besides, the interactions between various properties (For example, the influence of relative density on fracture toughness, thermal conductivity on wear properties, etc.) are discussed in this paper. It is hoped that this paper can provide theoretical basis for the research in this field and the preparation of high-performance cemented carbides.

2. Materials and methods

2.1. Materials preparation

The raw materials used in this experiment were WC-11Co cemented carbide powder and few-layer MLG; their dimensions are shown in Table 1. Figure 1a,b show the morphology of unprocessed WC-11Co powder and MLG. Due to the uneven size of the initial cemented carbide powder and the overlap between MLG sheets, high-energy ball milling was selected to prepare the powder mixture. Ball milling can provide a large shear force to separate MLG sheets as well as stir the powders to make a homogeneous mixture. Before ball milling, the MLG powder was poured into a 2 mg/mL polyvinylpyrrolidone (PVP)/ethanol solution. After ultrasonic dispersion for 40 min, the MLG suspension and the weighed carbide powder were poured into tanks for ball milling at a speed of 180 r/min for 12 h. After the above steps were completed, the tanks were removed from the ball mill and placed in a vacuum drying oven for 7 h at 75°C. Then, the tanks were loaded onto the ball mill again for processing at 350 r/min for 10 min (separating the powder from the milling balls). Finally, the powders were passed through an 80-mesh sieve to obtain MLG/WC-11Co cemented carbide powder mixtures with MLG contents of 0, 0.05, 0.1 and 0.15 wt%. The morphology of the mixed powders is shown in Figure 1c. The prepared powders were sintered by hot pressing in a vacuum sintering furnace. Schematic diagrams of the sintering equipment and sintering temperature and pressure are shown in Figure 2a,b.

2.2. Characterization

In this experiment, SEM (SUPRA 40, ZEISS) and TEM (Tecnai G2 F30 S-Twin, FEI) were used to observe the microstructure of samples. MLG was detected using a Raman spectrometer (LabRAM HR Evolution, HORIBA Jobin Yvon S.A.S.). The phase composition of the samples was analyzed by XRD (Empyrean Alpha-1, Malvern Panalytical) and selected area electron diffraction, and the grain sizes of the samples were calculated by using the intercept method and ImagePro software. The actual density of each sample was evaluated by a density measuring instrument (MH-120C, MAYZUN), and the relative density of the samples was obtained by dividing the actual density by the theoretical density. The HV₁₀₀ Vickers hardness of these samples was determined by a Vickers hardness tester (FV-810, Future-Tech Corp.), and the fracture toughness was calculated by the indentation crack method. The calculation formula is as follows [16,17].

| Table 1. Information of raw materials. |
|----------------------------------------|
| **Thickness** | **Size** | **Source** |
| WC-11Co powder | 1.2 μm | Zunyi Zhongbai cemented carbide Co., Ltd (China) |
| Multi-layer MLG | 1 ~ 5 nm | Suzhou Heng Qiu Technology Co. (China) |

![Figure 1](image-url)  
*Figure 1.* Powder morphology: (a) original WC-11Co powder; (b) raw MLG; and (c) powder mixture after ball milling.
\[
K_C = \beta (HP/L)^{1/2}
\]

where \( \beta = 8.89 \times 10^{-2} \), \( H \) is the Vickers hardness value, unit: N/mm\(^2\), \( P \) is the load, unit: N, and \( L \) is the sum of crack lengths at four corners of indentation, unit: \( \mu m \). A multifunctional friction and wear tester (MFT-5000, RTEC) was used to conduct friction experiments and record the friction coefficient in real time. A laser confocal microscope (OLS-5000, OLYMPUS) was used to measure the cross-sectional areas of the wear tracks, and the wear volume was obtained by multiplying the measured value of the cross-sectional area by the length of the wear track.

3. Results and discussion

3.1. Grain size and relative density

Figure 3(a-e) show the metallographic diagrams of samples with different MLG contents and the measurement results for WC grain sizes. The grain sizes of all samples with MLG are smaller than that of the specimen without MLG. In WC-Co cemented carbides, the growth of WC grains is mainly attributed to the dissolution and precipitation of small grains. That is, smaller WC grains dissolve and reprecipitate on the surfaces of larger grains during sintering, increasing the sizes of the larger particles. This phenomenon is known as Ostwald ripening [18–20]. Figure 3f shows the microtopography of the sample with 0.1 wt% MLG where bright white MLG is visible in the middle of the black matrix. Figure 3g,h show selected electron diffraction patterns on both sides of MLG. The calibration results for diffraction spots show that the two sides of MLG are WC grains. This indicates that the MLG added to the WC-11Co matrix adheres to the surfaces of WC grains rather than reacting with the matrix. Thus, adhesion of MLG to WC grains effectively hinders the migration of grain boundary and their dissolution and reprecipitation during the sintering process, which inhibits the
growth of WC grains [13,15]. In addition, some researchers have pointed out that MLG increases the cooling rate during sintering, thus inhibiting the growth of grains [14]. When the MLG content is 0.15 wt%, the grain sizes are larger, which is related to the agglomeration of MLG particles [10,13]. After agglomeration, the specific surface area of MLG is not as large as before agglomeration, and the coating effect on WC grains is far less than that of unagglomerated MLG; thus, agglomerated MLG cannot inhibit the dissolution and reprecipitation of WC grains effectively. As a result, the larger grains of WC can become even larger by consuming smaller grains of WC, and the average grain size increases.

Figure 4a shows graphs of the relative densities of the samples. Compared with the original sample without MLG, the densities of the other three samples with MLG are higher to varying degrees, which is related to the excellent thermal conductivity of MLG [10,17]; the theoretical thermal conductivity of MLG is as high as 5300 W/m K [21–23]. When MLG is present in the powder, it plays the role of “heat conducting plate”. Therefore, in the sintering process, the mixed powder with MLG enters the liquid state faster than pure WC-11Co cemented carbide powder. Thus, under the very large pressure exerted by the pressure bar, the gas in the powder has more time to flow and be extruded, and the liquid phase Co has more time to fill the interstices, which decreases the porosity and increases the density of the sintered sample. However, if too much MLG is added, then it easily agglomerates, which reduces its ability to increase the thermal conductivity of cemented carbide [10]. Therefore, the time of matrix in the liquid state is shortened, which is not conducive to densification of the matrix and is the reason for the lower density of the sample with 0.15 wt% MLG vs. the sample with 0.1 wt% MLG.

### 3.2. Hardness and fracture toughness

#### 3.2.1. Hardness

Figure 4b shows the hardness and fracture toughness of samples with different MLG contents. The Vickers hardness of the samples first increases and then decreases with increasing MLG content, and the hardness value is the highest when the MLG content is 0.1 wt%, which is related to the grain size and density of the samples. As mentioned above, MLG can inhibit grain growth and increase the density. According to Hall-Petch theory [10,12], when the grain is smaller, the number of grain boundaries will be larger, so the obstruction effect of grain boundaries on dislocation will be more obvious, and the plastic deformation of the material will be more difficult. Therefore, the sample with smaller grain size will have larger hardness. In addition, when the WC grains are smaller, the total area of the WC grains increases accordingly. This means that there is a greater probability of the Vickers hardness indenter contacting the hard phase WC during the pressing process, resulting in a higher hardness. Furthermore, an increase in relative density means that the lower the porosity of the matrix is, the more compact the sample, the more difficult the pressing process of the hardness tester, and the smaller the indentation, which raises the measured hardness value. As can be seen from Figure 4c, the hardness of the sample gradually increases with the increase of density, but the relationship between hardness and relative density is not linear. Hence we can infer that relative density is the factor affecting hardness, but it is not the only factor. Which is the main factor affecting the hardness of the sample, relative density or grain size? According to the experimental results, we can know that the change of relative density of the samples is not significant (the difference between the maximum and minimum is only three percentage points), and the hardness is more significantly affected by the grain size. Therefore, we judge that grain size is the main reason affecting the hardness of the sample. In general, we suggested that because of the smaller grain size and higher relative density of samples that contain MLG, they are harder than the MLG-free sample. As the sample with 0.1 wt% MLG has the smallest grain size and the largest density, its hardness is the highest of those in this study. According to 3.1, when the graphene content is 0.15 wt%, the mean grain size of the sample is larger than that of the sample with 0.1 wt% graphene content, while the density was
smaller than that of the sample with 0.1 wt% MLG content. Which may be the reasons for the decrease in hardness of the sample with 0.15 wt% graphene content.

3.2.2. Crack bridging and crack deflection enhance fracture toughness

Figure 4b shows that the fracture toughness of the specimens containing MLG is greater than that of the specimen without MLG. Figure 5a,b show the crack morphology of the sample with 0.1 wt% MLG. It is obvious in this figure that crack bridging and crack deflection are visible at the crack. This is because MLG has excellent mechanical properties (the theoretical elastic modulus can reach 1 TPa [24–26]). When the crack extends to MLG, the stress at the crack tip is difficult to break the MLG. Therefore, the crack continues to expand by crossing or bypassing MLG, which consumes crack propagation energy and is unfavorable for subsequent crack propagation. When a crack crosses and bypasses MLG, crack bridging and crack deflection remain. When the MLG content is too large, it has a negative impact on the fracture toughness of the matrix. As shown in Figure 5c, when the MLG content is 0.15 wt%, the MLG agglomerate easily. Agglomerated MLG is an impurity phase that can easily lead to the formation and propagation of cracks in cemented carbides, resulting in a decrease in the fracture toughness of the matrix. Hence, the fracture toughness of the 0.15 wt% MLG sample is lower than that of the 0.1 wt% MLG sample.

3.2.3. Phase constitutions and relative density affect fracture toughness

TEM was used to observe the MLG-free sample and the sample with 0.1 wt% MLG, and the results are shown in Figure 6(a-c). As these figures show, Co3C is present in the sample without MLG. In the sample with MLG, the Co phase does not react and has face centered cubic (FCC) structure. Face centered cubic Co has 12 slip systems, and the atoms are connected by metal bonds, which makes it have good plasticity [27,28]. The stress concentration at the crack tip can be effectively alleviated by plastic deformation so that the

![Figure 5](image-url)

Figure 5. (a),(b) Crack morphology and local EDS scanning results of the sample with 0.1 wt% MLG; (c) crack morphology and local EDS scanning results of the sample with 0.15 wt% MLG.

![Figure 6](image-url)

Figure 6. (a) TEM images of the morphology and electron diffraction spots of the MLG-free sample; (b) TEM image of the morphology and electron diffraction spots of the sample with 0.1 wt% MLG; (c) high-resolution image of the red box in Figure (b); (d), (e) schematic diagrams of crack propagation in samples with different densities.
matrix can maintain good fracture toughness. However, when Co transforms into Co₃C, there are only three slip systems, and the atoms are connected by ionic bonds, so the plasticity is much less, which leads to lower fracture toughness of the matrix in comparison to the sample with FCC Co. The reaction of the Co phase to form Co₃C is closely related to the inexistence of MLG in the matrix. As shown in Figure 6c, MLG adheres to the surface of the Co phase in the cemented carbide matrix, which prevents the diffusion of elemental C from WC into the Co phase where it reacts to form Co₃C. In addition, MLG can also hinder the mutual diffusion and growth of the Co phase so that the grain size remains in a small range. It has been shown [29] that when the Co particle size is very small, FCC Co has a lower surface free energy and is more stable at room temperature than larger Co particles. Therefore, the Co phase in this paper is FCC Co instead of conventional hexagonal close packed (HCP) Co. In conclusion, MLG can prevent the Co phase from reacting and enable it to maintain FCC structure, thus improving the fracture toughness.

In addition to the above toughening mechanism, the increase in the relative density has a positive influence on the fracture toughness of the matrix. As shown in Figure 6d,e, compared with the sample with higher density, the sample with lower density has higher porosity and a smaller contact area between the crack tip and matrix. Therefore, under the same crack propagation conditions, the matrix with lower density withstands greater stress and more easily cracks, which decreases the fracture toughness of the matrix. As mentioned above, the sample with MLG is denser, so its fracture toughness is higher than that of the sample without MLG. However, it can be seen from Figure 4c that although the fracture toughness of the three samples with higher relative density is also higher, the fracture toughness is obviously not proportional to the relative density. Therefore, density is not the only factor affecting fracture toughness. This is consistent with the idea proposed in this paper that in addition to density, crack deflection and crack bridging induced by MLG and phase composition of the sample also affect fracture toughness.

3.3. Tribological performance

3.3.1. MLG adheres to the wear track and protects the surface

As mentioned above, when the amount of MLG is 0.1 wt%, the density, hardness and fracture toughness are the best of the samples tested in this study. Therefore, samples with MLG contents of 0 wt% and 0.1 wt% were selected for a test to compare friction and wear. Figure 7 shows the 3D images and cross sectional images of wear tracks taken by laser confocal microscopy. As shown in Figure 7a,b, the wear track of the sample without MLG is particularly obvious, with a depth of more than 30 µm. Figure 7c,d show that the wear depth of the sample with MLG is less than 5 µm. Such a sharp contrast indicates that the addition of MLG considerably improves the wear resistance of WC-11Co cemented carbide.

Figure 8a,b show the surface morphology of the wear track of the sample with 0.1 wt% MLG where there are some bright white flakes on the surface of the wear track. Combined with the EDS scanning results of points A, B and C in these figures, it is
apparent the carbon content of these bright white areas is much higher than that of the matrix. Figure 8c shows Raman spectra of the wear tracks of the original MLG and the sample with 0.1 wt% MLG. The D, G and 2D peaks of the latter are the same as those of original MLG at the same wavenumbers. These results indicate the presence of MLG on the wear track. Therefore, in the process of friction testing, MLG is pulled out of the matrix by the Si3N4 ball and attached to the surface of the sample, which effectively hinders direct contact between the Si3N4 ball and the matrix. Because MLG has excellent mechanical properties, it resists destruction by Si3N4 ball, thus having a good protective effect on the matrix. In addition [17], MLG layers easily separate under shear force during friction because van der Waals forces are responsible for the interaction between MLG layers, as a result, there is an increase the area covered by MLG, further enhance the protection effect on the matrix.

3.3.2. Phase composition affects wear resistance

To further explore the effect of MLG on the wear resistance of cemented carbide, XRD was used to evaluate the phase compositions of the two samples in this experiment; the results are shown in Figure 9. There is no obvious difference in the overall phase compositions of the two samples. However, in the sample without MLG, there is a weak diffraction peak corresponding to $W_2Co_3C$, which indicates a small amount of $W_2Co_3C$ in the sample. The diffraction peak of $W_2Co_3C$ does not appear in the blue curve in Figure 9, which indicates that the addition of MLG effectively inhibits the formation of this phase. Figure 10(a-d) show selected electron diffraction and TEM morphology results for the sample without MLG. The figures demonstrate that $W_2Co_3C$ and $Co_3C$ are present in the sample without MLG, and the two phases are in close proximity. This phenomenon demonstrates that in the liquid phase sintering process, WC dissolves into the adjacent Co grains in the form of W and C. Under high temperature and high pressure conditions, part of the elemental C reacts with Co to form a stable $Co_3C$ phase. As a result, the original WC grains react with Co to form $W_2Co_3C$ due to the loss of elemental C during the subsequent cooling process. Figure 10(e-h) show selected electron diffraction and TEM morphology results for the sample with 0.1 wt % MLG. The cemented carbide with MLG retains its original phase composition without the formation of $W_2Co_3C$ and $Co_3C$. Figure 10(g,h) show the presence of MLG on the grain boundaries of WC and Co. This indicates that MLG can effectively prevent the dissolution of elemental C from WC into Co during the sintering process so that $W_2Co_3C$ and $Co_3C$ do not form in the sintered WC-11Co cemented carbide. $Co_3C$ does not have excellent plasticity, so it cannot relax stress concentration through plastic deformation (as can Co) during the friction process. Thus, it is difficult for $Co_3C$ to have a positive impact on the friction properties of WC-Co cemented carbide. In addition, $W_2Co_3C$ is a common carbon-deficient phase that forms during the preparation of WC-Co cemented carbide. Due to the poor mechanical properties of $W_2Co_3C$, it is easily breaks and separates from the matrix to form wear debris under the influence of positive pressure and shear force during the processes of friction and wear, thus bringing adverse effects on the wear resistance of the matrix. In conclusion, the addition of MLG effectively inhibits the formation of $W_2Co_3C$ and $Co_3C$, thus greatly improving the wear resistance of the samples.

Figure 8. (a), (b) Morphologies of wear tracks and local EDS scanning results of the sample with 0.1 wt% MLG; (c) Raman spectra of raw MLG and wear track of the sample with 0.1 wt% MLG.

Figure 9. XRD patterns of 0 wt% and 0.1 wt% MLG samples.
3.3.3. Oxidation degree and mechanical properties affect wear resistance

The wear resistance of the samples is directly related to the degree of oxidation during friction. To explore the difference in oxidation degree between the two samples during the friction process, SEM was used to observe the wear surface of the MLG-free sample and the sample with 0.1 wt% MLG, and EDS scanning was performed, as shown in Figure 11(a-f). As shown in Figure 11(a-c), the wear surface of the MLG-free sample is covered by bright white and dark oxides, and the morphological characteristics that were present before
friction testing are no longer visible. EDS scanning results show that oxygen covers almost the entire surface of the wear track. The oxygen content is up to 18.4%, which indicates that the sample underwent a considerable amount of oxidation during friction testing and. Figure 11d shows the wear morphology of the sample with 0.1 wt% MLG. It can be seen that after the friction test, the surface morphology of the sample does not change much compared with that before the friction test. There are only some slightly dark adhesive wear areas on the surface of the wear track. Figure 11e,f show that elemental oxygen is mostly concentrated in the local adhesive wear area, while the oxygen content is extremely low in other areas (only 3.74%). The above phenomenon indicates that the main wear mechanism of the samples with 0.1 wt% graphene is not oxidative wear, but slight adhesive wear. Why are there such differences between the two samples? We suggest that this is mainly because the addition of MLG improves the thermal conductivity of cemented carbide. As shown in Table 2, the thermal conductivity of the sample with 0.1 wt% MLG content is nearly 10 W/(m × K) higher than that of the sample without MLG. This indicates that the sample containing MLG can more rapidly transfer heat generated by the friction process to the whole matrix, thus reducing the surface temperature and the oxidation degree of the sample. This means that it is more difficult for oxidative wear to occur during the friction process. Comparing Figure 12(a-h) shows that due to the poor thermal conductivity of the MLG-free sample, an obvious oxide layer forms on the wear surface. Due to the poor mechanical properties of the oxide layer, it is easily destroyed and generates oxidative wear in the process of continuous friction with the Si₃N₄ ball. Therefore, cracks, pits and other forms of damage are apparent in the morphology of the wear track. As shown in Figure 12(e-h), due to the excellent thermal conductivity of the sample with MLG, the matrix does not undergo much oxidation during the friction test, so the excellent properties of Co and WC can be fully utilized in the friction test. Because Co phase keeps good bonding effect in unoxidized WC-Co cemented carbides. Therefore, it is difficult for the WC grains to be pulled out of the matrix by the friction ball. And under the action of positive pressure and shear force, the interaction of “sticking-tearing-sticking again-tearing again” occurs between the friction ball and Co phase with good wettability, resulting in adhesive wear of the sample. This is reason for why the sample with 0.1 wt% MLG content has slight adhesive wear. As shown in Fig. S1. and Fig. S2., it can be seen from the figures that the Co content in the worn area is indeed lower than that in the unworn area, which confirms our view again. on the surface of the wear track of the sample, there are obvious slip bands and stratiform fractures of WC grains, indicating that the matrix without obvious oxidation has undergone plastic deformation that effectively alleviates the stress concentration generated by the friction process and thus maintains good wear resistance by the matrix. In addition to the above mechanisms, the wear resistance of cemented carbide is closely related to its hardness and fracture toughness. As discussed above, the addition of MLG can improve the hardness and fracture toughness of cemented carbide. This indicates that compared with the sample without MLG, it is more difficult for the Si₃N₄ ball to press into the surface of the sample with 0.1 wt% MLG during sliding, and more difficult for cracks to form and expand on its surface, which is also one of the reasons for the better wear resistance of this sample.

| Content of MLG (wt%) | Density (g/cm³) | Thermal diffusion (mm²/s) | Cp (J/g·K) | Thermal conductivity (W/(m·K)) |
|---------------------|----------------|--------------------------|-----------|-------------------------------|
| 0                   | 13.9234        | 16.545                   | 0.344     | 79.245                        |
| 0.1                 | 14.3383        | 17.73                    | 0.35      | 88.976                        |

Figure 12. (a), (b), (c), (d) Wear track topography of the sample with 0 wt% MLG; (e), (f), (g), (h) wear track topography of the sample with 0.1 wt% MLG.
3.3.4. The coefficient of friction

Figure 13a shows the wear volumes and the mean friction coefficients during the stable stage (approximately 300–2500 s) of the MLG-free sample and the sample with 0.1 wt% MLG. The wear volume of the sample with MLG is much lower than that of the sample without MLG, but the mean friction coefficient of the former is higher than that of the latter. Combined with Figure 13b, the result shows that during the initial stage of stabilization (approximately 300–900 s), the average friction coefficient $f_{0.1}$ of the sample with MLG is 0.618, while the counterpart $f_{0.0}$ of the sample without MLG is 0.628. This is because during the early stage of the friction experiment, MLG can lubricate the surface of the wear track so that the friction coefficient of the specimen containing MLG is lower than that of the specimen without MLG. However, after 900 s, the friction coefficient of the MLG-free sample gradually decreases and eventually remains at a relatively low value. Combined with Figure 13c,e, these results show that there is much wear debris on the surface of the wear track of the uncleaned MLG-free sample. Figure 13d,f show that there is almost no abrasive debris on the surface of the sample with 0.1 wt% MLG. Therefore, the reason why the mean friction coefficient of the MLG-free sample is lower than that of the MLG-containing sample is that after 900 s, solid lubrication by the wear debris on the former surface is more obvious than lubrication by the MLG on the latter. To facilitate understanding, a schematic diagram is shown in Figure 14, in which Figure 14a is a schematic diagram of the friction device, and Figure 14(b-e) are schematic diagrams of the wear of the samples without and with 0.1 wt% MLG, respectively. The figures show that when there is a large amount of wear debris on the surface of the sample, it accumulates on the surface of the wear track and can have a solid lubricating effect between the $Si_3N_4$ ball and the matrix, making the friction mode gradually change from initial sliding friction to a combination of sliding friction and rolling friction, resulting in the decrease in the friction coefficient. However, due to the good wear resistance of the sample containing MLG, only a small amount of debris forms during the friction test, so the friction mode is always sliding friction; hence, its friction curve remains stable throughout the test. Therefore, a lower friction coefficient does not mean that the sample is more wear resistant, and the level of wear resistance is closely related to the nature of the matrix. In addition, although a large amount of wear debris has a solid lubricating effect on the surface of the wear track, those particles are not conducive to the

![Figure 13](image-url)
heat dissipation of the matrix [30], which aggravates the oxidation of the surface of the wear track and has adverse effects on wear resistance. Hence, it is not accurate to evaluate the wear resistance of samples by only the friction coefficient.

4. Conclusions

By means of SEM, TEM, XRD, Raman spectroscopy, etc., the effects of MLG on the grain size, density, hardness, fracture toughness and tribological performance of WC-11Co cemented carbide were studied. The results are as follows:

1. MLG adhered to the surfaces of WC grains, which hindered their dissolution and precipitation during the sintering process and thus inhibited the growth of grains and improved the hardness of the sample.
2. MLG enhanced heat conduction, making the powder reach the liquid state faster during the sintering process and providing sufficient time for the flow and discharge of gas, which was conducive to the densification of the matrix.
3. Crack bridging and crack deflection induced by MLG improved the fracture toughness of the matrix. Additionally, MLG inhibited the transformation of the Co phase into Co3C during the sintering process and made Co phase maintain a face centered cubic structure with good plasticity to exert a toughening effect.
4. MLG hindered direct contact between the Si3N4 ball and the matrix, inhibited the formation of W6Co3C and Co3C in the WC-11Co cemented carbide, and reduced the degree of oxidation of the sample during friction testing, thus improving the wear resistance of the sample.
5. From 300 to 900 s during the friction test, MLG acted as a lubricant, and the friction coefficient of the sample with 0.1 wt% MLG was slightly lower than that of the sample without MLG. However, with the increase in the volume of the wear debris on the MLG-free sample, the solid lubricating effect of the wear debris on the surface of the wear track was greater than that of MLG, resulting in a lower mean friction coefficient than that of the sample with MLG.

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References

[1] Han XQ, Lin N, Chen M, et al. In situ synthesis of dicobalt phosphide on tungsten carbide-cobalt cemented carbide substrates as a hydrogen evolution reaction electrocatalyst. Scripta Mater. 2021;204:114159.
[2] Ibe H, Kato Y, Yamada J, et al. Controlling WC/Co two-phase microstructure of cemented carbides additive-manufactured by laser powder bed fusion: effect of powder composition and post heat-treatment. Mater Des. 2021;210:110034.
[3] Ye Y, Xia H, Lin Y, et al. Refined WC grain size and improved mechanical properties in a hardmetal WC-8Co processed via short-time semi-solid hot pressing. J Alloys Compd. 2021;889:161560.
[4] Zhang Q, Huang K, Wang J, et al. Effect of pulse electromagnetic coupling treatment on thermal conductivity of WC-8Co cemented carbide. Ceram Int. 2021;47:22683–22692.
[5] Jiang W, Lu H, Chen J, et al. Toughening cemented carbides by phase transformation of zirconia. Mater Des. 2021;202:109559.

[6] Nguyen TP, Pahzouhanfar Y, Delbari SA, et al. Characterization of spark plasma sintered TiC ceramics reinforced with graphene nano-platelets. Ceram Int. 2020;46:18742–18749.

[7] Sun J, Zhao J, Huang Z, et al. Preparation and properties of multilayer graphene reinforced binderless TiC nanocomposite cemented carbide through two-step sintering. Mater Des. 2020;188:108495.

[8] Kvetková L, Duszová A, Hvizdoš P, et al. Fracture toughness and toughening mechanisms in graphene platelet reinforced Si3N4 composites. Scripta Mater. 2012;66:793–796.

[9] Stolyarov VV, Frolova AV, Sudzhanstaya IV. Dielectric properties of nanocomposite ceramics Al2O3/graphene processed by spark plasma sintering. Ceram Int. 2020;46:6920–6925.

[10] Su W, Li S, Sun L. Effect of multilayer graphene as a reinforcement on mechanical properties of WC-6Co cemented carbide. Ceram Int. 2020;46:15392–15399.

[11] Sun J, Zhao J, Gong F, et al. Design, fabrication and characterization of multi-layer graphene reinforced nanostructured functionally graded cemented carbides. J Alloys Compd. 2018;750:972–979.

[12] Zhang X, Zhu S, Shi T, et al. Preparation, mechanical and tribological properties of WC-Al2O3 composite doped with graphene platelets. Ceram Int. 2020;46:10457–10468.

[13] Li M, Song Z, Gong M, et al. WC+Co+graphene platelet composites with improved mechanical, tribological and thermal properties. Ceram Int. 2021;47:30852–30859.

[14] Sun J, Zhao J. Multi-layer graphene reinforced nano-laminated WC-Co composites. Mater Sci Eng A. 2018;723:1–7.

[15] Hezaveh T, Moazami-Goudarzi M, Kazemi A. Effects of GNP on the mechanical properties and sliding wear of WC-10wt%Co cemented carbide. Ceram Int. 2021;47:18020–18029.

[16] Shetty DK, Wright IG, Mincer PN, et al. Indentation fracture of WC-Co cermets. J Mater Sci. 1985;20:1873–1882.

[17] Sun J, Zhao J, Chen M, et al. Multilayer graphene reinforced functionally graded tungsten carbide nano-composites. Mater Des. 2017;134:171–180.

[18] Mannesson K, Jeppsson J, Borgenstam A, et al. Carbine grain growth in cemented carbides. Acta Mater. 2011;59:1912–1923.

[19] Borgh I, Hedström P, Borgenstam A, et al. Effect of carbon activity and powder particle size on WC grain coarsening during sintering of cemented carbides. Int J Refract Met Hard Mater. 2014;42:30–35.

[20] Müller D, Konyashin I, Farag S, et al. WC coarsening in cemented carbides during sintering. Part I: the influence of WC grain size and grain size distribution. Int J Refract Met Hard Mater. 2022;102:105714.

[21] Xu X, Pereira LF, Wang Y, et al. Length-dependent thermal conductivity in suspended single-layer graphene. Nat Commun. 2014;5:3689.

[22] Alexander A, Balandin SG, Bao W, et al. Superior thermal conductivity of single-layer graphene. Nano Lett. 2008;8:902–907.

[23] Wu N, Che S, Li HW, et al. A review of three-dimensional graphene networks for use in thermally conductive polymer composites: construction and applications. New Carbon Mater. 2021;36:911–926.

[24] Geim AK. Graphene: status and prospects. Science. 2009;324:1530–1534.

[25] Zhu Y, Murali S, Cai W, et al. Graphene and graphene oxide: synthesis, properties, and applications. Adv Mater. 2010;22:3906–3924.

[26] Hua D, Zhou Q, Wang W, et al. Atomic mechanism on the mechanical and tribological performance of amorphous/graphene nanolaminates. Tribol Int. 2022;165:107318.

[27] Deng Y, Xiong X, Zou JP, et al. Control of morphology and structure for β-Co nanoparticles from cobalt oxalate and research on its phase-change mechanism. J Alloys Compd. 2015;618:497–503.

[28] Su W, Zou J, Sun L. Effects of nano-alumina on mechanical properties and wear resistance of WC-8Co cemented carbide by spark plasma sintering. Int J Refract Met Hard Mater. 2020;92:105337.

[29] Osamu K, Hisateru S, Yutaka S. Size effect on the crystal phase of cobalt fine particles. Phys Rev B. 1997;56:13849–13854.

[30] Wang H, Gee M, Qiu Q, et al. Grain size effect on wear resistance of WC-Co cemented carbides under different tribological conditions. J Mater Sci. Technol. 2019;35:2435–2446.