Fabrication of graded WC-Ni₃Al cemented carbides by lamination pressing and spark plasma sintering

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Abstract: WC-Ni₃Al composite powders with different Ni₃Al contents were prepared by ball milling WC and Ni₃Al powder mixtures. Functionally graded WC-Ni₃Al cemented carbides (FGCCs) with Ni₃Al content gradient were prepared by lamination pressing different WC-xNi₃Al (x = 2, 10) powder mixtures and spark plasma sintering the layered compacts. The results show that there are some distinct gradient composition layers in the sintered bulk sample. With the increase of Ni₃Al content, the size of the WC grains decreases from 0.83 to 0.74 μm because Ni₃Al increases the free path of WC grains. And due to difference in Ni₃Al content and WC grain size, graded WC-Ni₃Al cemented carbides has a Vickers hardness of 1901.8 HV30 at the surface, which decreases to 1780.3 HV30 in the core. Nevertheless, the fracture toughness increases from 10.89 MPa·m¹/² at the surface to 13.34 MPa·m¹/² in the core. The present results show that FGCCs with high outer layer hardness and high inner layer toughness were successfully prepared.

1. Introduction
Cemented carbides are prepared by hard phase (WC, TiC, etc.) and binder phase metals (Co, Ni, Fe, etc.) through various sintering methods [1]. At present, WC-Co cemented carbides are widely used in high-speed cutting and wear protection fields due to its high hardness, fracture strength and wear resistance [2]. However, cobalt is easy to soften at high temperature so that it is difficult to maintain the same mechanical properties at low temperature. And its corrosion resistance and oxidation resistance are poor, which also restricts the application of WC-Co cemented carbides in complex working environments. Therefore, researchers have been looking for binder that can replace cobalt. The intermetallic compound Ni₃Al is promising because of its excellent high-temperature performance. Especially when the temperature is lower than 850 °C, its yield strength will increase with the increase of temperature [3]. Zhang et al. prepared WC-10Ni₃Al cemented carbides with a hardness of 20.4 GPa and a fracture toughness of 10.5 MPa·m¹/² by spark plasma sintering [4]. However, Su et al. prepared WC-8Co cemented carbides with 0.5 wt.% nano alumina by spark plasma sintering, which have a hardness of 1716 HV30, flexural strength of 2728 MPa, and fracture toughness of 12.95 MPa·m¹/² [5]. It is obvious found that WC-Ni₃Al cemented carbides still have a certain gap with WC-Co cemented carbides in terms of comprehensive mechanical properties, especially fracture toughness. Therefore, they cannot meet the requirements of industrial applications.

As it is known, high hardness and wear resistance require cemented carbides to contain more hard phases, but the toughness will be reduced. Conversely, high toughness requires high content of the binder
phase, which results in the poor hardness and wear resistance. Therefore, in the past few decades, the combination of excellent strength and toughness in cemented carbides have always been the research direction of researchers. One way to achieve that is to prepare nanocrystalline cemented carbides which obtain good wear resistance and high toughness by nanograin structure [6]. However, nanocrystalline WC-Ni3Al composite powders is difficult to prepare and WC grains are easy to grow during sintering. Another method is to prepare a layer of coating with higher hardness and wear resistance on the cemented carbide substrate [7]. However, the coating preparation method is so complicated that its cost is high, which limits the application of coating technology. And the third method is to prepare functionally graded cemented carbides (FGCCs). The composite powders with different binder phase contents are laminated one by one, and then sintered to form a graded cemented carbide with a controllable thickness each layer [8]. At present, the method for preparing gradient cemented carbides can conveniently and quickly meet the performance requirements of high surface hardness and good core toughness. But the preparation of gradient WC-Ni3Al cemented carbides are still seldom studied yet.

In this study, graded WC-Ni3Al cemented carbides were prepared by lamination pressing and spark plasma sintering, and the microstructure and mechanical properties of the graded WC-Ni3Al cemented carbide were investigated.

2. Experimental

2.1. Materials preparation

In order to make the graded WC-Ni3Al cemented carbides obtain hard surface and tough core, this study selected WC-2Ni3Al composite powders as outer layer, and WC-10Ni3Al composite powders with more binder as inner layer. We used commercial WC powders (~0.8 µm 99 wt.% purity, Xiamen Golden Egret Special Alloy Co., Ltd., China) and high-energy-milling Ni3Al powders as raw materials. Fig. 1 shows the SEM images of the raw powders. The WC-x wt.%Ni3Al (x = 2, 10) composite powders were ball milled in cyclohexane in a QM-3SP24 planetary ball mill (Nanjing Chishun Science & Technology Co., Ltd., China) at a 250 rpm speed using a ball-to-powder weight ratio of 3:1. The mixed slurry was placed in a vacuum drying oven at 70°C for vacuum drying, and after being completely dried, it is passed through a 100-mesh sieve to avoid agglomeration.

Fig. 1. SEM images: (a) WC and (b) Ni3Al powders.

The schematic diagram of FGCCs was shown in Fig. 2. In order to ensure that the graded cemented carbide had a certain bending strength, the inner layer was designed to occupy 3/5 thickness, the outer layer occupied 2/5 thickness. For subsequent grinding and polishing, the surface layer increased extra thickness of both sides by 0.5 mm. According to the theoretical density of WC-2Ni3Al and WC-10Ni3Al which was calculated by the rule of mixtures, we weighed the required powder weight of each component layer according to the volume of each layer, and pour the dry WC-xNi3Al (x=2,10) composite powders into a graphite mold with a outer diameter of 50 mm and an inner diameter of 22 mm. An axial pressure of 30 MPa was applied to compact the powders for 5 minutes each layer. Then the powders were sintered in a spark plasma sintering furnace (Dr. Sinter Model SPS-825 Spark Plasma Sintering System, Sumitomo Coal Mining Co. Ltd., Japan) in vacuum atmosphere (≤ 6 Pa) at 1380 °C for 5 min. During the spark plasma sintering, the axial pressure was also 30 MPa.
2.2. Materials characterization

The sintered blocks were processed by wire cutting for the sample size of 20×6.5×5.25 mm. Ground each side of the samples to 2000 mesh and then polished. Then the transverse rapture strength was performed on the universal testing machine. The hardness and fracture toughness of the FGCCs (along the gradient surfaces direction) were determined using standard methods. In detail, the hardness was tested using a Vickers Hardness Tester (Beijing Times Sihe Technology Co., Ltd.) under a 30 kg load at room temperature, and the fracture toughness of the samples was calculated by measuring the crack length around the indentation with a 30 kg load. The fracture toughness, \( K_{IC} \), was calculated using the following equation:

\[
K_{IC} = 0.0028 \frac{HP}{\Sigma L}
\]

Where \( H \) is the Vickers hardness (N/mm\(^2\)), \( P \) is the load (N), and \( \Sigma L \) is the total length of the apparent crack at the four corners (mm).

The phase composition of the sample was detected by X-ray diffractometer (XRD, Cu target, D8 Advance, Bruker Co., Germany). The microstructure and fracture morphology of the sample surface were observed by a high-resolution scanning electron microscope (HRSEM, Nova Nano 430, FEI, USA).

3. Results & Discussion

3.1. Phase composition and microstructure of FGCCs

Fig. 3 shows the sintering curve of the gradient WC-Ni\(_3\)Al bulk sample. It can be seen in Fig. 3 that the shrinkage rate of the composite powder fluctuates slightly before 650 °C, which can be explained as the composite powders will absorb some moisture during the ball milling process and the drying process. This moisture will vaporize during the heating process and cause the shrinkage rate changes lightly. When the temperature rises to 850 °C, the densification stage of the composite powder begins, and the shrinkage displacement gradually increases. After the temperature reaches 1350 °C, the shrinkage rate is close to 0 mm/min, with little change, indicating the end of the densification stage. Therefore, it is reasonable to sinter composite powders at 1380 °C for 5 min.
Fig. 4 shows the XRD patterns of the composite powders and the FGCCs sample. It can be seen that the intensity of the Ni₃Al diffraction peak in the composite powder increases with the increase of its content. After spark plasma sintering, the peak width of each diffraction peak of the bulk material becomes smaller, and the intensity of the Ni₃Al diffraction peak increases. This is due to the growth of WC grains during the sintering process.

Fig. 4. XRD patterns of the composite powders and the FGCCs sample.

Fig. 5 (a) depicts gradient cross-sectional micro morphology diagram of FGCCs. It can be obvious seen that layers are formed in the block. There are bright gray matrix phase and black phase in both layers, and the core layer contains more black phase. Combined with the EDS surface scanning distribution map of the core layer in Fig. 6, it can be found that the distribution of Al element and O element are relatively coincident, which infers that Al₂O₃ is produced in the sintered sample. The reason for its origination may be that O element adsorbed in the composite powders reacts with Al element at high temperature. The distribution of Ni element is relatively dispersed, indicating that the binder phase is better distributed between the WC grains. At the same time, Fig. 5(d) and (e) also gives the WC grain size of the core layer and the surface layer. Among them, the average WC grain size of the core layer is 0.74 μm. The average WC grain size of the surface layer is 0.83 μm, which is larger than that of the core layer. This indicates that when the binder phase Ni₃Al is more distributed, the mean free path of WC may be increased so that the aggregation and growth of WC grains during the sintering process may be inhibited.

Fig. 5. SEM images: (a) SEM image of the polished gradient surfaces, (b) SEM images of the core layer and (c) SEM images of the surface layer, (d) mean WC grain size of the core layer, (e) mean WC grain size of the surface layer.
3.2. Mechanical properties of FGCCs

Fig. 7 shows the hardness and fracture toughness of the graded cross-sectional surface. The results show that the hardness of the surface layer is higher than that of the core layer, and the fracture toughness of the core layer is higher than that of the surface layer. As it is known, low binder phase content and high WC content will increase the hardness of cemented carbides. Therefore, the hardness of the gradient WC-Ni3AI bulk material gradually decreases from the surface (1901.8 HV30) to the core (1780.3 HV30). Thanks to the increase of binder phase content, the fracture toughness of the core gradually increases from the surface layer (10.89 MPa m$^{1/2}$) to the core (13.34 MPa m$^{1/2}$). Therefore, the properties of prepared gradient WC-Ni3Al bulk is basically consistent with the pre-designed properties.

Fig. 8 depicts the crack propagation morphology of the surface layer and core layer. It can be seen from the crack path of the surface layer in Fig. 8(a) and (b) that intergranular fracture is the main fracture mode. Slight crack deflection is present in the crack propagation paths, which can increase the resistance of crack propagation. As shown in Fig. 8(c) and (d), the WC grain size of the core layer is smaller, the WC/WC grain boundary and the WC/binder phase interface are the preferred locations for crack propagation, forming intergranular fractures. Specially, when passing through the Al$_2$O$_3$ grains, it will...
Fig. 8. SEM images of crack propagation morphology: (a) and (b) the surface layer, (c) and (d) the core layer.

cause crack deflection and bridging. This indicates more power to extend the cracks. Therefore, mixed fracture (intergranular and transgranular) is the main fracture mode in the core layer. And the formed Al₂O₃ has significant effects on crack propagation, as a result of improving the fracture toughness of cemented carbides.

4. Conclusions
A gradient WC-Ni₃Al bulk material with good properties was prepared by lamination pressing and spark plasma sintering at 1380 °C for 5 min. The microstructure and mechanical properties of the bulk material were analyzed, and the conclusions were as follows:
(1) Due to the effect of rapid heating, a good composition gradient is maintained in the sintered block.
(2) The graded WC-Ni₃Al bulk material has a better surface hardness due to its low surface layer binder phase content and high WC content. At the same time, the core layer obtains better fracture toughness due to the smaller WC grain size and the deflection and bridging effect of self-generated Al₂O₃ on cracks.

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