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ARTICLE

Functionally Graded WC-Co/WC-Fe-Ni Double-Layer Cemented Carbides

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Abstract: We investigated the properties of functionally graded WC-based cemented carbide prepared with a new approach featured by sintering the WC-Co/WC-Fe-Ni double-layer compacts together. For this approach, the reasonable pressing pressure to prepare the alloys should be about 15 MPa, under which the two layers have consistent sintering shrinkages and the unexpected phenomena (e.g. layering and cracking) was not observed. The phase composition and microstructure analyses based on the X-ray diffraction, optical and scanning electron microscopy experiments indicate that the η or graphite phase does not exist in both WC-Co and WC-Fe-Ni layers, and that the interface of these two layers is well combined together. Meanwhile, a significant gradient of Fe, Ni and Co is observed at the interface between the above two layers, and this composition gradient results in a noticeable hardness gradient, which further leads to the WC-Co/WC-Fe-Ni double-layer cemented carbide being of high hardness, wear resistance and toughness.

Key words: WC-Co/WC-Fe-Ni; functionally graded cemented carbide; shrinkage; microstructure; mechanical properties

Due to its high hardness, strength, toughness and good wear resistance, the conventional WC-Co cemented carbide with uniform structure has been widely used in mining, drilling, cutting, machining, wear resistant parts, etc[1-4]. In order to extend service life and improve the production efficiency of the workpieces, the cemented carbides with a unique combination of hardness, toughness and wear resistance are required[4]. However, the hardness and fracture toughness are trade-off for uniform-structure cemented carbides[5]. Clearly, it is difficult for the conventional uniform structure system to meet the requirements for industrial applications due to the antagonism mentioned above. Currently, functionally graded double-layer cemented carbides offer a solution to the trade-off between hardness and toughness by varying the binder content and grain size between the two layers[6,7].

Therefore, in order to improve the overall properties of the cemented carbides, researchers have common interest to study functionally graded alloys[6-11]. Zhang et al[8] declared that a new type of double-layer gradient WC-Co-Ti(C, N)-ZrC cemented carbides were successfully prepared by liquid phase sintering. Oiadapo et al[9,10] demonstrated that a Co gradient could be formed by controlling the composition and holding time of WC-Co double-layers. Konyashin[7] stated that the wear resistance of gradient WC-Co cemented carbide in percussive drilling of quartzite and cutting of abrasive concrete was roughly 2~4 times as that of the corresponding conventional alloys with uniform Co distribution. Additionally, Mohammadpour et al[11] confirmed that the inserts have superior tool life and cutting performance due to the formation of a surface gradient layer with improved properties as well as crater wear resistance. However, compared with the uniform structure cemented carbides, extensive application of the graded materials is limited by their disadvantage in more complex production process, higher price and higher power consumption.

Among the Fe group metals, the combination of Fe and Ni is considered to be an ideal alternative for replacing of Co because of its low toxicity, low price and good wettability with WC[12,13]. Gao[2], Chang[13,14] and Schubert[15] re-

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ported that the WC-Fe-Ni cemented carbides possessed equivalent mechanical properties and corrosion resistance as compared with WC-Co alloys. Therefore, it is possible to produce graded double-layer cemented carbides with a tough layer, constituted by cheaper Fe-Ni binder with high content, stacked by a hard surface WC-Co layer. Moreover, to reduce manufacturing cost, a new process needs to be developed for the preparation of graded double-layer cemented carbides (one layer of WC-Co with low binder content and fine grains and the other layer WC-Fe-Ni with high binder content and coarse grains). However, the functionally graded WC-Co/WC-Fe-Ni double-layer cemented carbides were rarely reported in the past.

In this study, the reasonable pressing pressure was investigated for preparing the functionally graded WC-Co/WC-Fe-Ni double-layer cemented carbides. The composition and microstructure were analyzed. The variation of chemical composition (Fe, Ni and Co) and hardness along the direction of WC-Co layer to WC-Fe-Ni layer were also analyzed. Meanwhile, we discussed the mechanism of composition and hardness gradient formation between the WC-Co and WC-Fe-Ni layers.

1 Materials and Experimental Procedures

In this study, two types of WC powders with the average particle size of 1.42 and 2.68 μm and the Fe, Ni, Co powders (particle size≤1.1 μm) were used as raw materials. The nominal composition and average grain size of WC-Co/WC-Fe-Ni double-layer cemented carbides are given in Table 1. The mass ratio of Fe to Ni in the binder is 3:1. Mixed powders of each layer were prepared separately. The mixed powders of each layer were milled in a stainless steel tumbler in gasoline, protected under argon atmosphere for 22 h. The WC-Co balls were used as milling bodies. The ball-to-powder mass ratio was 3:1, and the rotation rate of the mill was 100 r/min. After the milling, 1 wt% buna rubber was added as pressing aid, and milled slurry was dried under vacuum at 70 °C for 2 h, and then granulated and sieved. To obtain proper pressing pressure of the double-layer alloys, firstly, the WC-Fe-Ni and WC-Co mixed powders were pressed under various pressures (i.e., 15, 20, 30, 45, 90 and 120 MPa). All these green compacts were prepared in the same sintering condition, then the shrinkage of as-sintered samples was measured, and consistent sintering shrinkages of the two layers were found. At last, the double-layer green compacts were manufactured by pressing WC-Co mixed powders under the proper pressure onto pre-pressed WC-Fe-Ni compacts in a cylindrical die. All green compacts were dewaxed and sintered in an industrial sinter-HIP furnace at 1420 °C for 60 min with an argon pressure of 5.0 MPa.

Table 1 Chemical composition and average grain size of WC-Co/WC-Fe-Ni double-layer cemented carbides

Layer	Initial WC powder size/μm	Composition/wt%	Total carbon content
1	1.42	WC-18Co	Stoichiometric
2	2.68	WC-25(Fe-Ni)	Stoichiometric

The hardness along the direction of layer 1 to layer 2 was determined by a Vickers hardness tester with a load of 98 N and dwelling time of 15 s. The transverse rupture strength (TRS) of layer 1, layer 2 and double-layer alloy were measured using rectangular specimens with dimensions of 5.25 mm×6.5 mm×20 mm and a three-point bending test. The fracture toughness (K_{1C}) of layer 1, layer 2 and double-layer alloy were obtained by single edge notched beam (SENB) method[2]. The wear properties test of the layer 1 and layer 2 was performed by an MM-200 ring-on-block tester under dry sliding conditions at ambient temperature with an applied load of 49 N at a sliding speed of 0.42 m/s for 2 h. A GCr12 die steel ring (hardness: HRC 58) was used as a counterface material. In order to avoid the interference caused by element diffusion, we separately prepared three kinds of alloys (WC-Co layer, WC-Fe-Ni layer and WC-Co/WC-Fe-Ni double-layer alloy). Then, phase composition of the three alloys was detected by a D/max-2500 X-ray diffractometer (XRD) with Cu Kα radiation (λ=0.154 06 nm), obtained from a tube operated at 250 mA and 40 kV. The XRD analyses were carried out with a step of 0.02° and a count time of 10 s with a scanning range between 10°~90° (2θ). To identify the η phase using optical microscope, the specimens were etched for 10~20 s in a Murakami's reagent (10 g $K_3[Fe(CN)_6]$+10 g KOH+100 mL water). The microstructure analyses were carried out by Sirion-200 scanning electron microscope (SEM). The average grain size of WC was measured by the linear intercept method. The Fe, Ni and Co element distribution in the WC-Co/WC-Fe-Ni double-layer cemented carbides was measured by electron probe microanalysis (EPMA, JXA-8230).

2 Results and Discussion

2.1 Pressing pressure to prepare double-layer cemented carbide

For preparing excellent WC-Co/WC-Fe-Ni double-layer cemented carbides, the technical key is to control the shrinkage of the different layers. The shrinkage of the materials can be controlled by pressing pressure. Hence, the relationships between pressing pressure and sintering shrinkage of WC-Co and WC-Fe-Ni layers were investigated. The sintering shrinkage of the each layer with various pressing pressures is presented in Fig.1. As shown, the two alloys have

have very similar sintering shrinkage when the pressure values are at a low level (about 15 MPa). When the pressing pressure is between 15~ 45 MPa, the sintering shrinkage difference of the two layers dramatically becomes larger. However, with further the increase of the pressing pressure, the shrinkage difference nearly keeps constant.

It is known that the WC grain size and binder content have significant influence on the sintering shrinkage of the cemented carbides. Due to the variation of porosity, the shrinkage of the specimens with different WC grain sizes, under the same pressing pressure, is different. Cemented carbides with fine grain or high binder content have higher sintering shrinkage than the alloys with coarse grain or low binder content. The generation of stress at the interface may be caused by the difference in the shrinkage of two layers, which can cause the degradation of interface strength[16-18]. As shown in Fig.1, the reasonable pressing pressure to prepare the double-layer alloys should be about 15 MPa, under which the two alloys have consistent sintering shrinkage. The prepared WC-Co/WC-Fe-Ni double-layer cemented carbide is presented in Fig.2. As shown, under about 15 MPa pressing pressure, the double-layer alloys can be successfully prepared at 1420 °C for 60 min.

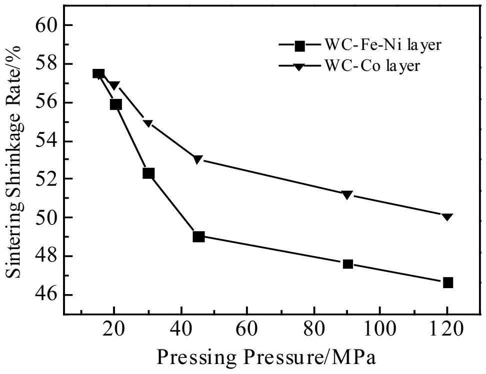

Fig.1 Relationship between sintering shrinkage and pressing pressure of WC-Fe-Ni and WC-Co layers

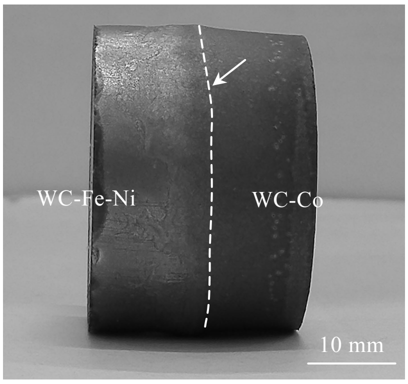

Fig.2 Prepared WC-Co/WC-Fe-Ni double-layer cemented carbides

2.2 Phase constitution and microstructure analysis

The phase composition has a great effect on the mechanical properties of cemented carbide. So, it is worth investigating the phase composition of the graded WC-Co/WC-Fe-Ni double-layer cemented carbides with the help of XRD analysis. Fig.3 shows the X-ray diffraction patterns of WC-Co layer, WC-Fe-Ni layer and gradient layer. From Fig.3a and 3b it can been observed that the crystal structures of binder phase in WC-Fe-Ni layer are fcc γ-(Fe,Ni) solid solution, and the crystal structures of binder phase in WC-Co layer are fcc-Co and ε-Co. Meanwhile, from the XRD diffraction pattern of gradient layer (shown in Fig.3c), the gradient layer mainly consists of γ-(Fe,Ni), α-(Fe,Ni) and fcc-Co phase. And the diffraction peaks of undesired η or graphite phase can not be found in Fig.3. The crystal structure changes in the gradient. There are two crystal structures of pure Co: one is hexagonal close-packed (ε-Co), stable below 417 °C and the other is face centered cubic (α-Co), stable at the higher temperatures[17]. The introduction of Fe and Ni resulting from the diffusion can stabilize the fcc-Co, due to the shift of transition temperature (T_t) to a lower temperature[19]. Therefore, it is easy to explain why the diffraction peaks of ε-Co can hardly be observed.

The optical micrographs of WC-Co/WC-Fe-Ni double-layer cemented carbides after etching with Murakami reagent are presented in Fig.4. Fig.5 shows SEM images of the double-layer alloy with different regions. The microstructures of WC-Co layer and WC-Fe-Ni layer are shown in Fig.5a and Fig.5b, respectively. Microstructure of the double-layer specimen near the interface is presented in Fig.5c. Metallography and SEM analysis show that the double-layer alloy has a WC and binder two-phase structure containing no free graphite or η phase, which is consistent with the XRD results (Fig.3). The layer 1 has finer microstructure (1.32 μm) than layer 2 (1.98 μm). Additionally, it can be clearly seen from Fig.5 that the double-layer alloy has a two-phase structure with WC (gray) and binder phase (black). The interface of the two-layer structure with coarse and fine WC grain size is obvious and the wavy interface is observed. Moreover, the microcracks, layering or other type of defects are not found at the interface (see Fig.4 and Fig.5). The interface of these two layers is well sintered together, which is beneficial to enhance the interface strength of the graded double-layer alloy.

2.3 Mechanical properties

The mechanical properties of layer 1, layer 2 and interface layer are listed in Table 2. As seen in Table 2, the layer 1 exhibits higher hardness and lower fracture toughness compared with that of layer 2. Meanwhile, the TRS of layer 1 (2834 MPa) is inferior to that of layer 2 (3077 MPa). It also can be drawn from Table 2 that the mechanical

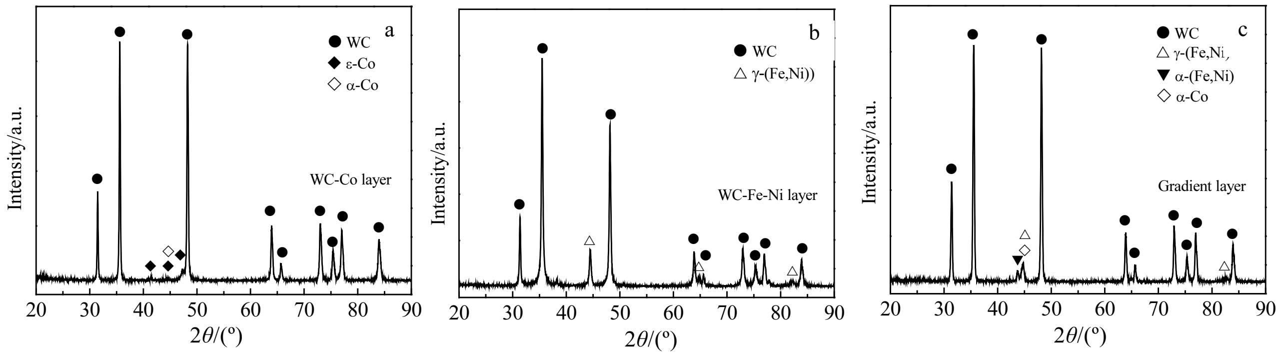

Fig.3 XRD patterns of WC-Co/WC-Fe-Ni double-layer cemented carbides: (a) WC-Co layer, (b) WC-Fe-Ni layer, and (c) gradient layer

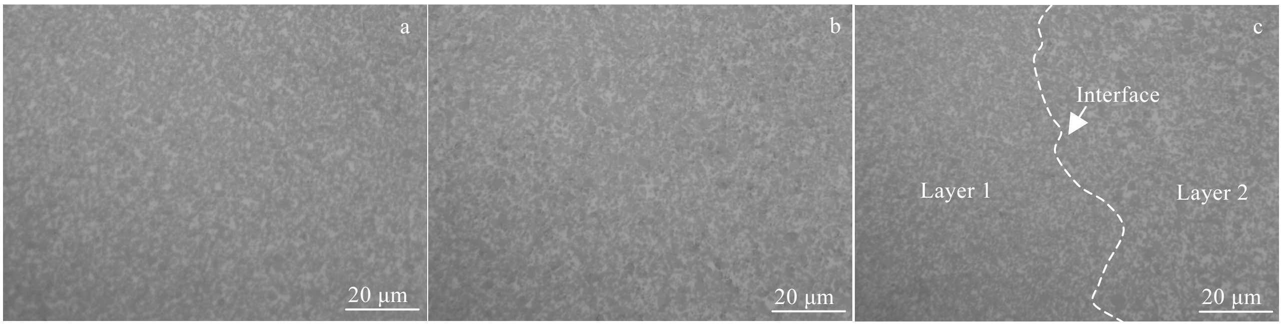

Fig.4 Optical micrographs of WC-Co/WC-Fe-Ni double-layer cemented carbides etched with Murakami's reagent: (a) WC-Co layer, (b) WC-Fe-Ni layer, and (c) interface between the two layers

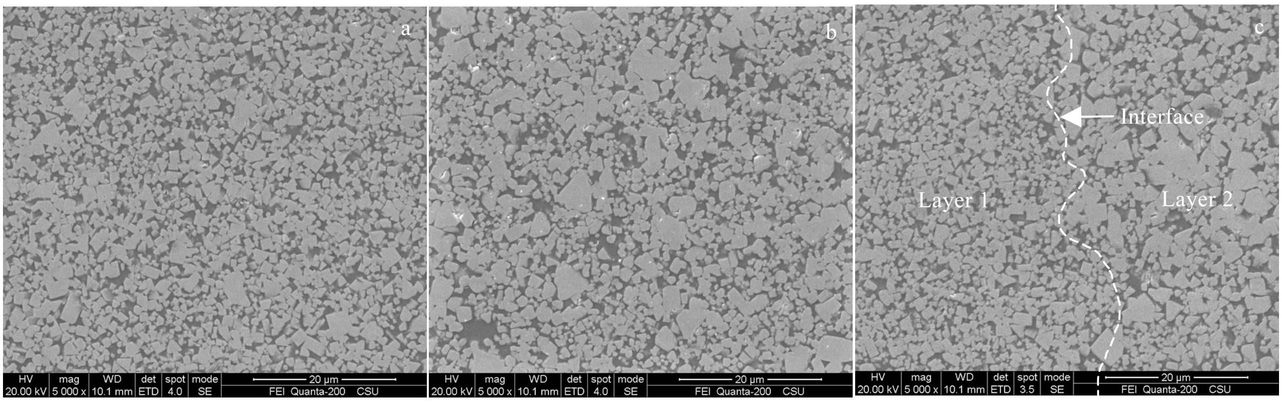

Fig.5 SEM images of graded WC-Co/WC-Fe-Ni double-layer cemented carbides: (a) WC-Co layer, (b) WC-Fe-Ni layer, and (c) interface between the two layers

properties (e.g. K_{1C} and TRS) of the interface layer are intermediate between that of layer 1 and layer 2. It is known that the grain size and binder content are two critical aspects for the properties of cemented carbides[20]. Generally, the mechanical properties of cemented carbides strongly depend on the microstructure, which are governed by the size of WC grains as well as the binder content[20]. The cemented carbides with coarse grain and high content binder possess great toughness, while the alloys with fine grain and low binder content have excellent hardness and wear resistance[4,7]. During three-point bending test, the alloys would undergo plastic deformation, crack initiation, and crack growth processes before fracture. For the alloy with higher binder content, it can withstand greater plastic deformation and consume more energy during deformation, so the alloy with higher binder content exhibits a higher TRS.

The wear characteristics of layer 1 and layer 2 were evaluated by performing ring-on-block wear tests. The corresponding wear rate and friction coefficient results of layer 1 and layer 2 are presented in Table 2. As shown, layer 1 exhibits lower wear rate (7.5×10^{-7} mm^3/N·m) and friction coefficient (0.49) compared with those of layer 2. Obviously, layer 1 with lower binder content and finer grain has higher wear resistance. Fig.6 presents the SEM images of the worn surface of layer 1 and layer 2 after wear tests, and from these images, it is clear that the worn surfaces of the two layers are consistent with the wear rate results (Table 2). As seen in Fig.6a and 6b, the worn surfaces of layer 1, are relatively smooth with only a small amount of loose wear debris and pits, which can be found on the wear surfaces. While severe wear occurs in the layer 2 with massively loose wear debris covering on the worn surface (Fig.6c and 6d). Generally, the alloys with higher hardness possess better wear resistance[7,21]. In addition, a low friction coefficient is beneficial for reducing the friction force[2], thereby decreasing worn and enhancing the wear resistance of layer 1. So, layer 1 has superior wear resistance as a result of the lower binder content and finer WC grains.

2.4 Element distribution and hardness variation

To investigate the variation of composition and hardness along the direction of WC-Co layer to WC-Fe-Ni layer, EPMA line scanning and hardness analysis were performed on the WC-Co/WC-Fe-Ni double-layer alloy. The corresponding results are given in Fig.7. As shown in Fig.7, the contents of Fe, Ni, Co, W and C nearly keep constant in both layers 1 and 2, while the Fe, Ni and Co elements show a clear gradient change across the interface between these two layers. The W and C elements are not markedly changed with the increase of the distance along the direction from layer 1 to layer 2. Specifically, in the gradient layer, the contents of Fe and Ni continuously increase with the distance far from layer 1. By contrast, the Co shows an opposite tendency with the distance. As shown, the thickness of compositional gradient is about 8.5 mm. The total carbon content in both layers at green state is stoichiometric; thereby, the effect of carbon content on the formation of double-layer structure can be ignored. The above observed composition gradient can be

Table 2 Mechanical properties of layer 1, layer 2 and interface layer

Layers	Hardness, HV/×10 MPa	K_{1C}/MPa·m$^{1/2}$	TRS/MPa	Wear rate/×10^{-7} mm^3·(N·m)$^{-1}$	Friction coefficient
1	1082±11	19.6±0.94	2834±78	7.5±0.3	0.49
2	845±16	25.4±0.87	3077±26	20.4±1.2	0.62
Interface	-	22.3±1.02	2922±54	-	-

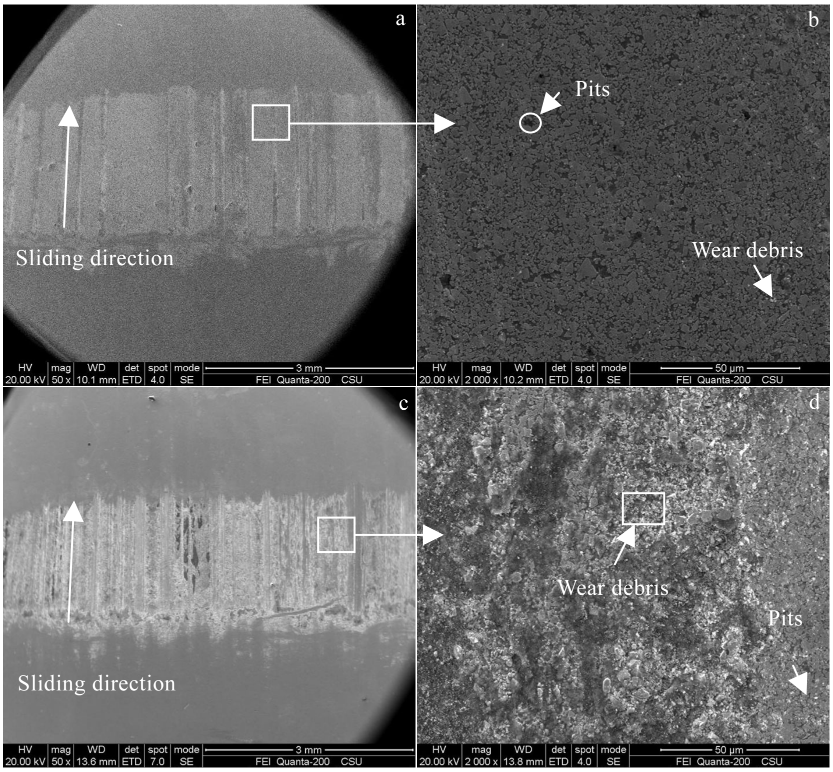

Fig.6 SEM images and corresponding partial enlargements of worn surfaces: (a, b) layer 1 and (c, d) layer 2

attributed to the element diffusion, which occurs in the stage of the liquid phase sintering of the double-layer alloy. During the sintering process, the huge difference in the element concentration (Fe, Ni and Co) between the two layers induces the diffusion of Fe and Ni into layer 1, and the diffusion of Co into layer 2. It is just the interdiffusion behavior leading to the significant composition gradient. The Fe, Ni and Co gradient can be formed by introducing an initial difference in the element content within WC-Co/WC-Fe-Ni double layer prior to sintering. The diffusion kinetics of Fe, Ni and Co could be expressed by the modified Arrhenius equation[22], which is applicable to the cases of liquid phase diffusion. Furthermore, when there is a difference in WC grain size in the two layers, the binder will migrate from coarser grain part (layer 2) to finer grain part (layer 1) due to the difference in capillary force[23]. Therefore, when there is identical initial carbon content but a difference in initial binder content and grain size between the two layers, the compositional gradient is jointly determined by the difference in concentration gradient and capillary force between the two layers. However, some studies indicate that the WC-Co bi-layer with stoichiometric carbon content but different initial Co content had completely homogeneous Co content across the two layers after liquid phase sintering[9,23], which is inconsistent with the EPMA results shown in Fig.7. This may be due to the huge difference in the element concentration between the two layers, slowing down the homogenization process of the chemical composition.

As seen in Fig.7, a clear hardness gradient can also be observed in the double-layer alloy. In both layers 1 and 2, the hardness keeps a nearly constant value, and the hardness in layer 1 is about 2400 MPa higher than that in layer 2. As seen in Fig.5, the average grain size of layer 1 (1.32 μm) is obviously much smaller than that of layer 2 (1.98 μm). The difference in the hardness values of the two layers can be attributed to the difference in the grain size and binder content corresponding to each layer. In the gradient layer, the hardness shows a continuous decrease with the increase of the distance from layer 1 to layer 2. The hardness and the chemical compositions results reveal that the variation tendency of the hardness is approximately consistent with that of the Co, while it contradicts to that of Fe and Ni. This suggests that the hardness change of the graded alloy across the interface is dominated by the composition diffusion. The combination of the WC-Co layer (layer 1) and WC-Fe-Ni layer (layer 2), observed in Fig.5 and Fig.7, will form a graded double-layer cemented carbide with high hardness, wear resistance and also good toughness. Therefore, the low cost and high performance of such alloy makes it a quite promising material in the high abrasive and impact load environments.

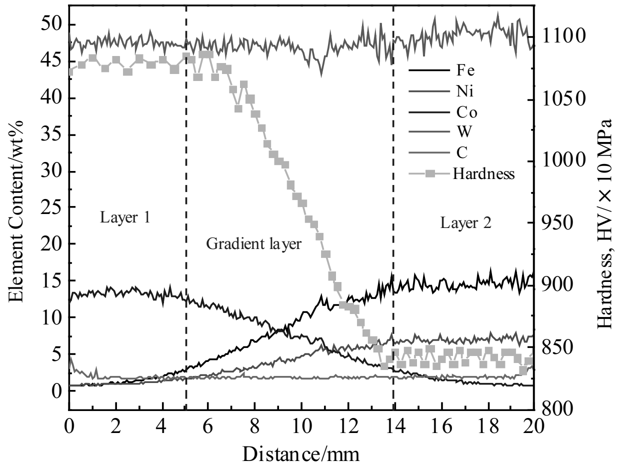

Fig.7 Variation of Fe, Ni, Co, W and C element content and hardness along the direction of layer 1 to layer 2

3 Conclusions

1) We successfully prepared a functionally graded WC-Co/WC-Fe-Ni double-layer cemented carbide by controlling a pressing pressure of 15 MPa.

2) The difference in the initial compositions and WC grain size leads to a gradient layer, which is featured by the composition and hardness gradients, formed between the WC-Co and WC-Fe-Ni layers. Moreover, the hardness gradient is mainly attributed to the Fe, Ni and Co gradient.

3) This newly designed functionally graded alloy provides a viable solution to the trade-off between the wear resistance and toughness.

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功能梯度 WC-Co/WC-Fe-Ni 双层硬质合金的研究

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摘　要：使用新的制备方法成功制备了功能梯度 WC-Co/WC-Fe-Ni 双层结构硬质合金。冷压成型所需的压制压力需要保持在 15 MPa，在这个压力下 WC-Co 和 WC-Fe-Ni 层的烧结收缩率相同，制备的双层合金没有分层和裂纹等不利现象出现。采用 X 射线衍射（XRD）仪、光学显微镜（OM）和扫描电子显微镜（SEM）等实验手段研究了双层合金的相组成与微观结构。发现合金中没有 η 或者石墨相的存在，而且，WC-Co 和 WC-Fe-Ni 层间的界面处结合良好。同时，在 WC-Co/WC-Fe-Ni 双层结构硬质合金的界面处有明显的连续变化的 Fe, Ni 和 Co 成分梯度，两层间的成分梯度导致界面附近的硬度梯度的形成。制备的功能梯度 WC-Co/WC-Fe-Ni 双层结构硬质合金同时具有高的硬度、耐磨性和韧性。

关键词：WC-Co/WC-Fe-Ni；功能梯度硬质合金；收缩；微观组织；力学性能

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