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ARTICLE

Effect of Ni Content on Microstructure and Properties of WC-Ni Composites Prepared by Electroless Plating and Powder Metallurgy

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Abstract: WC-Ni composite powders were prepared by electroless plating with a simplified chemical method. The morphologies of original, pretreated WC powder, WC-Ni powders and surface morphologies, fracture surface and composition of WC-Ni composites were analyzed by FE-SEM. EDS and XRD. Different contents of Ni doped WC composites were prepared after sintering. The relative density and properties of the WC-Ni composites were also discussed. Results show that the WC powder is uniformly covered by Ni particles. After powder metallurgy (PM), the fabricated composites perform a well-dispersed surface morphology. With the increasing of Ni content bending strength enhances without reducing hardness. Trans-granular fractures are observed on the fracture surface of the WC-Ni composites.

Key words: WC-Ni composites; electroless plating; powder metallurgy

Tungsten carbides are widely employed in tribological fields because of their good performance and good wear resistance[1–5]. For cemented carbides, the properties can be modified by the presence of a second phase[6]. Cobalt, as the second phase, shows good wettability and adhesion with tungsten carbides, and the dissolution of WC in the Co phase results in WC-Co cemented carbides with high hardness, high strength, and high wear resistance[7-11]. Due to the high cost of cobalt, the use of Fe or Ni to replace cobalt possible in WC-Co cemented carbides has been studied to improve the binding strength[12,13]. And Ni as the most promising substitute of Co has been viewed by many scientists. WC-Ni alloys were prepared using high-frequency induction-heated sintering which acquired a significantly high hardness nevertheless of the complex process and facility[14]. WC-Ni powder and WC-Ni cemented carbides were produced using powder metallurgy. While this experiment involves ball milling and liquid phase which may lead to the nickel grow up to large size aggregates and affect the properties of composites after sintering[15].

In this study, a new process was used to reduce the costs and simplify the preparation process of WC-Ni cemented carbide. Electroless nickel plating was performed on the WC powder surface, followed a simple pretreatment of WC powder at room temperature assisted with ultrasonic. After powder metallurgy, an additive-induced refined microstructure and enhancement of the properties, such as relative density, micro-hardness, and bending strength was also analyzed.

1 Experiment

Commercial WC powder (grain diameter of 3.0 to 5.0 μm) were used. The non-catalytically active surface was pretreated prior to electroless plating in order to produce

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surface defects. WC powders were immersed in a mixed aqueous solution of hydrofluoric acid (60 mL/L) and nitric acid (30 mL/L) during pretreatment (activation). The whole procedure was assisted with ultrasonic wave. Pretreated powders were washed 3 times using deionized water, and then dried. Table 1 shows the composition of the used solutions. Four different nickel contents of powders were prepared in the study. The mass fractions of nickel were 3%, 5%, 7%, and 9%. Hydrazine hydrate (80 mL/L) was added to the plating solution, and the chemical reaction started at room temperature. pH value of solution was maintained between 11 to 12 by adding NaOH. In order to obtain uniformly dispersed particles and reduce agglomeration, electroless plating was performed via an ultrasonic bath (model: JK-450B; frequency: 40 kHz; power: 400 W). The experimental schematic diagram is shown in Fig.1.

The powders were subsequently dried in a DHG series heating and drying oven (DHG-9070) at 40 ℃ for 2 h. The Ni-coated WC powders were compacted into a size of 40 mm × 8 mm under a pressure of 331 MPa by a 769YP-60E tablet machine. The green compacts were placed in a pipe furnace (GSL-1700X), and pre-sintered at 500 ℃ for 2 h using hydrogen as a protective gas. Polyvinyl alcohol vaporized and escaped during this pre-sintering process. Then the green compacts were sintered by liquid phase sintering (LPS) in vertical vacuum sintering furnace (KGPS-100) at 1800 ℃ for 2 h and used argon as a protective gas. The sintering process is shown in Fig.2 including sintering temperature and holding time.

Table 1 Composition of the electroless nickel plating bath

Chemical	Formula	Concentration/g·L^{-1}
Nickel sulfate	$NiSO_4 \cdot 6H_2O$	1.38~4.43
Sodium citrate	$Na_3C_6H_5O_7 \cdot 2H_2O$	24
2,2-Dipyridyl	$C_{10}H_8N_2$	0.02~0.04

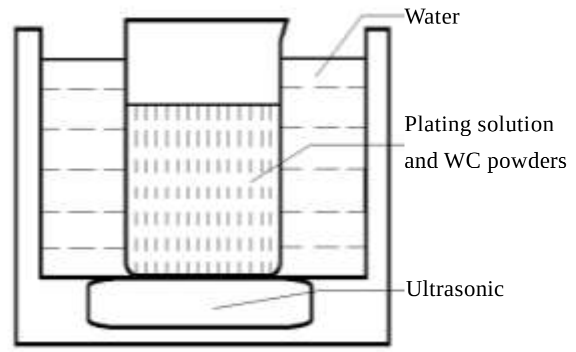

Fig.1 Schematic diagram of the ultrasonic aided plating device

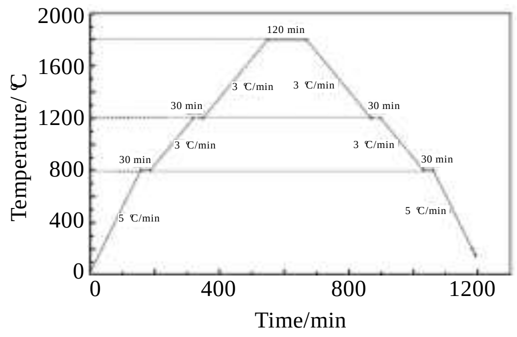

Fig.2 Sintering temperature and holding time of liquid phase sintering (LPS)

The relative densities of the WC-Ni composites were measured using Archimedes' principle. Polished sintered specimens were subjected to Vickers micro-hardness testing by MH-3L, which measured from the center to the specimen edges with a loading force of 2.94 N held for 15s. The three point bending test performance was measured by slow loading at a speed of 0.5 mm/min until specimens was broken using the MTS-809 machine. Size of test specimens was 35 mm×8 mm×4 mm.

The morphology of the original WC, pretreated WC and WC-Ni composite powders and the phase of the WC-Ni composites after sintering were analyzed by scanning electron microscopy (SEM-UL) with 5.0 kV, energy dispersive spectroscopy (EDS) with 15.0 kV and X-ray diffraction (XRD), respectively.

2 Results and Discussion

2.1 Morphologies of WC-Ni composite powders

Fig.3 presents the scanning electron microscopy (SEM-UL) morphologies of the original WC powder, WC powders after pretreatment, and WC powders after electroless Ni plating via simplified pretreatment. Fig.3a shows that the powders are uniformly distributed in the field of view. Based on high-magnification SEM image, the powders are mostly polygonal particles with a grain diameter of 3.0 to 5.0 μm and show a smooth mechanical surface. Fig.3b displays the SEM morphology of WC powders after pretreatment. The original particles have mostly etched to be irregular shapes. These irregular particles are uniformly dispersed with the polygonal particles, as seen in the high-magnification surface morphology image. Compared with the original particles, the etched surface of particles exhibits excellent activity, which resulted from the increased superficial area and surface defects in the form of steps. Generally speaking, successful palladium-free electroless plating is dependent on the catalytic ability of the surface to plate. Catalytic capacity is expressed by the magnitude of activity, which is

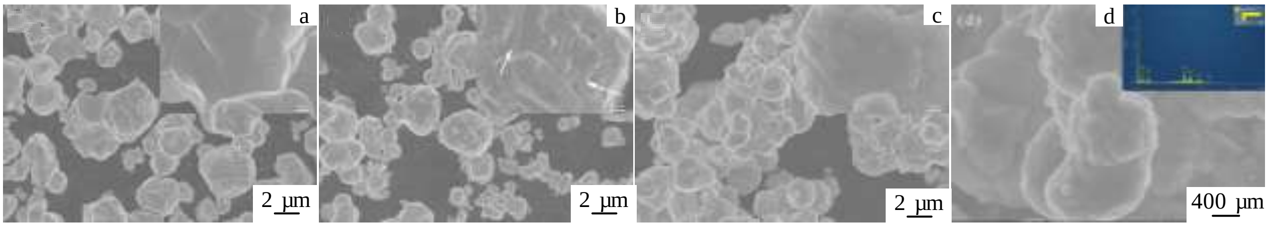

Fig.3 Surface morphologies image of the WC powder: (a) original WC powder, (b) pretreated WC powders, (c) WC powders after electroless Ni plating, and (d) high magnification image of Fig.3c coupled with EDS

the number of surface defects (i.e., surface atoms or atomic groups with unsaturated coordination at the edge, step, or edge of the adsorbate island). These parts easily adsorb foreign substances to build keys[16]. The characteristics of these surfaces are beneficial to adsorb, nucleate, and grow Ni particles during electroless plating (Arrowed in Fig.3b). Fig.3c shows the SEM morphology of WC powders after electroless Ni plating via a simplified pretreatment method. All WC particles are coated by a layer of Ni. High-magnification image shows that Ni is uniformly coated on the WC particles, and the plating layer is completely dense (as shown in Fig.3d).

2.2 Analysis of the WC-Ni composites after sintering

Fig.4 shows SEM image and EDS map of the sample with Ni (3wt%) after sintering. The purple points are uniformly distributed in the second field of view. This image shows that the Ni coating is evenly distributed across the samples. Fig.5 displays X-ray diffraction (XRD) pattern of WC-Ni sample with 9wt% Ni after sintering. It demonstrates the absence of other elements in WC-Ni composites, and the exclusion of intermetallic compounds but inclusion of WC and Ni. Based on the voidage, the relative densities of WC doped with different Ni contents have high values, even reach to 99% (WC-3wt%Ni).

Fig.6 shows the bending strength and micro-hardness curves of the specimens with different Ni contents. The

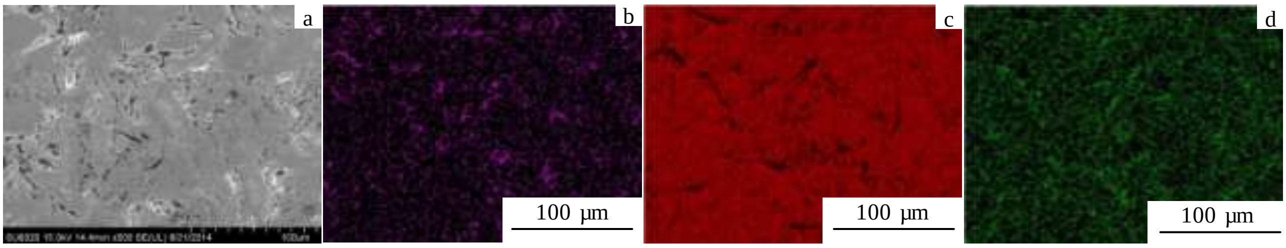

Fig.4 SEM image (a) and EDS map of the sample with Ni (3wt%) after sintering: (b) Ni, (c) W, and (d) C

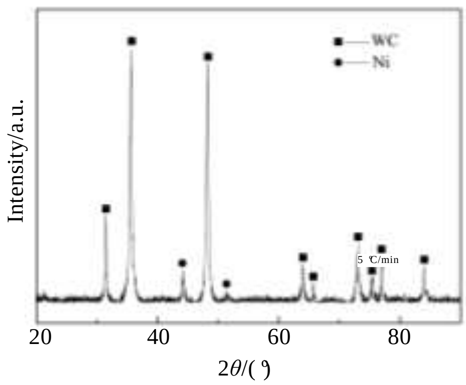

Fig.5 XRD pattern of the WC-9wt% Ni composites

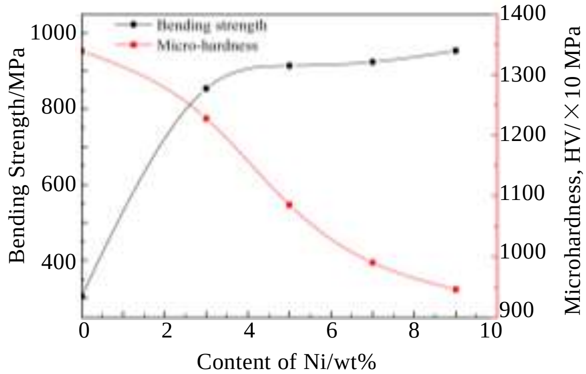

Fig.6 Bending strength and micro-hardness curves of the coated specimens with different Ni contents

black curve represents the bending properties, while the red curve represents micro-hardness. The bending strength of pure WC is not very high. When the Ni content is 3wt%, the bending strength greatly increases. Bending strength of the samples further increases as the Ni content increases from 5wt% to 9wt%. In terms of hardness, the curve shows that the hardness of WC samples decreases with increasing nickel content. In terms of increasing the bending strength of the samples without reducing excessive hardness, the content of nickel electroless plating has a great effect on the bending properties; Studies shows the increased contents of Ni should have concurrently the positive and negative effects for WC composites [17,18]. Consequently, WC-3wt%Ni composite performs the best properties. FE-SEM was also used to characterize the morphology of the fracture surface for further studying the bending properties of samples. Fig.7 shows the fracture surface of pure WC samples after the bending test. Fig.7a shows a low magnification image of many complete particles that are uniformly arranged together with no binder. Fig.7b shows a high magnification image of the fracture surface. The grain boundaries are clearly visible and the grain surface is smooth. A grainy morphology is displayed, which is typical inter-granular fracture. Fig. 8 shows the SEM morphology of the fracture surface with Ni-coated WC after the bending test. Fig. 8a is a low magnification image of the WC grains coated by a binder (Ni) completely and densely. No contact is observed between the WC grain surfaces (indicated by the arrow in Fig.8a). Fig.8b is a higher magnification image of Fig.8a. Many bright lines can be seen on the Ni coating, which indicates that the Ni coating results in plastic deformation and ductile tearing. WC grains demonstrate an apsidal surface resulting from crack propagation paths

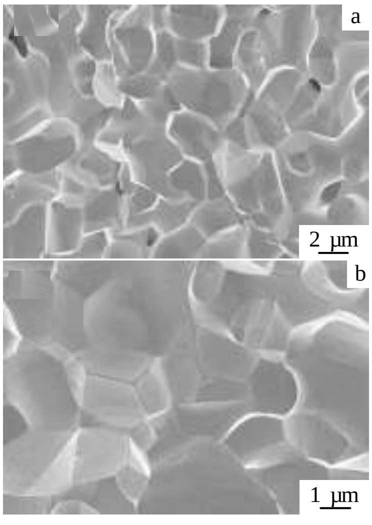

Fig.7 Surface morphology of fractured pure WC sample

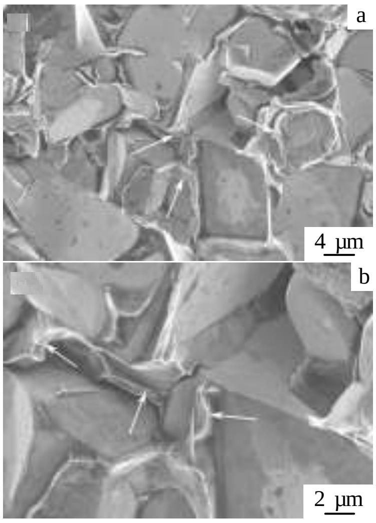

Fig.8 Surface morphology of fractured WC-Ni composite

across the WC grains. The fracture mode is a trans-granular fracture (indicated by the arrow in Fig.8a). And according to the reports, the Ni as a binder phase can make a significant effect on WC composites[19,20]. Given the uniformity of the binder phase (Ni) in inter-granular fracture, an inter-granular fracture does not occur, and a trans-granular fracture is observed, which is a fracture of high-energy absorption processes.

3 Conclusions

1) After powder metallurgy, the relative densities of WC doped with different Ni contents have high values, even reach to 99% (WC-3wt%Ni).

2) The composition of WC-Ni composite is pure enough to exclude any other elements except W, C, Ni. With the increasing of Ni content bending strength enhances without reducing excessive hardness.

3) Trans-granular fractures are observed because of the uniformity of binder phase (Ni).

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Ni 含量对化学镀结合粉末冶金法制备的 WC-Ni 复合材料组织和性能的影响

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摘　要: 采用简化预处理辅助化学镀法制备了WC-Ni复合粉体，结合压制烧结法获得了不同Ni含量的WC-Ni复合材料。通过FESEM, EDS和XRD检测手段分析了原始WC粉、WC-Ni复合粉体形貌和WC-Ni复合材料的表面形貌和断口特征。研究了不同Ni含量对WC-Ni复合材料组织和性能的影响规律。结果表明，Ni颗粒均匀包覆在WC粉体表面，WC-Ni复合材料具有细小均匀的晶粒分布；随着Ni含量的增加，WC-Ni复合材料的抗弯强度增加，硬度基本保持不变，断口形貌表现出穿晶断裂特征。

关键词: WC-Ni 复合材料；化学镀；粉末冶金

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