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RESEARCH ON SHAPING TECHNOLOGY OF NANOCOMPOSITE WC-6Co POWDER AND PROPERTIES OF SINTERED COMPACTS

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The influences of powder extrusion molding (PEM), die pressing and cold isostatic pressing (CIP) on the green compacts and the sintered compacts of nanocrystalline WC-6Co composite powder produced by spray pyrogenation-continuous reduction and carburization technology were researched. The results showed that the pore volume distribution, density and scanning electron microscopy (SEM) morphologies of fractured surface of powder extrusion molding or die pressing followed by the cold isostatic pressing consolidation green compacts were better than that of powder extrusion molding or die pressing. The green compacts were sintered by using vacuum sintering plus hot isostatic pressing (HIP), the sintered specimens were characterized by testing density, Rockwell A hardness, saturated magnetization, coercivity force, transverse rupture strength (TRS) and atomic force microscope (AFM) images, the results showed that sintered specimen of the green body that prepared by powder extrusion molding or die pressing followed by cold isostatic pressing had excellent properties of high strength and high hardness, transverse rupture strength of sintered specimen was more than 3100 MPa, Rockwell A hardness of sintered body was more than 93. Ultrafine WC-6Co cemented carbide rods with excellent mechanical properties and fine microstructure were obtained.

Keywords: WC-6Co; nanocomposite powder; shaping technology; mechanical properties; microstructure.

1. Introduction

The ultrafine grained WC-Co ceramic–metal is one of the best materials with both high hardness and high toughness. It consists of wear-resistant particles bonded together by a soft ductile metal and is widely applied into many fields for its excellent properties and finds increasing usage in areas such as miniature drills for highly integrated printed circuit boards (PCBs), pins for dot-printers, wood machining, dental work and wear parts, etc.[1–4]

In recent years, shaping techniques of cemented carbide rods are focused very much by materials researchers around the world, and it developed very fast. The progressive miniaturization of printed circuit board design requires ever-smaller cutting tools. In order to meet performance requirements in terms of wear resistance, rigidity and toughness, cemented carbide rods with an extremely fine grain size should be specifically developed. Ultrafine or nanocrystalline WC-Co composite powder should be used in order to obtain cemented carbide rods with extremely fine grain size and excellent mechanical properties.[5]

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Sintering of cemented carbides is conducted most commonly in vacuum.[6,7] However, the WC grain size in sintered WC-Co cemented carbide becomes much larger than that in pre-sintered powders due to high interface energies between nanocrystalline WC grains as well as differences in individual grain sizes, constituting the driving force for the growth process. Many researchers have developed novel approaches to control the rapid grain growth, such as adding grain growth inhibitors (VC, Cr_3C_2, TaC or their combinations), conducting the sintering at lower temperatures with the aid of plasma pressure compaction,[8] spark plasma sintering (SPS),[9] microwave process.[10]

This paper focuses on powder extrusion molding (PEM), die pressing and cold isostatic pressing (CIP) of rods of nanocrystalline WC-6Co composite powder produced by spray pyrogenation-continuous reduction and carburization technology, and sintering of green compacts by vacuum sintering plus hot isostatic pressing.

2. Experimental

Nanocomposite WC-6Co powder produced by spray pyrogenation-continuous reduction and carburization technology was used for this study. The powder was ball-milled in acetone for mixing with paraffin for 48 h and then dried at 90°C in a vacuum oven, and was shaped by PEM, die pressing and CIP. The green compacts were consolidated in vacuum sintering process at 1380°C for 60 min; then were followed by HIP at 1320°C for 60 min with an Ar pressure of 150 MPa, in order to improve the carbon content, some carbon powders were placed beside the specimens.

The starting WC-Co powder was characterized for shape and particle size by an atomic force microscopy (AFM) (Digital Instruments NanoScopeIV, VEECO company, USA)(tapping mode), the particle size of that was also characterized by a BET analyzer.

Green samples were characterized for microstructure, grain size and porosity by a scanning electron microscopy (SEM). Specimens were with a size of diameter of 3.25 mm and height of 38 mm. The specimens were also observed by AFM (CSPM 3000, Ben Yuan Ltd., China) (tapping mode) after ground by diamond grinding wheel. The density was determined according to ISO3369-1975. Transverse rupture strength (TRS) (according to ISO 3327-1982) and Rockwell A hardness (HRA) of sintered specimens (according to ISO 3738/1-1982) were measured. Saturated magnetization was measured by using saturation induction measuring system, and coercivity force (according to ISO3326-1975) was also measured by using förster-koerzimat 1.095 system.

3. Results and Discussion

The properties of the nanocomposite powder are summarized in Table 1. The specific surface area of the nanocomposite powder is 10.0497 $m^2 \cdot g^{-1}$ and the equivalent mean particle size is about 40 nm. AFM analysis indicates that the grain size distribution of the nanocomposite powder is homogeneous, and the grain shape can be classified as irregular. The nanocomposite powder consists of weak agglomerated particles, and the average grain size is about 40 nm. It coincides with the result of the BET analysis.

Table 1. Properties of WC-6Co nanocomposite powder.

Properties	Surface area (m^2/g)	Total carbon content (wt%)	Free carbon content (wt%)	Total oxygen content (wt%)	Cobalt content (wt%)	ρ_{TD} (g/cm^3)
Values	10.0497	5.80	0.22	0.26	6.15	14.82

TD, theoretical density (calculated value).

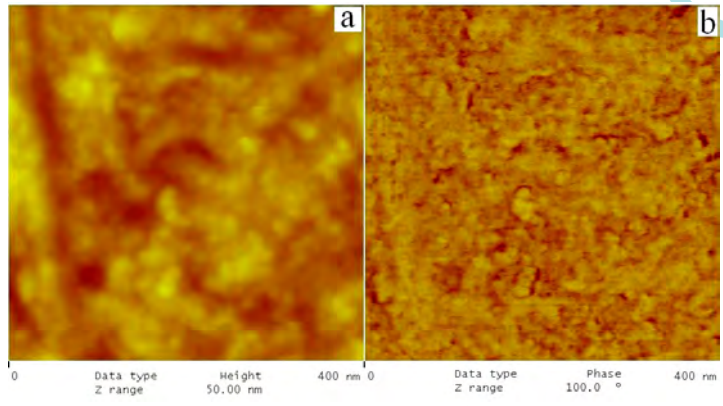

Fig. 1. AFM images of nanocrystalline WC-6Co composite powders (a) height image and (b) phase image.

As shown in Fig. 1(b), there are two phases, one is Co phase, the other is WC phase, and the WC particles were homogeneously dispersed within Co phase in the nanocrystalline WC-6Co composite powders.

As shown in Fig. 2, the pore volume distribution of green compacts prepared by PEM or die pressing followed by CIP (b, d) are better than that of green compacts prepared by PEM (a) or die pressing (c). It is obviously that the green samples prepared by PEM or die pressing followed by CIP are denser than that prepared by die pressing or PEM. There are pore volume distribution such as pores between agglomerates, pores in agglomerates and even bridged pores in green compacts that prepared by PEM or die pressing, but there are few pores between grain in green compacts that prepared by PEM or die pressing followed by CIP, especially in that prepared by die pressing plus CIP, and, pores between agglomerates and even bridged pores are almost broken completely.

During the vacuum sintering process, at about 1300–1400°C partial melting occurs, the cobalt and WC phases form a pseudo-binary eutectic.[2] Smaller WC grains dissolve due to their higher dissolution potential and precipitate after diffusion through the binder at coarser WC grains. As the WC dissolved fraction increase with the binder liquid content, the WC size distribution at the sintering process depends on the binder liquid fraction. Nucleation is easier for graphite than for WC, the WC precipitation activated by previous deposit of C nuclei acting as defect on WC particles has been suggested.[11] High carbon content or liquid binder increases the intensity of this dissolution-precipitation

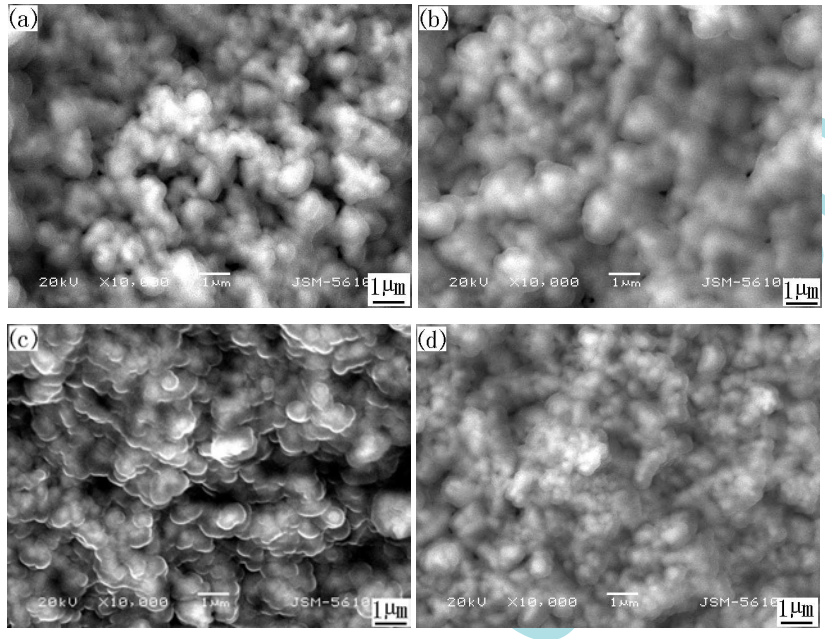

Fig. 2. SEM micrographs of the fractured surface of green compacts of nanocrystalline WC-6Co composite powder before debound (a) PEM; (b) PEM plus CIP; (c) die pressing; and (d) die pressing plus CIP.

process and therefore the WC growth rate. More WC is dissolved until the eutectic concentration is reached. This Co-rich eutectic liquid containing W and C in solution helps in densification and the development of a rigid skeletal structure. A further increase in temperature results an additional dissolution of WC and complete melting of the Co phase. In this stage, rapid final densification occurs and the sintered body is practically pore-free. More homogeneous pore volume distribution of green compacts is, more homogeneous microstructure of sintered compacts is. Pores between agglomerates and even bridged pores are almost broken completely by CIP, and the organic lubricant introduced to get sound compacted pieces and impurities (Oxygen O, water vapor H_2O) are easily eliminated, then the microstructure defect of cobalt lake, abnormal growth of the WC grains can be eliminated effectively, because the pores between grains are filled up with the Co-rich eutectic liquid homogeneously, and local overabundance Co-rich liquid phase is avoided, then dissolution and precipitation of the WC grain easily get to equilibrium. Larger VC amounts introduced in the WC-Co mixtures generate materials containing three phases at the LPS temperature: WC, liquid and (V, W) C, whose W content can reach up to some 20 at.%. V promotes the formation of η that occurs for a W/C ratio lower than in the ternary system in the solid state and at the liquid-phase sintering (LPS) temperature. The grain growth inhibitors such as VC and Cr_3C_2 disperse more homogeneously in whole sintered compact easily, and local grain growth inhibitor content is not higher, so the grain growth inhibitors can inhibitor grain growth effectively

without the formation of extra stable phases that could cause brittleness.[12] The carbon content is not simultaneously affected by the organic lubricant that has been almost debound completely.

During the HIP treatment process, because CIP consolidation compacts have smaller cobalt lake, and it is easily eliminated by HIP process, and the WC grains grow little; but cobalt lake in the compacts prepared by only PEM or die pressing is bigger, it is very difficult to eliminated, the WC grains grow easily because the overabundance Co-rich liquid phase. From Figs. 3(a) and 3(c), it is seen that microstructure defect of cobalt lake still exist, but from Figs. 3(b) and 3(d), cobalt lake is almost eliminated completely.

Table 2. Properties of WC-6Co cemented carbide material.

Shaping Technology	Density (%TD)	TRS (MPa)	Rockwell A hardness (HRA)	Saturated magnetization (%)	Coercivity force (kA/m)
Die pressing	97.4	2450	93.1	84	37.7
PEM	97.0	2240	92.8	86	38.5
Die pressing plus CIP	99.5	3120	93.6	88	37.9
PEM plus CIP	98.5	3010	93.4	87	38.8

TD, theoretical density.

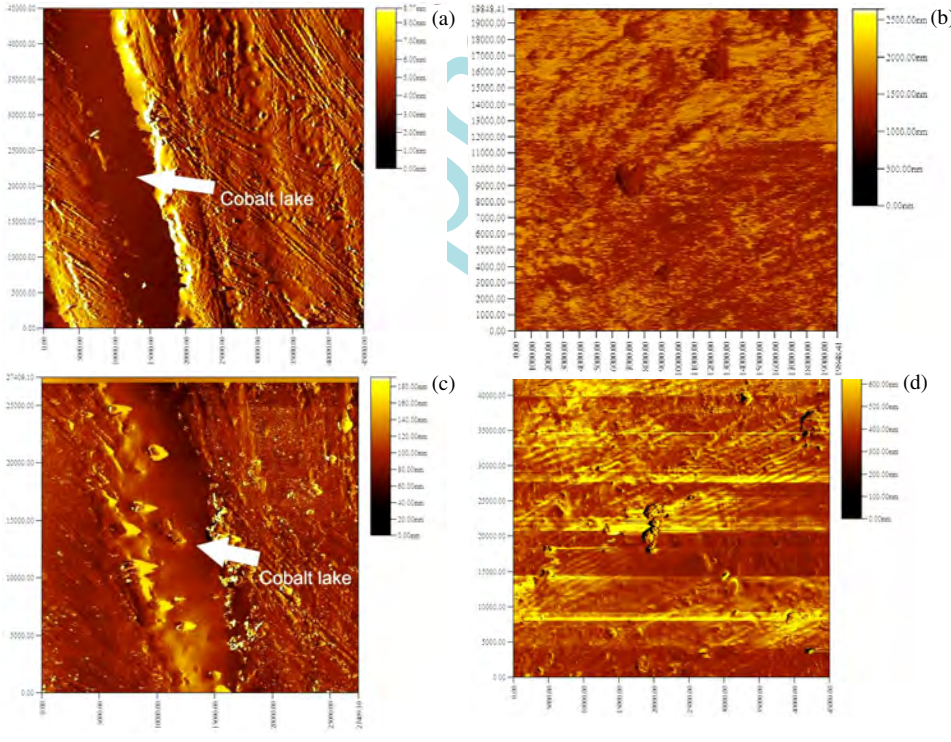

Fig. 3. AFM phase images of the WC-6Co cemented carbide rod materials prepared by vacuum sintering plus HIP (a) PEM; (b) PEM plus CIP; (c) die pressing; and (d) die pressing plus CIP.

Table 2 shows properties of WC-6Co cemented carbide material that prepared by different shaping technologies. Higher sintering pressure of HIP treatment process resulted in a harder sintered product with higher strength. This should be attributed to lower porosity, smaller average grain size and little microstructure defect (Fig. 3).

4. Conclusions

The CIP consolidation cemented carbide rods prepared by nanocrystalline WC-6Co composite powder produced by spray pyrogenation-continuous reduction and carburization technology have high strength (TRS = 3010–3120 MPa) and high hardness (HRA = 93.4–93.6).

In order to improve the mechanical properties of ultrafine WC-Co cemented carbide rods, oxygen content should be controlled as low as possible, and carbon content should be controlled with a concentration higher than the theoretical value, taking into account the oxygen concentration in nanocrystalline WC-6Co composite powder.

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