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Materials

Atomic force microscope study of WC-10Co cemented carbide sintered from nanocrystalline composite powders

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Abstract: In order to compare the spark plasma sintering (SPS) process plus hot isostatic press (HIP) with vacuum sintering plus HIP, an investigation was carried out on the topography, microstructure and gain size distribution of nanocrystalline WC-l0Co composite powder and the sintered specimens prepared by SPS plus HIP and by vacuum sintering plus HIP by means of atomic force microscopy (AFM). The mechanical properties of the sintered specimens were also investigated. It is very easy to find cobalt lakes in the specimen prepared by vacuum sintering plus HIP process. But the microstructure of the specimen prepared by SPS plus HIP is more homogeneous, and the grain size is smaller than that prepared by vacuum sintering plus HIP. The WC-10Co ultrafine cemented carbide consolidated by SPS plus HIP can reach a relative density of 99.4%, and the transverse rupture strength (TRS) is higher than 3540 MPa, the Rockwell A hardness (HRA) is higher than 92.8, the average grain size is smaller than 300 nm, and the WC-10Co ultrafine cemented carbide with excellent properties is achieved. The specimen prepared by SPS with HIP has better properties and microstructure than that prepared by vacuum sintering with HIP.

Key words: WC-10Co; nanocrystalline composite powder; atomic force microscopy (AFM); spark plasma sintering (SPS); hot isostatic pressing (HIP)

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1 Introduction

In recent years, increasing efforts are directed towards the synthesis of nanomaterials because of their improved properties comparing with conventional coarse-grained polycrystalline materials. Nanomaterials exhibit increased strength/hardness, enhanced diffusivity, improved ductility/toughness, reduced density and elastic modulus, increased electric resistivity and specific heat capacity, superior soft magnetic properties *etc.*

Tungsten carbide-cobalt cemented carbides have both high hardness and high toughness, and are widely applied in many fields owing to its excellent properties, such as miniature drills for highly integrated printed circuit boards (PCBs), pins for dot-printers, wood machining, dental work, cutting tools, rock drill tip and other wear resistant parts [1-2]. The current trend in the hardmetal industry to finer and finer-grained alloys has put high demands on the manufacturing process, for both powders and alloys [3-4]. Nanocrystalline WC-Co composite powders have been produced by spray thermal decomposition-continuous reduction and carburization technology [5]. And the WC particle size can be reduced below 50 nm. However, the WC grain size in sintered WC-Co hardmetals is much larger than that in pre-sintered powders due to high interface energies between the nanocrystalline WC grains as well as differences in individual grain sizes, constituting the driving force for the growth process. Therefore, even though the initial WC size is smaller than 50 nm, the grain size increases rapidly up to 400 nm or larger during the conventional liquid phase sintering. Even though the grain growth inhibitors were added in WC-Co, WC grain size increases up to 300 nm during the liquid phase sintering process [6-7].

Spark plasma sintering (SPS) is fundamentally different from conventional heating. Spark plasma is generated by high-pulsed electric current through the compact, and the SPS enables a powder compact to be sintered by Joule heat. When spark discharge appears

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in the gaps between the particles of a compact, the local temperature may arrive at several to ten thousand degrees. This causes vaporization and melting of the surfaces of the particles during the SPS process; constricted shapes or "necks" are formed around the contact area between the particles. These necks gradually develop and plastic transformation progresses during sintering, resulting in a sintered compact of over 99% density. The SPS process has been applied to fabricate various types of materials, *e.g.* Ti_3SiC_2, Al_2O_3, A1N, ZrO_2, WC-10Co and TiO_2 *etc.* [8].

Atomic force microscopy (AFM) provides a new method to observe the microstructures of materials, and it has changed modern natural sciences by contributing to the major progress in understanding the structure and properties of condensed matter. AFMs are nowadays part of the standard equipment in almost every research or development departments dealing with the characterization or engineering of materials surfaces and interfaces [9-12].

An investigation was carried out on the topography, microstructure and gain size distribution of nanocrystalline WC-10Co composite powder and the sintered specimens prepared by SPS process plus HIP (hot isostatic press) and by vacuum sintering plus HIP by means of AFM, the mechanical properties of the sintered specimens were also investigated.

2 Experimental

WC-10Co nanocrystalline composite powder produced by spray thermal decomposition-continuous reduction and carburization technology was used for this study. The powder was ball-milled in acetone for 48 h and then dried at 90°C in a vacuum oven. The green compacts were consolidated in SPS process at 1100°C under a pressure of 50 MPa for 10 min or in the 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 120 MPa. In order to improve the carbon content, some carbon powders were placed beside the specimens. The shape and particle size of the starting WC-10Co powder was characterized by using a CSPM-3000 atomic force microscope (Ben Yuan Ltd. China) (contact mode), and the particle size was also characterized by using a BET analyzer. SPS sintered specimens with a diameter of 30.5 mm and a height of 5.5 mm were cut into specimens with a size of 20 mm×6.5 mm×5.25 mm by electrospark wire-electrode cutting; vacuum sintered specimens were also with the same size. Specimens were characterized for microstructure, and grain size by a CSPM-3000 atomic force microscope (Ben Yuan Ltd. China) (tapping mode). The density was determined according to ISO3369-1975. The transverse rupture strength (TRS) (according to ISO 3327-1982), and the Rockwell A hardness (HRA) (according to ISO 3738/1-1982) were measured. Magnetic saturation induction by using SATURATION INDUCTION MEASURING SYSTEM and magnetic coercivity (according to ISO3326-1975) by using FöRSTER-KOERZIM AT 1.095 SYSTEM were also measured.

3 Results and discussion

3.1 AFM study of WC-10Co nanocomposite powder

The composition (wt%) of the nanocomposite powder is total carbon, 5.46; free carbon, 0.18; oxygen, 0.22; Co, 10.15; VC/Cr_3C_2, 0.40/0.40; surface area, 5.9800 $m^2 \cdot g^{-1}$. The carbon content was controlled a little higher than the theoretical value, taking into account the oxygen concentration in it. The specific surface area of the WC-10Co nanocrystalline composite powder is 5.9800 m^2-g^{-1} and the equivalent mean particle size is about 60 nm. **Figure 1** shows the AFM micrographs of WC-10Co nanocomposite powder. **Figure 2** shows the grain distribution of the nanocrystalline tungsten carbide-cobalt composite powder. Spray thermal decomposition-continuous reduction and carburization technology can assure that nanocrystalline grain growth inhibitors such as VC, Cr_3C_2 disperse uniformly in WC-Co nanocomposite powder.

AFM analysis indicates that the grain size distribution of the as-produced nanocrystalline composite powder is homogeneous. The nanocrystalline composite powder consists of agglomerated particles, and the average agglomerated grain size is about 120 nm. There are a lot of weak or strong agglomerations in nanocrystalline composite powder without ball-milled, but the extent of agglomerations seems to be less pronounced in the ball-milled powder, so ball milling is very important to improve the density of green and sintered specimens.

Figure 2 shows the histogram of particle size distribution of the nanocrystalline WC-10Co composite powder without ball-milled determined by AFM with a size interval of 50 nm. It is concluded that the nanocrystalline WC-10Co composite powder without ball-milled has a mean particle size of about 120 nm. It does not coincide with the result of the BET analysis because the powder for the BET analysis was ball-milled in acetone for 48 h.

3.2 AFM study of WC-10Co cemented carbide prepared by SPS plus HIP

Figure 3 shows the AFM images of the surface of

WC-10Co prepared by SPS plus HIP. It can be seen that the microstructure of the sintered specimen is homogeneous, and microstructure limitations of cobalt lake, η phase or free carbon are almost eliminated completely. During the sintering process, smaller WC grains dissolve due to their higher dissolution potential and reprecipitate after diffusion through the binder at coarser WC grains.

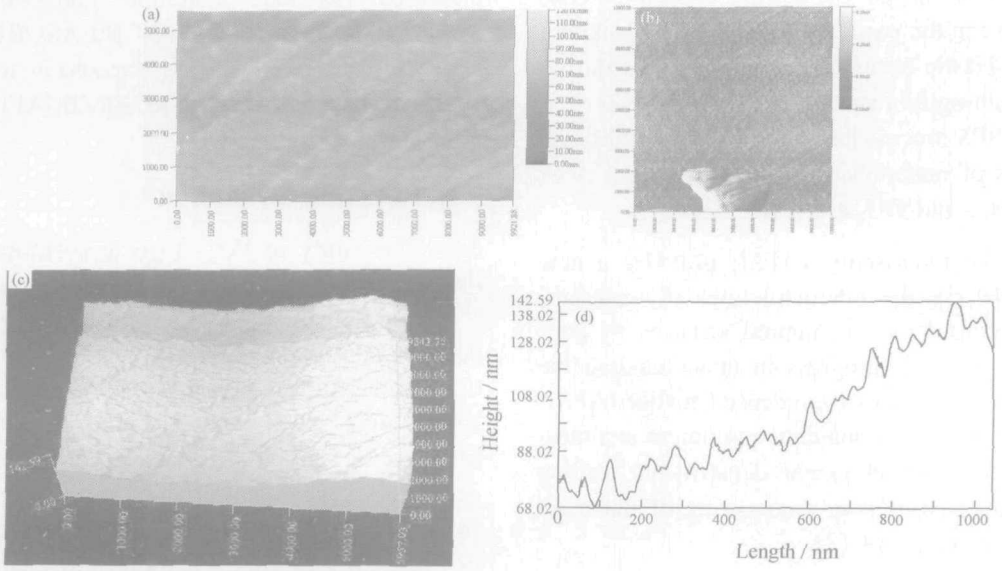

Figure 1 AFM images of the nanocrystalline tungsten carbide-cobalt composite powder without ball-milled: (a) height image; (b) friction force image; (c) 3D image; (d) section analysis.

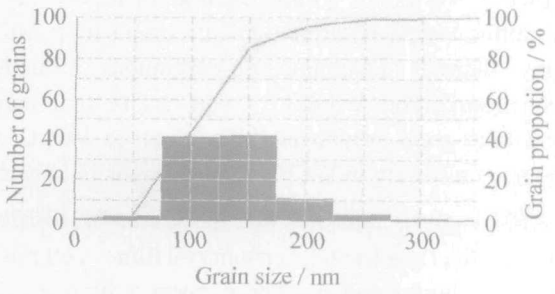

Figure 2 Histogram of grain size distribution of the nanocrystalline tungsten carbide-cobalt composite powder.

Figure 4 shows the histogram of particle size distribution of the ultrafine WC-10Co cemented carbide consolidated by SPS plus HIP determined by AFM. The ultrafine WC-10Co cemented carbide has a mean grain size of 280 nm, which is about several times of that of the start nanocrystalline composite powder.

3.3 AFM study of WC-10Co cemented carbide prepared by vacuum sintering plus HIP

Figure 5 shows the AFM images of ultrafine WC-10Co cemented carbide consolidated by vacuum sintering plus HIP. From figure 5, it is very easy to see the microstructure limitation of cobalt lakes.

Spray thermal decomposition-continuous reduction and carburization technology can make the WC particle sizes be reduced below 60 nm. However, the WC grains in sintered WC-10Co hardmetals become much larger than those in pre-sintered powder due to the high interface energies between nanocrystalline WC grains as well as differences in individual grain sizes, constituting the driving force for the growth process. Therefore, even though the initial WC size is smaller than 60 nm, the grain size increases rapidly up to about 450 nm or larger during the vacuum sintering plus **HIP** (see **figure 6).** The average grain size of the WC-10Co cemented carbide prepared by vacuum sintering plus HIP is much coarser than that prepared by SPS plus HIP. The discontinuous WC grain growth is easily found in figure 6.

3.4 Discussion

Table 1 depicts the properties of the WC-10Co cemented carbide prepared by different sintering processes. Properties of the specimen prepared by SPS plus HIP are better than those of the specimen prepared by vacuum sintering plus HIP. This should be attributed to a lower porosity, a smaller average grain size, no η phases, little discontinuous WC grain growth, and little cobalt lakes.

During the sintering process, 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 in an additional dissolution of WC and complete melting of the Co phase. In this stage, rapid final densification occurs and the sintered specimen is practically pore-free.

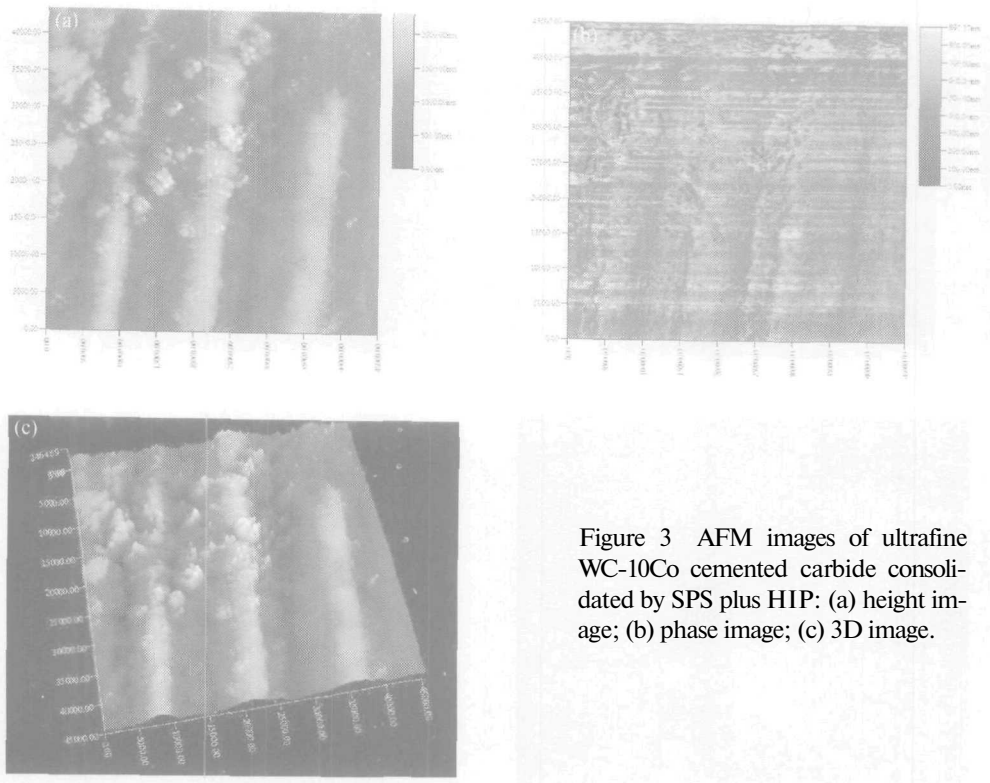

Figure 3 AFM images of ultrafine WC-10Co cemented carbide consolidated by SPS plus HIP: (a) height image; (b) phase image; (c) 3D image.

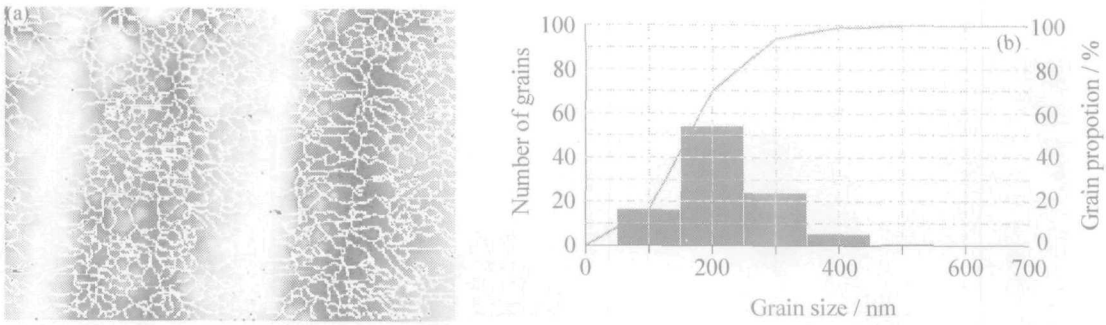

Figure 4 Grain size distribution of ultrafine WC-10Co cemented carbide consolidated by SPS plus HIP: (a) grain size analysis; (b) grain size distribution histogram.

Even though conventional cemented carbide powder consolidation is based on liquid phase sintering (LPS), pronounced densification occurs even in the solid state during the heat-up to the eutectic temperature. It is reasonable; therefore, that more effective control of grain growth can be obtained if the liquid phase is formed at lower temperature. It is obviously that the sintering temperature of vacuum sintering (1380°C) is much higher than that of SPS process (1100°C), so the average grains of the specimen prepared by vacuum sintering is coarser than that prepared by SPS process. The temperature of HIP process is 1320°C, HIP process improves the density, low porosity and eliminate η phase or free carbon, but the grain grows slightly, then makes the properties of WC-10Co cemented carbide be improved greatly.

In order to retard the grain growth and improve the properties of the specimens, the grain growth inhibitors should be admixed as early and as uniformly as possible to the WC-Co mixture or to the WC powder or co-carburize the WC with the additives [13-14]. Spray thermal decomposition-continuous reduction and carburization technology can assure that nanocrystalline grain growth inhibitors such as VC, Cr_3C_2 disperse uniformly in WC-Co nanocomposite powder, and it deals with complex starting solution that contains two or more precursor compounds. According to the experimental results, VC and Cr_3C_2 content can be controlled by changing the concentration of the complex starting solution. The grain growth inhibitors retard the grain growth, and low negative effects on properties of WC-Co ultrafine cemented carbide simultaneously.

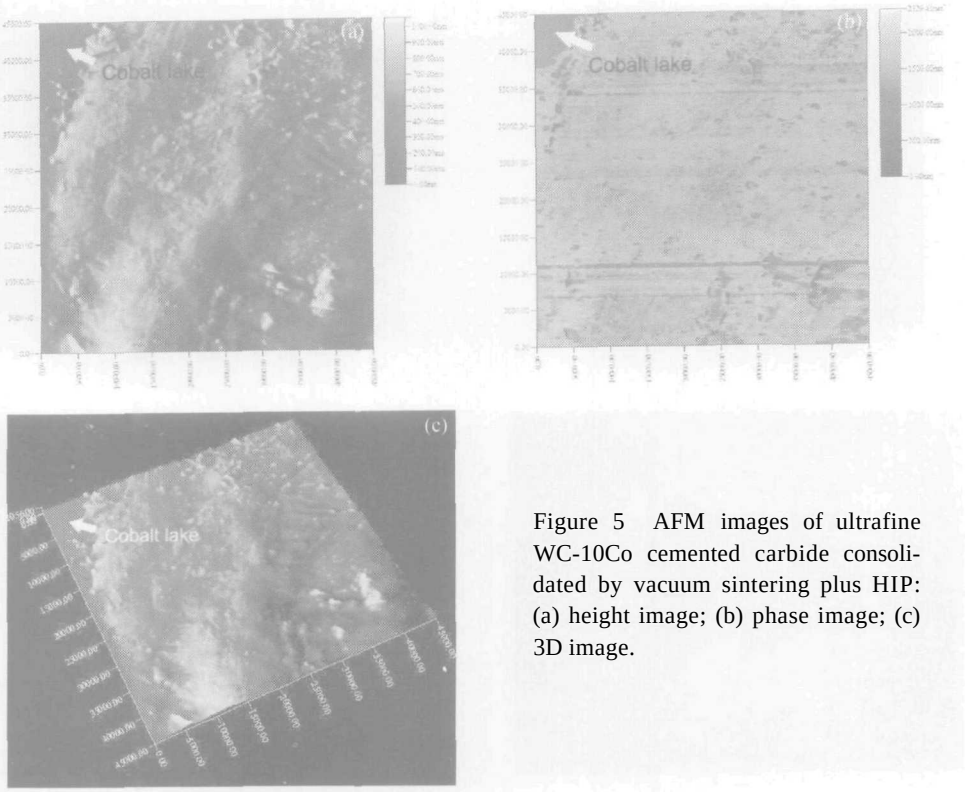

Figure 5 AFM images of ultrafine WC-10Co cemented carbide consolidated by vacuum sintering plus HIP: (a) height image; (b) phase image; (c) 3D image.

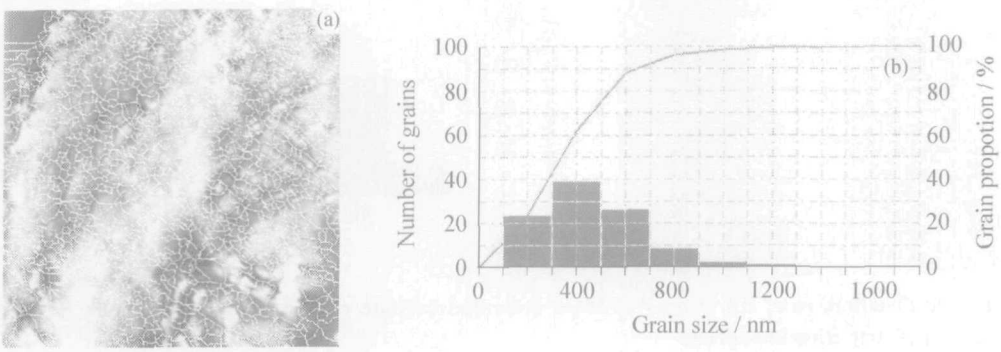

Figure 6 Grain size distribution of ultrafine WC-10Co cemented carbide consolidated by vacuum sintering plus HIP: (a) grain size analysis; (b) grain size distribution histogram.

Table 1 Properties of ultrafine WC-Co cemented carbide

Pressure	Vacuum sintering plus HIP	SPS plus HIP
Measured density / ($g \cdot cm^{-3}$)	14.25	14.33
Density / %TD	98.8	99.4
Average grain size / nm	450	280
TRS / MPa	3140	3540
HRA	92.4	92.8
Saturated magnetization / %	85	86
Coercivity force / ($kA \cdot m^{-1}$)	26.2	27.1

Note: TD—theoretical density; TRS—transverse rupture strength.

4 Conclusions

(1) The WC-10Co nanocrystalline composite powder produced by spray thermal decomposition-continuous and carburization technology was consolidated by the SPS plus HIP, and the WC-10Co ultrafine cemented carbide with an average grain size of about 280 nm, high strength (3540 MPa), high hardness

(HRA 92.8) was obtained.

(2) Comparing with the sintered specimen prepared by vacuum sintering plus HIP, the SPS plus HIP not only decreases the average grain size but also improves the properties of the cemented carbide.

(3) In order to improve the mechanical properties, the oxygen content should be controlled as low as possible and the carbon content should be with a concentration higher than the theoretical value in nanocrystalline composite powder, taking into account the oxygen concentration in it.

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