

SINTERING OF NANOCRYSTALLINE WC-Co COMPOSITE POWDER

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Abstract. The aim of this work is to investigate the mechanism of densification of WC-Co nanocomposite at temperatures about the liquid-solid boundary. The processing method of spray thermal decomposition – continuous reduction & carburization was used to produce the nanocrystalline WC-Co composite powder. They were sintered in vacuum with SIP or with HIP treatment. Density, hardness, transverse rupture strength, magnetic saturation induction and magnetic coercivity were measured. The microstructure of the sintered composites were studied by SEM and TEM. Results show that the chemical-uniformly dispersed particles and the formation of liquid phase at lower temperatures play a crucial role in low temperature consolidation.

1. INTRODUCTION

The need for hardmetals with improved properties, particularly increased hardness and strength coupled to increased ductility and toughness, has focused attention on the development of grades with finer and finer-grained powders and cemented carbides. Nowadays, submicron and ultrafine grades of WC-Co, with a WC grain size of 0.4 – 1.0 μm , still dominate the market for cemented carbides. Essentially, they are desired to be sintered from WC-Co superfine powder with a WC grain size up to 0.3 μm or nanocomposite powder with a grain size below to 0.1 μm (100 nm) [1].

There is a growing demand for the finer grade materials in the following applications: miniature drills for highly integrated printed circuit boards (PCBs), pins for dot-printers, wear-resistant parts and coatings, rock drills, tools for cutting cast irons, Al-Si alloys, plastics and wood. This turns out to be one of the driving forces for the fast growing technologies for synthesizing nano WC and nanocomposite WC-Co powders, such as the rapid carbo-

thermal reduction (RCR) process patented by Dow Chemical Company, USA [2], the chemical vapor reaction (CVR) process used by H. C. Stark, Germany [3], carbon coated precursors process [4], mechanical alloying (MA) / high energy ball-milling process [5,6], *in-situ* carbon source method [7], precursor-derived method [8], solution synthesis method [9], integrated mechanical and thermal activation (IMTA) process [10, 11], spray conversion process (SCP) [12,13], direct carburization process in a rotary kiln used by Tokio Tungsten Co., Ltd., Japan [14-17], and spray thermal decomposition - continuous reduction and carburization process patented by authors [18-25].

Sintering of cemented carbides is conducted most commonly in vacuum [26-31]. But one of the crucial aspects in fine-grained hardmetal sintering is the strong tendency of the very fine WC grains to coarsen, due to their high interface energies as well as differences in individual grain sizes, constituting the driving force for the growth process. Many researchers have developed novel approaches to con-

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trol 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 (P^2C) [32], spark plasma system (SPS) [33], plasma activated sintering (PAS) [34], pulse current process [35], microwave process [36] and hot isostatic pressing (Sinter + HIP or sinterhip / SIP) [16, 37-39].

The last technology is now wide-used practically to produce high performance materials in the world. The present investigation has been carried out in order to study this sintering mechanism and prepare materials from nanocrystalline WC-Co composite powder produced by spray thermal decomposition – continuous reduction and carburization technology.

2. EXPERIMENTAL PROCEDURES

WC-9.45Co-1.0VC/ Cr_3C_2 (wt.%) nanocomposite powder produced by spray thermal decomposition - continuous reduction and carburization technology was used for this study. The powder was ball-milled in acetone for mixing with paraffin for 24 h. After milling it was dried at 45 °C in a vacuum oven. Then the powder was palletized to small spherical shape of about 150 μm . The compacted powder was consolidated by sintering in vacuum with HIP treatment or by sinterhip (SIP) process.

The starting WC-Co powder was characterized for shape and particle size by a transmission electron microscopy (TEM). And the particle size of it was also characterized by a BET analyzer. Sintered samples were characterized for microstructure, grain size and porosity by a scanning electron microscopy (SEM) and a TEM. The density was determined by Archimedes' principle, using water immersion. The rockwell A hardness (HRA) (@60kg), transverse rupture strength (TRS) (according to ISO 3327), magnetic saturation induction and magnetic coercivity were also measured.

3. RESULTS AND DISCUSSION

The properties of the nanocomposite powder are summarized in Table 1. Carbon content was controlled with a concentration higher than the theoretical value, taking into account the oxygen concentration in it. The specific surface area of the nanocomposite powder is 5.8576 m^2/g and the equivalent mean particle size is about 70 nm. TEM (22 k \times) analysis indicates that grains of the nanocomposite powder are in the 50-70 nm range

Table 1. Properties of WC-9.45Co (0.5VC+0.5 Cr_3C_2) (wt.%) nanocomposite powder.

Properties	Values
Surface Area (m^2/g)	5.8576
d_{BET} (nm)	70
Total Carbon (wt.%)	5.55
Free Carbon (wt.%)	0.13
Total Oxygen (wt.%)	0.15
Co (wt.%)	9.45
ρ_{th} (g/cm^3)	14.64

and the grain size distribution is homogeneous. The grain shape can be classified as irregular (see Fig.1).

Fig. 2 shows SEM micrographs of the fractured surface of the WC-Co material prepared by vacuum sintering (a, b) or by sinterhip (c, d). It can be seen that most of the grains are around 200-300 nm, which is about several times that of grains of the starting nanocomposite powder. It is obviously that the sample prepared by sinterhip is denser than that prepared by vacuum sintering.

Fig.3 shows TEM micrographs (40 k \times) of the WC-Co material prepared by sinterhip (SIP). Most WC particles exhibit simple geometric forms with

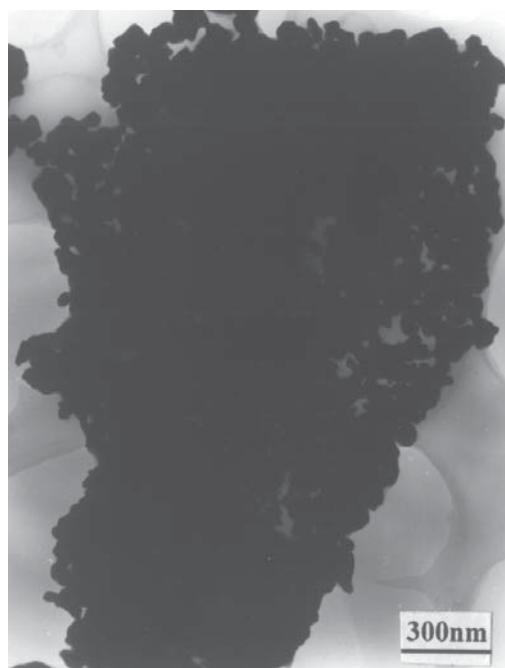
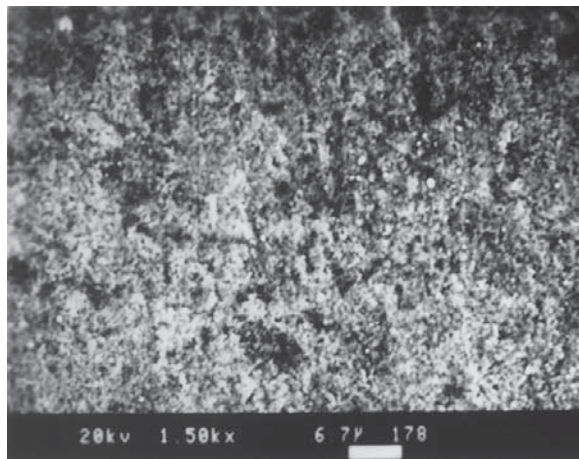


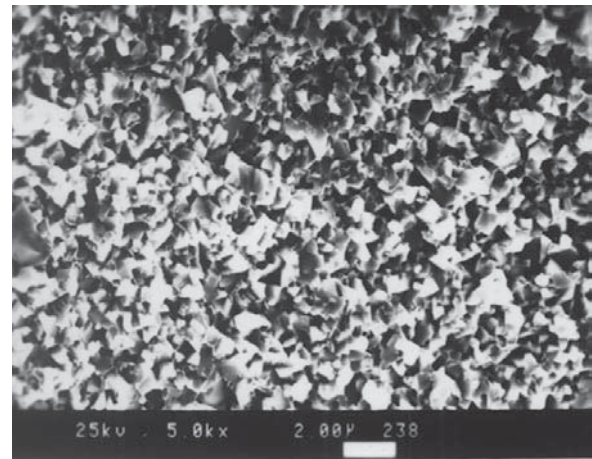
Fig. 1. TEM micrograph (22.0 k \times) of the WC-Co nanocomposite powder.

Table 2. Properties of WC-9.45Co (0.5 VC + 0.5 Cr₃C₂) (wt.%) material.

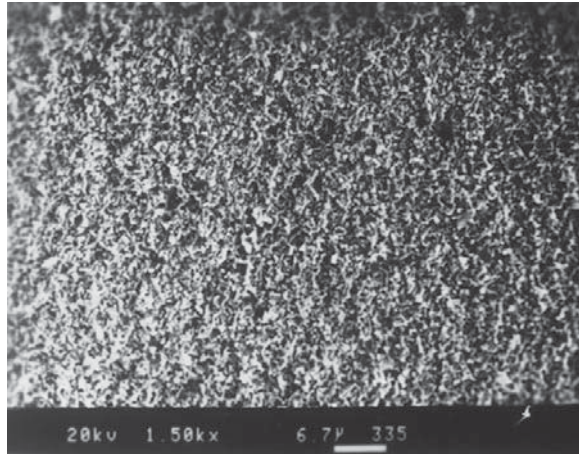
No.	Sinte- ring process	Sinte- ring temp. °C	Sinte- ring time (min.)	Pressure (MPa)	Measured density (g/cm ³)	Relative density(%)	Magnetic saturation induction (%)	Magnetic coercivity (kA/m)	HRA	TRS (MPa)
1	vacuum	1380	45	6.7·10 ⁻⁶	14.32	97.8	77	27.6	92.6	2300
2	sinterhip	1380	45	5.5(Ar)	14.45	98.7	86	27.4	92.8	3430
2	sinter+HIP	1350	40	150(Ar)	14.48	98.9	87	27.0	92.9	3660



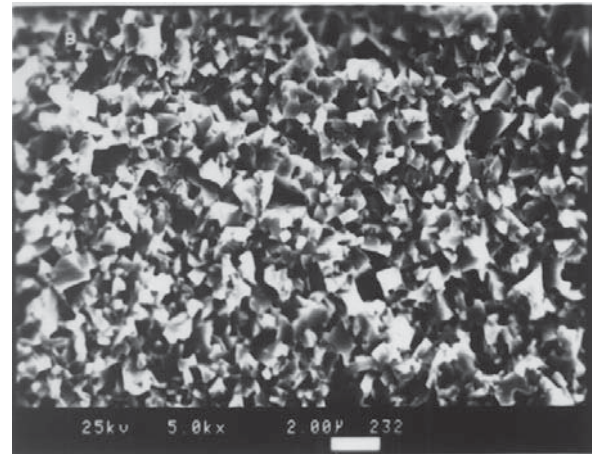
a)



b)



c)



d)

Fig. 2. SEM micrographs of the fractured surface of WC-Co material. (a) and (b): vacuum sintered; (c) and (d): sinterhiped (SIPed).

straight edges, which are the same as in conventional samples except for a much smaller grain size. It is worth paying attention to the fact that some WC particles do not develop well-defined straight edges. An explanation is that a fine WC particle has a much larger solution pressure to drive

more W-C atoms at the edges of the particles to dissolve in the binder (Co). Few dislocations and stacking faults were observed within WC grains. The microstructure of the carbide and binder phases is critical to the mechanical behavior of the composite.

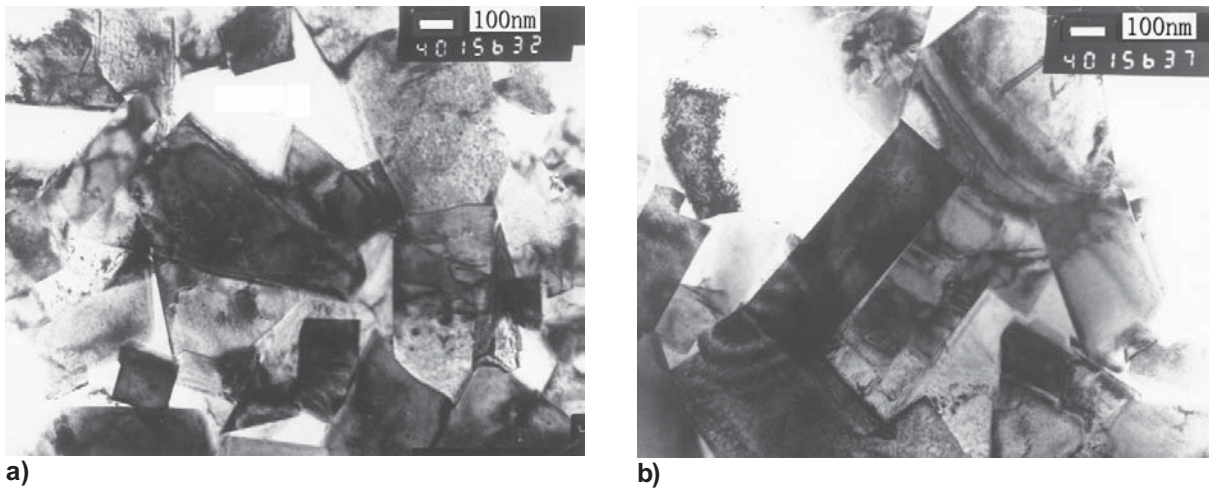


Fig. 3. TEM micrographs (40 k \times) of the WC-Co material prepared by sinterhip process.

Table 2 depicts properties of WC-9.45Co (0.5 VC + 0.5 Cr₃C₂) (wt.%) material. Higher sintering pressure resulted in a harder sintered product with higher strength. This should be attributed to lower porosity and smaller average grain size (see Fig. 2).

The vacuum sintered samples were loaded in a HIP-ing device and heated (30 °C below vacuum sintering temperature) again under Ar pressure 150 MPa. Results show that the TRS value increased exceptionally and HRA value increased slightly.

Considering this rather expensive two-stage treatment, sinterhip (SIP) process was introduced to substitute it. Sinterhip represents that low-pressure isostatic pressing up to 5.5 MPa follows closely normal vacuum sintering. The TRS and HRA values of the sintered samples are more higher than that by vacuum sintering, even though they are decreased slightly than that by sinter + HIP process.

The magnetic saturation induction and density can be used to determine precisely the cobalt and carbon content. And the magnetic coercivity is a function of cobalt and carbon content as well as grain size [40]. When sintering condition varied from vacuum to sinterhip or HIP, the magnetic saturation induction of densified samples increased and the magnetic coercivity decreased successively. This meant that more and more WC dissolved in the Co binder phase whereas less and less free carbon content retained in samples. So the grain growth and mechanical properties changed relevantly.

With solid solution grain growth inhibitors and in improved carbon balance procedure, therefore, we have achieved nearly full density of samples with the grain size below 300 nm.

At about 1300-1400 °C (binary eutectic temperature WC-Co 1310 °C; ternary eutectic temperature W-Co-C 1275/1280 °C) partial melting occurs, the cobalt and WC phases form a pseudo-binary eutectic [1]. More WC is dissolved until the eutectic concentration (54 vol.% Co and 46 vol.% WC) 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 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.

However, accompanying densification, significant microstructural coarsening takes place via a solution-reprecipitation mechanism in which smaller WC grains with higher solubility dissolve in the liquid and reprecipitate to form larger WC grains. Therefore, it is imperative that the solution-reprecipitation stage be controlled so as to achieve a fully dense structure without significant grain growth [37-38].

Even though conventional hardmetal powder consolidation is based on liquid phase sintering (LPS), pronounced desiccation 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 temperatures. It is important to achieve a completely uniform dispersion of the inhibitor phases in the starting powder. The spray thermal decomposition – continuous reduction and carburization technology deals with complex starting solutions that contain two or more

precursor compounds. It tends to suppress phase separation.

4. CONCLUSIONS

Nanocomposite WC-Co powder can be sintered to 98.9% density of cemented carbide with an average grain size of 200-300 nm. These superfine grained materials have superior strength (3430-3660 MPa) and high hardness (HRA = 92.6-92.9). The uniformly dispersed grains and formation of liquid phase at lower temperatures play a crucial role in low temperature consolidation.

Further research is needed in investigating the microstructure at the various stages of the sintering process in order to understand the cause of the different sintering mechanisms.

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