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Fabrication and mechanical properties of WC-Co-Al_2O_3 nanocomposites by spark plasma sintering①

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Abstract: Small amounts of nanocrystalline Al_2O_3 particles were doped in WC-Co nanocrystalline powders to study their reinforcing effects, and spark plasma sintering technique was used to fabricate the WC-Co-Al_2O_3 nanocomposites. Experimental results show that the use of Al_2O_3 nanoparticles as dispersions to reinforce WC-Co composites can increase the hardness, especially the transverse rupture strength of the WC-Co hardmetal. With addition of 0.5%(mass fraction) Al_2O_3 nanoparticles, the spark plasma sintered WC-7Co-0.5Al_2O_3 nanocomposites exhibit hardness of 21.22 GPa and transverse rupture strength of 3 548 MPa. The fracture surface of the WC-7Co-0.5Al_2O_3 nanocomposites mainly fracture with transcrystalline rupture mode. The reinforcing mechanism is maybe related to the hindrance effect of microcracks propagation and the pinning effect for the dislocations movement, as well as the residual compressive strength due to the Al_2O_3 nanoparticles doped.

Key words: nanocomposites; WC-Co-Al_2O_3; mechanical properties; spark plasma sintering
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1 INTRODUCTION

WC-Co based nanostructured cemented carbides or cermets are used as precision machine tools, dies, and high-pressure valves for the oil field industry, thin hard metal wires, microtwist drills for printed circuit boards and printer heads[1, 2]. It is recognized that the technical challenge in preparation of nanostructured WC-Co cermets is not in the production of nanocrystalline WC-Co powders, but in the uniform retention of extremely fine microstructures in the consolidation of WC-Co nanocomposites[2-4]. Researches on nanostructured WC-Co cermets show that they exhibit a higher hardness and their undiminished toughness is not inherently higher than the conventional counterparts[1], as anticipated. Much progress has been made in consolidating nanocrystalline ceramics and cermets powders by many consolidation techniques[5-8] during the past several years. These studies have highlighted the problem of consolidating the nanopowders into fully dense ceramics and cermets without excessive grain growth. Spark plasma sintering(SPS), a fast consolidation technique, which can enhance sintering kinetics and reduce the time for grain growth[8, 9], is considered an advanced sintering technique for preparation of nanocrystalline ceramics and cermets.

Alumina based ceramic composites reinforced with refractory carbides have already been developed as an alternative to cemented carbides[10-12]. Additionally, small amounts of nanocrystalline Al_2O_3 particles were doped to reinforce the Ni binder phase of WC-Ni cermets, so the excellent mechanical properties have been achieved[13]. It is indicated that if small amount of nanocrystalline Al_2O_3 particles were added in the WC-Co nanocomposites to reinforce the Co binder phase, better mechanical properties combination of the WC-Co nanocermets could be obtained.

In this paper, small amounts of Al_2O_3 nanoparticles were mixed in the WC-Co nanopowders and the WC-Co-Al_2O_3 nanocomposites was fabricated by spark plasma sintering technique. The densification, grain growth, mechanical properties and reinforcing mechanisms of the nanocomposites consolidated by the novel pressing technique were examined and discussed.

2 EXPERIMENTAL

Nanocrystalline WC-7Co(mass fraction, %) powders were prepared by thermochemical methods. In the carbonization process, 0.4% VC and 0.6% Cr_3C_2(mass fraction) were added as grain growth inhibitors into the WC-Co composite powders. Nanocrystalline α-Al_2O_3 powders used as do-

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ping components were prepared by sol-gel method. The Al_2O_3 powders were dispersed in alcohol for 15 min using ultrasonic shaker firstly. Then, WC-Co nanocrystalline powders doped with inhibitors were mixed with the Al_2O_3 powders and the mixtures were dispersed ultrasonically for 30 min. Finally, the mixed powders were ball milled for 120 min in ethanol media. The mixtures were dried naturally and broken up using pestle. For this study, 0.3%, 0.5%, 0.7% and 1.0% (mass fraction) Al_2O_3 powders have been mixed with WC-Co powders.

The spark plasma sintering was carried out under vacuum in a Dr. Sinter Model SPS-1050 spark plasma sintering system (Sumitomo Coal Mining Co, Japan). The sintering temperature was set at 1 100 ℃ with holding time of 10 min and axial pressure of 80 MPa. The applied electronic current of SPS was about 1 kA and the heating rate was maintained as 100 K/min. The SPS specimen size is 20 mm in diameter and 7 mm in thickness. For comparison, nanocrystalline WC-7Co without Al_2O_3 additions was also spark plasma sintered under the same conditions.

The final densities of the sintered compacts were determined using Archimedes method. The hardness was measured by Vickers pyramid hardness testing machine under load of 300 N. The transverse rapture strength was examined by three point bending method with a span length of 15 mm. The nanocrystalline WC-Co and Al_2O_3 powders were morphologically observed by transmission electron microscopy (TEM, Model JEM-1200EX, Japan) and characterized by X-ray diffraction pattern (XRD, Model D/max-γB, Japan) with Cu K_α radiation. The fractured morphologies of the sintered composites were observed using scanning electron microscopy (SEM, Model JSM-6301, Japan). The average grain size of WC in the sintered composites was measured by the mean linear intercept method from the SEM images.

3 RESULTS AND DISCUSSION

3.1 Powder characteristics

The morphologies of nanocrystalline WC-7Co and Al_2O_3 powders are shown in Figs. 1(a) and (b), respectively. The WC-Co powders are in near sphere shape, as shown in Fig. 1(a), and the particle size is about 40 nm. The Al_2O_3 powders display polygon shape and show particle diameter of about 80 nm, as presented in Fig. 1(b).

Then the nanopowders were characterized by X-ray diffractometry (Fig. 2). The grain size of the nanocrystalline WC-Co, Al_2O_3 powders can be calculated by Scherer equation. It is calculated that the gain size of WC powders is 40 nm, and that of

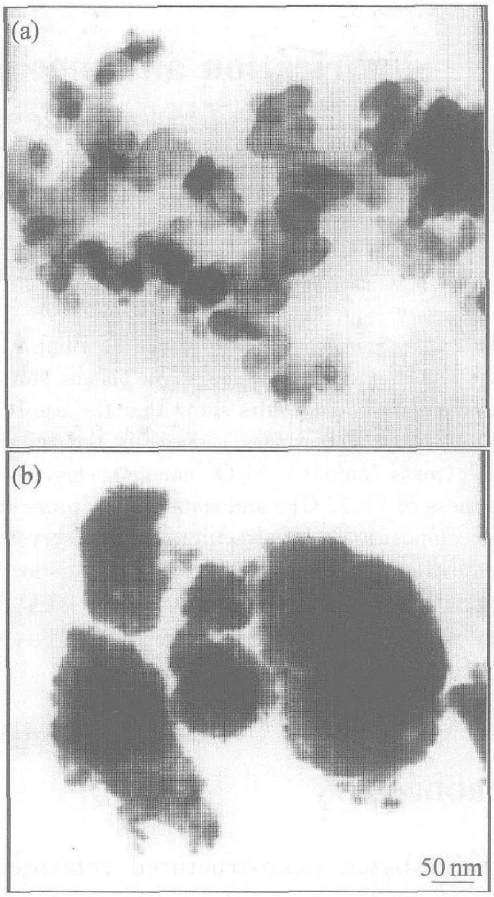

Fig. 1 TEM morphologies of starting nanocrystalline powders
(a) —WC-Co; (b) —Al_2O_3

Al_2O_3 powders is 10 nm, which means that the WC-Co particles in Fig. 1(a) are composed of single particle, but the Al_2O_3 particles are agglomerated ones in the TEM images.

3.2 Densification and grain growth

The relative density of WC-Co nanocomposites with different contents of nano-Al_2O_3 dopant consolidated by spark plasma sintering is shown in Fig. 3. It is noted that the relative densities of the spark plasma sintered nanocomposites are all very high (almost full density, > 99.0%), although the sintering temperature is as low as 1 100 ℃ and the soaking time is only 10 min. It can be due to the special sintering mechanism of spark plasma sintering, for the on-off DC pulse energizing method can generate spark plasma, spark impact pressure, Joule heat, and electrical field diffusion effect[9], as well as the axial pressure applied, by which the densification process is promoted at low temperatures. The relative density of the composites is decreased with the content increment of nano-Al_2O_3. The hard alumina nanoparticles in the composites need more liquid phase to wet and bind them. But the liquid binder phase is definite at the given temperature. Thus, the relative density of WC-Co-Al_2O_3 nanocomposites is decreased for the

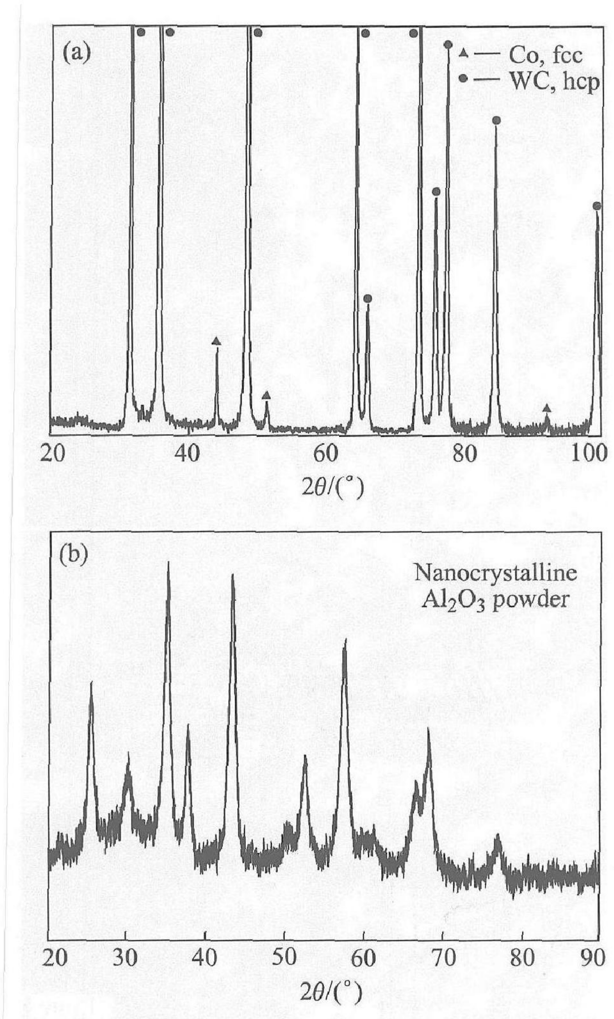

Fig. 2 X-ray diffraction patterns of nanocrystalline powders
(a) —WC-Co; (b) —Al_2O_3

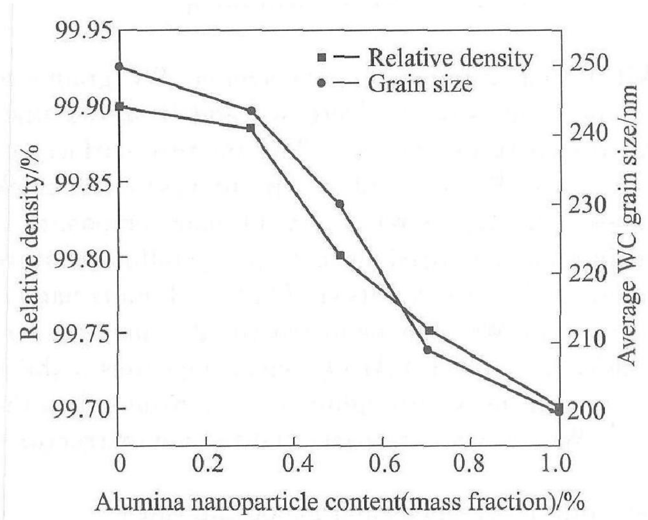

Fig. 3 Variations of relative density and grain size of nanocomposites with nano-Al_2O_3 content

worse wetting effects. The grain size of the nanocomposites is also shown in Fig. 3. It can be seen that the nano-Al_2O_3 doped cermets possess finer WC grain than the undoped counterparts. The higher the alumina content, the finer the WC grain of the nanocomposites. The grain size of 0.5% Al_2O_3 doped one is about 230 nm, and 1.0% doped one has grain size of 200 nm. Grain growth is the result of grain boundary migration. The quick grain boundary migration of nanograined WC is retarded by addition of nanocrystalline Al_2O_3 particles in the WC-Co composites, as a result, the grain growth is inhibited to some extent.

3.3 Mechanical properties

The variations of hardness and transverse rupture strength of WC-Co nanocomposites consolidated by SPS with nano-Al_2O_3 content are shown in Fig. 4. It is shown that the hardness is increased with the content of alumina increasing. With addition of 1.0% (mass fraction) Al_2O_3 nanoparticles, the hardness increases to 22.46 GPa. For the reason that the grain size of WC cemented carbides is refined by incorporation of nanocrystalline alumina, the hardness increasing obeys the Hall-Petch relationship. However, the transverse rupture strength of the composites increases until the maximum value appears, and then follows a decreasing trend. This means that with incorporation of optimum hard and brittle nano-Al_2O_3 particles, the toughness can be improved.

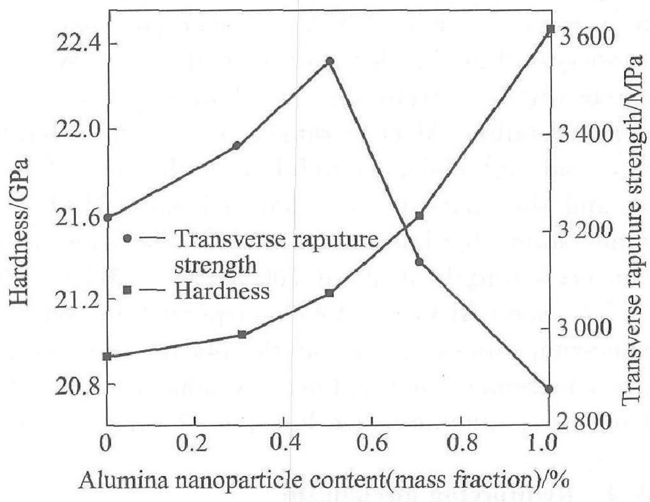

Fig. 4 Variations of hardness and transverse rupture strength of WC-Co nanocomposites with nano-Al_2O_3 content

As shown in Fig. 4, the hardness and transverse rupture strength are both increased with 0.5% nanocrystalline Al_2O_3 addition. Especially the transverse rupture strength of the WC-Co-Al_2O_3 nanocomposites is as high as 3 548 MPa, much higher than the undoped counterparts. However, 1.0% nanocrystalline Al_2O_3 doped cermets show much higher hardness of 22.46 GPa but lower transverse rupture strength of 2 875 MPa, compared with the pure WC-Co nanocermets sintered under the same condition. This is because that the spontaneous agglomeration of Al_2O_3 nanopowders leads to nonuniform distribution of alumina particles in the binder phase if more nanocrystalline Al_2O_3 particles are doped. Moreover, more Al_2O_3 nanoparticles embedded in the Co binder phase will decrease the wetting ability, as mentioned above. Therefore, the hardness increases but transverse rupture strength decreases. Accordingly, the use of nanocrystalline Al_2O_3 doped in the WC-Co nanocomposites as dispersions to reinforce the nano-WC-Co hardmetal has good effect of increasing the conventional mechanical properties, especially, the transverse rupture strength of the WC-Co nanocermets, as anticipated.

Tungsten carbide (WC) has been well known for its exceptional hardness and wear/erosion resistance; however, its low toughness causes brittle fracture. It is present in Table 1 that the spark plasma sintered nano-WC at 1 900 ℃ exhibits hardness of as high as 24.49 GPa and transverse rupture strength of about 950 MPa[9]. By addition of ductile metals such as Co can improve the toughness of WC ceramics. In Table 1, the transverse rupture strength of the WC-7Co nanocermets increases to 3 230 MPa, but at the mean time its hardness reduces, compared with the pure nano-WC. In order to further increase the mechanical properties of nano-WC-Co cemented carbides, nanocrystalline Al_2O_3 is doped in the nano-WC-Co composites to strengthen the binder phase. The nanocrystalline Al_2O_3 ceramics possess high hardness and high chemical stability, as listed in Table 1, and the spark plasma sintered nano-Al_2O_3 ceramic shows hardness of 20.40 GPa and transverse rupture strength of about 700 MPa[14]. With only 0.5% nano-Al_2O_3 particles dispersed in WC-Co nanocomposites, after spark plasma sintering, great increment of toughness is achieved, and the hardness is undiminished but has a little increase.

3.4 Reinforcing mechanism

The microstructures of fracture surfaces in the WC-7Co and WC-7Co-0.5Al_2O_3 spark plasma sintered nanocomposites are shown in Fig. 5. With addition of nanocrystalline Al_2O_3 particles in the WC-Co nanocomposites, the average WC grain size of the composites is decreased and it shows finer microstructures (Fig. 5). The fracture surfaces of pure nano-WC-Co follow an intergranular crack mode, but that of WC-Co-Al_2O_3 nanocomposites is mainly characterized by a transcrystalline rupture manner. By incorporation of 0.5% alumina nanoparticles in WC-7Co nanostructured cemented carbides, the WC-Co-Al_2O_3 nanocomposites exhibit better hardness-to-toughness relationships than the pure WC-7Co counterpart, and the microstructures

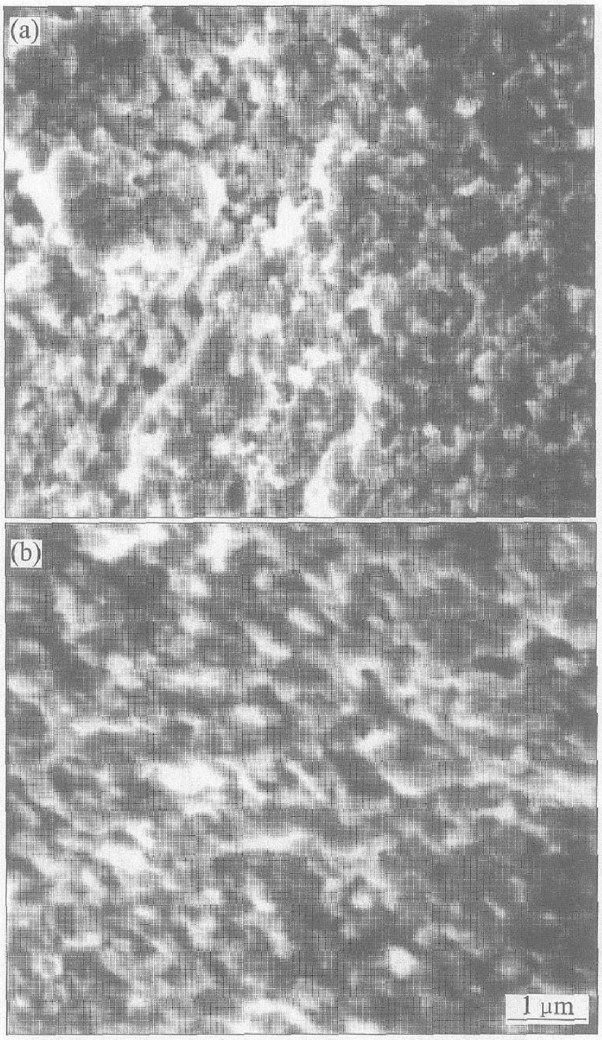

Fig. 5 Fracture surface morphologies of spark plasma sintered WC-Co(a) and WC-Co-Al_2O_3(b) nanocomposites

Table 1 Properties comparison of spark plasma sintered ceramics and nanocomposites

Material	Processing conditions	Relative density/%	Average WC grain size/nm	Hardness(HV)/GPa	Transverse rupture strength/MPa
Nano-WC	1 900 ℃	98.0	400	24.49	~ 950
Nano-WC-7Co	1 100 ℃, 10 min, 80 MPa	99.9	250	20.93	3 230
Nano-Al_2O_3	1150 ℃, 3 min, 63 MPa	99.8	349	20.40	~ 700
Nano-WC-7Co-0.5Al_2O_3	1 100 ℃, 10 min, 80 MPa	99.8	230	21.22	3 548

are also modified. The reinforcing mechanism is maybe related to the presence of nanocrystalline Al_2O_3 particles in the Co binder phase of WC-Co nanocermets, which can hinder the propagation of the microcracks. Furthermore, Al_2O_3 nanoparticles have pinning effect for the movement of dislocations in the Co binder phase deformed under the external forces. Finally, the expansion coefficients between Al_2O_3 and WC-Co are different, so the addition of nanocrystalline Al_2O_3 in WC-Co nanocomposites can result in the existence of residual compressive strength in the nanocomposites. Al_2O_3 is characterized by higher chemical stability at elevated temperatures and higher hot hardness than carbides[15], therefore it is expected that the WC-Co-Al_2O_3 nanocomposites will show better hot hardness than the WC-Co nanostructured cemented carbides. This study on the WC-Co-Al_2O_3 nanocomposites suggests that nanocrystalline Al_2O_3 powers can be used as dispersions to reinforce the WC-Co nanocomposites with increasing both the hardness and toughness.

4 CONCLUSION

Small amounts of nanocrystalline Al_2O_3 powders as dispersions can be used to reinforce the WC-Co nanocomposites with increments of the hardness and transverse rupture strength. The spark plasma sintered WC-7Co-0.5Al_2O_3 nanocomposites exhibit better hardness and toughness combinations with hardness of 21.22 GPa and transverse rupture strength of 3 548 MPa, whose fracture surfaces mainly fracture with transcrystalline rupture mode. The reinforcing mechanism is also discussed.

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