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Fabrication of ultrafine grain WC alloys by spark plasma sintering

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Abstract: Ultrafine grain WC alloys were prepared by high energy ball milling and subsequent spark plasma sintering from elemental mixed powders of nominal composition of WC-6Co-1.5Al(%, mass fraction). The influences of spark plasma sintering parameters on the density, hardness, bend strength and microstructure of sintered WC alloys were also investigated. The results show that there existed a proper time combination of pulse current and constant current employed for sintering. When the peak, base, frequency and occupational ratio of pulse current, constant current, total sintering time and sintering pressure were chosen as 3000 A, 360 A, 50 Hz, 50%, 1500 A, 6 min and 30 MPa, respectively, the optimal sintering was a combination application of 1min pulse-current and subsequent 5 min constant-current. The density, hardness and bend strength of the as sintered alloys could get up to 14.224 g/cm^3, HRA94 and 1660 MPa, respectively, and the average grain size of WC was only about 500 nm.

Key words: high energy ball milling; spark plasma sintering; ultrafine grain; WC-6Co-1.5Al cermets; microstructure and properties

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1 Introduction

Recently, owing to the rapid development of manufacturing, the ultrafine grain or nanocrystalline WC-base cemented carbides with high hardness, high toughness and sound anticorrosion have been studied extensively[1,2]. By far, it is still not reported that bulk cemented carbides with the grain size of less than 100nm and with high integrated performances have been fabricated, though the WC-base composite powders with average grain size of about 25 nm have been prepared successfully[3,4]. The WC grain size in as sintered alloys becomes much larger than that in precursor powders due to the surface and/or interface effect of ultrafine or nanometer WC grains. So, during the sintering process of ultrafine or nanocrystalline cemented carbides, obstructing WC grains growth become the key to obtain good performance alloys. New developed spark plasma sintering technique is a ideal choice to consolidate nanocrystalline powders, because its chacteristics of near net shaping, rapid sintering, and environmental friendship. It has been tested that spark plasma sintering mainly associated with particle surface activation and rapid consolidation, was obvi-

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ously superior in preparation of fine, ultrafine and nanocrystalline bulk materials[4-6]. In order to obtain fine grains of WC-base cemented carbides, and resultingly improve their mechanical properties, spark plasma sintering was used to sinter WC-6Co-1.5Al cermets in present work. And the effects of sintering parameters on the properties of sintered alloys were also studied.

2 Experimental procedure

WC-6Co-1.5Al(%, mass fraction) powders were blended for 24 h from commercial powders of WC, Co and Al (all particle size$\leqslant$3μm, and purity$\geqslant$99%) in a low energy mixer. Then, the mixed powders were moved into a high energy attritor to mill with cemented carbide milling balls. Figure 1 shows the morphology of mixed powders and 15 h milled powders. It could be observed that milling improved the particle size distribution of powders. After milling not only did the particle sizes ranged narrowly but also the powder particles became finer. D/max-1200 X-ray diffraction (XRD) analyzer was also used to characterize the sample powders. According to the half-high width of diffraction peak, the WC grain size among powders milled for 15 h was calculated and was about 25 nm.

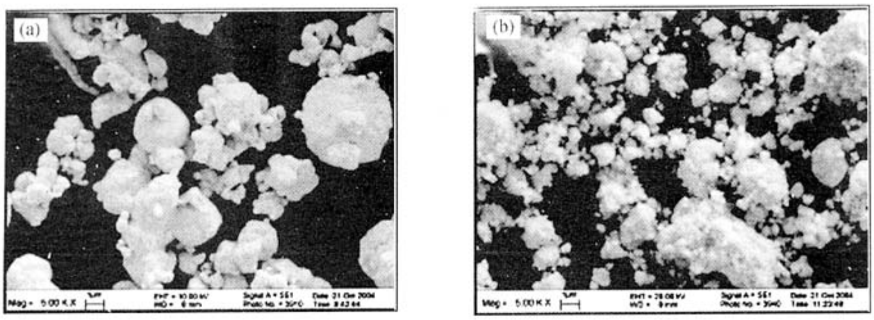

Fig. 1 SEM images of powders
(a)—mixed; (b)—milled for 15 h

To consolidate milled powders, 20 g powders every time were removed into a die of Φ21mm and then sintered in a SPS device under a pressure of 30 MPa. During the sintering process, the current was applied as shown in Fig. 2. The peak, base, duty ratio and repetition frequency of pulse current were chosen as 3000 A, 360 A, 50% and 50 Hz, respectively, and the subsequent constant current was 1500A except for special marking. The total sintering time was kept 6 min. In present work, only the sintering characteristic

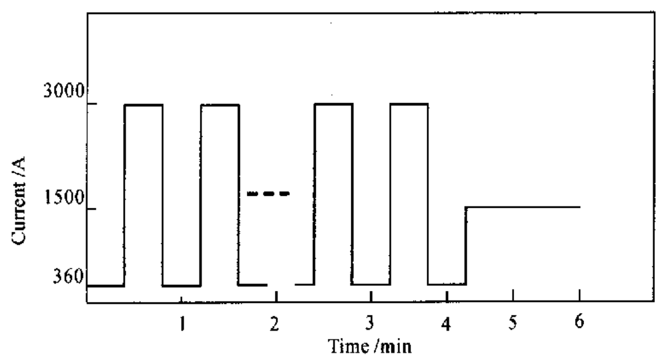

Fig. 2 Schematic diagram of current sintering process

of 15 h milled powders were investigated.

Density measurements were conducted based on the Archimedes' principle. Morphology of bend fracture surface was observed by a LEO 1530 VP scanning electron microscope. Bend strength and hardness of sintered alloys were examined on a Xinsansi－CMT5105 mechanical property testing and a HDI－1875 Rockwell apparatus.

3 Results and discussion

3.1 Density

The effect of sintering process on sintered density is shown in Fig. 3. It can be found that the density of sintered alloy came to the maximum of 14.224 g/cm^3, when a 1 min pulse-current and subsequent 5 min constant-current sintering was adopted. However, with the pulse current sintering time being further prolonged the sintered density decreased. When only pulse current was supplied during sintering, the sintered density fell down to the minimum, being 9.0 g/cm^3. It is because that the discharge plasma generated by pulse current among the powder particles has effects of cleaning and activation to the powder granules, and discharge shock pressure yielded by pulse current also resulted in denseness of local stress and energy, promoting the diffusion of grain boundary and bulk powders, as a result, elevating densification process of powders[4-6]. Whereas, as the average of pulse current used in present work was small, the Joule heat generated by pulse current was not sufficient in per volume of powders correspondingly, so a requisite sintering temperature could not be obtained only by single pulse current sintering for 6 min. Consequently milled powders could not be sufficiently consolidated and densified using pulse current sintering of such a short time. Although constant current can not generate discharge plasma to activate powder particles, it results in a rapid temperature rising. Thus, a proper coupled application of pulse current and constant current was necessary, such as 1min pulse-current and consequent constant-current sintering. It not only took full advantage of spark plasma generated by pulse current among the powder particles, but also benefited from rapid heating effect of constant current. As a result, the sintered temperature got up to 1175℃, and the powders were sintered sufficiently.

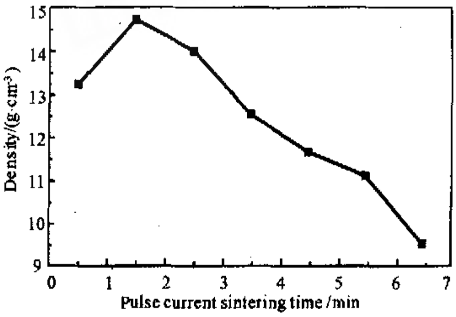

Fig. 3 Effect of pulse current on sintered density (total sintering time 6min)

3.2 Mechanical properties

Fig. 4 shows the variations of hardness and bend strength of sintered alloys with pulse current sintering time. When a 1min pulse-current and subsequent 5 min constant-current sintering was adopted, the hardness and bend strength of sintered alloys reached maxima simultaneously, being HRA94 and 1660 MPa, respectively. Nevertheless, the further increasing of pulse current sintering time resulted in decrease of hardness and bend strength of sintered alloys.

Fig. 5 shows the morphologies of bend fracture surfaces of sintered alloys. When a 5min pulse-current and subsequent 1min constant-current sintering was adopted, the starting morphology of powder particle even could be distinguished in the as sintered sample, as shown in Fig. 5(a), which was attributable to low sintering temperature caused by the constant current sintering so short time. With the constant current sintering time being prolonged, the final sintering temperature increased rapidly. When the constant current sintering time was prolonged to 5 min, that is, pulse current sintering time was shortened to 1min correspondingly, the final sintering temperature rose up to 1175℃. As the sintering temperature was relatively low, the grain growth of WC was inhibited well. So, the average grain size of WC was only about 500 nm after being sintered, as shown in Fig. 5(b). Meanwhile, the sintered density was enhanced, which depended on the appropriate coupled effects of pulse current and constant current. Therefore, the hardness and bend strength of the as sintered alloy was obviously improved. When the constant current sintering time was further prolonged to 6 min, that is, pulse current

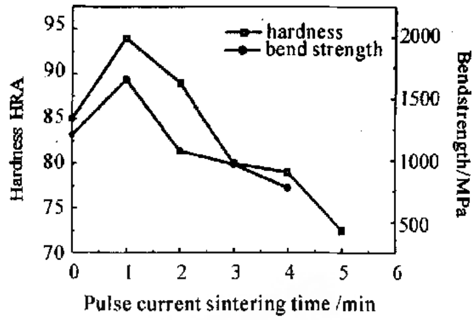

Fig. 4 Effect of pulse current sintering time on hardness and bend strength of sintered alloys (total sintering time 6min)

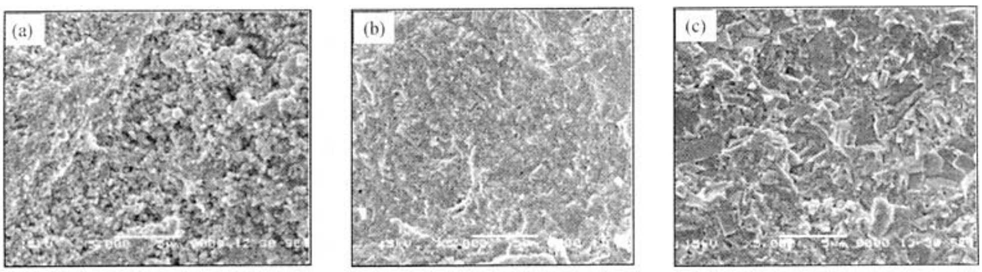

Fig. 5 Fractographs of alloys sintered by
(a) — 5 min pulse-current and subsequent 1min constant-current; (b) — 1 min pulse-current and subsequent 5 min constant-current; (c) — 1560 A constant current for 6 min

sintering was canceled, the sintering was insufficient and the sintered density decreased as described in Fig. 3, owing to lack of discharge activation of pulse current. It was not difficult to imagine that the mechanical property of the as sintered alloy was lower. When a single constant current was used to sinter powders by keeping the total sintering time being 6min, a higher sintered density with 14.705 g/cm^3 aslo could be achieved by increasing current values to 1560 A. It was because that with the sintering current increasing, the final sintering temperature increased, and resultingly the plastic deformability of powders and the diffusion velocity of atoms were improved, in spite of lacking activation effect of pulse current. However, because the sintering temperature was so high, reaching 1375℃, that the grains of WC grew rapidly. As shown in Fig. 5(c), the average grain size of WC went up to about 1 μm, though the sintering time was only 6 min and the intermetallic compounds of cobalt and aluminium formed during sintering could prevent the grain growth[7-8]. Consequently, the hardness and bend strength of sintered alloys decreased inversely. It is obvious that promising WC alloys could not be obtained only by using intensive constant current sintering.

4 Conclusions

(1) The milled WC-6Co-1.5Al%(mass fraction) powders could be sintered at lower temperature and in shorter time by SPS. When a proper coupled application of pulse current and subsequent constant current sintering was adopted, the density, hardness and bend strength of the sintered cemented carbides reached

14.224 g/cm³, HRA94 and 1660 MPa, respectively. Meanwhile, the average grain size of WC was only about 500 nm, because both Co-Al compounds caused during sintering and the rapid sintering of SPS in lower temperature inhibited the grain growth of WC phase.

(2) Under the sintering conditions of 30 MPa axial external pressure, 6min total sintering time, pulse current with the peak, base, frequency and duty ratio being 3000 A, 360 A, 50 Hz and 50%, and constant current of 1500 A, the optimal sintering process was 1 min pulse-current sintering plus subsequent 5 min constant-current sintering.

(3) When a single constant current sintering of 6 min was adopted, although the sintered density could be enhanced by increasing current intensity, the property of the sintered alloy substantially decreased instead, owing to evident growth of WC grains.

Acknowledgements

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