

FABRICATION OF BINDER-FREE ULTRAFINE WC-6CO COMPOSITES BY COUPLED MULTI-PHYSICAL FIELDS ACTIVATION TECHNOLOGY

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ABSTRACT

A novel sintering method, named as coupled multi-physical fields activation technology, has been introduced for the forming of various material powder systems. Compared with the conventional ones, this technique presents more advantages: lower sintering temperature, shorter forming time, and remarkable inhibition of the grains coarsening. In the study, the cylinders of $\Phi 4.0\text{mm} \times 4.0\text{mm}$ had been formed with ultrafine WC-6Co powders. The relative properties of sintered WC-6Co cemented carbides, such as hardness and the microstructures, had been obtained. The study has shown that a relative density, 97.80%, of the formed samples, could be achieved when the case of temperature 850°C , heating rate 50°C/s , pressure 75MPa and Electro-heating loop 6 times, were used. More importantly, the circumscription for the growth of grain size of WC, attributed to the effect of electrical field, renders coupled multi-physical fields activation technology applicable for getting WC-6Co cemented carbides with fine grain size and good properties.

Keywords: Coupled Multi-physical Fields Activation, Ultrafine WC-6Co powders, Microstructures.

1 INTRODUCTION

WC-Co composites are widely used as cutting tools and dies due to their high wear resistance and toughness (Pan 2011). And WC-Co composites are normally prepared by a powder metallurgy route, which is a procedure consisting of a series of long-time processes, such as synthesis of WC powder, mixing with metal, granulation, pressing and sintering. Moreover, the carbonization temperature of WC is as high as $1400\text{-}1600^\circ\text{C}$. In order to improve its properties and simplify the preparing procedure, the consolidation of WC-Co powder has been studied by a variety of techniques including the hot isostatic pressing (HIP) (Trung 2013), as well as unconventional processes such as microwave sintering and spark plasma sintering (SPS) (Machado 2009), rapid omni compaction (ROC) and ultrahigh pressure rapid hot consolidation (UPRC). However, the hardness and toughness are in

contradiction with each other for the conventional coarse-grained WC-Co alloys (Zhao et al. 2008). To-date, numerous processes have been dedicated to study the densification and grain growth control during sintering of the WC-Co powders in order to achieve the goal of obtaining fully dense WC-Co materials.

One of the keys for controlling the grain growth of WC-Co composites is a suitable selection of additives as grain growth inhibitors, such as Vanadium carbide (VC) and chromium carbide (Cr_3C_2). Meanwhile, the grain growth can be inhibited by using special sintering technologies allowing very high heating rates, increasing the densification rate, even at lower sintering temperature and shorter holding times, such as microwave sintering, spark plasma sintering (SPS), and so on. Moreover, Bonache *et al.* (2011) has investigated the effect of grain growth inhibitors on the WC grain growth and its mechanical properties when they are combined with the use of PECS sintering technique. The results has demonstrated showed that the addition of inhibitors, especially VC, is an efficient method for controlling the grain growth in the solid state, even by rapid sintering processes.

Recently, a coupled multi-physical fields activation technology was proposed for the forming of components for various material systems such as metals, ceramics and WC-Co composites, as illustrated in Figure 1. The advantages of this technique over the conventional ones include lower sintering temperature, shorter forming time, and remarkable inhibition of the grains coarsening. In the coupled multi-physical fields activated sintering, the powders are sintered under simultaneous influences of the current, high temperature and forming-pressure. Firstly, loose powders are placed directly into a die, and then the heating is generated by passing an AC current through the die to providing the necessary temperature in the powders, and a pressure is applied onto the powders at the same time. The whole forming process only took less than 4 minutes. Direct manufacture from powders and no additional binders added to the powders indicate that the proposed technique is an energy conserving and environmentally friendly forming process.

It can be easily noticed the significant differences between the proposed new sintering method and SPS are the amplitude of the electric current, the heating rate and the pressure. Firstly, SPS uses a pulsed electric current to stimulate spark discharge in gaps between the particles. Therefore, the pressure (15-50MPa) applied cannot be too high, otherwise the sparks will disappear. However, the AC current with low voltage and high current, used in the coupled multi-physical fields activated sintering, has little effect on pressure. Secondly, in the proposed sintering method, a heating rate as high as $50^\circ\text{C}/\text{s}$ and an electric current as high as 10^5A can be used, which are greatly higher than those used in SPS.

This paper is to report a study on the properties and XRD results of the WC-6Co cemented carbide fabricated by the novel powder sintering method. The microstructure evolution and grain size inhibition are also discussed.

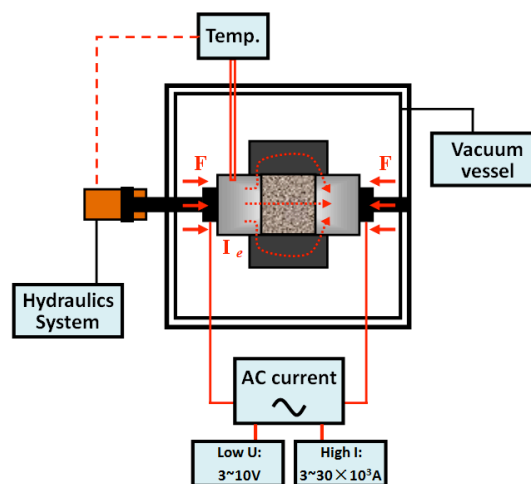


Figure 1: Schematic of the coupled multi-physical fields activation sintering and forming.

2 EXPERIMENTAL PROCEDURES

Commercial WC powder and Co powder (all of them with a 99% purity and an average grain size of $0.3\mu\text{m}$) were used as the raw materials. They were mixed thoroughly with a composition of 94 wt% WC-6wt% Co, and dry milled for 6 hours.

Figure 2 shows the schematic of the tool-set applied in the experiments with a Gleeble-3500D thermal simulation machine from Dynamic System Inc., USA. The machine controls the heating process with a computer-controlled system which is able to preset a value of the heating rate, and the accuracy of the temperature control is within $\pm 3\text{ }^\circ\text{C}$. The electric field produced by the machine has low voltage and high current (3~10 Volts and 3000~30000A), and the as-received powders consisted of agglomerates which are sufficient to make up a sample with the size of $\Phi 4.0\text{mm}\times 4.0\text{mm}$ (solid cylinder). After weighting, the powder was put into a die. The die model is shown in Figure 2. The die filled with WC-6Co powders was then placed onto the Gleeble-3500D machine, and then it was heated rapidly to a certain sintering temperature at a preset heating rate in a vacuum ($<10^{-4}\text{Pa}$) (a high electric current passes through the die-set and powder system), and at the same time, a preset pressure was applied onto the punch and die-bottom-side. The pressure-temperature profile used during the sintering processing can be found in Figure 3, and hence, the sintering process can be very short, even less than 4 minutes. The detailed technological parameters of the experiment are shown in Table 1. The Electro-heating loop means the fluctuation of the temperature and cycles for a fixed times.

The sintered compact's relative density was measured by the electronic analytical balance TP-214. The pore size distributions were observed under a scanning electron microscope JSM-5900LV, JEOL (Japan). And the phases of the synthesized products were analyzed by X-ray diffraction (XRD, D/Max-III A).

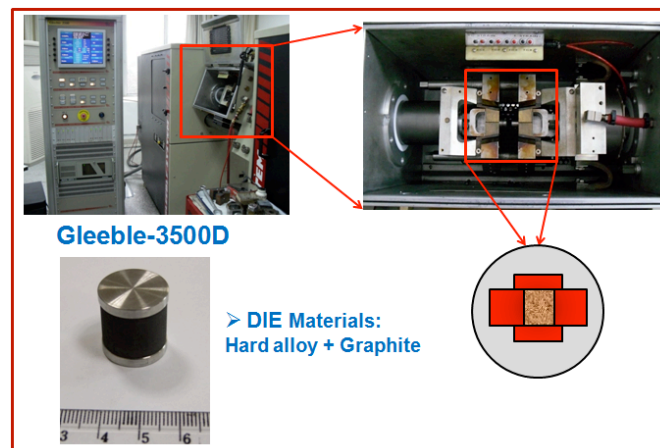


Figure 2: The coupled multi-physical fields activation technology production unit:Gleeble-3500D

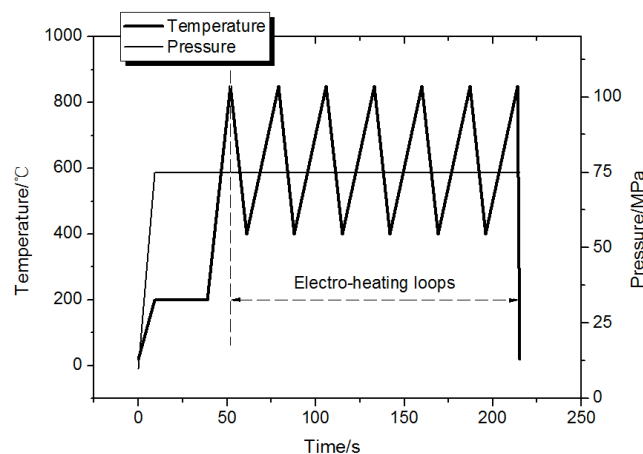


Figure 3: Pressure-temperature profile used during processing of the WC-6Co composites by the coupled multi-physical fields activation technology

Table 1: Process conditions and relative density of the formed samples

Specimen designation	Heating rate (°C/s)	Sintering temperature (□)	Pressure (MPa)	Times of Electro-heating loop (T~400□)	Relative density (%)
1#	50	850	75	1	92.90
2#	50	850	75	3	93.30
3#	50	850	75	4	93.80
4#	50	850	75	6	97.80

3 RESULTS AND DISCUSSION

3.1 Properties of the Sintered WC-6Co cemented carbide

The results selected from the experiments can be found in Table 1. The micro-formed samples show high relative density (92.90% to 97.80%). It can be found that dependence of the relative density onto the Electro-heating loop is strong and a tendency towards an increase in relative density as those two parameters was observed. The morphology of a formed sample can be seen from Figure 4.

Table 2 shows properties of WC-6Co cemented carbide material that prepared by different shaping technologies. It could be concluded that the effect of coupled multi-physical fields activation treatment process resulted in a harder sintered product with a relative low strength. This should be attributed to smaller average grain size (Figure 6 (e)) and very small material volumes involved.

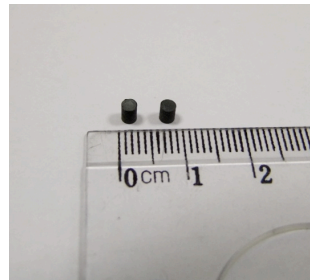


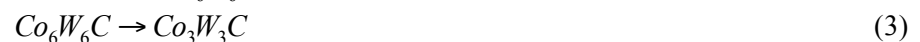
Figure 4: The formed samples (solid cylinder) with a size of $\Phi 4.0\text{mm} \times 4.0\text{mm}$

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

Shaping Technology	Relative density(%)	Rockwell A hardness (HRA)
Die pressing (Shi 2006)	97.40	93.1
PEM (Shi, 2006)	97.00	92.8
Die pressing plus CIP (Shi, 2006)	99.50	93.6
Coupled multi-physical fields activation	97.80	87.2

3.2 XRD Inspection of WC-Co System

During the sintering process, the reactions of WC and Co can be shown as follows (Bonache *et al.* 2011):



The XRD pattern of composition WC-6Co samples sintered by coupled multi-physical fields activation technology can be found in Figure 5. The XRD results show that there is no evidence of η

phase ($\text{Co}_3\text{W}_3\text{C}$ or $\text{Co}_6\text{W}_6\text{C}$) formation in the composition. The absence of secondary phases confirms that the WC-Co powder system had been sintered in solid phase. This clearly indicates that the incomplete densification in the solid state can be ascribed to the effect of coupled multi-physical fields activation, especially the high density current field, is associated with the limitation of the diffusion phenomena and migration of Co (Carroll 1999). On the other hand, it is difficult for WC-Co system to react because of the short time of heating period (a few seconds).

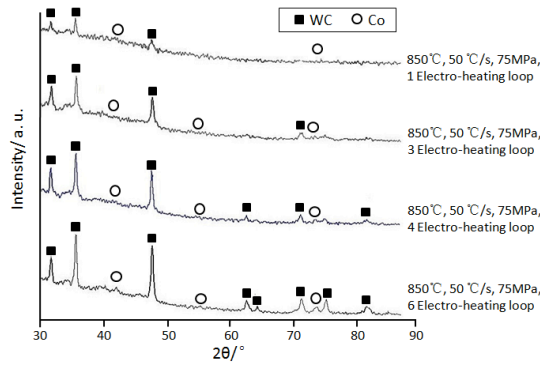


Figure 5: The XRD pattern of composition WC-6Co samples sintered by coupled multi-physical fields activation technology

3.3 Microstructure of the Formed Samples

Comparing the micrographs of the formed samples shown in Figure 6, the following conclusions could be found: (1) WC-6Co powders can be well sintered to dense compacts under the coupled actions from multi-physical fields within relatively short sintering time (e.g. < 4 minutes), while with a conventional sintering it could take a couple of hours.

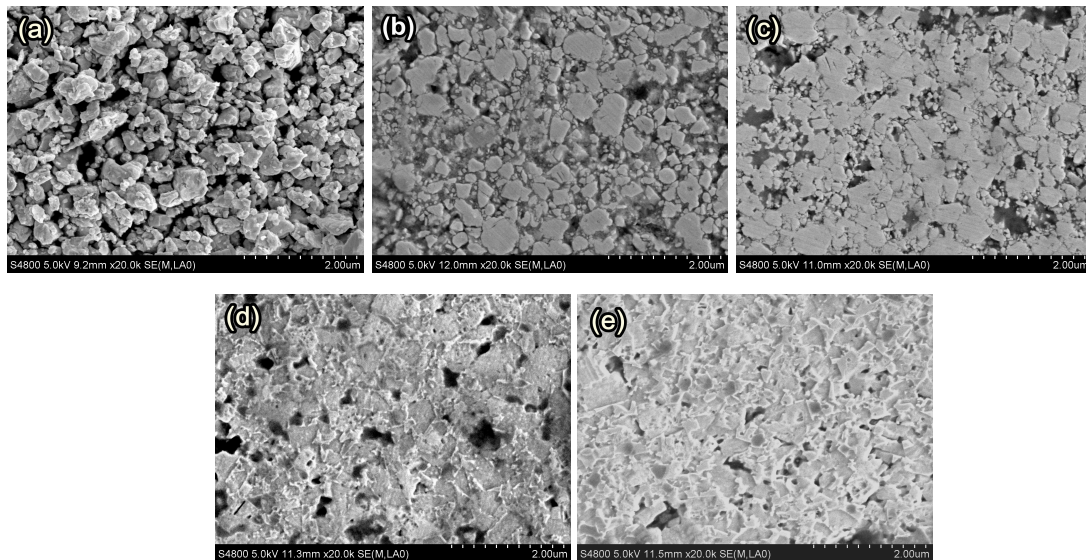


Figure 6: SEM micrographs of formed samples: (a) WC-6Co mixed raw powders; (b) WC-6Co sintered at 850°C, in 50°C/s and under 75MPa for 1 time Electro-heating loop; (c) WC-6Co sintered at 850°C, in 50°C/s and under 75MPa for 3 times Electro-heating loop; (d) WC-6Co sintered at 850°C, in 50°C/s and under 75MPa for 4 times Electro-heating loop; (e) WC-6Co sintered at 850°C, in 50°C/s and under 75MPa for 6 times Electro-heating loop

It is worth to mention that the pores in a composite decrease as the times of the electro-heating loops rise, which accompanies with the densification of compact. At the same time, when the times of the Electro-heating loop increased, the round WC grains combined together with Co binder phase in WC-6Co cemented carbides, for the liquid Co binder phase was formed during the sintering process.

(2) It was found that no coarsening of grains accompanied the process of the densification of the dense compact, obtained from the comparison between the grain size of Figure 6 (b), (c), (d) and (e) and the raw materials grain size of Figure 6 (a). Therefore, the coupled multi-physical fields activation technology is a suitable selection of controlling the grain growth of WC-6Co composites and remaining the good properties of density and hardness.

4 CONCLUSIONS

From the work completed in this study, the following conclusions can be drawn. Compared with conventional sintering methods, the coupled multi-physical activation technology is an efficient process, and it has lower energy consumption and little impact to the environment due to directly forming the component from loose binder-free powders. The WC-6Co cemented carbide can be made using this coupled multi-physical fields activation technology. And the density of the sample made from WC-6Co powder can reach over 97% when they were sintered at a relatively low sintering temperature (850°C), higher heating rate (50°C/s), pressure 75MPa and Electro-heating loop 6 times. The study on the characteristics of the micrographs of the formed samples suggests that the grain growth can be inhibited under the coupled multi-physical fields activations, which is fundamentally different from that in conventional vacuum sintering, as well as SPS. The effect of simultaneous pressure field, temperature field and electric field plays a vital role in controlling grain coarsening.

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