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Effect of direct current patterns on densification and mechanical properties of binderless tungsten carbides fabricated by the spark plasma sintering system

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ABSTRACT

Binderless tungsten carbide materials (bWCs) were fabricated by the spark plasma sintering (SPS) system. Ultrafine WC powders with adjusted oxygen contents and C/W atomic ratios were used as raw materials. Constant and pulsed direct current patterns (constant DC and pulsed DC) were chosen as the power supplies. The results indicate that for WC starting powders with either low (0.31%) or high (0.95%) oxygen contents, a relative density larger than 99.0% can be reached by pulsed DC at 1820 °C. Nevertheless, the severely oxidized WC powders cannot be well-densified by constant DC. A high degree of densification of bWCs facilitates the collaborative improvement of the toughness and hardness. The existence of W_2C facilitates the improvement of the hardness at the high expense of the toughness. The existence of graphite phase is substantially detriment to the toughness. The grain coarsening facilitates the improvement of the toughness with sacrificed hardness. The related mechanism is discussed.

1. Introduction

WC–Co cemented carbides are widely used as cutting, mining and forming tools because of the high hardness, excellent wear resistance as well as easy tailored properties [1,2]. While cemented carbides often suffer galvanic corrosion because of a higher oxidation potential of the binder phase compared to the tungsten carbide based hard phase in aggressive media [3,4]. Once the binder phase dissolved, the mechanical properties deteriorate severely [5,6]. Hence, by reducing or eliminating the amount of binder phase, corrosion resistance of the cemented carbides can be improved.

Binderless tungsten carbides are defined as series of bulk WC materials (bWCs) without or with < 0.5 wt.% metal binders [7]. Due to the absence of metal binder, bWCs are promising materials in extremely tough environments, such as mechanical seals under high burthen [1], nozzles for abrasive water-jet [8,9] as well as in the fabrication of optical glass lens molds [8,10]. With the progress of technology and equipments as well as the urgent demands of more excellent materials in special fields, bWCs have attracted great attentions and interests from researchers and the industry. Cold isostatic pressing–hot isostatic pressing [11,12], cold pressing–vacuum sintering [1,13], hot pressing [10,14,15], high frequency induction electric current sintering [16] and especially spark plasma sintering (SPS) [7–9,17–22] have been developed for consolidating bWCs.

SPS is a preferred methodology for scientists to consolidate ceramics, like bWCs, due to several advantages such as high heating rate and unique heating mechanism in comparison with the conventional sintering processes [23,24]. Recently, the reported literatures focused mainly on the effect of the particle size on the sintering behavior and properties of bWCs [17–19]. The bWCs from nano-scaled and ultrafine WC powders are the typical successful case fabricated by SPS technique. Another interest is the effect of the alloy additives, taking Cr_3C_2 [8], VC [8,20], La_2O_3 [21], or multi component additive [8,22] as examples, on the densification, abnormal grain growth inhibition and the related properties. However, the study concerning the effects of precisely controlled oxygen content or C/W atomic ratio on the sintering behavior and properties were seldom reported. Owing to the high specific surface area, nano-scaled and ultrafine WC powders are easy oxidized in room temperature during production, packing, transporting, storing and the later using. Warren, et al. [25,26] reported that the oxide of WC at room temperature is in the form of WO_3, and that the finer the WC powders, the more easily oxidized. Quality control can hardly be guaranteed by using severely oxidized WC powders as raw materials.

Additionally, as a new sintering technology for consolidating bWCs, SPS is favorable for scientists. The effect of consolidation parameters, e.g. temperature [18] of SPS on the consolidating behavior and properties of the as-sintered bWCs has been a hot topic in recent years. However, the effect of the conditions of electric current on the densification or

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Table 1
Information of the powders, power patterns and ID of the as-sintered specimens.

WC powder				Power pattern	ID of the as-sintered specimens
Notation	Oxygen content (wt.%)	Total carbon content (wt.%)	C/W atomic ratio		
P1	0.31	6.22	1.00	Constant DC	bWC1
P1	0.31	6.22	1.00	Pulsed DC	bWC2
P2	0.95	6.41	1.00	Constant DC	bWC3
P2	0.95	6.41	1.00	Pulsed DC	bWC4
P3	0.95	6.18	0.96	Pulsed DC	bWC5
P4	0.93	6.52	1.02	Pulsed DC	bWC6

Remarks: The C/W atomic ratio is defined as a value of theoretical molar mass of residual carbon after being completely consumed by the reduction of oxide versus the molar mass of tungsten.

properties of bWCs was seldom reported in literatures. SPS system can provide two basic patterns of electricity, i.e., constant DC and pulsed DC produced by constant DC passing through a pulse generator. The both patterns of DC can be employed as the power supply for the consolidation [27]. However, for most of papers concerning consolidation of bWCs by SPS systems, conditions of power supply were not clearly described. The effects of diverse DC patterns on sintering behavior of WC powder, especially those oxidized could be different.

In the present work, ultra fine pure WC powders with low and tailored high oxygen contents, as well as varied C/W atomic ratios were densified by SPS system with constant DC and pulsed DC as the power supplies, respectively. Effects of both the power patterns and oxygen content of WC powders on densification behavior and mechanical properties were investigated.

2. Experimental details

A commercial ultrafine WC powder without the addition of the grain growth inhibitor was used as the raw material. The chemical constituents and grain size of the WC powder according to the supplier quality certificate are: WC > 99.5 wt.%, total carbon 6.16 wt.%, free carbon 0.04 wt.%, oxygen 0.21 wt.%, FSSS (Fisher particle size) 0.51 μm and BET specific surface area 2.36 m^2/g.

In order to tailor high oxygen content for the investigation, the as-supplied WC powder was oxidized in a tube furnace with flowing argon atmosphere at 350 °C for 45 min. The purity of the argon was approximately 99%, obtained by controlling the flowing rates of oxygen and high purity argon (99.99%). The as-supplied and oxidized WC powders were subsequently mixed with different amounts of carbon black, respectively, by means of ball-milling for 12 h in alcohol medium, which was conducted in high purity argon atmosphere. The total carbon and oxygen contents of the ball-milled powders were analyzed employing CS-600 Carbon/Sulfur Determinator (Leco®, America) and ON900 Oxygen/Nitrogen Determinator (Eltra®, Germany), respectively. The selected mixed WC powders (i.e., P1, P2, P3 and P4) for the consolidation and their oxygen and total carbon contents are detailed in Table 1.

The mixed WC powders were consolidated in a graphite die with an inner diameter of 20 mm and by a SPS system produced by KCE®-FCT, Germany. The schematic drawing of the SPS system is shown in Fig. 1. The technique and process are described as follows: the internal surface of the mould was covered with graphite paper to avoid the contact between the powders and the surface, which facilitates the sintered specimen to be ejected off the die. The powders were loaded in the graphite mould and then pre-pressed with a pressure of 6 MPa. In order to minimize the radiation heat loss during the heating and dwell process, the external surface of the die was completely covered by carbon felt.

Constant DC and pulse DC were adopted. The parameters of both patterns are shown in Table 2. The setting heating curve was from room temperature to 1600 °C and then to 1820 °C with a heating rate of 200 °C/min. The soaking time on 1600 °C and 1820 °C were 10 and 6 min, respectively. After the sintering, the specimens were cooled down to room temperature together with the water-cooled pistons. The actual temperature was detected with a pyrometer focused on the interior of upper punch where the distance was 15 mm from the

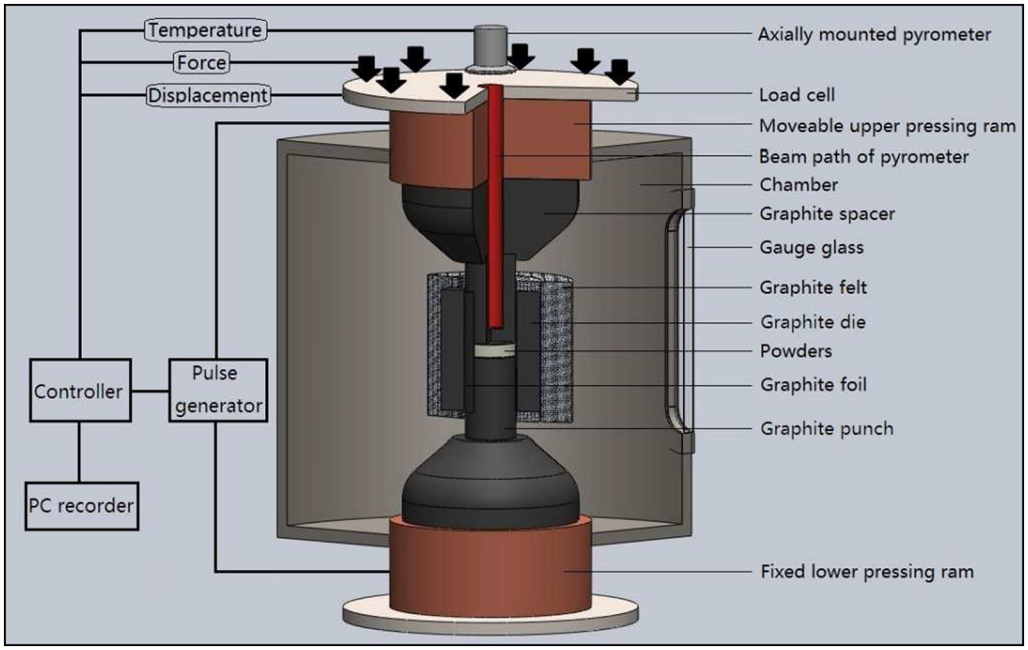

Fig. 1. Schematic drawing of the SPS system used in the research.