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Temperature distribution and neck formation of WC–Co combined particles during spark plasma sintering

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Abstract

Based on the experimental investigations, a model that describes the distributions of the current intensity and the temperature increase among the different raw powder particles, as well as its evolution during the spark plasma sintering (SPS) process, has been developed. As calculated by the model, in a WC–Co combined (Co-film coated WC) particle, a majority fraction of the WC particle is heated by the thermal energy transferred from the Co film. The rapid melting and joint of the Co films lead to the fast formation of the sintering necks of the combined particles. The temperature of the combined particles may reach the eutectic temperature of WC and Co and the melting temperature of Co at relatively lower sintering temperatures, thus the powder particles can be densified rapidly at the temperatures apparently lower than those in the conventional sintering techniques. The physical essence of the neck formation and the unique densification feature of the SPS process is presented by combing theoretical analysis and experimental studies.

Keywords: Spark plasma sintering; WC–Co cermets; Temperature distribution; Neck formation

1. Introduction

Cermets, or cemented carbides, is a class of materials with high industrial importance, and used widely in metal processing, mining, wearing-resistance parts and other applications that require the combination of high hardness and reasonable toughness [1]. With the development of manufacturing, there has been an increasing tendency towards exploiting the advantages of their high toughness, strength and rigidity coupled with high hardness and wearing resistance [2]. However, the ultra-fine hard metal grades are extremely sensitive to processing conditions and are even more prone to grain growth during consolidation [2]. It is known that the high properties of WC–Co cermets essentially depend on the grain structure of the sintered body. Since it is a disadvantage for cermets applications that the powder particles coarsen during sintering, many efforts have been contributed to improve processes that growth of WC grains can be hindered [3].

Spark plasma sintering (SPS) is an advanced sintering technology that has been rapidly developed in recent years. It has the key advantage of the very high degree of densification obtained at low sintering temperatures and within a short time, compared with the conventional sintering methods. Generally, the SPS process applies simultaneously a low voltage, pulsed direct current of high intensity and uniaxial pressure, which offers the possibilities of using rapid heating rates (e.g. achieving 1000 °C/min) and very short holding times (e.g. 3–5 min) to obtain highly densified bulk materials [4–6]. Owing to above features of SPS technology, the grain growth in the sintering samples can be controlled, fine grain structures, hence high mechanical properties of the bulk material are expected to obtain.

Recently, ultra-fine and even nanocrystalline binder-less WC [7] and WC–Co alloys [8–14] prepared by SPS technique have been reported. Most of these investigations were concentrated on the preparation procedures of the cermets, e.g. the optimization of SPS parameters. However, few studies have given a detailed description of the mechanisms of SPS synthesizing WC–Co cermets. For the single-phase conducting powders, we calculated the current distribution in the SPS process between the sample and the graphite die, as well as the self-Joule-heating effect of the particles, and found that there is a sharp temperature

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gradient from the particle interface to the particle center [15]. Accordingly, the mechanisms for the formation and growth of the sintering neck have been proposed to describe the densification process of conducting powders [15,16]. However, for SPS sintering WC–Co cermets, which has characteristics of sintering metal–ceramics composites, the current and the temperature distributions, as well as their evolutions with the densification process, to the best of our knowledge have not been systematically studied yet. In the present work, considering the different conducting features of WC, Co and the graphite die, we study the temperature distribution between WC and Co powder particles, as well as the temperature distribution evolution of the particles during SPS process. The essence of the neck formation and the unique densification feature of the SPS process is aimed to find out.

2. Experimental procedures

Commercial WC powder (Xiamen Golden Egret Special Alloy Co., Ltd., China) and Co powder (Institute of Non-ferrous Metals and Alloys, China) were used as the raw materials for ball milling, followed by SPS sintering. The WC powder particles have a purity of 99.98% and an average diameter of 200 nm. The Co powder particles have a purity of 99.5% and an average diameter of 28 nm. The high-energy ball milling was carried out at the room temperature for mixing the WC and Co particles, with apparatus of Pulverisette 4 (Fritsch, Germany) using cermets balls and vials. The ball-to-powder weight ratio of 3:1, the rotation frequency of 500 r/min, and time of 24 h were used for the ball milling. For the ball-milling process, the pure alcohol was used as the milling medium to prevent power particles from agglomerating.

The sintering apparatus of SPS-3.2-MV (Sumitomo Coal Mining Co., Ltd., Japan) was used, with a sequence consisting of twelve pulses (with a pulse duration of 3.3 ms) followed by two periods of zero current which is termed as 12:2 for the pulse sequence. For the sintering parameters, a constant pressure of 30 MPa was used, and the final sintering temperatures of 600, 800, 1000 and 1200 °C, which were selected to represent different sintering stages in a whole consolidation process, could be precisely obtained by controlling the heating time through the designed program. No holding time was used in order to keep the sintering process continuous. The electrical resistivities of the die and the samples sintered at different temperatures were measured by the conductance-testing instrument (model ZEM-2, ULVAC, Japan). To examine the microstructures of samples at different sintering stages, the samples were carefully broken off with fingers from an indentation, and observed on the fractured morphology with the scanning electron microscope (SEM) (model JEOL6500F, Japan).

3. Experimental results

The fracture surface morphology and the relative density of the WC-10 wt.%Co samples at different sintering temperatures are shown in Fig. 1. At a temperature of 600 °C the powder particles are at the early compact stage of sintering (Fig. 1a). At the temperature of 800 °C (Fig. 1b), there are changes in the morphology of the powder sample, where the sintering necks are found to form, and local melting at the surface of particles is observed, as indicated by the arrows marked in the picture. At the sintering temperature of 1000 °C, there are more melting features found at the surfaces of particles (Fig. 1c). With the further increase of the sintering temperature, e.g. above 1200 °C, the approximately fully densified sample is obtained. As the sintering temperatures (e.g. 800, 1000 or 1200 °C in Fig. 1) are much lower than the melting temperature of Co (1495 °C), the melting of Co film coating the WC particles indicates that an extraordinarily high temperature is generated at the particle surface, which is higher than the melting point of Co. Accordingly, an inhomogeneous temperature distribution should exist in the WC–Co combined particles (here representing the Co-film coated WC particles) at the stage of neck formation. The above characteristics found in early stages in the SPS process are quite different from those in the conventional sintering of WC–Co powder particles in the respects of the full densification temperature and the sensitivity of the densification degree to the sintering temperature. In order to study the unique densification mechanism of metal–ceramics composite powders in the SPS process, especially the mechanism in the early stages of neck formation and neck growth, a theoretical model will be developed in the following section.

4. Modeling of temperature distribution between WC and Co

To clarify the SPS mechanisms for multi-component materials, the temperature distribution between different components in the sintering process needs to be described. Due to the difference of the resistances of WC and Co, there may be existed the gradient of the temperature increase between WC and Co as a result of the local current distribution. From our ball-milling experiments, it is found that the Co particles were compacted and deformed into a thin layer surrounding the WC particles (this configuration is so called the “combined WC–Co particles” in the present article) when the milling time exceeds 24 h. Assuming that the mass ratio between WC and Co remains constant in the ball milling, the number of Co particles surrounding a WC particle can be estimated as:

$$N = \frac{W_{\mathrm{Co}}\rho_{\mathrm{WC}}r_{\mathrm{WC}}^3}{W_{\mathrm{WC}}\rho_{\mathrm{Co}}r_{\mathrm{Co}}^3} \tag{1}$$

where W_{Co} and W_{WC} are the masses, ρ_{Co} and ρ_{WC} are the densities, r_{Co} and r_{WC} are the particle radii of Co and WC, respectively. The radius of the WC–Co combined particle is thus estimated by

$$r = \left(Nr_{\mathrm{Co}}^3 + r_{\mathrm{WC}}^3\right)^{1/3} = \left(\frac{W_{\mathrm{Co}}\rho_{\mathrm{WC}}}{W_{\mathrm{WC}}\rho_{\mathrm{Co}}} + 1\right)^{1/3}_{r_{\mathrm{WC}}}. \tag{2}$$

The local intensity of the current that passes through the WC–Co combined particle, I_{p}, can be estimated [15] by the inner diameter of the die (which is the same as the sample diameter), ϕ, and intensity of the current that flows through the sintering