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VC and Cr_3C_2 doped WC-based nano-cermets prepared by MA and SPS

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Abstract

WC powders with average crystallite size of 10 nm were obtained through planetary ball milling of micron sized WC powder. Nanosized-WC powders were then mechanically milled with both 9 and 12 wt% Co, and the grain growth inhibitors VC and Cr_3C_2 in the range 0.2–0.8 wt%. Powder mixtures were then consolidated using spark plasma sintering (SPS) at two different temperatures, i.e. 1200 and 1300 °C. The microstructure, densification and mechanical properties of the resulting sintered nano-cermets were analyzed as a function of the type and amount of grain growth inhibitors, Co content, and sintering temperature. In general, the addition of VC and Cr_3C_2 was found to reduce densification. Nevertheless, the effect was found to be lower in Cr_3C_2 containing compositions with higher Co contents. The grain size variation was found by both a conventional line intersection method on FESEM micrographs, and by using grain analyzer software. VC was found to be comparatively more effective in restricting undesirable grain growth during the sintering processes. Moreover, the micro-hardness (H_{V30}) and fracture toughness were measured using micro-indentation and the results were compared for each composition to comparatively assess the individual effect of the inhibitors. Increasing the concentration of inhibitors was found to restrict grain growth even more and higher hardness values were obtained but only up to a critical inhibitor concentration, beyond which the hardness degrades.

Keywords: WC-based; Nanocrystalline alloys; Mechanical alloying; Spark plasma sintering

1. Introduction

Cemented carbides are known for their high hardness and toughness, and are widely used in cutting tool industry [1–3]. WC is a common choice for these carbides, as it exhibits high melting temperature (2785 °C) and high hardness values (16–22 GPa) [4]. WC, being very hard, is cemented with soft ductile metals such as Co, acting as a binding material and enhancing the mechanical properties and performance in cutting applications. Cobalt in particular is used to lower the consolidation temperature during sintering in the WC–Co system, in addition to enhancing the degree of densification of the composite [5]. Cobalt, as a second phase binding material, can be mixed with the WC, the hard matrix, through mechanical alloying, which results in a composite exhibiting a combination of improved hardness and toughness properties [6–9]. Mechanical alloying was preferred as it is known to be simple, versatile, economically viable and a scalable technique for production of large quantities of processed powders [10]. Higher amounts of binding materials in the mixture will lead to higher toughness values at the expense of hardness [4,5,11]. Therefore, controlling their amount in the mixed composition is very crucial in attaining adequate combination of properties in the resulted cermets. Multiple studies, in this regard, have been devoted to the analysis of the effect of binder addition on the cermets' properties [6,7].

One of the major challenges in developing usable materials via powder metallurgy route is consolidating the resulting powder mixtures, which is usually performed using a variety of techniques. These challenges are primarily related to the occurrence of undesirable grain growth during sintering, which is linked to following mechanisms. Firstly, the dissolution of the smaller particles which are having a larger ratio of surface atoms compared to larger particles and are more unstable due to larger surface energy; thus, tend to coalesce and promote

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grain growth.. Secondly, nanocrystalline WC–Co system has comparatively higher free surface energy and hence is more susceptible to grain growth. This will result in the loss of the nanostructure, degrading mechanical properties of the resulted cermets. Therefore, ultrafine-grained and nanostructured WC–Co composites have attracted great interest in the field of high-performance hard materials [12].

One of the preferred routes to overcome these issues is a non-conventional advanced sintering process, such as spark plasma-sintering (SPS), which is shown to be beneficial in a variety of studies [13,14]. SPS technique is chosen over conventional sintering processes because it exhibits higher heating rates and densification kinetics, in addition to lower sintering temperatures and shorter holding times under controlled high-pressure [15,16]. Further relevant reduction in co-efficient of friction and wear rate by 20 times in materials, when consolidated by the SPS technique was found by Espinosa-Fernández et al. [17]. Nevertheless, faster grain growth kinetics under SPS can also occur and add to the possibility of undesirable grain growth [18,19]. Therefore, limiting grain growth during the SPS process is a challenge for researchers when consolidating WC–Co cermets. To overcome this, the use of grain growth inhibitors during the sintering process helps reducing the exposed surface area of WC, thus limiting material transfer and hence grain growth rate [20]. Material transfer is also hindered as inhibitors reduce the WC solubility in cobalt. The cobalt binder possibly creates radicals over the WC surfaces and thus retard the solid transfer of material between grains [6]. Inhibitors also prevent transfer of phases and hence reduce the possibility of grain growth by creating an interface between WC and Co particles [19].

In addition, the amount and type of inhibitors added to the powder mixture, is another parameter that needs to be controlled, which if ignored may not inhibit grain growth leading to adverse effects [6], especially for the WC–Co system [21]. Different grain growth inhibitors have been used by researchers, and it has been found that VC and Cr_3C_2 are the most effective in restricting grain growth, due to their considerable solubility and mobility in liquid cobalt at lower sintering temperatures [19]. Nevertheless, systematic studies that highlight the specific role of these inhibitors need to be carried out. The effect of adding different kind of inhibitors to the WC-based cermets was presented in our previous work, however for fixed amounts aiming to assess their individual effect [22].

Therefore, the aim of the present study is to investigate the concentration effect of two grain growth inhibitors, i.e. VC and Cr_3C_2, in the range of 0.2–0.8 wt%, added to WC–9Co and WC–12Co nano-cermets. The powder mixtures were sintered at 1200 and 1300 °C via SPS to study the effect of different consolidation temperatures. The effect of changing the WC particle size from micron- to nano-scale was also investigated. Finally, an assessment of densification and mechanical properties was carried out.

2. Experimental procedure

The starting powder materials used in this study are listed in Table 1 and supplied by William-Rowland Co. UK. Nano-WC powders were prepared through ball milling of the micron-sized WC powders originally received from the manufacturer. Different amounts of both VC and Cr_3C_2, specifically 0.2, 0.4, 0.6, and 0.8 wt% were mechanically alloyed with WC–9Co and WC–12Co, as shown in Table 2. The milling experiments were carried out in a planetary ball mill (Fritsch Pulverisette 5) with an adjusted ball to powder ratio of 10:1. In addition, milling was performed in an inert Ar environment to reduce contamination of the powders. Ethyl-alcohol was added as a process control agent (PCA) in order to avoid excessive cold welding of the powders. Enhanced homogeneity powders mixture along with effective dispersion of WC within the Co matrix was achieved by using high energy probe sonication.

Each milled powder composition was placed in a cylindrical $20 \times 50 \times 50$ mm^3 graphite die, setup with graphite thin layer

Table 1
Characteristics of starting powder.

Powder	Purity	FSSS (μm)
WC	99.99%	3.5
Co	99.9%	1.3
VC	99.9%	2.02
Cr_3C_2	99.9%	1.82

Table 2
Sample composition and sintering temperature.

No.	Sample composition	Sintering temp. (°C)
01	WC(10 nm)–9Co–0.2VC	1200
02	WC(10 nm)–9Co–0.4VC	1200
03	WC(10 nm)–9Co–0.6VC	1200
04	WC(10 nm)–9Co–0.8VC	1200
05	WC(10 nm)–9Co–0.2Cr_3C_2	1200
06	WC(10 nm)–9Co–0.4Cr_3C_2	1200
07	WC(10 nm)–9Co–0.6Cr_3C_2	1200
08	WC(10 nm)–9Co–0.8Cr_3C_2	1200
09	WC(10 nm)–9Co–0.2VC	1300
10	WC(10 nm)–9Co–0.4VC	1300
11	WC(10 nm)–9Co–0.6VC	1300
12	WC(10 nm)–9Co–0.8VC	1300
13	WC(10 nm)–9Co–0.2Cr_3C_2	1300
14	WC(10 nm)–9Co–0.4Cr_3C_2	1300
15	WC(10 nm)–9Co–0.6Cr_3C_2	1300
16	WC(10 nm)–9Co–0.8Cr_3C_2	1300
17	WC(10 nm)–12Co–0.2VC	1200
18	WC(10 nm)–12Co–0.4VC	1200
19	WC(10 nm)–12Co–0.6VC	1200
20	WC(10 nm)–12Co–0.8VC	1200
21	WC(10 nm)–12Co–0.2Cr_3C_2	1200
22	WC(10 nm)–12Co–0.4Cr_3C_2	1200
23	WC(10 nm)–12Co–0.6Cr_3C_2	1200
24	WC(10 nm)–12Co–0.8Cr_3C_2	1200
25	WC(10 nm)–12Co–0.2VC	1300
26	WC(10 nm)–12Co–0.4VC	1300
27	WC(10 nm)–12Co–0.6VC	1300
28	WC(10 nm)–12Co–0.8VC	1300
29	WC(10 nm)–12Co–0.2Cr_3C_2	1300
30	WC(10 nm)-12Co-0.4Cr_3C_2	1300
31	WC(10 nm)–12Co–0.6Cr_3C_2	1300
32	WC(10 nm)–12Co–0.8Cr_3C_2	1300

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