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Characterization of nano-cemented carbides Co-doped with vanadium and chromium carbides

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ABSTRACT

Cemented carbides are ultra-hard composites used in a variety of applications that call for tough and wear-resistant materials. Conventional cemented carbide typically consists of grains of tungsten carbide (WC) embedded in a cobalt (Co)-based binder matrix. Often compounds are added that inhibit the growth of the WC grains and thus ensure a fine and homogeneous grain structure, to optimize hardness and toughness. Here, we report a detailed study of the structure and properties of cemented carbides that contain combined grain-growth inhibitors, i.e. vanadium carbide (VC) and chromium carbide (Cr_3C_2). The concentrations were varied and the mixtures were sintered at 1200 °C and 1300 °C to achieve optimum combination of properties. Alloy systems with a combination of both VC and Cr_3C_2 grain-growth inhibitors displayed superior mechanical properties compared to those in which only one inhibitor compound was present. The inclusion of VC produced lower densification with finer grains, whereas the incorporation of Cr_3C_2 produced a harder and tougher carbide. The compound WC–12Co–0.2VC–0.8Cr_3C_2 reached nearly full densification, with an average grain size of 50 nm, a microhardness of 1690 H_{v30} and a fracture toughness of 12.5 MPa·$m^{1/2}$. It is proven in this work that achieving a balanced concentration of both inhibitors is extremely vital to reach an optimum combination of properties.

1. Introduction

WC–Co cemented carbides are widely used in machining, cutting, mining and drilling tools as well as for wear-resistant equipment. Their wide application stems from their combination of desirable properties, including large hardness, wear-resistance and fracture-toughness values [1–4]. Moreover, their great hardness (16–22 GPa) and stability at high working temperatures have led to a dominance of WC over other common types of hard carbides, such as SiC, TaC and TiC [5].

Aside from possessing high hardness values, cemented carbides must exhibit appreciable fracture toughness to enable efficient use in applications where they experience a range of loads and jerks. For this reason, they are mixed during processing with ductile metals (binders) such as iron, nickel and Co. However, high concentrations of these binders in the composite mixture can result in increased toughness at the expense of reduced hardness [4,5]. Therefore, finding appropriate concentrations of the soft metallic binding material is essential for controlling the microstructure, and hence the properties, of the resulting composites [6,7]. Among other binding materials, cobalt is commonly added to WC-based composites to enhance their toughness values, to lower the consolidation temperature during sintering of the WC–Co system and to enhance the densification of the composite [4].

WC-based carbides can be synthesized using a variety of methods, such as in-situ reactions [8] and powder metallurgy [7]. In powder processing techniques, powder particles of alloys' constituents are cold-welded, fractured and re-welded during ball mill operations [6–10], leading to uniform dispersion of second-phase particles. Mechanical alloying, which is a powder processing technique, is simple, versatile and economically viable and can be scaled up for the production of large quantities [11]. One of the primary challenges in powder processing is to consolidate the processed powders without allowing the high temperatures associated with sintering to induce undesirable microstructural changes. In general, powder mixtures can be consolidated through either conventional or non-conventional sintering processes. Non-conventional sintering processes have the advantage of offering larger heating rates, higher diffusion kinetics, lower sintering temperatures and lower dwell times. All of these sintering parameters contribute to the fabrication of finer-grained microstructure sand the possible retention of nanostructures [7,12]. Therefore several non-conventional advanced sintering techniques, such as microwave and spark plasma sintering (SPS) have been used to process WC–Co composites [13–15].

During sintering of carbide composites, undesirable grain growth can occur and result in substantial deterioration of the carbide's mechanical properties [16,17]. Grain growth can result from the dissolution of smaller particles because they have fewer attached atoms than do large particles, which are more stable and reduce the overall energy of the system. In addition, nanocrystalline WC–Co systems exhibit

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comparatively high free-surface energies and hence are more susceptible to grain growth [17,18]. It should be noted that the use of SPS to sinter composites can induce grain growth because the grain growth kinetics are faster under SPS than under other sintering techniques [16,19].

One way to limit grain growth during sintering is to add grain-growth inhibitors to the powder composition. Grain growth is primarily restricted by reducing the exposed WC surface area, which limits material transfer among particles. Moreover, inhibitors help to create radicals over WC surfaces and thus diminish both the solubility of WC in cobalt and the solid transfer of material between grains [6]. These inhibitors form an interface between the WC and Co particles that prevents the transfer of phases and hence reduces the possibility of grain growth [19]. Nevertheless, the addition of inhibitors must be moderate, or excessive addition can have an adverse effect and end up not inhibiting grain growth as desired [6], especially in WC–Co systems [20]. Early research that employed different grain-growth inhibitors found that VC and Cr_3C_2 are the most effective in restricting grain growth, owing to their appreciable solubility and mobility in liquid cobalt at lower sintering temperatures [21–23]. However, choosing the right type and quantity of grain growth inhibitor remains a challenge, especially when using a variety of processing routes and trying to optimize processing [24,25].

In our previous work [26], we studied the effect of adding different concentrations of VC and Cr_3C_2 as grain growth inhibitors on the final microstructure of WC-based nanocomposites. However, it would be of great interest to investigate the effect of adding both inhibitors at the same time. Therefore, the aim of the present study is to investigate the combined effect of VC and Cr_3C_2 grain-growth inhibitors on the mechanical properties of WC–Co nanocomposites. The two inhibitors were added in varying combinations to WC–Co carbide with Co concentrations of 9 wt.% (WC–9Co) and 12 wt.% (WC–12Co). Each powder mixture was consolidated using SPS at temperatures of 1200 °C and 1300 °C and the resulting densification and mechanical properties were studied. The effect of the initial WC crystal sizes on the overall behavior of the composites was analyzed (with crystal size ranging from the micron-scale to the nano-scale). In addition, the effect of varying the binder quantity and sintering temperature on the synthesized composites was investigated.

2. Experimental procedure

2.1. Composite preparation

The elemental powder materials used for the study are listed in Table 1 and provided by William-Rowland Co., UK. As in our previous work [23], as-received WC powders were milled from 3.5 μm to approximately 10 nm by planetary ball milling (Fritsch Planetary Mill, Pulverisette-5, Germany). Such route has proven to be effective in resulting nanocrystalline WC powders, relative to other new chemical-based methods that can achieve as small as 20–80 nm in size [27]. Milling occurred in an argon atmosphere for up to 72 h using WC balls and vials (balls having a uniform size of 8 mm diameter) with a ball-to-powder ratio of 10:1 and a rotational speed of 300 rpm. The particle sizes of the milled WC powder were measured using a particle-size analyzer and the powder morphology and phase analyses were conducted using XRD (Bruker AXSD-8 with Cu-Kα radiation)

Table 1
Starting powders used to form nano-crystalline carbide composites.

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.

Sample	Carbide composition	Sintering temperature (°C)
1	WC (10 nm)–9Co–0.5VC–0.5Cr_3C_2	1200
2	WC (10 nm)–9Co–0.8VC–0.2Cr_3C_2	1200
3	WC (10 nm)–9Co–0.2VC–0.8Cr_3C_2	1200
4	WC (10 nm)–9Co–0.5VC–0.5Cr_3C_2	1300
5	WC (10 nm)–9Co–0.8VC–0.2Cr_3C_2	1300
6	WC (10 nm)–9Co–0.2VC–0.8Cr_3C_2	1300
7	WC (10 nm)–12Co–0.5VC–0.5Cr_3C_2	1200
8	WC (10 nm)–12Co–0.8VC–0.2Cr_3C_2	1200
9	WC (10 nm)–12Co–0.2VC–0.8Cr_3C_2	1200
10	WC (10 nm)–12Co–0.5VC–0.5Cr_3C_2	1300
11	WC (10 nm)–12Co–0.8VC–0.2Cr_3C_2	1300
12	WC (10 nm)–12Co–0.2VC–0.8Cr_3C_2	1300

and FESEM (JEOL JSM-6460), respectively. Subsequently, the nano-WC powders were mechanically alloyed with varying concentrations of Co (from 9 to 12 wt.%). Different combinations (0.2, 0.5 and 0.8 wt.% to achieve a maximum concentration of inhibitors as 1 wt.% in each case) of both VC and Cr_3C_2 were added to the WC–Co composites using ethyl-alcohol as the medium. The final compositions of all the synthesized nanocomposites are listed in Table 2. To increase homogeneity of these mixed powders and the effective dispersion of WC within the Co matrix, high-energy probe sonication was used. It is important also to mention that milling was conducted in a dry environment and no process control agent (PCA) were added as WC would not be experiencing excessive cold welding.

All powder compositions were consolidated using SPS at 1200 °C and 1300 °C (Table 2) in order to investigate the effect of sintering temperature on the microstructure and mechanical properties of the resulting carbides. The powder mixtures were placed into a cylindrical graphite die with thin graphite-sheet inserts (dimensions 20 × 50 × 50 mm). The sintering machine (Type HP D-50, FCT Systeme, Rauenstein, Germany) was maintained under a vacuum of 1 hpa (1 mbar) with a constant pulsed electric current of 0.5 Amp. a constant pulse duration of 10 ms and a pulse pause at 5 ms.

One of the key advantages of using SPS for sintering is that it enables distributed heating of the particles within the composite from the surface to the inner regions of the sample. In addition, the shortened processing time prevents undesirable grain growth and a corresponding loss of the nanostructure. Sintering was carried out at 1200°C and 1300 °C with a heating rate of 100 °C per minute for 10 min at a pressure

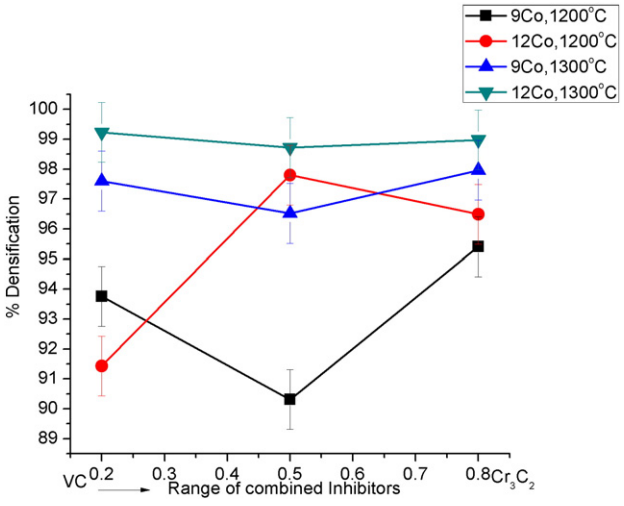

Fig. 1. Carbide densification as a function of inhibitor concentration, sintering temperature and Co content. The concentration of VC increases towards the right hand side of the X-axis.