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Short communication

Microstructural control of ultrafine and nanocrystalline WC–12Co–VC/Cr_3C_2 mixture by spark plasma sintering

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Abstract

The aim of this present work is to study the effect of VC and/or Cr_3C_2 in densification, microstructural control and mechanical behaviour of WC–12Co ultrafine and nanocrystalline mixtures, consolidated by spark plasma sintering at 1100 °C, applying a pressure of 80 MPa in combination with a heating rate of 100 °C min^{-1}. Nanocrystalline and ultrafine mixtures with an average size of 30 nm and 100–250 nm, respectively, with the addition of 1 and 0.5 wt.% of VC/Cr_3C_2 grain growth inhibitors, respectively, were investigated. The density, microstructure, hardness and fracture toughness of the consolidated samples were measured and observed. The addition of VC inhibitor allows an excellent grain growth control keeping microstructures with an average grain size of 154 nm. The hardness values and fracture toughness obtained were about 2000 HV_{30} and above 10 MPa $m^{1/2}$, respectively.

Keywords: A. WC–Co cemented carbides; B. Grain growth inhibitors; C. Spark plasma sintering; D. Microstructure; E. Mechanical properties

1. Introduction

WC–Co hardmetals are widely used as cutting tools and dies due to their high wear resistance and toughness [1–3]. The hardness and strength of WC–Co hardmetals can be improved by decreasing the WC grain size to the nanometer scale. Manufacturing WC–Co cemented carbides with fine grain size, even with the nanometer scale, is a good method to improve its properties.

The production of bulk nanocrystalline (grain sizes < 100 nm) cemented tungsten carbides remains a technological challenge because of the rapid grain growth during sintering. This coarsening of nanosized powders is an issue that affects not only the cemented tungsten carbide, but also the manufacture of bulk nanocrystalline materials of a broad range of ceramic and metallic materials. Compared to the sintering of conventional micron-sized powders, the sintering of nanosized powders has an additional challenge of retaining nanoscaled grain sizes upon achieving full densification [4,5]. To control the grain growth in ultrafine WC–Co composites, one of the keys is a suitable selection of the second-phase additives as grain growth inhibitors. By far vanadium carbide (VC) and chromium carbide (Cr_3C_2) are the most effective grain growth inhibitors due to their high solubility and mobility in cobalt phase at lower temperatures [6–9]. In addition, the grain growth can be inhibited to a certain extent by using special sintering technologies to accelerate the heating rate, increase the densification rate, decrease the sintering temperature and shorten the holding time, such as microwave sintering [10], rapid hot pressing sintering [11], spark plasma sintering (SPS) [12], and so on. Especially, the spark plasma sintering, which is also known as pulse electric current sintering (PECS), is a newly developed sintering method, which enables a powder compact to be sintered by Joule heat by high pulsed electric current through the compact and has been described recently for the sintering of composites, functionally graded materials and nanocrystalline materials. It is therefore highly interesting to investigate the effect of grain growth inhibitors on the WC grain growth and mechanical properties of WC–Co materials consolidated by PECS [13].

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In this paper, the ultrafine and nanocrystalline WC–Co powders adding the various amounts of inhibitor VC/Cr_3C_2 were consolidated to full density by SPS at 1100 °C under a maximum pressure of 80 MPa. The purpose is to produce nearly full density and fine grain size samples. The effect of the amount of inhibitor addition on the density, microstructure, fracture toughness and hardness was investigated.

2. Experimental

The raw materials were two different powders (i) WC–12Co mixture nanocrystalline powders with WC grain size of 30–80 nm (N) obtained by the spray conversion process and manufactured by Inframat Advanced Materials, (ii) WC–12Co mixture ultrafine powders with WC grain size of 100–250 nm (UF) obtained by vapour phase synthesis and manufactured by Nanostructured & Amorphous Materials, Inc. The appropriate amounts of vanadium carbide and chromium carbide were added to the raw powders, which were used as grain growth inhibitors. Free carbon was added to all compositions fabricated from N powder in order to adjust carbon content in the sintered sample.

The raw powders were milled for 2 h in a Fritsch Pulverisette 7 planetary ball mill using WC media of 5 mm diameter, isopropyl alcohol as the liquid medium and under argon atmosphere. The ball-to-powder weight ratio was 10:1 and the rotation speed was 700 rpm. After wet milling, powder mixes were dried at 120 °C for 3 h under protective argon atmosphere.

The powder samples were placed into a graphite die with an inner diameter of 20 mm and uniaxially cold pressed at 15 MPa. Then, they were introduced into a spark plasma sintering apparatus HP D 25/1 (FCT Systeme) under low vacuum (10^{-1} mbar) and sintered at 1100 °C for 5 min under an applied pressure of 80 MPa and a heating rate of 100 °C min^{-1}. Powder morphology and microstructures of the sintered materials have been characterized by field emission scanning electron microscopy (FESEM), Hitachi S4100. The mean WC grain size has been measured by lineal intercept method according to the standard specification ASTM E112. The uncertainty for the mean grain sizes has been calculated for a 95% confidence interval. The density has been determined by Archimedes' principle using alcohol immersion according to the ISO 3369 standard. The uncertainly for density values has been calculated for a 95% confidence interval. The porosity has been obtained using quantitative metallography of polished surfaces according to the ISO 4505 standard. Vickers hardness measurements have been carried out by applying a load of 30 kg and the standard specification ASTM E92-72. Indentation fracture toughness K_{IC} has been estimated by applying the Palmqvist model to cracks generated by indentation [14].

3. Results and discussion

Designation, compositions, relative density, porosity and mean grain size of the WC–12Co mixtures consolidated by SPS at 1100 °C are shown in Table 1. The nanocrystalline mixtures reach a high density, but only the mixture without the inhibitor (N) presents full densification. The reduction of the density value of the sintered samples with inhibitors is associated with the limitation of the phenomena of diffusion and migration of Co [15]. However, the density values achieved are much higher than those obtained by other authors [4,5,16]. This is probably due to nano-powder use and a higher pressure in the consolidation process. Sintered samples from UF mixtures show residual porosity.

The displacement, pressure and the temperature with the holding time during the SPS cycles for the compositions obtained from the N mixture, are shown in Fig. 1. The addition of inhibitors does not significantly affect the shrinkage of the mixtures. Only the NV mixture introduced a delay in the displacement curve, although the maximum difference does not exceed 3%. The behaviour of ultrafine material without additives (UF) is similar to N nanocrystalline mixtures. However, the addition of inhibitors in UF mixtures produces a difference of more than 7% to 1100 °C. This effect in the kinetics of densification is probably due to the high amount of additives in these compositions [16].

The microstructure of the sintered materials from N and NV compositions can be observed in Fig. 2. In both samples, the microstructural inhomogeneity can be appreciated. Cobalt segregations and lack of wettability are typical of the solid phase sintering which increases the contiguity between carbides, promoting coalescence phenomena.

Fig. 2 shows the effect of VC on grain growth inhibition by SPS. This has allowed the obtaining of cemented carbides near-nanocrystalline (NV) with an average grain size of 154 nm, one of the smallest ones reported in the literature [15]. The mechanisms of grain growth inhibition are not clearly

Table 1
Composition, relative density, porosity and sintered grain size of the WC–12Co mixtures consolidated by SPS at 1100 °C.

Samples	Mixture, WC–12 wt.%Co	Additives (wt.%)			Relative density (%)	Porosity	Mean WC grain size (nm)
		Cr_3C_2	VC	C			
N	N	0	0	0.8	99.94 ± 0.09	<A02 <B02	216 ± 12
NCr	N	1	0	0.8	99.74 ± 0.10	A04 B02	207 ± 10
NVCr	N	0.5	0.5	0.8	99.15 ± 0.10	A06 B02	190 ± 11
NV	N	0	1	0.8	98.95 ± 0.11	A06 B02	154 ± 10
UF	UF	0	0	0	98.56 ± 0.12	A06 B02	248 ± 12
UFCr	UF	0.5	0	0	98.18 ± 0.15	A06 B04	240 ± 12
UFV	UF	0	0.5	0	97.99 ± 0.16	A06 B04	235 ± 13

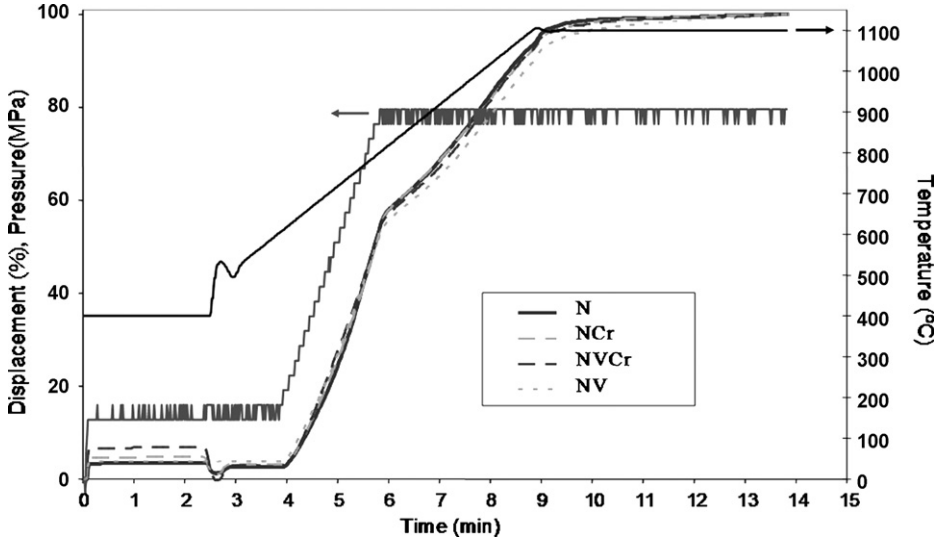

Fig. 1. Displacement, pressure and temperature versus time during SPS for N mixtures.

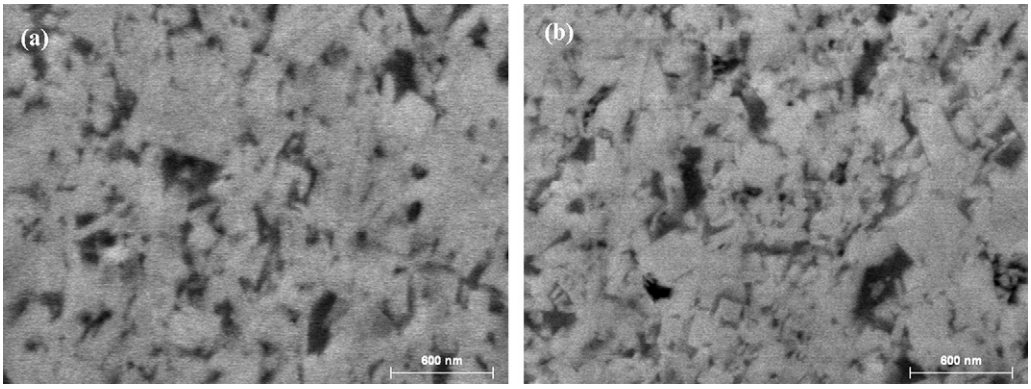

Fig. 2. FESEM micrographs of consolidated materials by SPS: (a) N, (b) NV.

determined [4,11,17]. They may be due to the formation of a thin film (Cr/V,W)C_x on the surface of WC crystals, limiting phenomena diffusion involved in grain growth [15]. Sintered materials from UF mixtures exhibit average grain sizes in the range 235–250 nm. These powders show a grain growth lower than nanocrystalline powders, associated with slower grain growth kinetic at low temperature due to its higher initial grain size. This effect of initial grain size coupled with the presence of Cr and V in the starting mixture justifies the limited effect of extra addiction of inhibitors on final microstructure.

The hardness and fracture toughness of the samples are compared in Fig. 3. The materials obtained from N mixture have excellent hardness, due to high densification and reduced grain growth. The VC inhibitory effect allows obtaining values of hardness close to 2000 HV_{30}. This improvement in hardness is accompanied by a loss of fracture toughness. However, the fracture toughness values obtained are higher than 10 MPa $m^{1/2}$. The materials obtained from the UF mixture present hardness values below those of the N mixture. Therefore, reducing the size of the raw material is important. The similar values of fracture toughness may be due to loss of strain capacity of the binder for the highest concentration of Cr_3C_2/VC or changes in the mechanisms of deformation and crack propagation by the effect of interfaces [15,18].

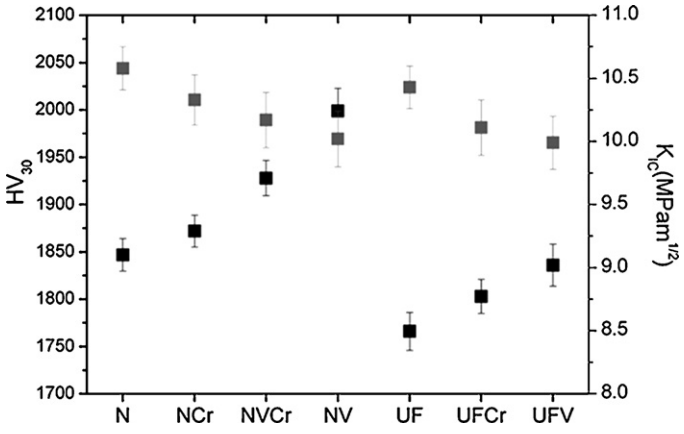

Fig. 3. Hardness and fracture toughness values of the sintered samples.

4. Conclusions

Nearly fully densified WC–12Co cemented carbides with VC or Cr_3C_2 addition were obtained by solid-state SPS at 1100 °C. The addition of inhibitors, especially VC, is more efficient in the control of grain growth in the solid state may be due to the formation of a thin film (Cr/V,W)C_x on the surface of WC. The grain growth control has enabled to obtain near-nanostructured materials with average WC grain size of 154 nm with excellent values of hardness and fracture toughness.

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