**Microstructural control of ultrafine and nanocrystalline WC-12Co-VC/$Cr_2C_3$ mixture by spark plasma sintering**

V. Bonache[1*], M.D. Salvador[1], V.G. Rocha[2], A. Borrell[3]

[1]Instituto de Tecnología de Materiales (ITM). Universidad Politécnica de Valencia. Camino de Vera, s/n, 46022 Valencia, Spain

[2]Fundación ITMA, Parque Tecnológico de Asturias, 33428 Llanera (Asturias), Spain

[3]Centro de Investigación en Nanomateriales y Nanotecnología (CINN) (Consejo Superior de Investigaciones Científicas - Universidad de Oviedo - Principado de Asturias), Parque Tecnológico de Asturias, 33428 Llanera (Asturias), Spain

*Corresponding Author:

Name: Victoria Bonache

Phone: +34 692512435

Fax: +34 963877629

E-mail: vicbobe@doctor.upv.es

Postal Address:

Instituto de Tecnología de Materiales

Edif. 5E. 1ª Planta

Universidad Politécnica de Valencia

Camí de Vera s/n. E-46022

Valencia, Spain.

**ABSTRACT**

The aim of this present work is to study the effect of VC and/or $Cr_2C_3$ in densification, microstructural control and mechanical behaviour of WC-12Co ultrafine and nanocrystalline mixtures, consolidated by spark plasma sintering at 1100 ºC, applying a pressure of 80 MPa in combination with a heating rate of

100 ºC/min. Nanocrystalline and ultrafine mixtures with an average size of 30 nm and 100-250 nm, respectively, with the addition of 1 and 0.5wt.% 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:** Grain growth; Microstructure; Spark plasma sintering; 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 carbide, 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 [6-8]. 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 [9], rapid hot pressing sintering [10,11], 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].

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 ºC 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 were investigated.

## 2. Experimental

The raw materials were two different powders i) WC-12Co mixture nanocrystalline powders with particle 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 particle 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 atmosphere of argon. 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 ºC for 3 h in protective argon atmosphere.

The powder samples were placed into a graphite die with an inner diameter of 20 mm and cold uniaxially 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 ºC for 5 min under an applied pressure of 80 MPa and a heating rate of 100 ºC $min^{-1}$. Characterization of powder morphology and microstructures of the sintered materials have been characterized by field emission scanning electron microscopy (FE-SEM), Hitachi S4100. The estimation of WC grain size has been measured using two methods: lineal intercept method according to the standard specification ASTM E112 and image analysis Image-Pro Plus software. The density has been determined by Archimedes' principle using alcohol immersion according to the ISO 3369 standard. The porosity has been obtained using quantitative metallography of polished surfaces according to the ISO 4505 standard. Vickers hardness measurements have been carried out 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 ºC are shown in Table 1. The nanocrystalline mixtures reach a high density, but only the mixture without the inhibitor (N) present 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-powders 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 Figure 1. The addition of inhibitors does not significantly affect the contraction of the mixtures. Only the mixture (NV) 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 ºC. 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 (N) and (NV) can be observed in Figure 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.

Figure 2 shows the effect of VC on grain growth inhibition by SPS. This has allowed the obtaining of cemented carbides nanocrystalline (NV) with an average grain size of 154 nm, one of the smallest ones reported in literature [15]. The mechanisms of grain growth inhibition are not clearly determined [4,11,17]. Although, 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].

The hardness and fracture toughness of the samples are compared in Figure 3. The materials obtained from a mixture (N) 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 mixture (N). 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 $Cr_2C_3$/VC or changes in the mechanisms of deformation and crack propagation by the effect of interfaces [18].

## 4. Conclusions

Nearly fully densified WC-12Co cemented carbides with VC or $Cr_3C_2$ addition were obtained by solid-state SPS at 1100 ºC. 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.

## Acknowledgements

The work is supported financially by the Spanish Ministry of Science and Innovation by means of the project MAT 2006-12945-C03-C02. A. Borrell, is grateful to this Ministry for the mobility grant to the Institute of Materials Technology (ITM) of the Polytechnical University of Valencia, Spain.

## References

[1] C. Jia, L. Sun, H. Tang, X. Qu, Hot pressing of nanometer WC-Co powder, International Journal of Refractory Metals and Hard Materials 25 (2007) 53-56.

[2] H.C. Kim, I.J. Shon, J.K. Yoon, J.M. Doh, Consolidation of ultra fine WC and WC-Co hard materials by pulsed current activated sintering and its mechanical properties, International Journal of Refractory Metals and Hard Materials 25 (2007) 46-52.

[3] H.C. Kim, I.K. Jeong, I.J. Shon, I.Y. Ko, J.M. Doh, Fabrication of WC-8 w.t.%Co hard materials by two rapid sintering processes, International Journal of Refractory Metals and Hard Materials 25 (2007) 336-340.

[4] D. Sivaprahasam, S.B. Chandrasekar, R. Sundaresan, Microstructure and mechanical properties of nanocrystalline WC-12Co consolidated by spark plasma sintering, International Journal of Refractory Metals and Hard Materials 25 (2007) 144-152.

[5] S.G. Huang, K. Vanmeensel, L. Li, O. Van der Biest, J. Vleugels, Influence of starting powder on the microstructure of WC-Co hardmetals obtained by spark plasma sintering, Materials Science and Engineering A 475 (2008) 87-91.

[6] A.G.P. Da Silva, C.P. De Souza, U.U. Gomes, F.F.P. Medeiros, C. Ciaravino, M. Roubin, A low temperature synthesized NbC as grain growth inhibitor for WC-Co composites, Materials Science and Engineering A 293 (2000) 242-246.

[7] C.W. Morton, D.J. Wills, K. Stjernberg, The temperature ranges for maximum effectiveness of grain growth inhibitors in WC-Co alloys, International Journal of Refractory Metals and Hard Materials 23 (2005) 287-293.

[8] D.F. Carroll, Sintering and microstructural development in WC/Co-based alloys made with superfine WC powder, International Journal of Refractory Metals and Hard Materials 17 (1999) 123-132.

[9] C. Lin, E. Kny, G. Yuan, B. Djuricic, Microstructure and properties of ultrafine WC-0.6VC-10Co hardmetals densified by pressure-assisted critical liquid phase sintering, Journal of Alloys and Compounds 383 (2004) 98-102.

[10] E. Breval, J.P. Cheng, D.K. Agrawal, P. Gigl, M. Dennis, R. Roy, A.J. Papworth, Comparison between microwave and conventional sintering of WC/Co composites, Materials Science and Engineering A 391 (2005) 285-295.

[11] S.G. Huang, J. Vleugels, L. Li, O. Van der Biest, Proceeding of the 16th international Plansee seminar. 2 (2005) 378-389.

[12] S.I. Cha, S.H. Hong, B.K. Kim, Spark plasma sintering behavior of nanocrystalline WC-10Co cemented carbide powders, Materials Science and Engineering A 351 (2003) 31-38.

[13] A. Michalski, D. Siemiaszko, Nanocrystalline cemented carbides sintered by the pulse plasma method, International Journal of Refractory Metals and Hard Materials 25 (2007) 153-158.

[14] D.K. Shetty, I.G. Wright, P.N. Mincer, A.H. Clauer, Indentation fracture of WC-Co cermets, Journal of Materials Science 20 (1985) 1873-1882.

[15] Z.Z. Fang, X. Wang, R. Taegong, K.S. Hwang, H.Y. Sohn, Synthesis, sintering, and mechanical properties of nanocrystalline cemented tungsten carbide - A review, International Journal of Refractory Metals and Hard Materials 27 (2009) 288-299.

[16] L. Sun, C.C. Jia, M. Xian, A research on the grain growth of WC-Co cemented carbide, International Journal of Refractory Metals and Hard Materials 25 (2007) 121-124.

[17] L. Sun, C.C. Jia, C.G. Lin, R.J. Cao, VC addition prepared ultrafine WC-11Co composites by spark plasma sintering, Journal of Iron and Steel Research International 14 (2007) 85-89.

[18] J.M. Sanchez, A. Ordoñez, R. Gonzalez, HIP after sintering of ultrafine WC-Co hardmetals, International Journal of Refractory Metals and Hard Materials 23 (2005) 193-198.