Materials Research. 2017; 20(3): 780-785
DOI: http://dx.doi.org/10.1590/1980-5373-MR-2016-0889

The Effect of Cr_3C_2 and TaC Additives on Microstructure, Hardness and Fracture Toughness of WC-6Co Tool Material Fabricated by Spark Plasma Sintering

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Received: November 29, 2016; Revised: March 8, 2017; Accepted: April 5, 2017

Spark plasma sintering has been used to successfully produce WC-6Co-xCr_3C_2, WC-6Co-xTaC (x = 0.2, 0.6, 1.0) and WC-6Co-xCr_3C_2-xTaC (x = 0.1, 0.3, 0.5) cemented carbides. The spark plasma sintered compacts were investigated by scanning electron microscopy, hardness tests and fracture toughness tests. The results were compared to an additives-free WC-6Co cemented carbide consolidated under the same process parameters and commercial ISO K10 inserts. By using Cr_3C_2 and TaC additives, it is possible to improve the hardness and fracture toughness of WC-Co cemented carbides. The best combination of hardness (1936 ± 15 HV_{30}) and fracture toughness (10.38 ± 0.46 $MPa{\cdot}m^{1/2}$) was obtained by the WC-6Co-1Cr_3C_2.

Keywords: *Spark plasma sintering, Cemented carbide, Chromium carbide, Tantalum carbide, Mechanical properties*

1. Introduction

Several authors' studies[1-3] have concentrated on the relationship of the microstructure and properties of the cutting zone in industrial applications. It is well known that WC-Co cemented carbides are usually used as tool materials for machining, mining, cutting and drilling tools as well as wear resistance parts. It is worth mentioning that the most likely dominant wear mechanisms of WC-Co tools at low speeds/temperatures during the machining process are abrasion, followed by adhesion at moderate speeds/temperatures and then diffusion at high speeds/temperatures. Of course, all of them cannot occur simultaneously, and the dominant wear mechanism depends on the machining conditions and work materials[4-5]. Morphologically, WC-Co cemented carbides consist of hard WC embedded in ductile Co[6-9]. Increasing the WC fraction can increase hardness and wear resistance, while fracture toughness can increase by increasing the Co content[9-10]. That is why WC-Co cemented carbides with 5-10 wt% Co are the most promising materials offering a very good balance of hardness and fracture toughness[10]. Moreover, to increase the hardness and fracture toughness, some authors modified the structure of these materials with additives such as Cr_3C_2[11], TaC[12-13], TiC[13], VC[12] and NbC[14]. Siwak and Garbiec in a previous study[15] proved that an addition of 2 wt% Cr_3C_2 and 2 wt% TaC to WC-5Co cemented carbides increased the hardness from 1512 to 2105 and 1725 HV_{30} respectively. The same relationship was confirmed by other authors. Su et al.[10] showed that an addition of 0.4 wt% TaC to WC-9Co increased the hardness from 927 to 1124 HV_{30}. The same effect was observed by Espinosa-Fernández et al.[11], where an addition of 1 wt% Cr_3C_2 to WC-12Co cemented carbides increased the hardness from 1503 to 1668 HV_{30} for conventional sintering and from 1847 to 1872 HV_{30} for spark plasma sintering. In recent years spark plasma sintering has become increasingly more attractive for the fabrication of WC-Co tool materials in view of the rapid heating and cooling, short holding time and controllable high compaction pressure over conventional powder metallurgy methods[16-17]. That is why in this paper the results on the spark plasma sintering of WC-6Co tool materials with additions of Cr_3C_2 and TaC additives are reported. The goal of the work was to study the effect of Cr_3C_2 and TaC additions to the basic WC-6Co cemented carbide on the microstructure and main mechanical properties such as hardness and fracture toughness.

2. Experimental Procedure

Nanocrystalline WC-6Co (99.9%, grain size 40-80 nm), microcrystalline Cr_3C_2 (99.9%, particle size ~6 μm) and microcrystalline TaC (99.9%, particle size ~3 μm) powders supplied by Inframat Advanced Materials, USA were used as the initial powders. The morphology of the powders was examined by scanning electron microscopy using a Vega 5135 (Tescan, USA) microscope with an energy dispersive X-Ray spectrometer. The WC-6Co and Cr_3C_2, WC-6Co and TaC, WC-6Co and Cr_3C_2 and TaC powders were mechanically mixed for 5 h using a mixer, similar to a Turbula shaker-

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mixer. The obtained powder mixtures were densified by spark plasma sintering using an HP D 25-3 furnace (FCT, Germany). The sintering temperature of 1450°C was reached at the heating rate of 600°C/min. The pressure level on the specimens was kept constant at 60 MPa throughout the sintering process. The vacuum level of the sintering chamber was set at 5 Pa. After a 5 min holding time, the spark plasma sintered compacts were rapidly cooled to room temperature. Cylindrical specimens with dimensions of 20 mm in diameter and 5 mm high were fabricated.

Vickers hardness measurements using a hardness tester FV-700 (Future-Tech, Germany) were carried out by applying a load of 294.2 N for 7 s. The fracture toughness (K_{1c}) was calculated based on the crack length measured from the corner of the indenter made by Vicker's indentation using the following equation (1):[18]

$$K_{1c} = 0,15 \cdot \sqrt{\frac{HV30}{\Sigma l}} \qquad (1)$$

where HV 30 is the Vickers hardness measured under a load of 294.2 N and Σl is the total length of cracks initiated from the corners of the indenter. The microstructure of the sintered materials was observed on polished cross-sectioned surfaces by scanning electron microscopy using an Inspect S (FEI, Netherlands) microscope. The scheme of the experimental procedure of fabricating the cemented carbide specimens and their examination is presented in Figure 1. A photograph of one of the obtained cemented carbide specimens is presented in Figure 2.

3. Results and Discussion

Figure 3 shows the second electron SEM micrographs of the initial powders morphology. The main component of premixed WC-6Co powder is WC, whose particles are multi-angular in shape in contrast to the Co powder particles which are spherical. The Cr_3C_2 powder particles are generally rounded and slightly agglomerated in contrast to the TaC powder particles which are spherical in shape but significantly agglomerated. The EDS analysis showed that only the main peaks corresponding to the basic elements are clearly visible in the spectra. It means that no contaminations were detected above the EDS detection limit.

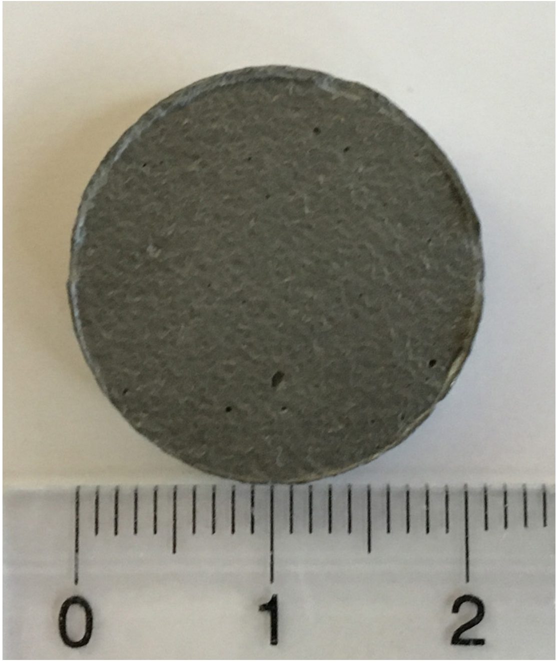

Figure 2. The photograph of one of the SPSed WC-Co cemented carbide specimen.

Figure 4 shows the backscattered electron SEM micrographs of the obtained sintered compacts. The microstructure observations allowed the authors to highlight the ceramic and the binder distribution. The bright and grey contrast phases are the WC ceramic and Co binder respectively. The black areas correspond to pores. Rumman et al.[19] explained that in WC-Co cemented carbides pores tend to decrease in size with an increasing compaction pressure. They applied a compaction pressure ranging between 30 and 80 MPa and obtained a reduction in porosity from 3.12 to 2.12%. Moreover, the pores found on the low compaction pressure specimens were bigger and less homogenously distributed as opposed to the high compaction pressure specimens. In this work, the microstructures are very fine, with a uniform grain-size distribution, only in the basic specimen and the specimen with the addition of 0.2 wt% Cr_3C_2. In other specimens with 0.2 wt% additives, porosity with pores up to a few µm is apparent within the microstructure. The cemented carbides with 0.6 wt% additives have bigger pores non-uniformly

Figure 1. The scheme of the experimental procedure of the fabricating the WC-Co cemented carbide specimens and their examination.

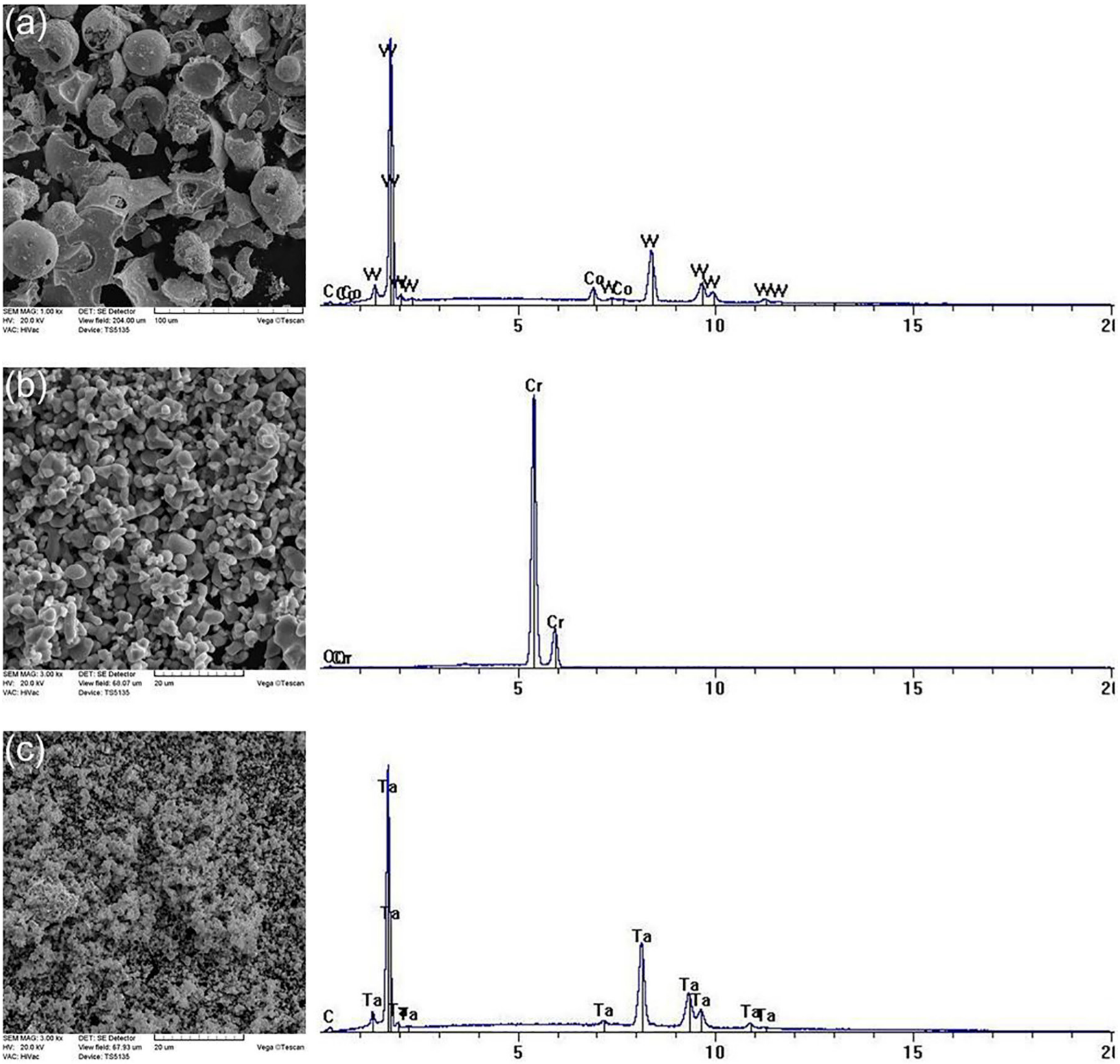

Figure 3. Second electron SEM micrographs and EDS analysis results of initial powders: (a) WC-6Co, (b) Cr_3C_2 and (c) TaC, various magnification.

distributed in the microstructure, whereas microstructural defects in the form of carbide agglomerates are noted in the WC-6Co-0.6TaC specimen. The same carbide agglomerates are also noted in the WC-6Co-0.5Cr_3C_2-0.5TaC specimen, but the size of these agglomerates is much higher. Probably one of the reason for carbide agglomerates formation is the mixing process in dry conditions and the resulting segregation. On the other hand, the same mixing process was used for preparing the WC-5Co-2Cr_3C_2 and WC-5Co-2TaC powder mixtures[15] and no carbide agglomerates were present in the microstructures. Anyway, one of keys to preventing the agglomeration phenomenon might be to use ultrasound in the process of mixing the suspension consisting of the initial powders and liquid as in work[19], where aluminum and alumina powders were ultrasound mixed using anhydrous methanol. The specimens with 1.0 wt% Cr_3C_2 and TaC show an obviously finer microstructure than those in the specimens with the 0.6 wt% of these additives, even in the WC-6Co-1TaC specimen microstructural defects are also present. It means that increasing the additive contents in the powder mixtures can prevent agglomerations of additive particles and lead to obtaining a fine microstructure without microstructural defects after the spark plasma sintering process, as shown in[15].

The calculated hardness and fracture toughness value of the additive-free WC-6Co and WC-6Co cemented carbides with additives up to 1 wt% are shown in Table 1. Figure 5 shows the hardness as a function of additive contents and Figure 6 shows the fracture toughness as the same function. As expected, the Vickers hardness increased with increasing

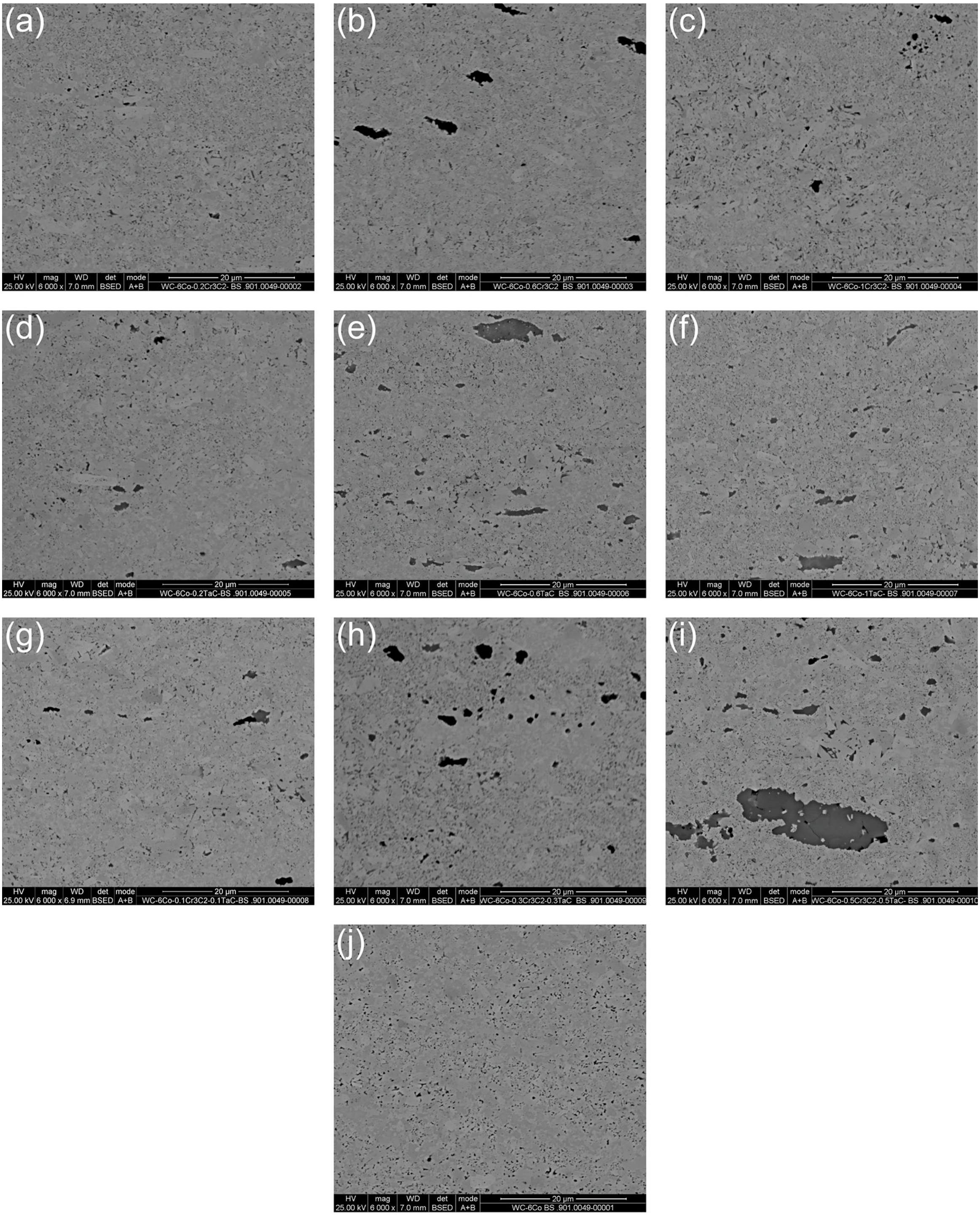

Figure 4. Backscattered SEM micrographs of spark plasma sintered WC-6Co-xCr_3C_2 (a) x = 0.2, (b) x = 0.6, (c) x = 1.0 and WC-6Co-xTaC (d) x = 0.2, (e) x = 0.6, (f) x = 1.0 and WC-6Co-xCr_3C_3-xTaC (g) x = 0.1, (h) x = 0.3, (i) x = 0.5 and (j) WC-6Co cemented carbides.

the additive contents. The basic WC-6Co cemented carbide has the hardness of 1728 HV_{30}. The hardness obtained in this work is higher than the value reported in the open literature for similar materials[8,20]. Furthermore, modification of the structure by the addition of 0.2, 0.6 and 1.0 wt% Cr_3C_2 has an influence not only on an increase in hardness but also on an increase in fracture toughness. The specimen with the highest content of Cr_3C_2 (1 wt%) is characterized by the highest hardness of 1936 HV_{30} and fracture toughness of 10.38 MPa·$m^{1/2}$ of the obtained materials. In turn, the obtained

Table 1. Hardness and fracture toughness of spark plasma sintered WC-6Co cemented carbides with varying weight content of Cr_3C_2 and TaC.

Material	Hardness, HV_{30}	Fracture toughness, $MPa{\cdot}m^{1/2}$
WC-6Co	1728 ± 16	9.71 ± 1.14
WC-6Co-0.2Cr_3C_2	1749 ± 29	10.32 ± 0.43
WC-6Co-0.6Cr_3C_2	1831 ± 26	10.02 ± 0.39
WC-6Co-1Cr_3C_2	1936 ± 15	10.38 ± 0.46
WC-6Co-0.2TaC	1784 ± 21	9.52 ± 0.67
WC-6Co-0.6TaC	1799 ± 20	9.76 ± 0.20
WC-6Co-1TaC	1790 ± 11	9.29 ± 0.18
WC-6Co-0.1Cr_3C_2-0.1TaC	1815 ± 19	9.32 ± 0.13
WC-6Co-0.3Cr_3C_2-0.3TaC	1732 ± 8	11.02 ± 0.47
WC-6Co-0.5Cr_3C_2-0.5TaC	1870 ± 21	9.48 ± 1.33

cemented carbides with the TaC additive, independent of the content of this additive, are characterized by a slightly lower fracture toughness than the basic cemented carbide and ranged between 9.29 $MPa{\cdot}m^{1/2}$ for the highest content of TaC and 9.76 $MPa{\cdot}m^{1/2}$ for the medium content. The hardness of these materials is slightly higher than that of the basic material and ranged between 1784 and 1799 HV_{30}. Higher hardness is noted for the cemented carbide with both the Cr_3C_2 and TaC additives and a value up to 1870 HV_{30} by WC-6Co-0.5Cr_3C_2-0.5TaC was achieved. The fracture toughness of this material is 9.48 $MPa{\cdot}m^{1/2}$. In turn, the lowest hardness of 1732 HV_{30} is noted for WC-6Co-0.3Cr_3C_2-0.3TaC and results directly from the porosity which is present in the microstructure (Figure 4h), because the porosity is a critical parameter that affects the hardness of cemented carbides[19]. On the other hand, this material is characterized by the highest fracture toughness of 11.02 $MPa{\cdot}m^{1/2}$ of the obtained specimens. For comparison, the hardness values in this work were compared against commercial inserts supplied by Baildonit, Poland from the ISO K10 group such as H10 (WC-6Co) and H10S (WC-4.5Co-4.5TaC-NbC), whose hardness was found to be 1600 and 1650 HV_{30} respectively[21]. The presented results of the commercial inserts clearly show the positive effect of additives on hardness. Obviously the WC-Co cemented carbides obtained by the authors are characterized by a much higher hardness. For another comparison, Mahmoodan et al.[22] investigated conventionally sintered WC-10Co-xCr_3C_2 ($x = 0.3, 0.6, 1.0$) cemented carbides and obtained a hardness not exceeding 1800 HV_{30} but the fracture toughness exceed 23 $MPa{\cdot}m^{1/2}$. Similar results were obtained by Sun et al.[23] where WC-11Co-xCr_3C_2 ($x = 0.2, 0.4, 0.6, 0.8$) ultrafine cemented carbides were fabricated by spark plasma sintering. The highest hardness of 1922 HV_{30} and fracture toughness of 14.14 $MPa{\cdot}m^{1/2}$ were noted for an ultrafine WC-11Co-0.6Cr_3C_2 cemented carbides. Of course, it should be kept in mind that direct comparison of other authors' results with the obtained mechanical properties is hampered due to, e.g. the differences in WC ceramic grain size, various contents of Co binder and used additives as well as the fabrication method and process parameters in each paper.

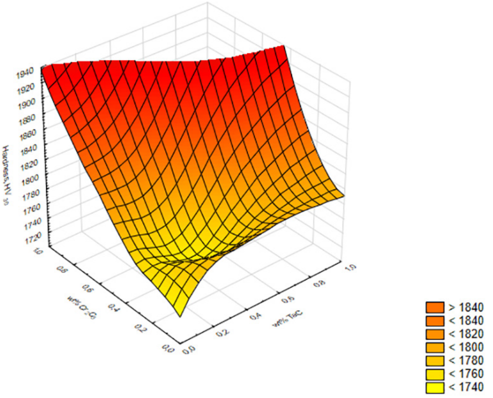

Figure 5. Hardness as function of additive contents of spark plasma sintered WC-6Co cemented carbides. Corresponding assay data are presented in Table 1.

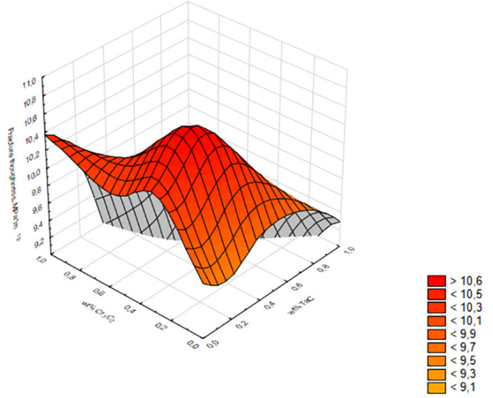

Figure 6. Fracture toughness as function of additive contents of spark plasma sintered WC-6 Co cemented carbides. Corresponding assay data are presented in Table 1.

4. Conclusions

Hardness is one of the most important factors that determine how well WC-Co tools will withstand extreme cutting conditions. In this work the effect of various weight contents of Cr_3C_2 and TaC additives on the microstructure, hardness and fracture toughness are analyzed. The obtained results clearly show that increasing the additive contents can prevent the agglomeration of carbides and lead to obtaining a fine microstructure with a higher hardness exceeding 1900 HV_{30} and a fracture toughness exceeding 9 $MPa \cdot m^{1/2}$. Moreover the cemented carbides with the Cr_3C_2 additive are characterized by better hardness and fracture toughness than with the TaC additive. The best combination of hardness of 1936 ± 15 HV_{30} and fracture toughness of 10.38 ± 0.46 $MPa \cdot m^{1/2}$ was obtained by the WC-6Co-1Cr_3C_2.

5. References

1. Krolczyk G, Nieslony P, Legutko S, Stoic A. Microhardness changes gradient of the duplex stainless steel (DCS) surface layer after dry turning. *Metalurgija*. 2014;53(4):529-532.
2. Krolczyk G, Legutko S, Nieslony P, Gajek M. Study of the surface integrity microhardness of austenitic stainless steel after turning. *Technical Gazette*. 2014;21(6):1307-1311.
3. Maruda R, Legutko S, Krolczyk GM, Hloch S, Michalski M. An influence of active additives on the formation of selected indicators of the condition of the X10CrNi18-8 stainless steel surface layer in MQCL conditions. *International Journal of Surface Science and Engineering*. 2015;9(5):452-465.
4. Arsecularatne JA, Zhang LC, Montross C. Wear and tool life of tungsten carbide, PCBN and PCD cutting tools. *International Journal of Machine Tools and Manufacture*. 2006;46(5):482-491.
5. de Melo ACA, Milan JCG, da Silva MB, Machado AR. Some observations on wear and damages in cemented carbide tools. *Journal of the Brazilian Society of Mechanical Sciences and Engineering*. 2006;28(3):269-277.
6. Liu W, Song X, Wang K, Zhang J, Zhang G, Liu X. A novel rapid route for synthesizing WC-Co bulk by in situ reactions in spark plasma sintering. *Materials Science and Engineering: A*. 2009;499(1-2):476-481.
7. Liu W, Song X, Zhang J, Yin F, Zhang G. A novel route to prepare ultrafine-grained WC-Co cemented carbides. *Journal of Alloys and Compounds*. 2008;458(1-2):366-371.
8. Raihanuzzaman R, Jeong TS, Ghomashchi R, Xie Z, Hong SJ. Characterization of short-duration high-energy ball milled WC-Co powders and subsequent consolidations. *Journal of Alloys and Compounds*. 2014;615(Suppl. 1):S564-S568.
9. Kim HC, Shon IJ, Yoon JK, Doh JM. 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*. 2007;25(1):46-52.
10. Su W, Sun YX, Yang HL, Zhang XQ, Ruan JM. Effects of TaC on microstructure and mechanical properties of coarse grained WC-9Co cemented carbides. *Transactions of Nonferrous Metals Society of China*. 2015;25(4):1194-1199.
11. Espinosa-Fernández L, Borrell A, Salvador MD, Gutierrez-Gonzalez CF. Sliding wear behavior of WC-Co-Cr_3C_2-VC composites fabricated by conventional and non-conventional techniques. *Wear*. 2013;307(1-2):60-67.
12. Mahmoodan M, Aliakbarzadeh H, Gholamipour R. Sintering of WC-10%Co nano powder containing TaC and VC grain growth inhibitors. *Transactions of Nonferrous Metals Society of China*. 2011;21(5):1080-1084.
13. van der Merwe R, Sacks N. Effect of TaC and TiC on the friction and dry sliding wear of WC-6 wt.% Co cemented carbides against steel counterfaces. *International Journal of Refractory Metals and Hard Materials*. 2013;41:94-102.
14. Genga RM, Akdogan G, Westraadt JE, Cornish LA. Microstructure and material properties of PECS manufactured WC-NbC-CO and WC-TiC-Ni cemented carbides. *International Journal of Refractory Metals and Hard Materials*. 2015;49:240-248.
15. Siwak P, Garbiec D. Microstructure and mechanical properties of WC-Co, WC-Co-Cr_3C_2 and WC-Co-TaC cermets fabricated by spark plasma sintering. *Transactions of Nonferrous Metals Society of China*. 2016;26(10):2641-2646.
16. Rumman R, Xie Z, Hong SJ, Ghomashchi R. Effect of spark plasma sintering pressure on mechanical properties of WC-7.5 wt% Nano Co. *Materials & Design*. 2015;68:221-227.
17. Zhao S, Song X, Wei C, Zhang L, Liu X, Zhang J. Effects of WC particle size on densification and properties of spark plasma sintered WC-Co cermet. *International Journal of Refractory Metals and Hard Materials*. 2009;27(6):1014-1018.
18. Schubert WD, Neumeister H, Kinger G, Lux B. Hardness to toughness relationship of fine-graded WC-Co hardmetals. *International Journal of Refractory Metals and Hard Materials*. 1998;16(2):133-142.
19. Garbiec D, Jurczyk M, Levintant-Zayonts N, Mościcki T. Properties of Al-Al_2O_3 composites synthesized by spark plasma sintering method. *Archives of Civil and Mechanical Engineering*. 2015;15(4):933-939.
20. Lee S, Hong HS, Kim HS, Hong SJ, Yoon JH. Spark plasma sintering of WC-Co tool materials prepared with emphasis on WC core-Co shell structure development. *International Journal of Refractory Metals and Hard Materials*. 2015;53(Part A):41-45.
21. BAILDONIT. Sintered carbide inserts for brazed tools. BAILDONIT: Katowice, Poland. 1-52. baildonit.com/images/katalogi/baildonit-katalog_plytki_lutowane.pdf
22. Mahmoodan M, Aliakbarzadeh H, Shahri F. Effect of Cr_3C_2 and VC on the mechanical and structural properties of sintered WC-%10wt Co nano powders. *World Journal of Nano Science and Engineering*. 2013;3(2):35-39.
23. Sun L, Jia C, Cao R, Lin C. Effects of Cr_3C_2 additions on the densification, grain growth and properties of ultrafine WC-11Co composites by spark plasma sintering. *International Journal of Refractory Metals and Hard Materials*. 2008;26(4):357-361.