Chiang Mai J. Sci. 2017; 44(4) : 1714-1721
http://epg.science.cmu.ac.th/ejournal/
Contributed Paper

The Effect of Substitution of WC by TiC in WC-Co Composite Tool Materials on Microstructure and Mechanical Properties

Jan Dutkiewicz* [a], Łukasz Rogal [a], P. Bobrowski [a], Małgorzata Szutkowska [b], Wojciech Leśniewski [c] and Piotr Dłuzewski [d]

[a] Institute of Metallurgy and Materials Science Polish Academy of Sciences 30-059 Kraków ul. Reymonta 25 Poland.

[b] Institute of Advanced Manufacturing Technology 30-011 Kraków, ul. Wrocławska 37a, Poland.

[c] Foundry Research Institute 30-418 Kraków ul. Zakopiańska 73, Poland.

[d] Institute of Physics of the Polish Academy of Sciences al. Lotników 32/46, 02-668 Warszawa, Poland.

*Author for correspondence; e-mail: j.dutkiewicz@imim.pl

Received: 14 July 2015
Accepted: 16 November 2015

ABSTRACT

WC-Co composites with TiC additions of 5-20 wt.% substituting WC were consolidated using Hot Isostatic Pressing (HIP) method at temperature of 1350°C and pressure between 50-150 MPa. The hardness of WC-Co consolidated samples increase from 1050 HV (without TiC consolidated at 50 MPa) up to 1330 HV at 5% TiC and up to 1600 HV with 20% of TiC. The higher hardness of samples with TiC additions can be explained by a higher consolidation pressure of 150 MPa leading to a lower porosity, but also to hardening due to TiC addition. Young modulus values are lower for samples with TiC attaining 420-490 GPa as compared to 570 GPa for conventional WC-Co samples. Samples with a crack formation behavior allowed to determine fracture toughness K_{IC} using crack length from hardness measurements. Results in the range 10, 9-11, 2 [$MPam^{1/2}$] for the samples containing 0-10 % TiC, indicated only insignificant decrease of this property with TiC content. Addition of TiC causes also 15-30 % lower density of composites in the range 10-12, 5 g/cm^3. The major identified phase is the hexagonal WC carbide separated by a narrow layer of Co binder and accompanied by single particles of TiC within Co. The size of WC particles was the same as applied in conventional composites i.e. 2-4 mm, while that of homogeneously distributed TiC were measured as slightly smaller, below 2 mm. Transmission electron microscopy investigations allowed to identify relatively high dislocation density in both cubic TiC and hexagonal WC carbides and different interfaces between WC and TiC carbides and Co binder however no additional phases were detected there. The crystallographic relationship [01-1] TiC || [100] WC was often observed. The appearance of solid solution of TiC with WC near WC/TiC interfaces was discussed.

Keywords: WC-TiC-Co composites, mechanical properties, TEM, SEM studies

1. INTRODUCTION

WC-TiC-Co is a kind of cemented carbide that has been widely used as a tool material for high speed machining applied mainly to high-strength-steel and other long-chipping-materials. These composites benefit from improvements with the addition of metallic carbides such as TiC, TaC, ZrC and NbC. Metallic carbides enhance the hardness and wear resistance of WC-Co based ceramic composites by inhibiting WC grain growth during sintering [1-4]. Powder mixtures containing 10-20 vol. % of cubic carbides and 10 vol % of binder phase show the best effect of grain growth inhibition when TiC was added to the powder mixture [5]. Earlier works indicate that the hardness of WC-TiC-10 wt% Co cemented carbide increased with decreasing the WC/TiC grain size ratio from 4 to 0.8 following the modified Hall-Petch type equation [3]. It was shown that the application of the mechanical alloying MA process during preparation of powder mixtures refined the microstructure, reduced the porosity, and increased the relative density, while yielding a hardness value higher than that of conventional grade 78WC-16TiC-6Co ceramic composite [6] and the density, hardness, and wear performance of the ceramic composites did not change remarkably with the type of TiC powder added to the mixture of WC and Co powders. The recent structural and corrosion studies [7] showed that the existence of TiC can inhibit the corrosion of carbide in hardmetals. WC-5TiC-Co ultrafine cemented carbides were compared with a conventional cutting tools of this composition. The ultrafine inserts showed higher hardness and transverse rupture strength as compared to the conventional insert [8]. The combined addition of TaC and TiC did not provide a significant improvement in the wear resistance while the larger carbide grain sizes and the TiC also made the alloy more susceptible to fracture and material removal [9].

From the above literature search it results that the information concerning the effect of TiC on the properties and microstructure are rather inconsistent. It is clear that the carbides grain refinement and the addition of TiC to WC-Co composites have a positive effect on mechanical properties and corrosion resistance, however there are limited information on the effect of TiC on fracture toughness, interface quality and the effect of various TiC additions on the mechanical properties change. Therefore in the present paper these aspects were considered concerning materials intended for mining tool materials.

2. MATERIALS AND METHODS

Table 1 shows chemical composition of the investigated WC-Co mixtures used for preparation of hard composites. One can see that the first 2 mixtures contain about 14 wt.% of Co, while the third one (B30) only 11-12,5 wt.% Co. The content of other elements is below 0.3% (chromium) and the other below 0.1%. The mixture YK15,6 was delivered by the Chinese producer Chongyi Zhangyuan Tungsten Co. Ltd and the other two German Burhaun company. SEM micrographs of the delivered WC-Co powder's mixtures indicate that the size of powders is variable between 0.5-5 mm. the measurements using Shimadzu type SA-CP3 allowed to determine the mean size of the mixture YK15, 6 as 3, 75 mm, that of B30/1 3, 57 mm and that of B30/2 2, 44 mm. These are considered optimal for the produced hard products. The structure of the consolidated samples was studied using a Philips CM20 transmission electron microscope (TEM), or FEI **TITAN**

CUBED 80-300 HRTEM equipped with EDS detector and astigmatism objective lens corrector, scanning electron microscope FEI equipped EDS detector, Leica optical microscope equipped with QUIN quantitative image analysis and X-ray diffractometer Philips PW1840 using mono-chromatic Cu-Kα radiation.

Table 1. Chemical composition of the investigated WC-Co mixtures

Symbol	Elements/phases								
	WC	Co	Fe	Ti	Mo	Nb	Ni	Cr	V
YK15,6	85,8	13,9 - 14,9	0,1	0,04	0	0,01	0,08	0,30	0
B30/1	84,2	14,4 - 19,0	0,1	0,05	-	0,02	0,24	0,36	0
B30/2	89,0	11,0 - 12,5	-	-		-	-	-	-

The samples were consolidated using Hot Isostatic Pressing (HIP) model AIP10-30H using pressure of between 50 - 150 MPa and temperature of 1350°C. The samples were placed in titanium containers, then separated by elastic graphite foil from the titanium in order to prevent chemical reaction between a composite and the die. Afterwards the titanium containers were welded to avoid the interaction with gas.

3. RESULTS AND DISCUSSION

Figure 1. shows results of hardness measurement of the WC-Co base composites with 5 wt. %, 10 wt % 15 wt.% and 20 wt. % of TiC additions. The composites were prepared either from YK15,6 or B30 WC-Co mixtures of composition given in the Table 1. The variation of mixtures have only an insignificant effect on hardness of consolidated composites. The addition of TiC causes increase of hardness of the composites from 1050 HV (for industrial product without TiC consolidated at 50 MPa) up to 1330 HV at 5% TiC and up to 1600 HV with 20% of TiC. This is in accord with previous studies [3-8] where it was reported that the addition of TiC causes hardness increase of WC-TiC-Co composites.

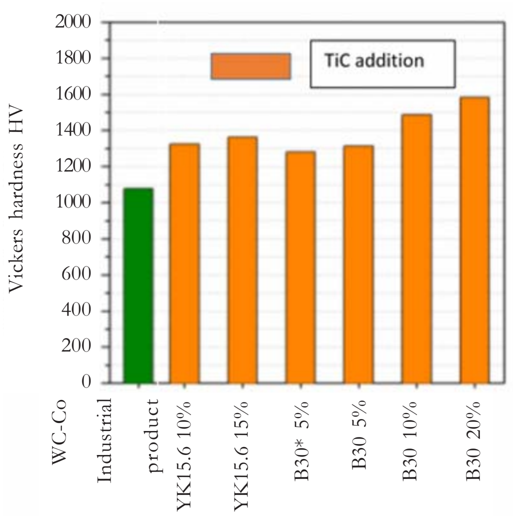

Figure 1. Graph illustrating changes of Vickers hardness with TiC additions between 5.20 wt% toWC-Co mixture YK 15.6 or B30.

Figure 2 shows an imprint of HV30 of the sample based on B30 with 10 % if TiC. One can clearly see the cracks formed at the edges of the imprint. The fracture formed at Vickers indentations were used to compute the fracture toughness by the Anstis method. Fracture toughness measured by the Anstis crack-length method is dependent on the elastic modulus of the material, micro indentation hardness and crack length, and the applied load. The fracture toughness measured in samples containing 5-10 % Ti showed very similar values between 10,7-10,9 [MPam$^{1/2}$], however when the addition of TiC was 20 wt. % the fracture toughness decreased down to 9,1 [MPam$^{1/2}$] and at 30 % of TiC down to 7,1 [MPam$^{1/2}$].

The crack did not appear in samples without TiC and therefore it was not measured using hardness method, but it is only slightly higher for similar composites (with similar Co content and grain size) between 11,8-12, 0 MPam$^{1/2}$ measured using three point bending method [10].

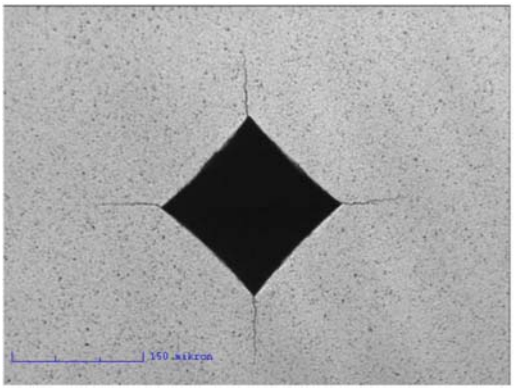

Figure 2. Photograph of an intend with cracks at theedges of the imprint allowing calculation of fracture toughness.

Figure 3 shows compression test curves obtained from samples of composites prepared from B30 WC-Co powder mixtures with additions of either 5% or 10 wt. % of TiC. One can see that the addition of 10 wt. % of TiC causes compression strength increase up to 4000 MPa, while at 5 % TiC addition it was measured at 3000 MPa. The differences in the supplement of cobalt did not have much influence of the compression strength. Contrary to the compression strength results the wear measurements (shown in Figure 4) performed using corundum ball on disc friction method of composites with a different TiC content indicated that the increase of the TiC content above 20 % causes increased wear of the disc, while wear of the ball is not much different. The addition of Co with TiC causes increased rate of wear.

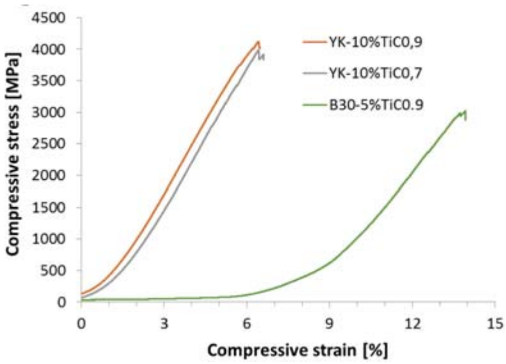

Figure 3. Stress-strain compression curves of composites based on B30 or YK WC-Co mixtures containing either 5 or 10 % of TiC.

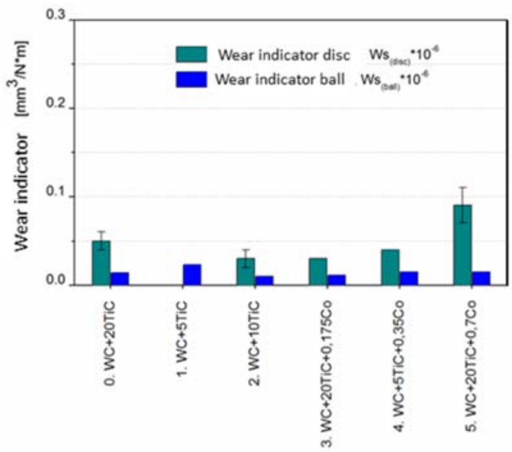

Figure 4. Indicators of ball and disc wear results performed for various WC-Co-TiC composites using corundum ball on disc method.

Figure 5 shows X-ray diffraction curves from WC-Co composites based on B30 mixture containing 5 % and 10 % of TiC HIPed at 150 MPa. The results show presence of the initial phases i.e. hexagonal WC and regular TiC and Co. No additional phases that could be formed as a result of reactions between composite components has been observed.

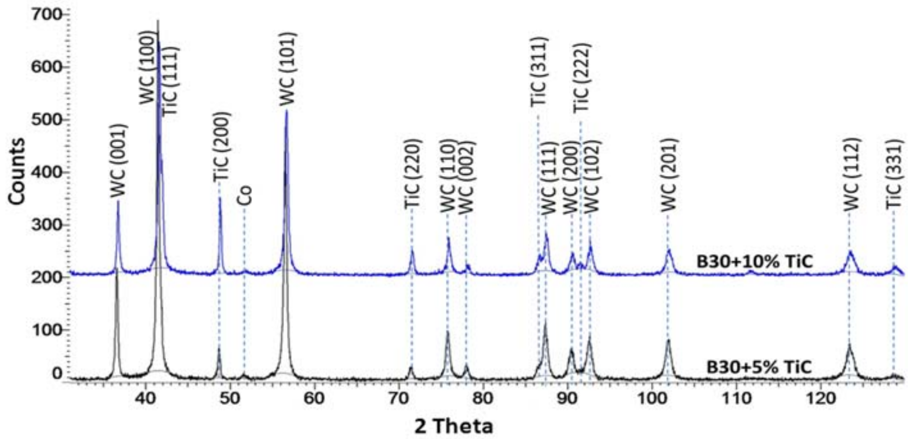

Figure 5. X-ray diffraction curves from composites B30 WC-Co with either 5% or 10% of TiC additions.

This observation was confirmed using SEM studies of investigated composites presented in Figures 6 and 7. Figure 6a shows a typical microstructure of WC-Co composite where two component phases i.e. WC (brighter) and Co (darker) can be seen. The average size of WC particles near 4 mm was confirmed. The composition of components was confirmed using EDS microanalysis in places marked 1 (WC) and 2 (Co). Figure 6b taken at the same magnification shows WC particles as slightly brighter as contrast has been changed to distinguish TiC fine particles. From EDS analysis performed from places 1, 2, 3 one can see that the dark particles in point 1 possess 51 at.% Ti, 48 at.% C and 0.5 at.% W and 0.5 at.% Co. The latter results could result from the surrounding radiation or phases below the existing phase, so one cannot conclude at this stage about the formation of the solid solution of TiC and WC. The size of TiC particles is similar to that of WC, however in such places like 3 there exist a mixture of cobalt, WC and TiC fine particles what is confirmed by the EDS chemical analysis, where it was found 43 at.% Ti, 43.5 at.% C, 10 at.% W and 3.5 at % Co. At this stage it is however difficult to state if there is a mixture of TiC and WC phases or a solution of WC and TiC. The much finer size of TiC particles may suggest a different structure. Figure 7 shows SEM microstructures of composites with 10 wt. % and 20 wt. % of TiC. One can see a similar microstructure like that in Figure 6b i.e. more frequent dark TiC particles, fine mixture of TiC, Co and WC phases and bright WC particles which is a dominant phase. The results of microanalysis are similar, but in the fine particles mixture like in place number 2 it is again difficult to judge if there is a solid solution of WC and TiC mixed with Co or a mixture of all existing phases of a smaller size. Figure 7b shows slightly different microstructure due to tendency of agglomeration of TiC phases which are in higher amount of 20 wt.%. The presence of agglomerates could be a reason of smaller resistance to wear due to possible removal of TiC agglomerates by corundum ball. There is less areas of fine particles mixture like in Figure 6b and 7a, however in area marked 4 where is a dominant cobalt binder, where some small percentage of tungsten was also detected. The presence of finer particles may also cause the increased resistance to wear as stated in previous works [7-9]. The interfaces of TiC and WC which can be seen more frequently in the sample of 20 % of TiC look rather clean without signs of mutual diffusion however the magnification was not high enough. Therefore the transmission electron microscopy was applied in order to determine the eventual solid solubility of carbides and a character of interfaces.

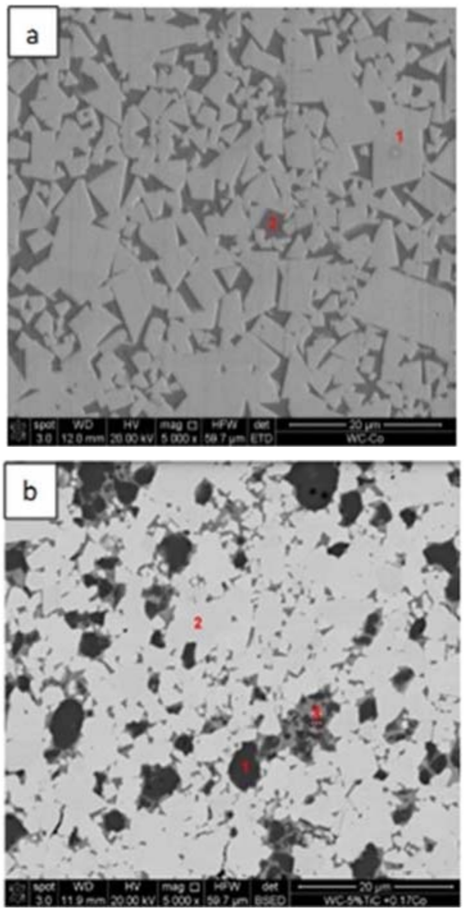

Figure 6. SEM micrograph of (a) industrial WC-Co composite based on B30 mixture and (b) Sample based on B30 with 5% TiC HIPed at 150 MPa.

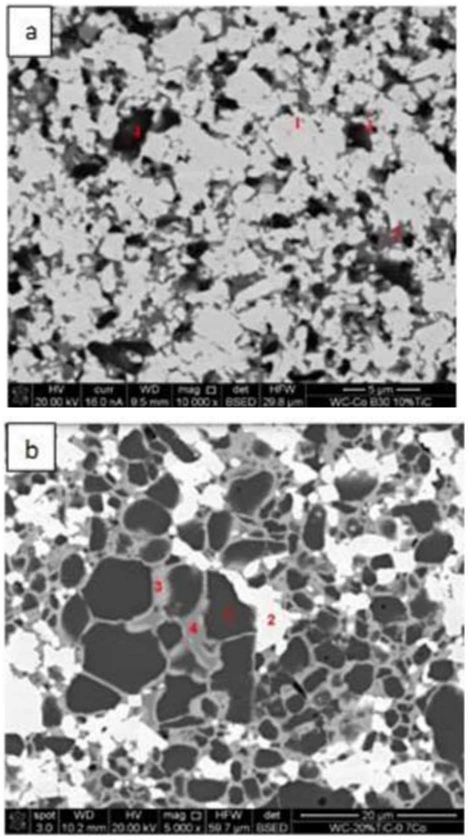

Figure 7. SEM micrograph of (a) WC-Co-10 % TiC composite based on B30 mixture and (b) Sample based on B30 with 20% TiC.

Figure 8 shows TEM micrograph from the composite prepared from B30 WC-Co mixture with added 10 % of TiC. One can see WC/TiC interface. As results from the diffraction patterns TiC carbide of a regular crystal lattice is of [01-1] zone axis orientation and hexagonal WC of [100] zone axis orientation can be seen. There is some relationship in crystallographic directions [010]WC || [200]TiC, what may indicate that some directions preferably grow, however it was not confirmed in a large amount of samples. The interface shows several ledges what indicate the contribution of diffusion in formation of the interface. A relatively high density of dislocations is observed not only in TiC in Figure 8, but also in cobalt and WC formed at high temperature and high pressure of 150 MPa. The contrast changes within TiC shows also presence of other phases confirming mixture of phases observed in TiC rich areas using SEM (Figsure 6b and 7a).

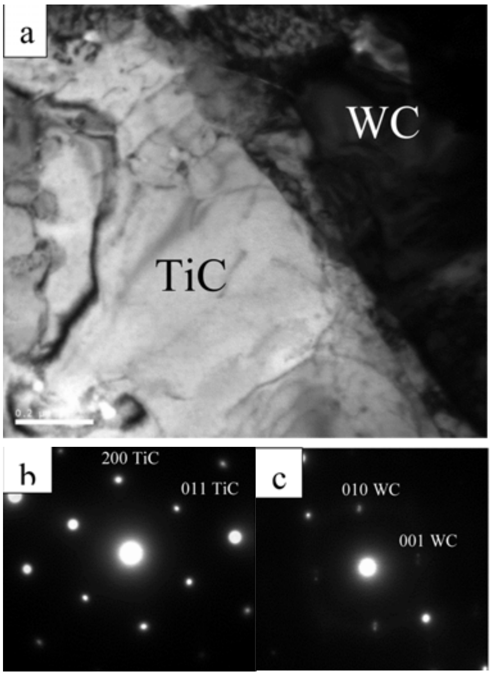

Figure 8. (a) TEM micrograph in the bright field of the B30 WC-Co composite with 10% TiC, (b) SADP from TiC bright area (c) SADP from the WC dark part.

Figure 9 shows STEM micrograph from the WC-Co composite B30 (based) with 10% TiC. On the right side it is shown EDS mapping within the area marked "1" where results of the distribution of C, Ti and W can be seen as separate mages. One can see a small inclusion of WC within the TiC carbide. TiC is free from WC, however at the lower part the mixture of TiC and WC can be seen indicating diffusion of WC toward TiC. This observation was confirmed in other places. The presence of fine particles of carbides within the cobalt binder (below 500 nm) was confirmed in TEM studies and it could be a reason of a good mechanical properties due to strengthening of a binder. The second reason is a good diffusional interface between the carbides confirming their mutual diffusion.

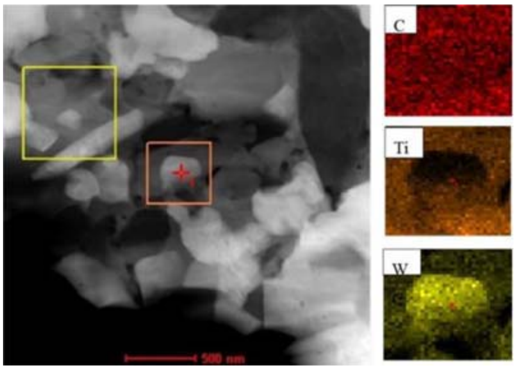

Figure 9. STEM micrograph from the B30 WC-Co composite with 10% TiC. On the right side STEM EDS results of the distribution of Ti, W and Co (from the top) along the line marked in the image.

Conclusions

1. The composites with additions of 5-20 wt % TiC showed increase of compression strength and hardness with increase of TiC content up to 20 %. The wear rate was slightly higher when the TiC addition approach 20 %. The fracture toughness only slightly decreases with TiC content up to 10 wt.%, however it drops more pronouncedly at higher TiC content 15-20 %.

2. The TiC carbides in composites containing 5-10 % TiC are mainly located as fine mixture of carbides and cobalt between WC particles. At higher TiC addition conglomerates of TiC carbides were observed causing deterioration of properties. Some mutual diffusion of TiC and WC was observed in the direction TiC into WC using STEM EDS studies, confirming diffusional character of the interface between carbides.

No additional phases were formed at the interfaces in the WC-Co composites due to TiC addition.

ACKNOWLEDGEMENTS.

The financial support from NCBiR Project GONAR: INNNOTECH-K2/IN2/20/181917/NCBR/13 allowing experimental work is gratefully acknowledged.

REFERENCES

[1] Toth L.E., *Transition Metal Carbides and Ntrides*. New York: Academic Press; 1971.

[2] Liu H., Wan D. and Hu D., *J. Mater. Process. Technol.,* 2009; **209(2)**: 805-10

[3] Lee K., Cha S.I., Kim B.K. and Hong S.H., *Int. J. Refract. Met. Hard Mater.,* 2006; **24**: 109-14

[4] Kim H.C., Kim D.K., Woo K.D., Ko I.Y. and Shon I.J., *Int. J. Refract. Met. Hard Mater.*, 2008; **26(1)**: 48-54.

[5] Weidow J., Zackrisson J. and Jansson B., Andren H.O., *Int. J. Refract. Met. Hard Mater.*, 2009; **27**: 244-248.

[6] Duman D., Gokce H. and Cimenoglu H., *J. Eur. Ceram. Soc.,* 2012; **32**: 1427-1433

[7] Lin N., He Y., Wu C., Liu S., Xiao X. and Jiang Y., *Int. J. Refract. Met. Hard Mater.,* 2014; **46**: 52-57.

[8] Guo Z., Xiong J., Yang M., Dong G. and Wan W., *Int. J. Refract. Met. Hard Mater.,* 2012; **35**: 262-269.

[9] Van der Merwe R. and Sacks N., *Int. J. Refract. Met. Hard Mater.*, 2013; **41**: 94-102.

[10] Chermant J.L. and Osterstock F., *J. Mater. Sci.,* 1976; **11**: 1939.