Study of the formation features of hard metal composites structure obtained from bimodal powder mixtures

Yu. I. Gordeev, V. B. Yasinskiy, N. E. Anistratenko, A. S. Binchurov
Siberian Federal University, 79, Svobodny pr., 660041 Krasnoyarsk, Russia

Abstract

A new method of forming dispersion-hardening oxide inclusions in the process of thermoreactive synthesis from aluminum nanoparticles introduced into WC-Co powder mixture is proposed. Such multiphase and fragmentarily nanostructured composite is characterized by additional heterogeneity, which is determined by the difference in sizes and elastic properties of the phases. In the structure of WC-Al_2O_3-Co composites a "barrier" effect is provided, the length of the carbide grains contacts is reduced. Carbide grains are separated by a thin cobalt layer with increased strength. In accordance with the results of numerical estimates using finite element analysis (FEA) method, the maximum stress intensity in tungsten carbide is 9.1 GPa (occurring at an external voltage of 3 GPa), which is 30% less than the maximum stress intensity in the basic material. The strength improvement predicted by the FEA method in fragmented nanostructured hardmetal composite correlates with experimental results of measurements of fracture toughness according to Palmqvist data. In case of the optimal amount of additives, the increase in crack resistance is equal to 50% compared with the basic material.

Introdusion

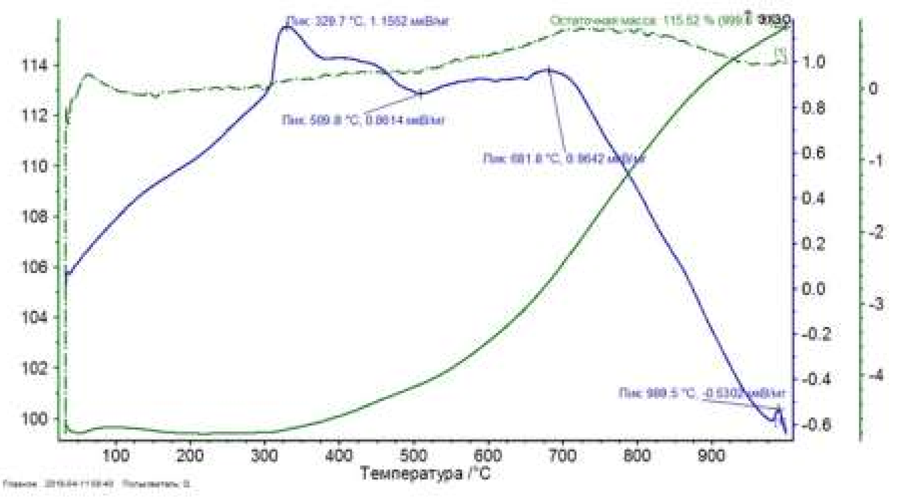
The tasks of quality improvement of hard metals can be effectively solved through the use of nano-sized tungsten carbide powders. However, it is well-known that when using traditional consolidation methods for obtaining a high density of the sintered composite, a high temperature and holding time during sintering are necessary, what leads to the increase of initial dimensions and the growth of carbide grains [1]. A possible option and effective technical solution to prevent recrystallization is the introduction of nanoparticles, i.e. inhibitors. Doping is carried out by various methods, such as chemical, mechanical (high-energy ball milling) and others [2]. Being dissolved in cobalt, alloying elements affect not only the microstructure, but also have a modifying effect on the consolidation processes and change the sintering kinetics, as well as mechanical and operational properties of the alloy [3-5]. The use of composite carbide-binder powders with simultaneous doping of inhibitors with nanoparticles (oxides, carbides, nitrides) also appears to be a highly promising direction [6-8]. Additional modification of the main mixture of WC, Co micron powders with nanoparticles also provides (besides preventing recrystallization) an improvement of the binder strength and the level increase of physical and mechanical properties of the composite as a whole. Such multiphased and fragmentarily nanostructured composite is characterized by the additional heterogeneity, which is determined by the difference in sizes and elastic properties of the phases [9].

Methods and equipment

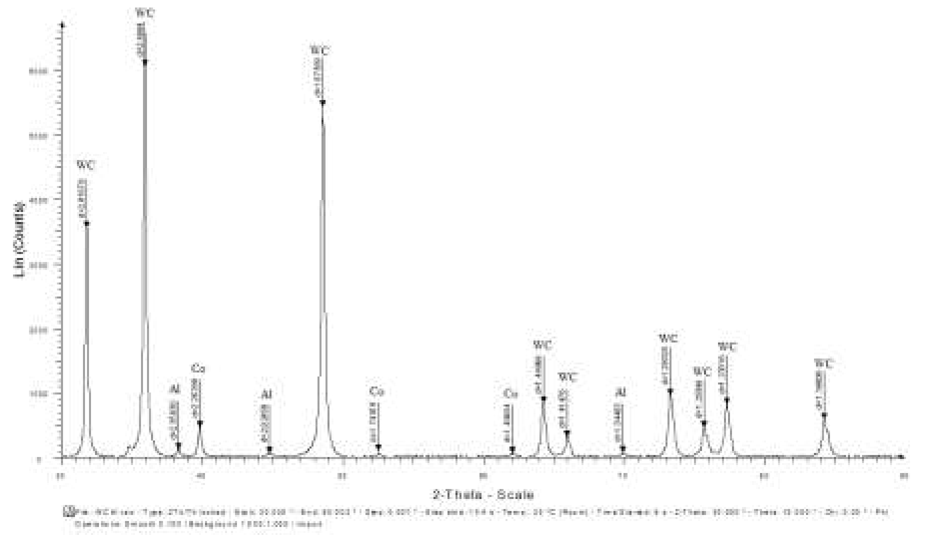
For obtaining hard metals with adjustable graininess, structure and improved properties, the modifying additives of nanoparticles are introduced into bimodal powder mixture. The mechanism of slowing down the growth of a carbide grain during sintering process is the inhibitor segregation at the emerging boundaries of WC-WC or WC-Co (in the volume of cobalt binder). In the course of experimental studies, two methods of introducing aluminum oxides modifying additives into the structure of a hardmetal composite were compared: at the stage of mechanical mixing WC-Co powders with nanoparticles of oxides, carbides (described in [8,9]), as well as a new method of forming dispersion-strengthening oxide inclusions in the process of thermoreactive synthesis from aluminum nanoparticles of W-Co powders introduced into the mixture. Bimodal powder mixtures (WC-Co) were obtained by the joint grinding and mixing of micron tungsten carbide powders to sizes (d_{WC} ~ 2 µm), cobalt (d_{Co} ~ 7 µm) and submicron composite powders (WC-Co) in fritch planetary ball mills in a liquid alcohol medium within 2 - 6 hours. Then modifying additives of aluminum nanoparticles (dAl ~ 0.08 µm with specific surface area about 12 m^2/g) were additionally introduced into the mixture in amount from 0,5 to 2% wt as suspension, and the resulting bimodal mixture was additionally stirred. Due to the size difference and specific surface area of the particles of the basic mixture and additional phase, it is possible to estimate the volume content of the nanophase in the composite - from 6 to 10% of vol. Changes in the structural-phase state of compacts and sintered samples obtained from the powder mixtures of tungsten carbide, cobalt and aluminum nanopowders were monitored by thermogravimetric method (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) using Jupiter STA449C derivatographs («Netzsch», Germany) and SDT Q600 V20.5 («Netzsch», Germany) in combination with X-ray phase analysis on D8 ADVANCE diffractometer (Germany) – figure 1. Additionally, shrinkage was monitored during sintering on DIL 402 dilatometer («Netzsch»). The complex use of these methods allows to establish the temperature-time intervals corresponding to significant changes of the phase state in the volume of composites. The microstructure of samples was examined on the polished surfaces by means of Hitachi TM1000 and JEOL JSM-7500FA scanning electron microscopes. The fractures analyses were carried out using JAMP 9500F microscope.

Results and discussions

In the process of heating during sintering in vacuum, the destruction of oxide films on the surface of aluminum nanoparticles occurs at relatively low temperatures - already at T^oC of about 350° C (peak 1, figure 1a). Subsequently, exothermic reduction-oxidation reactions take place between the aluminum and the oxide film on cobalt $2Al + 3CoO = Al_2O_3 + 3Co$, or with atmospheric oxygen absorbed on the surface of the mixture powders. As a result of the local release of additional heat in the microvolumes of the raw billet, a liquid-phase sintering process is carried out between carbide particles at low temperatures - even in the interval of 550 - 700 ^OC (peak 2, figure1) by the mechanism of mechanical repacking of the carbide phase particles. At the same time, segregation of oxide nanoparticles on the surface and between carbide grains occurs at an early stage of sintering, which in the course of subsequent sintering provides an inhibitory effect. The completeness of thermoreactive synthesis reaction of oxides from aluminum nanoparticles is also confirmed by the results of X-ray phase analysis of the samples when heated to a temperature of 1000 ^OC (figure 1b) - the availability of peaks of the α-Al_2O_3 phase.



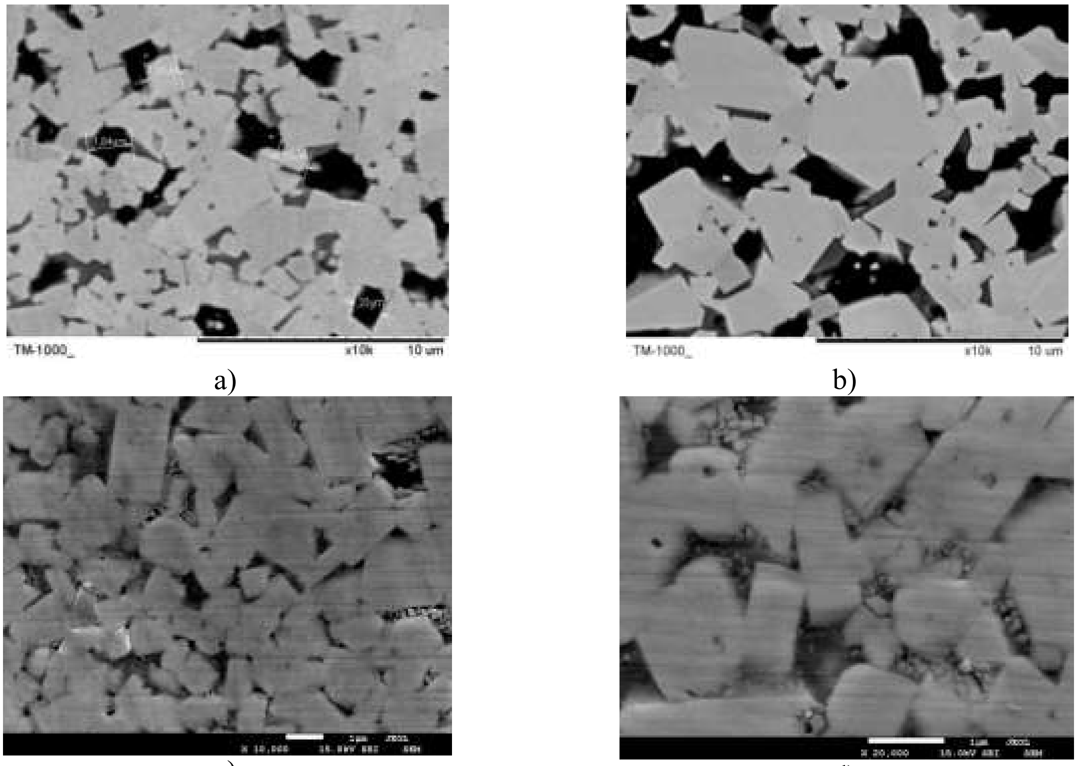
a)



b)

Figure 1. Results of thermal analysis a) and X-ray phase analysis (b) of the hard metal samples from WC-Co-Al bimodal mixtures

After final sintering at the temperatures about 1370 ^{O}C it is possible to form and keep the new type of a fragmentary nanostructured composite WC-Al_2O_3-Co, which is formed by the two interpenetrating scaffolds: carbide and mixed ceramic-metal (metal oxide Co-Al_2O_3). Typical images of the structure of such composites obtained from bimodal mixtures are shown in figure 2 (a, b) for the composition WC-8Co-2Al and in figure 2 (c, d) for the composition WC-8Co-0.5Al.



a)

b)

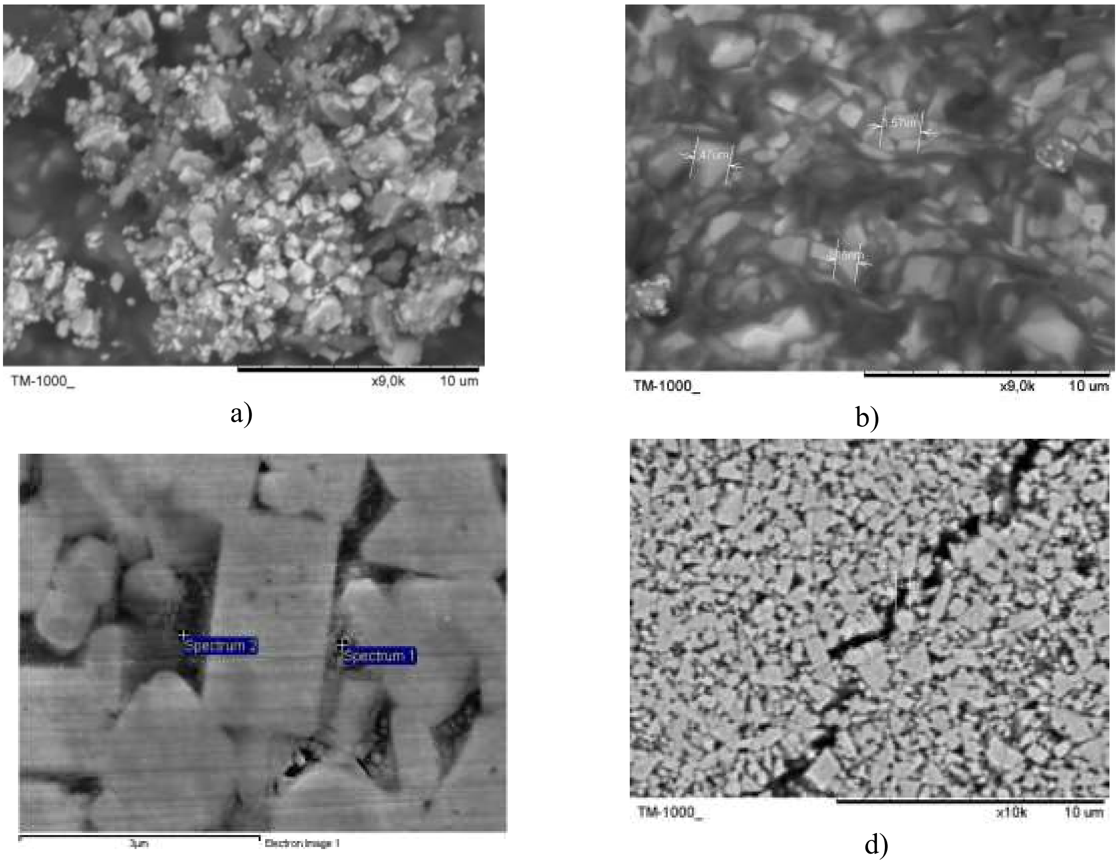
c)

d)

Figure 2. Microstructure of composites obtained from bimodal mixtures WC-Co-Al: (a, b) tungsten carbide grains bonded by mixed oxide-cobalt phase - dark background in the form of oxide inclusions; (c, d) the nature of the distribution of nanooxides in the cobalt layer

The results of the study of the structure parameters basing on typical images (figure 2) using AxioVision 4.6.3, module for the analysis of images Auto Measure on the basis of optical microscope Carl Zeiss Observer.Z1m. (Germany) show that the average size of a carbide grain of hardmetal composites WC-Co, modified by the nanoparticle additives, is equal to 0,8 – 1,2 µm (for WC-8%Co), average thickness λ_{Co} varies from 0,12 to 0,2 µm. (standard hard metals based on WC-Co have the average thickness of λ_{Co} - 0,5-0,6 µm).

Changes in size of the phases are accompanied by a decrease in the contact ability of carbide grains, total length of the interface borders WC-WC (to 0,3 in comparison with 0,56 in case of base microcrystalline hard metals WC-8%Co). Significant part of carbide grains has submicron size due to the inhibitory effect of oxide inclusions. They are more isolated from each other (compared to base materials). Bimodality by the size of grains of the solid phase (established at the stage of mixture preparation) is relayed in the form of the nanostructural fragmentation of dispersed oxide inclusions in the cobalt interlayer and submicron carbide grains, which is also confirmed by the electron microscopical image of fractures and chemical analysis results shown in figure 3c.



a)

b)

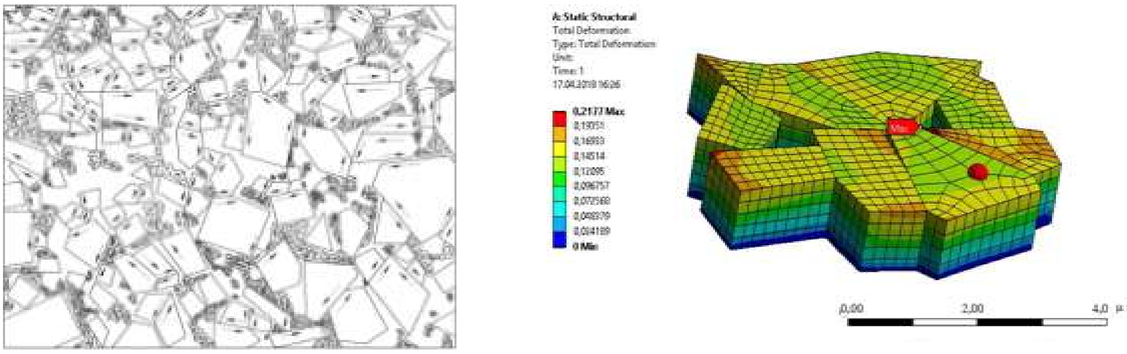
d)

Spectrum	C	Al	Co	W	Total
Spectrum 1	5.53	2.10	32.44	59.93	100.00
Spectrum 2	3.65	2.25	67.10	27.00	100.00

c)

Figure 3. Phase distribution of carbide composites WC-Al_2O_3-Co
a) dispersed inclusions of oxides at the fracture b) the nature of distribution of the cobalt bond (gray background) over the grains of the carbide phase; c) the results of the element-by-element analysis d) the nature of Palmqvist crack opening

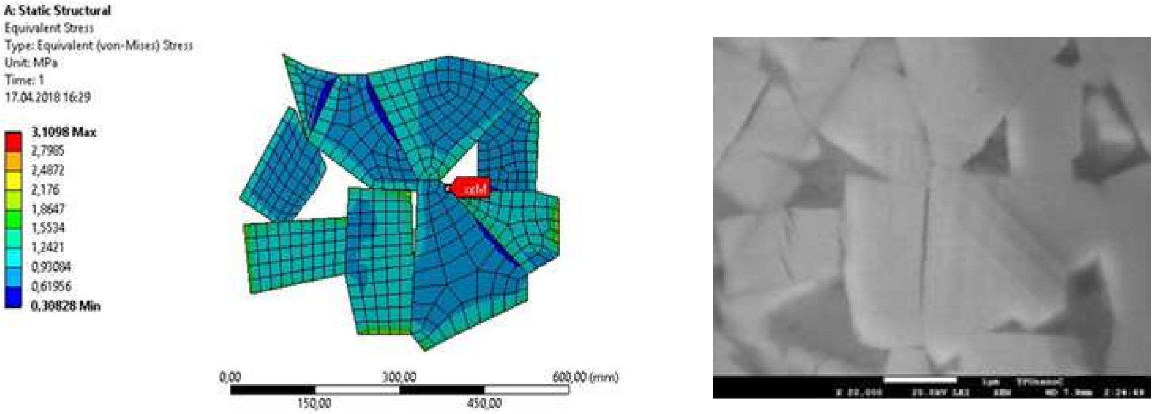
Since the thinner cobalt interlayer is dispersion strengthened, the nature of the stress-strain state in the local volumes (fragments) of Co-Al_2O_3-nano structure also changes. Calculations made using the finite element analysis (FEA) and ANSYS software products allow us to compare the strength of fragmentary nanostructured hardmetal composites with basic (WC-Co). In this case, for the analytical calculations, the microhardness values of the phase components can be used combining with the Palmqvist crack resistance measured data. Since the known microhardness values of tungsten carbide 20,6 GPa and the cobalt phase 7,5 GPa are significantly different, it is necessary to adapt these values to the known expressions for determining the integral parameter, i.e. crack resistance, by one of the known methods [9,10]. Using the finite element analysis (FEA) to estimate the stress state in the microstructure of the basic hard metal WC-8% Co with a carbide "skeleton" showed that the interface boundaries of carbide grains WC are stress concentrators and the weakest structural links in the volume of a hardmetal composite. At a load of 2 GPa, the stress intensity in the composite reaches 10.5 GPa, which leads to a displacement and the formation of microcracks along the boundaries. At the same time, hardmetal composites modified by nanoparticles are characterized by the destruction by another mechanism. The space between carbide grains is filled with cobalt material saturated with nanoparticles, therefore, besides disperse hardening of binder, a new oxide phase blocks the bias of carbide grains, figure 4 a, b, which is also confirmed by the results of numerical modelling of the mutual movement of carbide grains.



a) b)

Figure 4. Schemes of carbide grains bias as a result of external force impact (a – WC-Co-Al_2O_3-nano; b – bias of carbide grains under the load influence)

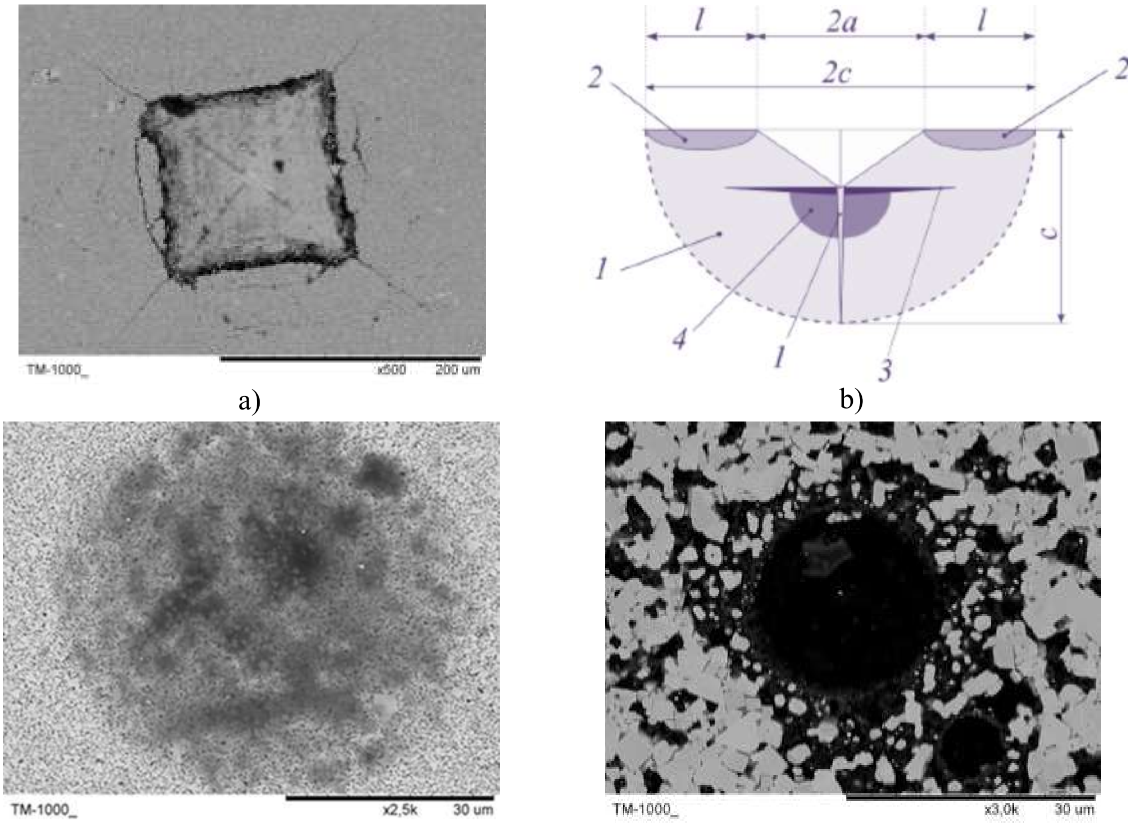
It is interesting to compare the experimentally observed effects of transcrystalline destruction of micron carbide grains (polycrystal) with the results of calculations by the FEA method when loading the model of the same structural fragment (figure 5a). Exactly at the maximum stress point the displacement and grain desctruction along crystallographic planes take place (figure 5b).



a) b)

Figure 5. Comparison of the results of a numerical experiment (a) and grain destruction in a real fragment of the microstructure (b).
A* - traces of intercrystalline destruction along crystallographic planes

In accordance with the results of numerical estimates, the maximum stress intensity in tungsten carbide is 9.1 GPa (arising under an external voltage of 3 GPa) - which is 30% less than the maximum stress intensity in a structure with a continuous carbide “skeleton”. In cobalt, under the same load, the stresses are concentrated in the area with the smallest thickness of the interlayers, their intensity reaches 7,4 GPa, which is very close to the value of their microhardness. It means that the destruction of such microstructure type (figure 6b) should start with plastic deformation of cobalt, and the destruction of tungsten carbide will start with a significantly greater load. Indirect confirmation of this is a morphology change of the indenter imprint and microstructure area adjacent to it. The imprint does not have a strongly pronounced faceting, instead of four Palmqvist cracks in the indentation zone, numerous hidden microcracks are formed. The image of the imprint and its model representation are shown in figure a, b. After the load removal (sometimes with some time delay), the areal structure (figure c) and the traces of lateral cracks relieved from residual internal stresses (figure 6d) may be observed on the grinding surface around the imprint along with the "normal" cracks (figure 6a).



a) b)

c) d)

Figure 6. Stress relaxation in the indentation zone on the surface of a fragmentary nanostructured hardmetal composite

Such effects may be also observed in other composite materials of increased hardness with nanostructural fragmentation of the grain structure [11]. The strength improvement predicted by the FEA method in fragmentary nanostructured hardmetal composite correlates with the experimental results of fracture toughness measurements according to Palmqvist. In case of the optimal amount of additives the fracture toughness growth is 50% in comparison with the basic material. This fact was further confirmed by microhardness numerical values of the individual structural fragments, as well as by the integrated index of Vickers hardness of ~ 1600-1650HV. New type of a hardmetal composite can be previously classified (defined) in the area between tool ceramics and hard metals.

References

1 C.J.R. González Oliver, E.A. Álvarez, J.L. García. Kinetics of densification and grain growth in ultrafine WC-Co composites // Int. Journal of Refractory Metals and Hard Materials 59 (2016) 121–131.

2 Panov, V.S., Zaitsev AA Trends of development the technology ultrafine and nanosized tungsten carbide WC-Co–A review //Proceedings of the universities. Powder metallurgy and functional coatings, 2014, no. 3, pp. 38–48.

3. Rempel', A.A., Kurlov, A.S., and Tsvetkov, Yu.V., Tungsten carbide nanopowder for WC–Co hard alloys, Proceedings of the Fourth All-Union Conference on Nanomaterials, Moscow: IMET RAN, 2011, p. 71.

4. Cholsong, P. Microstructure and properties of ultrafine WC-10Co composites with chemically doped VC / P. Cholsong, L. Ji, G. Zhimeng // Rare metals. –2011. –T. 30. –№ 2. –P. 183-188.

5. Huang, S.G. NbC as grain growth inhibitor and carbide in WC–Co hardmetals / S.G. Huang, R.L. Liu, L. Li [ect.] // International Journal of Refractory Metals & Hard Materials. –2008. –no.26. –pp. 389-395.

6. Sun, L. Effects of Cr_3C_2 additions on the densification, grain growth and properties of ultrafine WC-11Co composites by spark plasma sintering / L. Sun, C. Jia, R. Lin Cao, C. Lin // Int. J. Refract. Met. Hard. Mater. – 2008. – V. 26.– P. 357-361.

7 K. Essaki, E.J. Rees, and G.T. Burstein. Synthesis of Nanoparticulate Tungsten Carbide Under Microwave Irradiation // J. Amer. Ceram. Sos. – 2010. – T. 93. – № 3. – C. 692-695.

8 Gordeev, Y. I., Yasinski, V. B., Binchurov, A. S., Anistratenko, N. E., & Nikolaenko, I. V. (2018). Combined Application of Composite Powders WC-Co and Additives of Nanoparticles as an Effective Method of Improving the Properties of Hard Metals. In *Key Engineering Materials* (Vol. 769, pp. 134-140). Trans Tech Publications.

9 Gordeev, Y. I., Abkaryan, A. K., Binchurov, A. S., & Jasinski, V. B. (2014). Design and Investigation of Hard Metal Composites Modified by Nanoparticles. *Advanced Materials Research*, (1040).

10 Dvornik M.I., Mikhaylenko E.A. Study of the strength of VK8 hard metal by the finite element analysis // Chemical physics and mesoscopy. Volume 11, №4, 2009. C. 433-440.

11 Dvilis E.S., Khasanov O.L., Bikbaeva Z.G., Polisadova V.V., Struts V.K., Omarov G.Z., Khasanov A.O. Pattern of the B_4C Ceramics Surface Deformation at Local Loading. *Advanced Materials Research*. – 2014. – vol. 872. – p. 60-64.