Application of Nanoindentation for Constituent Phases Testing in Ceramic-Metal Composites

Irina Hussainova*, Iwona Jasiuk** and Medhat Hussainov***

*Tallinn University of Technology, Department of Materials Technology, Estonia, irhus@staff.ttu.ee
**University of Illinois, Department of Mechanical Science, Urbana, IL, USA, ijasiuk@illinois.edu
***University of Tartu, Institute of Physics, Estonia, medhat.hussainov@ut.ee

ABSTRACT

In this study, mechanical properties of the constituents of three-phase composite based on chromium carbides were measured by means of nanoindentation. Different loading scenarios were applied to different phases testing. The semi-ellipse method for accounting of pile-ups was applied to determine the hardness and modulus of elasticity of the constituents. After the contact area re-consideration, the properties of phases show good agreement with those obtained for the bulk form of the materials. Difference in values that are commonly referred and obtained during the test may point to the formation of new phases during sintering.

Keywords: nanoindentation, composite, hardness, pile-up, modulus of elasticity

1 INTRODUCTION

Many structural materials represent multiphase heterogeneous composites to tailor the properties needed for a specific application. Composite materials with well-controlled microstructures allow obtaining unique combinations of mechanical and/or thermal properties of a final product. Therefore, development of advanced composites requires a detailed knowledge of their constituents' properties as they are often somewhat different from the materials at their bulk form. Evaluation of in situ properties involves measurements in small volumes that can be accomplished by nanoindentation tests. Their main advantage is continues monitoring both the load and displacement of an indenter with high accuracy. Based on the analysis of loading – unloading data, elastic moduli (*E*) and hardness (*H*) as well as their distribution may be successfully determined [1].

The hardness of a material is usually defined as a load divided by a residual projected area. The correct determination of contact area is, therefore, of crucial importance for mechanical properties evaluation because of pile-ups appearing at the indent sides support part of the load and lead to overestimation of *E* and *H*.

In the present study, the nanoindentation techniques of different loading scenarios have been applied to chromium carbide based and nickel – chromium alloy bonded cermets to evaluate the micromechanical properties of the constituent phases. The aim of this paper is to report the experimental data on modulus of elasticity and hardness of cermets' constituents taking into consideration the indentations size effects and uncertainties in the projected area calculation due to pile – ups. Three-phase Cr_3C_2 – Cr_7C_2 – $CrNi_3$ composite, Figure 1, was chosen as a model material to study possibility of distinguishing between ceramic phases of quite similar properties (Cr_3C_2 – Cr_7C_2) as well as dissimilar constituents (carbides – binder alloy). Grain size of the carbides was in the range between 1 and 15 microns.

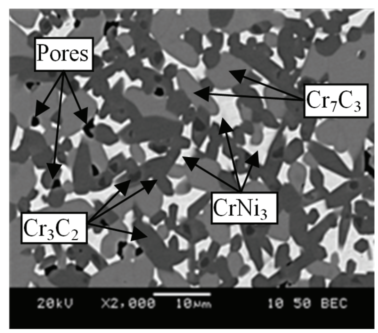


Figure 1: SEM image of the chromium carbide – based composite tested in the present study.

2 EXPERIMENTAL PROCEDURE

Prior to the testing, the samples were polished with a 0.25 µm diamond paste at a final step to obtain a smooth surface of nanometer-scale roughness.

A Hysitron Triboscope Nanomechanical Testing Instrument attached to a Veeco Nanoscope IV atomic force microscope (AFM) with a scanning probe microscope (SPM) controller was used to indent the composite by using a three-sided, pyramid-shaped diamond probe tip (Berkovich tip). The tests were load-controlled and conducted at room temperature. The area for testing was located by AFM imaging, and indentations marks were imaged by AFM after testing. In this study, two load scenarios were prescribed: (1) single – indent mode defined by loading segment duration of 10 s, a holding period at maximal load of 5 s, and unloading segment duration of 10 s; and (2) multi – indent mode defined by multiple step loading and which consisted of 10 loading segments, each up to a partial load and followed by a hold, and, respectively, 10 unloading segments as indicated in Figure 2. During nanoindentation tests the load on specimen and the depth of penetration were recorded and care was taken to properly calibrate for the range of the penetration depths recoded in both hard and soft phases. Because a small amount of cobalt and, therefore, small value of "mean free path", only scenario 1 with the maximum load of 2000 μN was applied during testing of the binder phase. Loading up to 8000 μN was used in scenario 2.

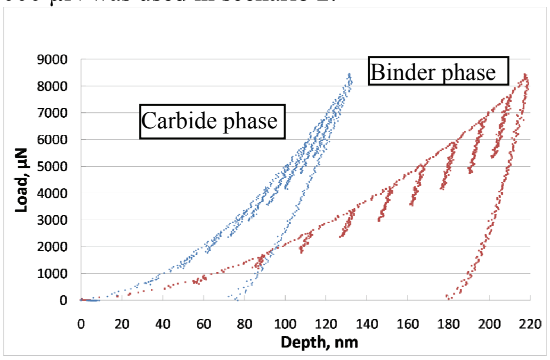


Figure 2: Load – displacement curves obtained during nanoindentation tests via scenario 2.

The analyzed area was firstly detected with the help of scanning electron microscope (SEM) JEOL 6060LV, Figure 3, guided by Vickers indents marks. This procedure is necessary to identify the phases despite the fact that it is time consuming. More than 20 indentations were performed for each phase and values of hardness and reduced moduli averaged. Figure 3 also represents the STM image of one of the tested zones with well recognizable indentation sites.

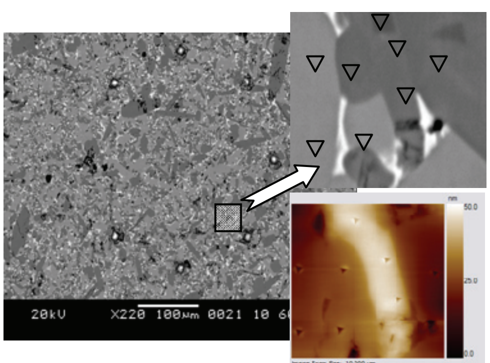


Figure 3: SEM and SPM images of the tested area.

The well-developed method for H and E determination based on the Oliver – Pharr approach [1], implying that contact stiffness of a material, S, can be experimentally obtained from the slope of unloading part of a load – displacement curve, was applied at the present study. For the Berkovich tip the contact area, A, is calculated as A = $24.56h_c^2$, where h_c is a contact depth. Based on the theory of rigid contact, the reduced modulus can be calculated as following:

$$E_r = S\sqrt{\pi} / 2\beta\sqrt{A} = \left[\frac{(1-\upsilon^2)}{E} + \frac{(1-\upsilon_i^2)}{E_i}\right]^{-1} , \quad (1)$$

where E_i and ν_i are Young's modulus and Poisson's ratio of the indenter (for diamond E_i = 1141 GPa and ν_i = 0.07).

To evaluate the true contact area, the AFM imaging was incorporated into measurements and simple, yet effective method proposed in [2] was applied for H and E re-calculations. The basic idea is approximating the area of the pile-up contact perimeter as a semi-ellipse and including this pile-up area in the analysis [2].

3 RESULTS AND DISCUSSION

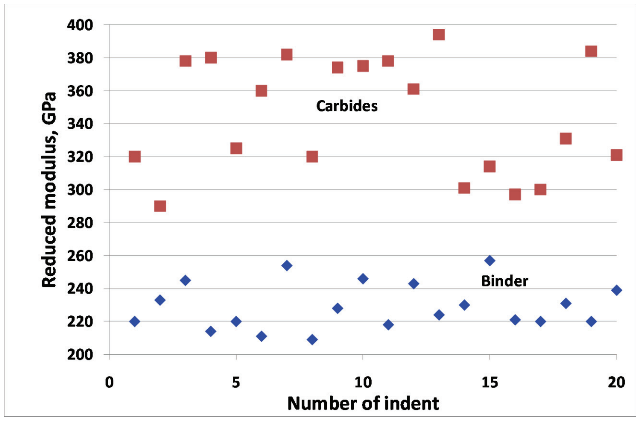
Figure 2 shows the representative load – displacement curves for different phases. Once a contact depth is known, the resulting radius of circle of contact is determined by simple geometry and used to determine the mean contact pressure or hardness H and reduced elastic modulus E_r (Eq. 1). Then, elastic modules are converted from reduced modules assuming a Poisson's ratio of 0.21 for both carbides and 0.3 for nickel alloy.

Analysis of the results obtained through the scenario 1 has revealed two well distinguished groups of parameters: one of them is ranged around a mean value of 5 (±2.7) GPa for H and 230 (±27) GPa for E_r while another one is grouped around 25 (±9) GPa for H and 360 (±50) GPa for E_r, Figure 4.

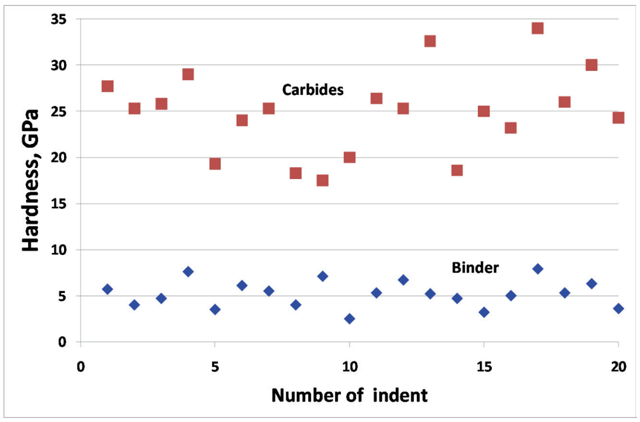
Quite large data scattering reflects the uncertainty in the spatial placement of indentations as under AFM the constituent phases are not clearly recognizable. The imprints in carbides subjected to a low load were not distinguished under SEM, also. Figure 4c shows the schematic diagram of possible indentation sites. Pores, presence of different phases in the nearest proximity of the tested area of material, interface and so on, all these features influence the results obtained.

To distinguish the carbide phases the higher load under scenario 2 was applied. Analysis of the data obtained from testing revealed three ranges of parameters for the studied cermet. The first one is grouped around the mean values of 28 (±3) GPa for H and 390 (±20) GPa for E_r; while another group exhibits values of about 22 (±2.5) GPa for H and 320 (±11) GPa for E_r. Undoubtedly, these parameters describe the carbides in the cermet materials. The third group corresponded to 5.5 (±3.6) GPa for H and 250 (±43) GPa for E_r. Figure 5 displays the modulus and hardness of the constituent phases measured at 20 arbitrary selected points in each phase.

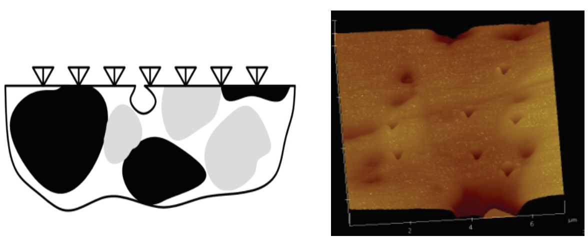
The residual imprints left by indent at 8000 μN are well visible under SEM and two carbide phases can be clearly indicated. At this load scattering of the data obtained for binder phase is much larger.



a



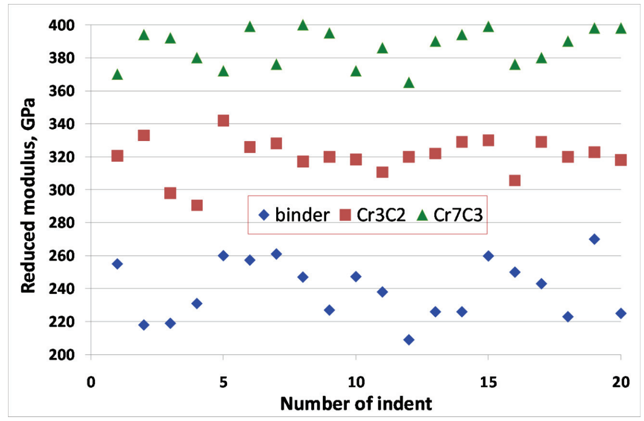
b



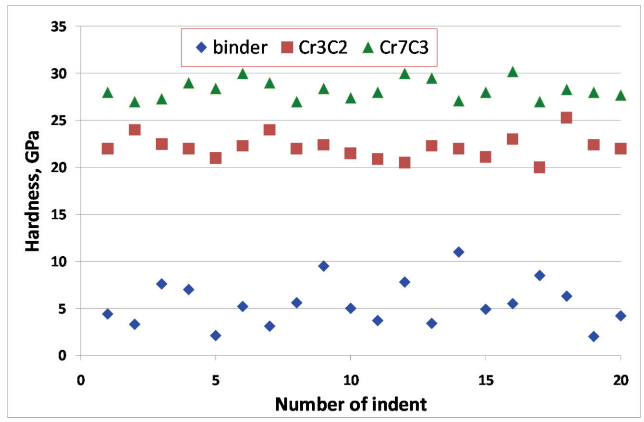
c

Figure 4: (a) – Reduced modulus of the constituents; and (b) – hardness as measured via scenario 1; (c) – schematic view of possible indentation sites.

That may be explained by low metal content leading to the strong "proximity effect" due to violation of the conditions $h/D \leq 1/10$, where h is a penetration depth and D is the radius of an indented particle. The neighboring matrix affects the measured values and test gives somewhat "joint" properties of the neighboring phases. A special care should be taken when the binder phase is tested. In the case when scenario 1 was applied, the contact depth was around 300 nm that is close to 1/10 of alloy islands between hard grains. In contrast, the properties of carbides have larger scattering when measured at low load.



a



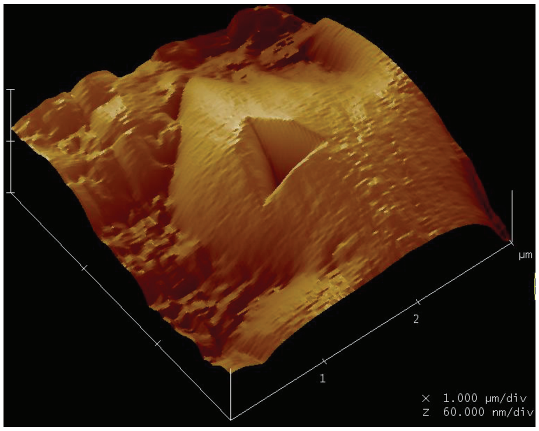
b

Figure 5: (a) – Reduced modulus of the constituents; and (b) – hardness as measured via scenario 2.

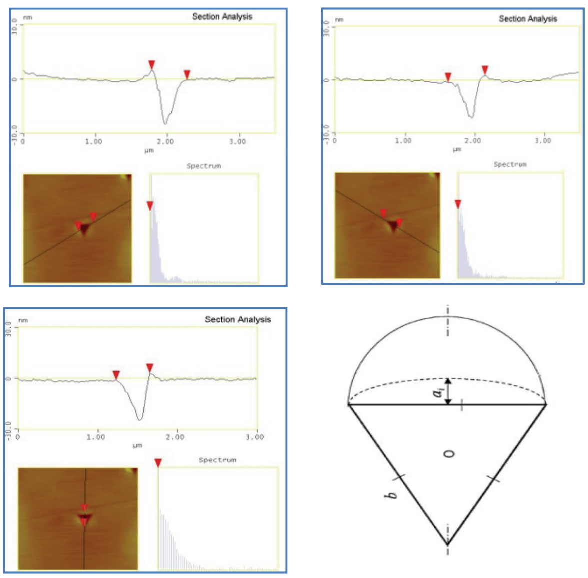
The hardness measured by the nanoindentation in the binder metal is much higher than that in the bulk alloy. The high hardness of the binder metal may be due to the solid solution of Cr and C in nickel during sintering, and to the surface preparation (polishing). Somewhat higher than expected hardness of both types of carbides may be attributed, to some extent, to the residual stresses present within the specimens as a result of processing (mismatch in coefficients of thermal expansion between phases) leaving carbides in compression [3]. However, the true values of hardness and modulus may only be obtained by taking the pile-ups into consideration.

Examination of the indentation sites indicates the pile-ups around the indents, Figure 6. Line profiles along a median of one of the indents are made with the help of AFM. The procedure for calculation of the contact area due to pile-ups is described in details elsewhere [2]. The present study follows the algorithm of the pile-up contact width determination as the width of the semi-ellipse projected by the squeezed out material as it shown in Figure 6b.

Assuming that the projected contact area, determined at contact depth, h_c, traces an equilateral triangle of side b, then for a perfect Berkovich tip, $A = 24.5\ h_c^2 = 0.433\ b^2$ and $b = 7.531\ h_c$. At each indentation, a_i for three sides may be different and, therefore, the total contact area can be calculated as $A = A_{impr} + A_{ad} = A_{impr} + 5.915h_c \sum a_i$, where A_{impr} is the area of imprint derived from the Oliver–Pharr method and A_{ad} is the total pile-up contact area.



a



b

Figure 6: (a) - 3D image showing pile-ups around a nanoindent; (b) – lateral images of an imprint and cross-sectional profiles for a real contact area calculation; and schematic approximation of the indent.

Moduli of elasticity and hardness values for the constituents as reported at the published literature [4] as well as determined before and after area correction are summarized in Table 1.

Values of H before pile-up corrections were higher than the upper limits given for these materials in the literature. After re-consideration of the contact areas a very good agreement with published data was found. Binder $CrNi_3$ solid solution shows the modulus of elasticity quite similar to that reported for bulk nickel-chrome solution.

Phase	Modulus of elasticity, GPa		
	Bulk [4]	Measured	Calculated
$CrNi_3$	210 – 255	230 ± 27	216.3±10.5
Cr_3C_2	373 – 386	320 ± 11	314.6±8.8
Cr_7C_3	340 – 400	390 ± 20	340.3±4.9
	Hardness, GPa		
$CrNi_3$	0.7 – 3	5 ± 2.7	2.5 ± 1.0
Cr_3C_2	10.2 – 18	22 ± 2.5	17.8 ± 1.6
Cr_7C_3	16 – 20	28 ± 3.0	22.5 ± 1.5

Table 1: Modulus of elasticity and hardness of the composite constituents.

However, the modulus measured for both modifications of chromium carbides is smaller than it could be expected. It is very possible that the solubility of nickel in carbide and its influence on the carbide properties results in the formation of carbide structures that differ from structures of commonly referred ones. EDS analysis of the elemental distribution indicates the presence of high amount of free carbon throughout the structure, solubility of nickel in hexagonal chromium carbide Cr_7C_3 and spurious phases formation.

4 CONCLUSIONS

The data analysis and re-calculation of the projected area are of primary importance for evaluation of the mechanical properties (E and H) extracted from the nanoindentation tests on the constituent phases of composites. All constituents show some degree of plastic deformation forming the pile – ups around nanoindents. The semi-ellipse method for accounting of pile – ups has been applied to multiphase material and after the contact area re-consideration, the hardness and module of phases show good agreement with published data. Difference in values that are commonly referred and obtained during the test may point to the formation of new phases during sintering and, therefore, to the possible different behavior of the bulk composite under loading from that as it may be expected at the design stage. Data extracted from nanoindentation may serve as the inputs for materials design and modeling.

5 ACKNOWLEDGEMENTS

Estonian Science Foundation under grants No 8211, JD120 and T062 are acknowledged for financial support of this research.

REFERENCES

[1] W.C. Oliver, G. Pharr, J.Mater.Res., 7, 1564, 1996.
[2] K.O. Kese, Z.C. Li, Scipta Materialia, 55, 699, 2006.
[3] I.Hussainova, I. Jasiuk, M. Sardela, M. Antonov, Wear, 267, 152, 2009.
[4] MatWeb. Searchable database of materials sheets. Obtained through Internet: www.matweb.com (accessed 04/08/2010).