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Hardmetals with nanograin reinforced binder: Binder fine structure and hardness

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Abstract

Ultra-coarse grained WC–Co hardmetals with nanograin reinforced binder and the trade name Master Grades were recently developed and implemented in industry on a large scale. The results on the binder fine structure of the binder of the Master Grade obtained by TEM and HRTEM indicate the presence of nanoparticles of several nanometers in size embedded in a matrix of fcc Co. The micro-hardness of the binder of conventional hardmetals with various carbon contents is found to vary from $HV_{0.05} = 360$ to $HV_{0.05} = 470$, whereas that of the nanograin reinforced binder is equal to $HV_{0.05} = 780$. The nanohardness of the binder of a conventional ultra-coarse grade and the Master Grade is found to be roughly 7.5 GPa and 10.2 GPa and their Young's modulus is equal to 390 GPa and 410 GPa correspondingly.

Keywords: Binder; Nanograins; Master Grades; Hardness; Microstructure

1. Introduction

The need for improved cemented carbides for various applications, particularly for mining and construction, is rapidly growing. Wear and failures of cemented carbide buttons and inserts in drilling bits, road-planing picks, coal-cutting picks, etc., are the major factors determining the effectiveness of mining and construction tools. Such tools work under extremely harsh operating conditions including temperatures of nearly 1000 °C, high impact loads, thermal shock, intensive abrasive wear and severe fatigue. WC–Co cemented carbides is the only type of hard materials that can be employed in such an unfavorable environment due to the unique combination of physical, mechanical and performance properties. However, in many cases, conventional WC–Co cemented carbides now operate above the limit of their physical, mechanical and performance properties resulting in short tool lives. Thus, the development of novel cemented carbides with improved combinations of hardness, fracture toughness and wear-resistance is now the task of great importance.

One of the major routes for dramatic improvements of physico-mechanical and performance properties of various materials is the development of nanostructured materials. The problem of the low lives of carbide tools could possibly be solved by developing nanograined WC–Co cemented carbides. There are a great number of initiatives evaluating the possibility of fabrication of nanostructured WC–Co cemented carbides from WC nanopowders. However, all the attempts to obtain nanograined cemented carbides from WC nanopowders have failed so far because of the

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intensive growth of WC nanograins during sintering. The finest cemented carbides obtained from nanopowders by conventional powder metallurgy techniques had a WC mean grain size of above 0.2 μm, so that they cannot be considered as nanomaterials.

Recently, we elaborated a fundamentally new approach to the development of nanostructured WC–Co hardmetals [1–5]. It includes binder reinforcement by hard nanoparticles of the θ-phase (Co_2W_4C). Novel WC–Co hardmetals with nanograin reinforced binder, designated as the Master Grades were developed and implemented in industry on a large scale. Results of numerous laboratory and field tests of the Master Grades in road-planing and concrete-, coal- and granite-cutting indicate that their wear-resistance is higher by a factor of 2–5 compared to conventional hardmetals of the same Co content and similar WC mean grain size. The significant improvement in wear-resistance of the new hardmetals is accomplished by a decrease of the number of broken road-planing and coal-cutting picks during the field tests resulting in a dramatic increase of their tool lifetime [1].

Here we present some results on the binder structure and hardness of the new hardmetals.

2. Experimental details

Transmission electron microscopy (TEM) of the binder of the new hardmetals was carried out by use of a Jeol-2000FX instrument and its high-resolution transmission electron microscopy (HRTEM) was performed on a JEOL-4000FX instrument. The specimens for transmission electron microscopy were prepared by successive dimpling and ion milling procedure on facilities from the Gatan Company. Fracture toughness was examined by the Palmqvist method after indentation of metallurgical cross-sections at a load of 1000 N. The binder micro-hardness was measured on a Leitz 7862 instrument at a load of 50 g on special model WC–50%Co samples having large areas of the Co-based binder. The model samples simulating conventional WC–Co hardmetals were made with various carbon contents by adding either carbon black or tungsten metal to the WC–Co mixture. The powder mixtures of all the samples were made by mixing 0.6 μm WC with Co in a Turbular mixer for 1 h. The model samples were sintered in Al_2O_3 crucibles at 1400 °C for 75 min (vacuum at a pressure of 10 mbar for 45 min + HIP in Ar at a pressure of 50 bar for 30 min). The Young's modulus and nanohardness of the binder of a conventional ultra-coarse grade with 6.5% Co and the Master Grade for road-planing were measured by use of add-on depth-sensing nanoindentation [6]. The spatially and depth resolved information on the micromechanical properties of the binder is determined by an nanoindentation device (Hysitron TriboScope) mounted on a scanner head of an atomic force microscope (AFM) (Park Scientific Instruments, AutoProbe CP). The immediate combination of this nanoindentation device with AFM allows imaging and indenting the surface with the tip, which enables the tip to be positioned for indentation with an accuracy of down to 20 nm. The measurements were carried out at a load of 500 μN using a Bercovich Indenter. The obtained load–displacement curves were corrected and analyzed according to the Oliver–Pharr-method [7,8]. The values of Young's modulus of the binder were calculated also by use of the method described in Refs. [7,8]. As a result of the nanoindentation measurements, two curves indicating the indenter displacement versus the applied force at loading and unloading are recorded. The nanohardness and Young's modulus values are determined by computer-aided mathematical treatment of the both curves.

3. Results and discussion

Fig. 1a shows the microstructure of the Master Grade for coal-cutting and tunnelling. The microstructure comprises rounded WC grains and large Co interlayers. As can be seen

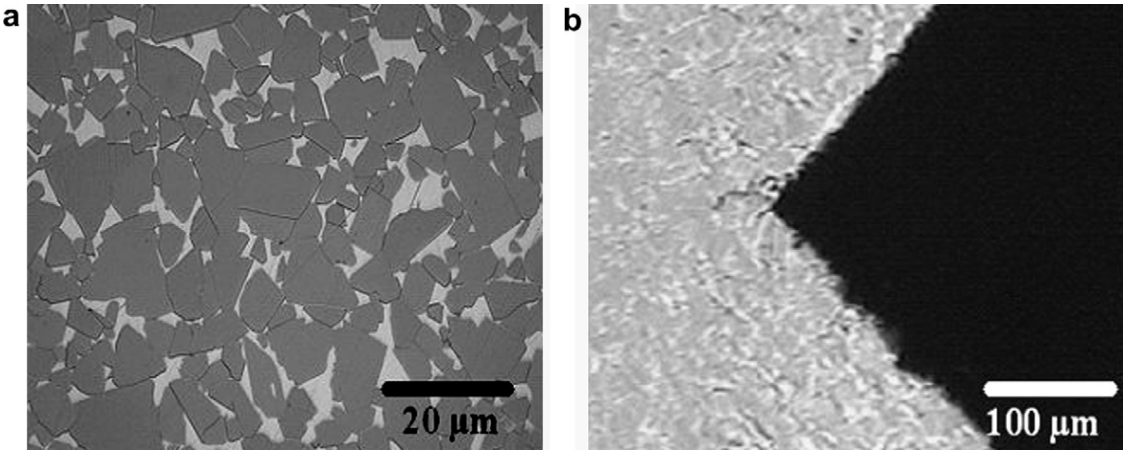

Fig. 1. Microstructure of the Master Grade for coal-cutting and tunnelling (a) and typical cracks near the Vickers indentation on the surface of the Master Grade at a load of 1000 N (b).

in Fig. 1b the Palmqvist cracks near the Vickers indentation on the new grade are very short, so that its Palmqvist fracture toughness K_{1C} normally exceeds 20 MPa m$^{1/2}$. In particular, K_{1C} of the sample shown in Fig. 1 is 20.4 MPa m$^{1/2}$. The hardness of the new grade for coal-cutting and tunnelling is $HV_{10} = 1050 \pm 50$, which, along with the binder nanograin reinforcement, ensures its high wear-resistance in cutting of abrasive rock. Note that the energy subjected to the surface of the new grade by indentation can be effectively dissipated by formation of numerous tiny micro-cracks near the Vickers indentation. The length of such cracks is usually comparable with the size of 2–3

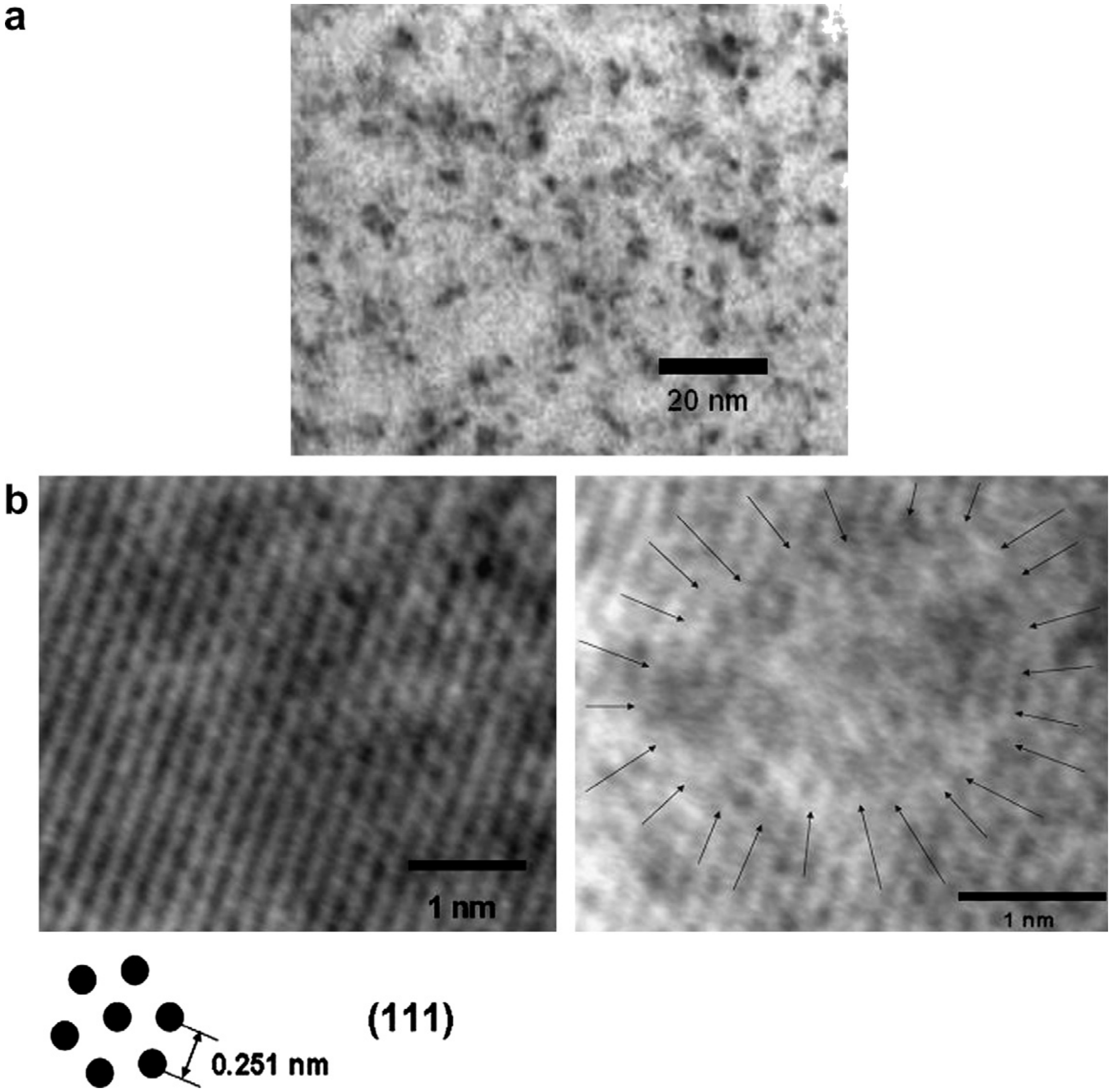

Fig. 2. Dark field TEM image (a) and HRTEM image (b) of the binder of the Master Grade. The dark field TEM image is taken using the (1 1 1) reflection of the θ-phase. The HRTEM image comprises the atomic structure of an fcc Co single-crystal with the orientation of (1 1 1) (left) and a nanoparticle embedded in the Co matrix (right); the interface between the nanoparticle and Co matrix is indicated by arrows.

Table 1
Composition and physical properties of the model WC–Co samples

No.	Sample	Phase composition	Hc Oe	Magnetic saturation μTm^3/kg, and % of its theor. value	
1	50% WC–50%Co	WC + Co	32.0	90.2	89
2	50% WC–50%Co–1.5% C	WC + Co + graphite	48.3	94.3	93
3	50%WC–50% Co–5% C	WC + Co + graphite	47.5	92.1	91
4	47.5% WC–50%Co–2.5%W	WC + Co	28.8	80.1	79
5	40%WC–50%Co–10%W	WC + Co + η-phase	27.4	71.0	70

carbide grains, and their propagation can effectively be suppressed by the thick Co interlayers. The high fracture toughness of the new grades is quite important when taking into account very high impact mechanical and thermal loads occurring in the performance of picks for coal-cutting and tunneling.

Fig. 2 shows a dark field TEM image and a HRTEM image of the binder of the Master Grade. It can be seen from the TEM image that the nanoparticles which are uniformly distributed in the binder have a size of roughly 1–5 nm. The HRTEM image shows a single-crystal of fcc Co with the crystal orientation of (1 1 1) and a nanoparticle of roughly 2 nm embedded in it. Such nanoparticles of the hard θ-phase can effectively harden and reinforced the Co-based binder without decrease of its fracture toughness. As a result, the high performance of the Master Grades with the nanograin reinforced binder compared to conventional WC–Co grades can be obtained.

It is well known that the binder hardness of WC–Co hardmetals depends on the carbon and consequently tungsten content in the binder (see e.g. [9–11]). Special model WC–Co samples with 50% Co were made in order to examine and compare the binder micro-hardness of the Master Grades with that of conventional WC–Co hardmetals with various carbon contents. These model samples simulating real hardmetals were made by adding carbon black or tungsten metal to WC–Co. A model sample with 50% Co simulating the binder of the Master Grades was also prepared.

Table 1 and Fig. 3 show the phase composition, coercivity, magnetic saturation and microstructure of the model samples with various carbon contents. It can be seen that two model samples, without W metal (sample 1) and with 2.5% W metal (sample 4), have a two-phase microstructure with no graphite or η-phase. The microstructure of the two other samples with additions of carbon black (sample 2 and 4) comprises graphite; these two samples have similar values of magnetic saturation and coercivity. The microstructure of the sample 5 with 10% W metal comprises η-phase both in form of large particles and fine inclusions. Note

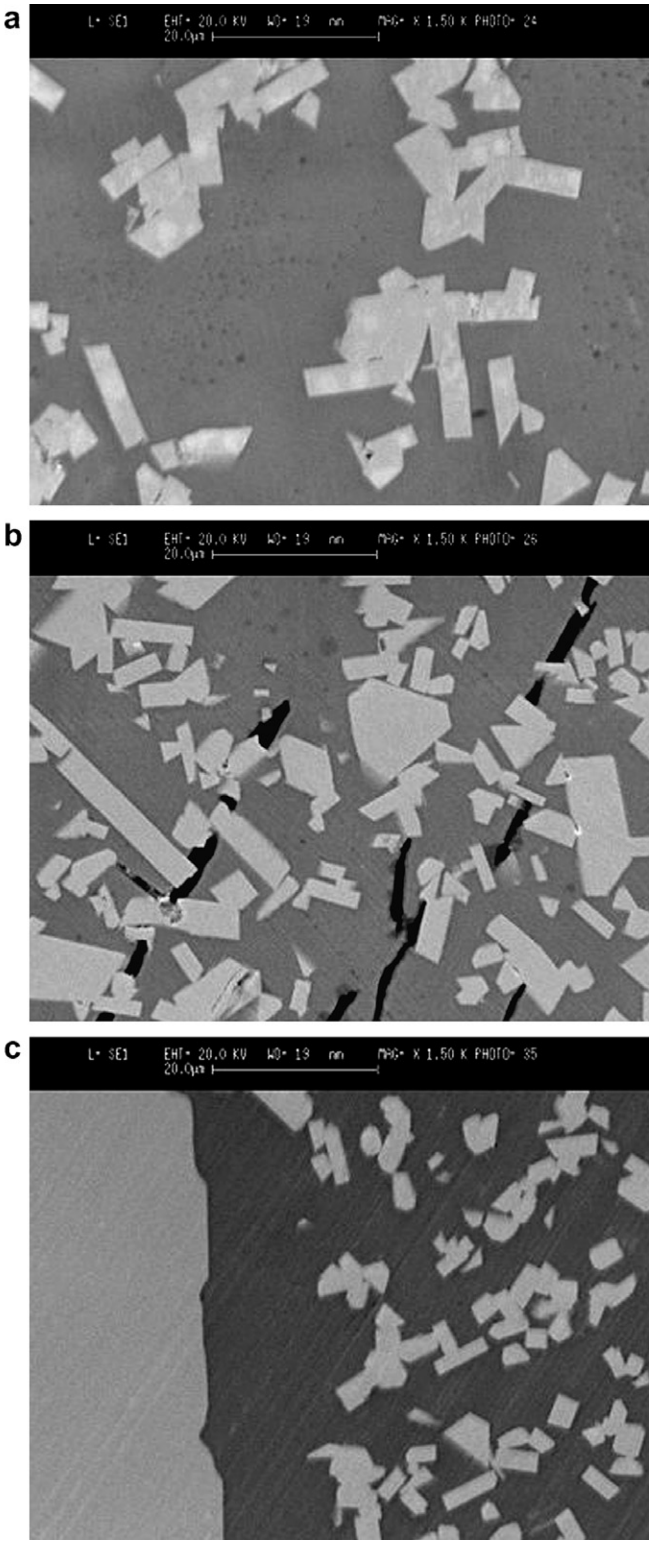

Fig. 3. Microstructure of the model samples, 1000×: (a) the two-phase sample 1; (b) the sample 2 containing some free carbon; and (c) the sample 5 containing η-phase. A large grain of η-phase is situated in (c) on the left and has a bright color.

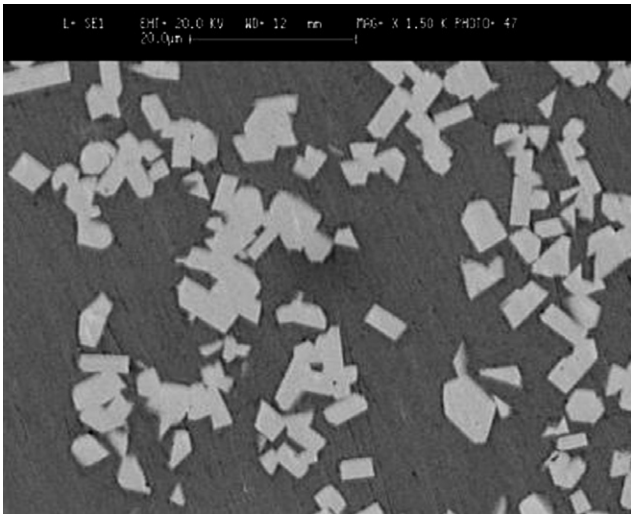

Fig. 4. Microstructure of the model sample simulating the binder of the Master Grades.

that the coercivity of the samples with free carbon is noticeably higher than that of the two-phase samples and the sample containing η-phase. It should be also noted that the magnetic saturation of the two-phase samples and even the samples containing free carbon is significantly lower than the theoretical value, that has to be equal to roughly 100.9 $\mu Tm^3/kg$ for the hardmetals with 50 wt.% Co. This is presumably a result of partial evaporation of Co during sintering and high W concentrations in the binder of all the samples. The binder micro-hardness of the model samples is equal to $HV_{0.05} = 360$ (samples 2 and 3 comprising graphite) and to $HV_{0.05} = 470$ for the two-phase sample 1 and 4, and the sample 5 containing η-phase. When taking into account the values of magnetic saturation of the model samples produced by adding carbon black, it can be concluded that the lower binder hardness of these samples is related to the low amount of tungsten dissolved in the binder.

Fig. 4 shows the microstructure of the model sample with 50% Co simulating the Master Grades. Its microstructure is similar to that of the model samples simulating conventional hardmetals, except that it comprises slightly rounded WC grains. The binder micro-hardness obtained on the model sample simulating the Master Grades is equal to HV = 780. This value is slightly higher than that obtained on samples of the Master Grades with large Co pool [1,2]. It should be noted that the accuracy of measurements of the binder micro-hardness in the present work is better than that of Refs. [1,2], as the binder areas of the model samples with 50% Co are significantly larger than those of the samples examined in Refs. [1,2]. The regions of the Co-based binder employed for the measurement of

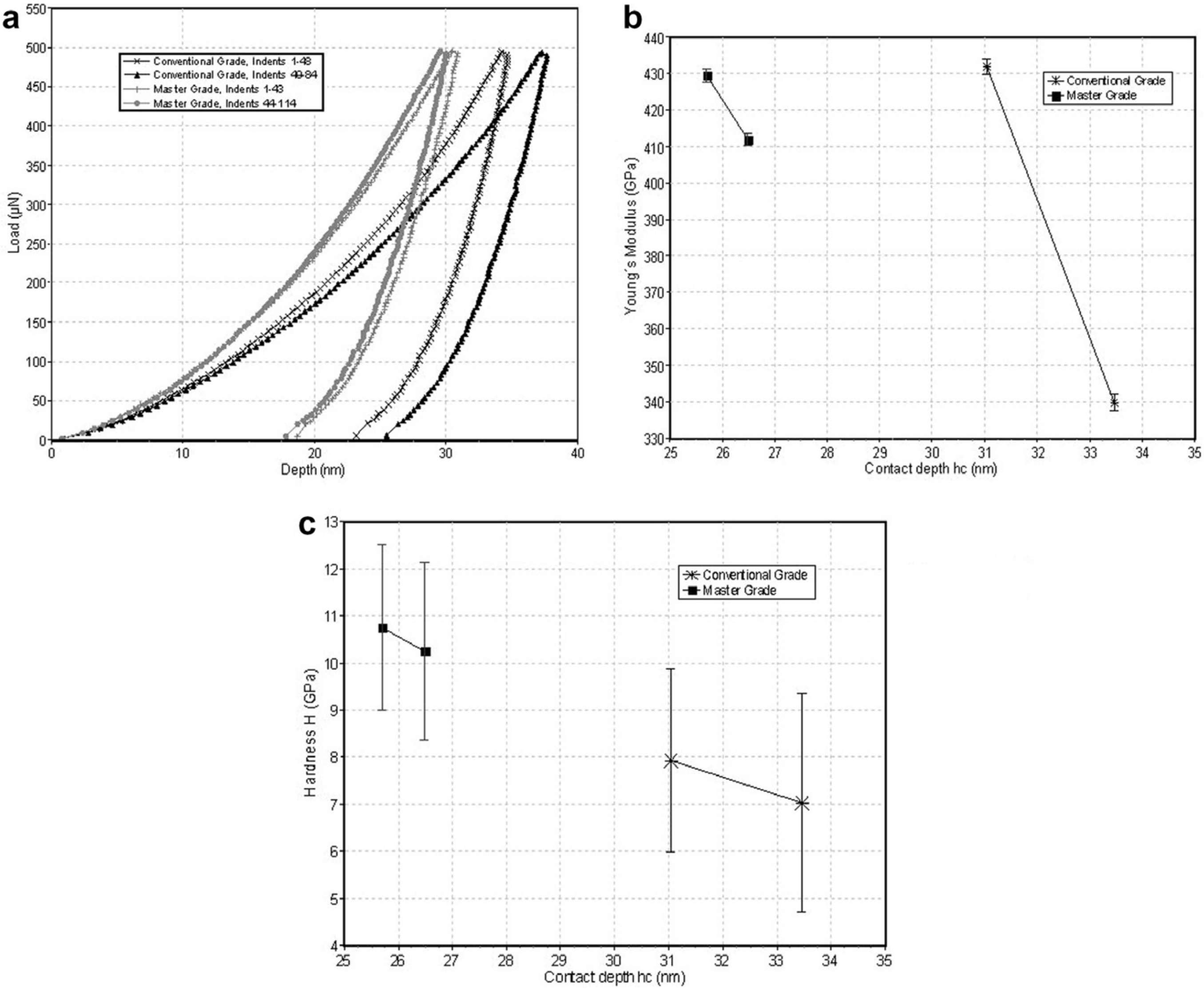

Fig. 5. (a) Curves characterizing the indenter displacement vs. contact depth, (b) Young's modulus and (c) nanohardness of the binder of a conventional ultra-coarse grade with 6.5% binder and the corresponding Master Grade. The curves characterizing the indenter displacement vs. contact depth for both the conventional grade and the Master Grade were obtained on the basis of results of two series of measurements indicated as "Indents 1–48" and "Indents 49–84" for the conventional grade and "Indents 1–43" and "Indents 44–114" for the Master Grade.

micro-hardness in the present work were at least 50 μm, which is significantly larger than those used in the previous works [1,2], where they were of the order of 30 μm. Thus, the influence of the neighboring WC grains on the micro-hardness results in the present work was insignificant when taking into account that the indentation sizes did not exceed 15 μm.

Fig. 5 shows the results of nanoindentation of the binder of a conventional ultra-coarse grade with 6.5% Co and the corresponding Master Grade. The curves characterizing the indenter displacement vs. contact depth for both the conventional grade and the Master Grade shown in Fig. 5a are obtained on the basis of results of two series of measurements indicated as “Indents 1–48” and “Indents 49–84” for the conventional grade and “Indents 1–43” and “Indents 44–114” for the Master Grade. The Young’s modulus of the binder of the conventional grade is found to be 390 GPa and that of the Master Grades to be 410 GPa; the higher modulus of the nanograin reinforced binder is presumably a result of the presence of the nanoparticles. However, the slight differences in binder elasticity are unlikely to affect performance. The binder nanohardness of the conventional grade is equal to 7.5 GPa, whereas that of the Master Grade is equal to 10.2 GPa. Both values of nanohardness are significantly higher compared to the micro-hardness values obtained on the model samples. Such a high difference can be explained by special features of the nanoindentation method, in which hardness is measured on the basis of the spatially and depth resolved information during the indentation.

4. Conclusions

The results of TEM and HRTEM of the binder of the Master Grade indicate the presence of nanoparticles of several nanometers in size embedded in the matrix of fcc Co. The micro-hardness of the binder examined by use of model WC–Co alloys containing 50% Co total with various carbon contents varies from $HV_{0.05} = 360$ to $HV_{0.05} = 470$ for conventional hardmetals and is equal to $HV_{0.05} = 780$ for the Master Grade. The nanohardness values of the binder of a conventional ultra-coarse grade and the Master Grade are found to be 7.5 GPa and 10.2 GPa and their Young’s modulus values are equal to 390 GPa and 410 GPa correspondingly.

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