WC-Co Hardmetals with Nano-Grain Reinforced Binder: Binder Structure on the Micro-, Nano- and Atomic-Level

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Ultra-coarse grained WC-Co hardmetals with nano-grain 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 obtained by high-resolution transmission electron microscopy indicate the presence of nano-particles of several nanometers in size embedded in the matrix of fcc Co. The micro-hardness of the binder of conventional hardmetals with various carbon contents is found to vary from roughly $HV_{0.1}$=360 to $HV_{0.1}$=460, whereas that of the nano-grain reinforced binder is equal to $HV_{0.1}$=770. The nano-hardness 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.

Introduction

The need for improved hardmetals for various applications, particularly for mining and construction, is rapidly growing. Wear and failures of hardmetal 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. Thus, the development of novel hardmetals with improved combination of hardness and fracture toughness is the task of great importance.

Recently, we elaborated a fundamentally new approach to the development of nano-structured WC-Co hardmetals [1, 2]. It includes the employment of the binder reinforcement by hard nano-particles of the θ-phase (Co_2W_4C). Novel WC-Co hardmetals with nano-grain reinforced binder designated as the MASTER GRADES were developed and implemented in industry on a large scale. Here we present some results on the binder structure of the new hardmetals as well as results on its micro- and nano-hardness.

Experimental Details

High resolution transmission electron microscopy (HRTEM) of the binder of the new hardmetals was carried out on the JEOL-4000FX instrument. The specimens for the TEM investigations were prepared by successive dimpling and ion milling procedure on the GATAN facilities. Fracture toughness was examined by the Palmquist method after indentation of metallurgical cross-sections at a load of 1000 N. The binder micro-hardness was measured by use of a Leitz 7862 instrument at a load of 100 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 hr. The model samples were sintered in Al_2O_3 crucibles at 1400°C for 75 min (vacuum + HIP). The Young's modulus and nano-hardness 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 the Hysitron TriboScope instrument.

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 it can be seen in Fig 1b the Palmquist cracks near the Vickers indentation on the new grade are very tiny and short, so that its Palmquist fracture toughness K_{1C} of the grade 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±50, which, along with the binder 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 to 3 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 real performance of picks for coal-cutting and tunnelling

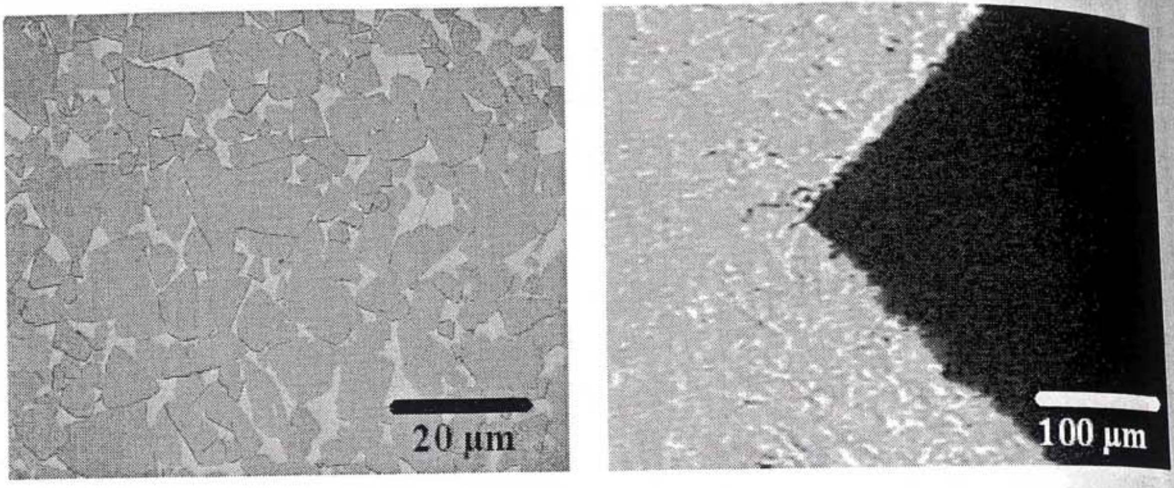

Figure 1. Microstructure of the Master Grade for coal-cutting und tunnelling (a) and (b) typical cracks near the Vickers indentation on the surface of the Master Grade at a load of 1000 N.

It is well known that the binder hardness of WC-Co hardmetals depends on the carbon and consequently tungsten content (see e.g. [3, 4]). 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; at the same time a model sample with 50% Co simulating the Master Grades was also prepared.

Table 1 and Fig. 2 show the phase composition, coercivity and magnetic saturation of the model samples as well as their binder micro-hardness. It can be seen that two model samples (sample 1 and 4) without W metal and with 2.5% W metal are two-phase with no graphite or η-phase, whereas the sample 4 has a lower magnetic saturation and slightly lower coercivity. The microstructure of the two other samples with additions of carbon black (sample 2 and 4) has either small or medium amounts of graphite; the 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 that the coercivity of all the samples decreases with decreasing the magnetic saturation, which is not typical for conventional hardmetals. 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 µTm³/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 even samples containing free carbon. The binder micro-hardness of the model samples is equal to $HV_{0.1}$=360 for the model samples 2 and 3 comprising graphite and $HV_{0.1}$=460 for the two-phase sample 1 and 4 as well as the sample 5 containing η-phase. The values of the binder micro-hardness of the model samples are noticeably higher than those obtained in ref. [3], where the micro-hardness of the binder of hardmetals with various carbon contents varied from nearly 250 to 350 kg/mm^2. The micro-hardness of our model samples was measured very carefully and the micro-hardness was calculated as an average value of measurements of at least 10 binder regions. The difference in the results obtained in ref. [3] and our results can presumably be explained by the lower W contents in the binder of the hardmetals examined in ref. [3].

Fig. 3 shows the microstructure of the model sample with 50% Co simulating the Master Grades. Its microstructure is similar to that of the model samples except for it comprises light rings and globules in the binder volume having a yellowish colour after etching in the Murakami reagent. These rings are presumably composed of agglomerates of nano-particles of the θ-phase, the concentration of which in some regions can exceed their average concentration in the binder phase. The binder micro-hardness obtained on the model sample simulating the Master Grades is equal to HV=770. This value is slightly higher than that obtained on hardmetal sample with large Co pool [1, 2]. It should be noted that the exactness of measurements of the binder micro-hardness obtained in the present work is higher 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].

Fig.4 shows the results of nano-indentation of the binder of a conventional ultra-coarse grade with 6.5% Co and the corresponding Master Grade. The Young's modulus of the binder of the conventional grade is found to be roughly 390 GPa and that of the Master Grades to be nearly 410 MPa. The binder nano-hardness 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 nano-hardness 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 nano-indentation method, in which hardness is measured on the basis of the indenter displacement.

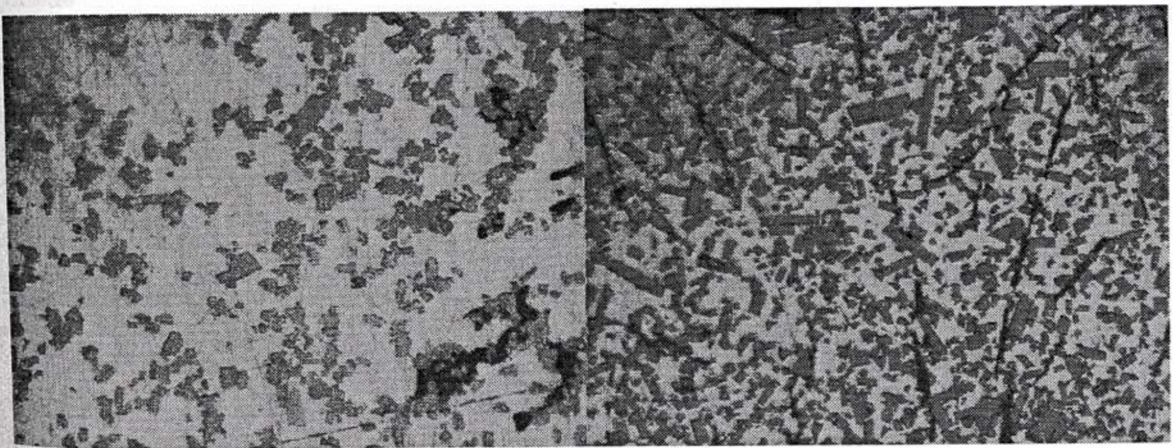

Figure 2. Microstructure of the model samples 5 containing η-phase (left) and 2 containing free carbon (right), x1000.

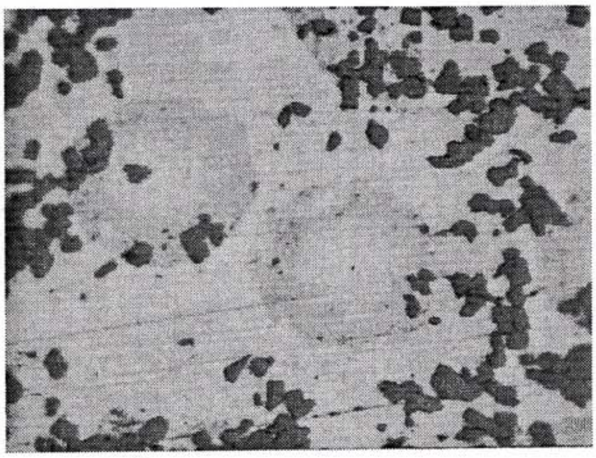

Figure 3. Microstructure of the model sample simulating the nano-grain reinforced binder of the Master Grades, x1000.

No.	Sample	Phase composition	Hc Oe	Magn. Saturation µTm³/kg; % of the theor. value		Binder micro-hardness HV $_{0.1}$
1	50% WC–50%Co	WC + Co	32.0	90.2	89%	460
2	50% WC–50%Co-1.5% C	WC + Co + graphite	48.3	94.3	93%	360
3	50%WC-50% Co-5% C	WC + Co + graphite	47.5	92.1	91%	360
4	47.5% WC-50%Co-2.5%W	WC + Co	28.8	80.1	79%	460
5	40%WC-50%Co-10%W	WC + Co + η-phase	27.4	71.0	70%	460

Table 1. Physical properties and binder micro-hardness of the model samples.

Fig.4 shows the results of nano-indentation of the binder of a conventional ultra-coarse grade with 6.5% Co and the corresponding Master Grade. The Young's modulus of the binder of the conventional grade is found to be roughly 390 GPa and that of the Master Grades nearly 410 MPa; the higher modulus of the nano-grain reinforced binder being due to the presence of the nano-particles. However, the slight differences in binder elasticity are unlikely to affect performance.

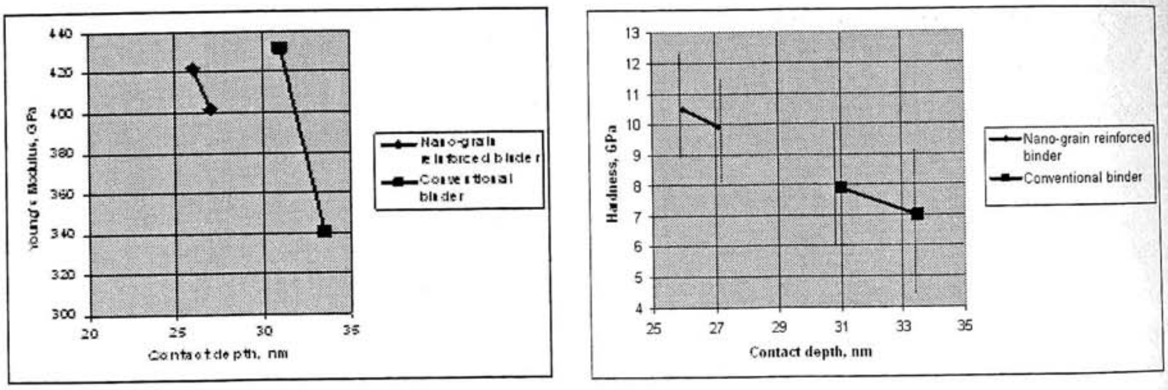

Figure 4. Young's modulus (left) and nano-hardness (right) of the binder of a conventional ultra-coarse grade and the Master Grade.

Fig. 5 shows HRTEM images of the Co-based binder of the Master Grade. Two regions of the Co-based binder composed of Co single crystals with the crystal orientations of (111) and (100) were examined. It can be seen that the binder comprises nano-particles of several nanometer in size. It can also be seen that the nano-particles do not have a distinct interface with the face-centered cubic (fcc) Co matrix, i.e. the nano-particles are coherent with the matrix.

Conclusions.

The micro-hardness of the binder examined by use of model WC-Co alloys containing 50% Co with various carbon contents varies from roughly $HV_{0.1}$=360 to $HV_{0.1}$=460 for conventional hardmetals and is equal to $HV_{0.1}$=770 for the Master Grades. The nano-hardness 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 roughly 390 GPa and 410 GPa correspondingly. The HRTEM results indicate the presence of nano-particles of several nanometers in size embedded in the matrix of fcc Co.

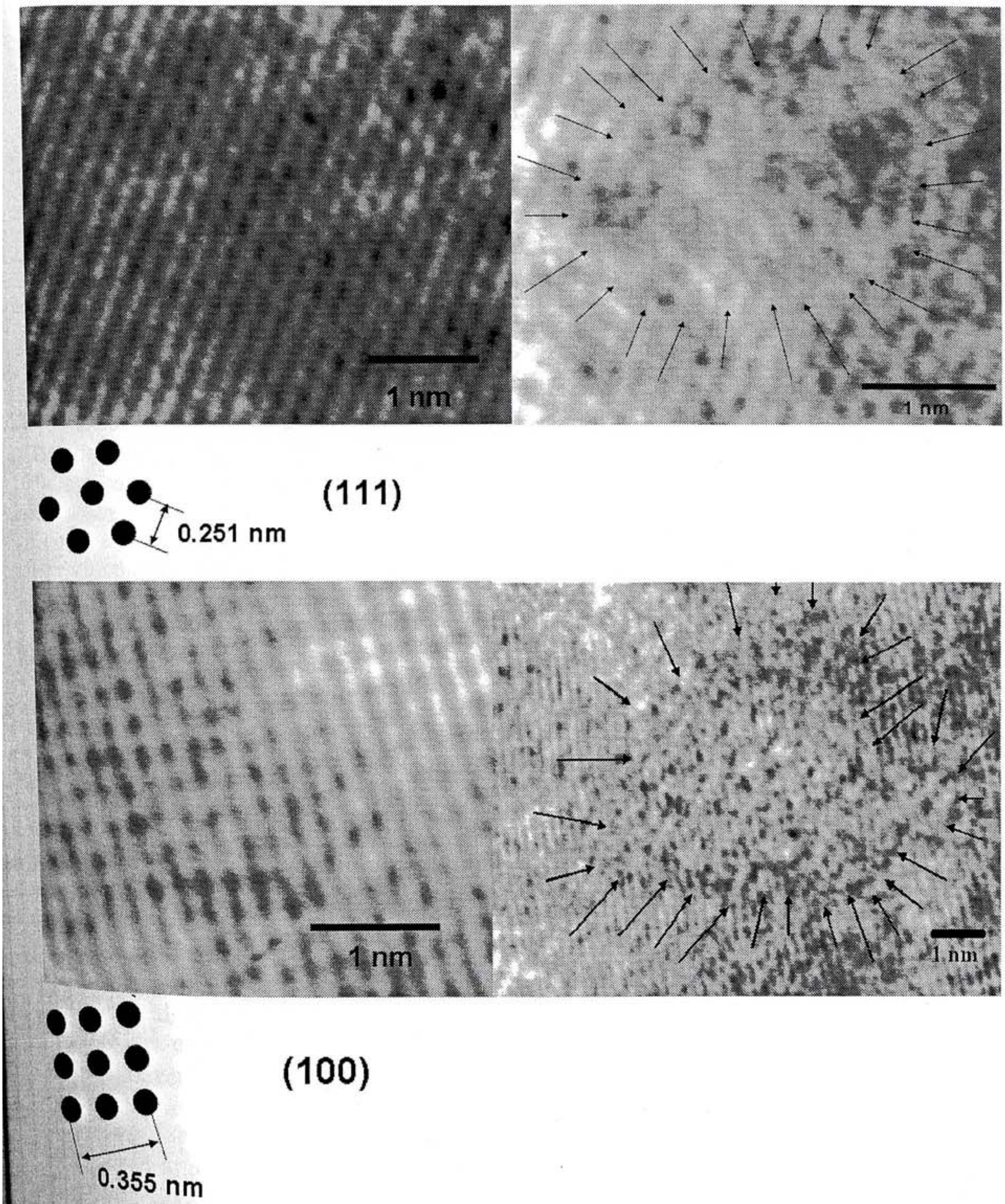

Figure 5. HRTEM images of the binder of the Master Grade in two regions having different orientations of the Co single-crystal. Left: the atomic structure of the fcc Co single-crystal and right: nano-particles embedded in the Co matrix; the interfaces between the nano-particles and Co matrix are indicated by arrows.

References

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