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Near-nano WC–Co hardmetals: Will they substitute conventional coarse-grained mining grades?

I. Konyashin *, B. Ries, F. Lachmann

Element Six Hard Materials, Element Six GmbH, Städeweg 12 – 24, D-36151 Burghaun, Germany

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ABSTRACT

Development of nanostructured hardmetals is a task of great importance. Nevertheless, in spite of some "euphoria" with respect to nanograined hardmetals, their potential application ranges are yet not clear. In some works, near-nano and nano hardmetals are believed can potentially substitute conventional medium- and coarse-grained WC–Co grades. In the present work near-nano hardmetals with WC mean grain size of nearly 200 nm and Co contents of 10–33 wt.% were produced and examined with respect to their hardness, fracture toughness, transverse rupture strength and wear-resistance. The near-nano hardmetal with 10% Co having a hardness of 20 GPa and fracture toughness of 9.5 MPa m$^{1/2}$ is characterised by exceptionally high wear-resistance obtained by use of the ASTM B611 test in comparison with an ultra-fine grade with 10%. The wear-resistance of the near-nano hardmetals in the ASTM B611 test significantly decreases with increasing the Co content and the wear rates of the difference between the wear rates of the grades with 10% and 33% Co is equal to nearly 44 times. The near-nano hardmetals with 25%, 28% and 33% Co having a moderate hardness and high fracture toughness corresponding to conventional coarse and ultra-coarse-grained mining grades have a very low wear-resistance in laboratory tests on concrete-cutting, granite-cutting and percussion drilling of quartzite. A number of grades with the very similar hardness of 13 ± 0.2 GPa, WC mean grain sizes varying from 0.2 to 4.8 μm and Co contents varying from 3% to 25% were produced and examined by use of the ASTM B611 test. The wear-resistance of the near-nano grade with 25% Co is found to be lower by more than three times compared to the coarsest grade with 3% Co at almost the same hardness. In this case, in spite of the very similar hardness of all the samples, the proportion of the soft binder phase on the surface subjected to abrasive particles when performing the test is significantly higher for the near-nano grade compared to the coarse- and ultra-coarse grained hardmetals. Thus, near-nano and presumably nano hardmetals are expected to never substitute conventional medium- and coarse-grained mining grades. The only application range, where near-nano and nano hardmetals can potentially substitute conventional grades, is an application range of hardnesses of above 18 GPa.

1. Introduction

There is a general trend in the modern hardmetal industry to produce WC–Co hardmetals with WC mean grain size as small as possible with the target of achieving the range of nanomaterials. In recent time, there was a significant research effort with respect to the development of nano hardmetals with WC mean grain size of 100 nm or near-nano hardmetals with WC mean grain size of nearly 200 nm. Numerous publications in this field are summarized in the review paper [1].

In the past two decades, there were a great number of works evaluating the possibility of fabrication of nanostructured WC–Co hardmetals from WC nanopowders (see e.g. [2–6]). In spite of the substantial research effort in the field of nanostructured WC–Co hardmetals, it did not result in obtaining nano or near-nano hardmetals up to recent times. All the attempts to obtain nanograined hardmetals from WC nanopowders failed because of the very intensive growth of WC nanograins during sintering as a result of the very high sintering activity of the nanostructured WC powders.

Only recently, nano or near-nano WC powders characterised by the very low activity with respect to re-crystallisation during liquid-phase sintering were developed and implemented [7,8]. Therefore, only since that time it has been possible to produce near-nano WC–Co hardmetals with extremely uniform and fine microstructure (see e.g. [9]).

In spite of some "euphoria" with respect to nano and near-nano hardmetals, their potential application ranges are yet not clear. In some works (see e.g. [1]), near-nano and nano hardmetals are believed can potentially substitute conventional medium- and

* Corresponding author.
E-mail address: igor.konyashin@e6.com (I. Konyashin).

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coarse-grained WC–Co grades. It is noted that applications of nanostructured hardmetals will include all areas where conventional WC–Co materials are used. Nevertheless, there is no information in the literature whether near-nano hardmetals will be able to substitute conventional medium and coarse-grained grades with high fracture toughness and relatively low hardness for wear and mining applications. Meanwhile, there is some concern, that the wear-resistance of near-nano hardmetals with moderate hardness, high fracture toughness and consequently high Co contents might be lower than that of conventional medium- and coarse-grained grades. This concern is based on the results of Refs. [10,11] providing evidence that the abrasion resistance of WC–Co hardmetals having the same hardness decreases with decreasing the WC mean grain size and consequently increasing the Co content. Nevertheless, only a limited number of hardmetal WC mean grain sizes, namely 0.6, 1.0, 3.0 and 5.0 μm, were examined in Refs. [10,11] and no near-nano hardmetals were tested. In contrast to the results of Refs. [10,11], Gee et al. believe that mainly the hardmetal hardness has an effect on the hardmetal wear-resistance measured by use of the ASTM B611 test [12].

The major objective of the present work is to produce and examine near-nano hardmetals with various Co contents and consequently different combinations of hardness and fracture toughness in order to establish in which application ranges the near-nano hardmetals can potentially substitute conventional WC–Co grades.

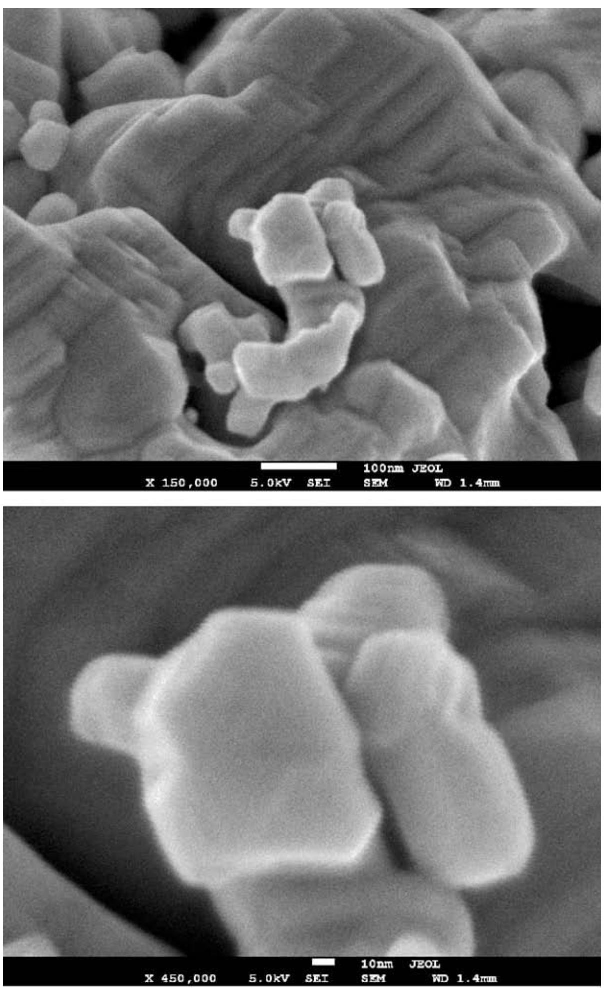

Fig. 1. Morphology of the WC powder (4NP0, H.C. Starck), HRSEM.

2. Experimental details

The WC powder (4NP0, H.C. Starck) with specific surface area (BET) of 4.08 m^2/g and total carbon content of 6.15%, and fine-grained Co powder (EF, Umicore) were employed for fabrication of the near-nano hardmetals. The WC powder was milled with 10–33 wt.% Co and various amounts of VC and Cr_3C_2 in a ball mill in hexane at the ball-to-powder ratio of 6:1 for 24 h. The contents of VC and Cr_3C_2 were equal to 1.0 and 0.3 wt.% for the alloy with 10% Co and were increased for the alloys with higher Co contents proportionally to the Co content, in order that the concentrations of V and Cr dissolved in the binder phase would be equal for the alloys with the various Co contents. After subsequent drying of the slurry, samples were pressed and sintered in a laboratory furnace (Vakuumanlagen Solms) in a graphite crucible at temperatures of 1360–1460 °C in vacuum with consequent HIPing.

After sintering, metallurgical cross-sections were prepared and examined on an optical microscope and the JEOL 7500F Field Emission SEM. The measurement of WC mean grains size was carried out by the conventional linear intercept method. Before carrying out the measurement procedure the SEM images were marked by two different colours to distinguish the binder and carbide phase. Hardness measurements were carried out according to the DIN ISO 3878 at a load of 20 kgf with the precision of roughly ±10 Vickers units. The indentation fracture toughness was measured by the Palmqvist method at a load of 30 kgf with the precision of roughly ±5% after annealing of the cross-sectional samples in a vacuum at 800 °C for 60 min. Transverse rupture strength (TRS) was examined according to the ISO 3327 standard. Wear-resistance was examined according to the ASTM B611-85 standard. The near-nano hardmetals were examined also in laboratory performance tests on cutting of abrasive concrete and granite, and percussion drilling of quartzite. The height loss of hardmetal inserts was a measure of wear in the tests on concrete- and granite-cutting performed under the following parameters: cutting speed – 1.5 m/s, depth of cut – 2.5 mm, feed – 2.5 mm. The gauge loss was a measure of wear in the test on percussion drilling. The drilling test was carried out by use of a conventional drilling rig operating at the following parameters: blow energy – 200 J, torque

Table 1
Composition and properties of the near-nano hardmetals.

Alloy	Co content (wt.%)	Density (g/cm^3)	Magnetic coercivity (kA/m)	Magnetic moment ($\mu T\ m^3\ kg^{-1}$)	SMS (%)	D_{WC} (μm)	HV_{20} (GPa)	K_{1C} ($MPa\ m^{1/2}$)	Wear ($cm^3/rev \times 10^{-4}$)
1	10	14.31	39.8	1.29	80	0.20	20.0	9.5	0.12
2	13	13.88	38.2	1.68	80	0.20	18.5	9.5	0.35
3	15	13.69	36.5	1.93	80	0.20	17.4	9.4	0.59
4	19	13.25	32.5	2.50	82	0.20	15.5	9.6	1.49
5	22	12.87	24.5	3.00	85	0.22	14.0	10.9	2.52
6	25	12.65	18.0	3.40	85	0.22	12.8	12.4	3.82
7	28	12.24	17.9	3.47	83	0.22	11.4	13.6	4.32
8	33	11.84	15.4	4.40	83	0.25	10.7	24.0	5.27