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NEW TUNGSTEN CARBIDE MATERIAL WITH NANOSCALE GRAIN SIZE FOR FOCUSING TUBES

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ABSTRACT

Wear resistance of focusing tubes is an important factor influencing cutting quality and production costs in abrasive water jet cutting. Due to their unique hardness-toughness combination, tungsten carbide-based focusing tubes show superior wear resistance, compared to even super-hard ceramic materials. CERATIZIT is the leading European manufacturer for such WC-based water jet nozzles. In this paper, a new tungsten carbide material will be presented, which has been specially designed for this application. With a mean WC grain size of 150nm, entering *de facto* the 'nano' arena, hardness over 2800HV10 has been determined for this material. This outstanding hardness value leads to extreme abrasion resistance, far above other conventional WC/Co cemented carbides parts and outperforms the previous generation of ultrafine grained water-jet nozzles.

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1. INTRODUCTION

Abrasive water jet (AWJ) technology is more and more regarded as a clean task, being emission-free compared to thermal cutting processes. A wide range of materials can be cut, from stone, to composites, plastics, metals … up to a thickness of 150mm for a stainless steel slab for example. For metals or aluminium alloys, a special advantage of AWJ cutting is that the process is cold, avoiding thermal stresses or heat affected zones. All the AWJ cutting heads have nearly the same basic design and the same principle of operation : a high-velocity water jet passing through a small orifice entrains air, carrying with it abrasive particles, from a mixing chamber into a focusing tube, or nozzle, in which a fraction of the kinetic energy of the WJ is transferred to the abrasive grit, forming a thin, focused and coherent AWJ at nozzles outlet. The development of extremely hard, wear and erosion resistant materials for nozzles was a critical issue to the successful exploitation of AWJ for precision cutting. Inner bore walls of focusing tubes have to withstand both [1] :

- impact wear from abrasive particles in their conical inlet and down to about the first one third of their length. In this area, coarse abrasive particles are travelling mainly with water droplets and air, surrounding the central water jet causing impact erosion at the periphery of the water jet, because of large and various angles of impact against tube walls

- and also abrasive sliding wear, from about one third of the length down to the orifice outlet. In this area, energy exchange between air and high velocity water jet results in abrasive particles communition, leading to micron and submicron fragments causing abrasive wear

This implies that candidate materials for focusing tubes have to combine both extremely *high hardness* to resist to abrasion and *sufficient fracture toughness* to avoid material removal by micro-fractures as demonstrated by Bao et al. [2]. CERATIZIT is manufacturing carbide nozzles for decades, and due to decreasing particle size of WC powders available on the market and to continuously improved alloy composition and sintering technologies, nanostructured carbide nozzles can be produced now. In this paper the most recent developments will be presented, together with laboratory wear tests to illustrate the potential of this newly launched ‘WC-based’ grade, ULTRAMANT 3000.

2. EXPERIMENTAL PROCEDURES

Microstructural investigations of polished cross-sectioned samples were performed by means of light optical microscope (LOM) and scanning electron microscope (FE-SEM JSM6330F, JEOL, Japan), using Energy Dispersive Spectroscopy for micro-analysis. Density of sintered compacts has been measured in distillated water, using Archimedes method. Classification of the WC grain sizes established by the German ‚Fachverband für Pulvermetallurgie’ [3] has been adopted (cf Table 1). Despite the nano-category, defined as WC grain size below 0.2µm, may be criticized as it is widely large, this classification is already used extensively by hardmetal producers. Grain size distribution of sintered and fully dense compacts have been done by image analysis on SEM micrographs of polished surfaces, slightly etched to reveal grain-boundaries, and using a semi-automatic analyser (AxioVision, Carl Zeiss Vision GmbH, Germany).

Table 1. Classification of the WC grain sizes, according to the FPM [3]

Grain size	<0.2μ	0.2-0.5μ	0.5-0.8μ	0.8-1.3μ	1.3-2.5μ	2.5-6.0μ	>6.0μ
Designation	Nano	Ultrafine	Submicron	Fine	Medium	Coarse	Extra-C

Vickers hardness HV was determined using a semi-automatic hardness tester using ISO 3878 specification, with different indentation loads from 2kgf up to 30kgf (AVK-C2, Mitutoyo, Japan). HV results are the mean of at least three individual indentations. Concerning toughness, there is no ISO international standard test method for hardmetals. Two different approaches have been used to assess the toughness of these super-hard WC-based grades.

The indentation fracture toughness K_{IC} has been calculated from radial cracks originating from the corners of HV impressions. For a given indentation load, the shorter the cracks the tougher the substrate. The formula of Shetty et al [4] has been used to convert the sum of crack lengths into Palmqvist fracture toughness, according to :

$$K_{IC}\ (MNm^{-3/2}) = A \,.\, \sqrt{HV} \,.\, \sqrt{(P/\Sigma l)} \qquad (1)$$

where A=0.0028 for K_{IC} expressed in $MNm^{-3/2}$ (or MPa.√m) [5], HV is the hardness (N/mm²), P is the load (N), and Σl is the sum of the crack lengths (mm). Crack lengths measurements were carried out on LOM at a magnification of 1000x for better accuracy. Palmqvist tests are widely used to assess the toughness of hardmetals, since only limited amounts of material are needed.

Additionally, fracture toughness has been also calculated using Single Edge V-Notched Beam (SEVNB) specimens, following DIN 51109 specification, established for advanced technical ceramics. The test involves the introduction of a crack into the specimen by an approved method, and the propagation of the crack by application of a rising load up to the fracture of the testpiece in a four-point bend test. The plane strain fracture toughness K_{IC} is the critical value of the plane strain stress intensity factor K_I at which the crack begins to extend under the influence of this rising load, and is calculated as follows :

$$K_{IC}\ (MNm^{-3/2}) = Y \,.\, F / (b.\sqrt{w}) \qquad (2)$$

where Y is a stress intensity shape factor, F is the maximum applied load at fracture (MN), b and w respectively the specimen width and height. Sharp-notched geometry (radius ≤10μm) was ensured by using a razor blade sprinkled with diamond paste, on a V-notch polishing device. This avoids over-estimation of fracture toughness because of too wide notch-root radius, as reported by Damani et al. [6]. Reported values are the mean of at least five specimens fractures, the notch geometry being carefully controlled by LOM before the four-point bend test.

3. MACRO-ABRASIVE WEAR TESTS

There are many wear resistance tests which have ben applied to cemented carbides, such as "dry" pin-on-disc and "wet" ASTM B611 tests. Only this latter test is fully internationally recognized, though results cannot be universally applied to all wear situations. In this test which may be regarded as a "macro"-abrasive wear test, specimen is pressed with a 20kg load against a steel wheel, rotating at 100rev/min and in the presence of an abrasive slurry, consisting of coarse alumina grit of about 30mesh in distilled water. F40 alumina grit has been used here (cf fig.1), with mean diameter of about 450µm (Supplier : H.C. Starck, Germany).

Figure 1. F40 Abrasive grit used for the ASTM B611 wear tests

Figure 2. Typical wear scars observed on cemented carbides

The value of wear resistance is expressed by a wear number W (cm^{-3}), defined as the reciprocal of the wear volume and is calculated as follows :

$$W = d / L \quad (3)$$

where d is the specimen density (g/cm^3) and L is the weight loss (g) after 1000rev. Typical wear scars produced by the ASTM B611 test on WC/Co carbide specimens are illustrated on fig.2.

4. RESULTS AND DISCUSSION

4.1. Selection of WC Powders

Submicron (0.8-0.5µm) and ultrafine (0.2-0.5µm) grained hardmetals based on WC/Co have been developed in the 80s and in the 90s for at first special applications such as wood cutting tools or microdrills for printed circuit boards (PCBs) in the electronics industry. Due to the very high hardness, including hot hardness, bending strength and wear resistance, new applications for ultrafine grained hardmetals have been found in wear applications but also for producing carbide round tools such as drills, mills and reamers for cutting applications, with excellent performance.

To follow the trend of the hardmetal industry looking for ever finer and finer grained cemented carbides, WC raw powders producers, including CERATIZIT, are developing specific manufacturing processes to enter the ‘nano’ arena, like gas-phase carburization for H.C. Starck (Germany) and Treibacher Industrie AG (Austria), Calcination-Reduction-Carburization process for Bergla (Wolfram Bergbau und Hütten GmbH, Austria) or direct carburization for A.L.M.T. Corp. (Japan) to name a few processes and companies.

The reduction of WC powder particle size over the last 20years, for producing carbide focusing tubes, is illustrated on SEM micrographs of figure 3. New AWJ nozzle materials with increased lifetime have been obtained, due to this WC powder particle size reduction.

Submicron (0.8-0.5µm) since 1988	Ultrafine (0.2-0.5µm) since 1996	Nano (<0.2µm) since 2003

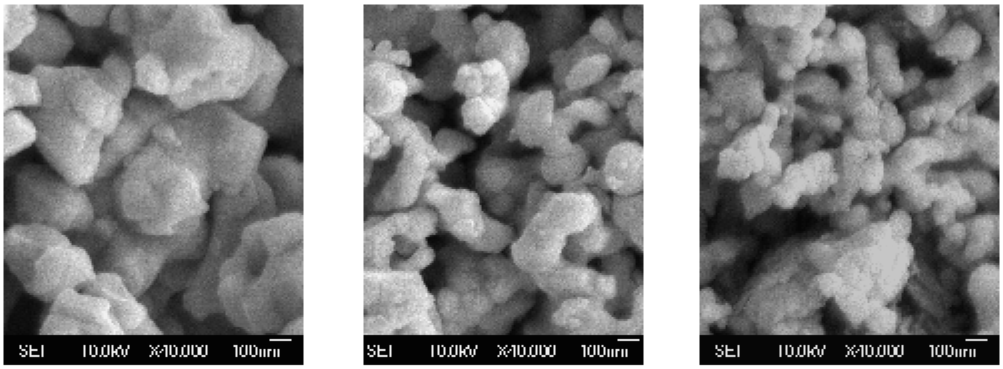

Figure 3. Overview of Submicron, Ultrafine and Nano-WC powders (scale bars = 100nm), used at CERATIZIT for producing AWJ nozzles

4.2. Microstructural Investigation of ULTRAMANT3000

ULTRAMANT3000 AWJ nozzles are produced by powder metallurgy and modern extrusion technology. This forming process is a critical step to convert the initial powders mixture into first a plastic feedstock material and then into extrusion moulded rods. A lot of efforts were necessary to find suitable plastification and lubricant agents for such initial 'nano' WC particles.

Full densification is then ensured by sinter-HIP process, allowing defect-free parts without macro-porosities and residual micro-porosity better than A02B00C00 (ISO4505 standard). Contrary to conventional WC/Co cemented carbides, 'WC-based' ultrahard grade ULTRAMANT3000 do not contain free metallic cobalt after sintering. Secondary and intergranular phases other than WC grains are evenly distributed throughout the microstructure, as revealed by chemical etching (fig.4A). Thanks to optimised composition and processing route, resulting microstructures observed by means of LOM are very homogeneous, without any coarse WC grains (fig.4B) that can be detrimental for the abrasion wear resistance.

In an attempt to determine an average WC grain size by image analysis, SEM micrographs have been used at a magnification of 20,000x for UMG01 and ULTRAMANT3000 (fig.4C). There is still no agreed standard for measurement of grain size in WC/Co cemented carbides. The use of linear intercepts (LI) or the calculation of equivalent circle diameters (ECD) are the most commonly used methods to obtain grain size distributions from micrographs. ECD measurements can be seen on Table 2, for both UMG01 and ULTRAMANT3000 grades. The new grade developed for AWJ nozzles exhibits a grain size reduction of about 30%, as compared to UMG01 grade, and is entering the 'nano' range, as defined in [3], whatever is the selected parameter ECD (148nm) or LI (128nm).

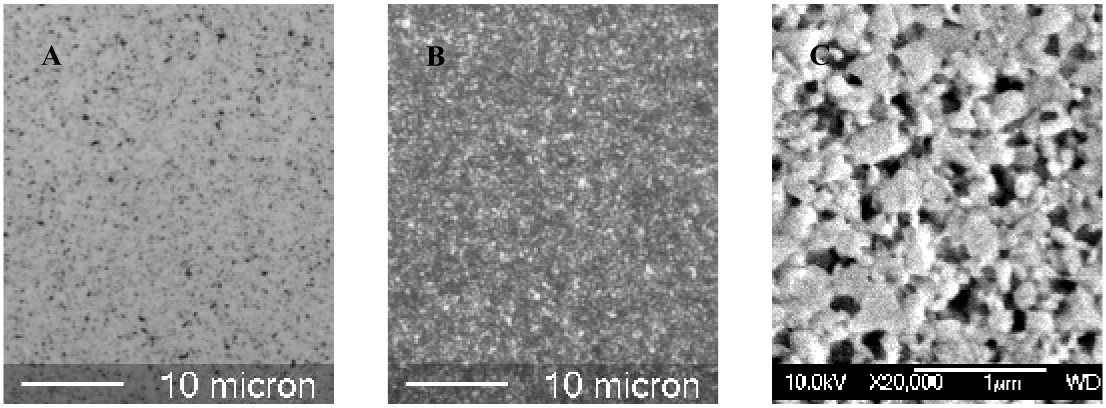

Figure 4. LOM micrographs revealing secondary and intergranular phases (4A, etched), microstructure (4B, etched) and corresponding SEM micrograph (4C, etched)

From simple 2D geometrical considerations, ECD and LI values can be related by : ECD = $2/\sqrt{3}$ LI. Recently, such a relation has been validated by B. Roebuck and his colleagues [7] at the National Physics Laboratory (NPL, Teddington, UK), in WC/Co hardmetals with different average grain size. One SEM image of each sample was analysed by two different operators, using both ECD and LI methods to determine grain size distributions. A clear linear relationship has been found, with mean ECD = 1.15 mean LI over the experimental range 0.5-5.0µm, in good agreement with the empirical $2/\sqrt{3}$ (=1.155) coefficient.

Table 2. ECD measurements on ultrafine UMG01 and nano ULTRAMANT3000 grades.
* mean LI calculated from formula LI = $\sqrt{3}/2$ ECD (cf text)

Parameters	UMG01	ULTRAMANT3000
HV10	2661	2811
Counts	701 grains	705 grains
mean ECD	207nm	148nm
min. ECD (nm)	54	42
max. ECD (nm)	521	428
mean LI * (nm)	179nm	128nm

4.3. Mechanical Properties of ULTRAMANT3000

4.3.1. Vickers Hardness

Loads of 30kgf, as recommended by ISO3878, and 10kgf are the most commonly indentation loads used by hardmetal producers; conversion between HV10 and HV30, and reciprocally, being done internally with existing conversion tables, covering the standard HV range for cemented carbides (HV30 ~800-2200). Since lower loads are often used for ceramics and brittle ultra-hard composites, such as silicon or boron carbides, different indentation loads have been tested, from HV2 to HV30 :

Table 3. Vickers Hardness HV as a function of indentation loads
Reference : ULTRAMANT 3000, Batch C

Load	2 kg	5 kg	10 kg	20 kg	30 kg
HV	2922 ±47	2891 ±58	2854 ±49	2818 ±16	2795 ±27

As can be seen in Table 3, HV hardness over 2900 can be measured on ULTRAMANT 3000 substrate, depending on the selected indentation load. These outstanding HV values for a 'WC-based' alloy are surpassing all the standard HV range for WC/Co carbides, and also the hardness determined on WC single crystals (with HV~2200-2500 depending on the crystallographic planes considered) [8]. HV10 hardness specification is indicated in Table 4, for this new ULTRAMANT3000 grade.

Table 4. HV10 hardness *specifications* for CERATIZIT grades

Grade	SMG02	UMG01	ULTRAMANT3000
Structure	Submicron	Ultrafine	Nano
HV10	2300 ±100	2675±75	2825 ±75

4.3.2. SEVNB Fracture Toughness

SEVNB fracture toughness has been determined for both conventional WC/Co cemented carbides, with low cobalt content, and 'WC-based' grades UMG01 and ULTRAMANT3000. HV5 hardness has been checked on the same specimens used for the SEVNB tests. For very-fine grained hardmetals, toughness is decreasing slowly with increasing hardness of WC/Co substrates, as widely documented in literature and as can be seen in Table 5. Nearly equivalent SEVNB values have been determined for the two 'WC-based' grades, with fracture toughness tending towards a limiting or asymptotic value of about 5.0MPa.√m.

Table 5. Fracture toughness K_{IC} determined with the SEVNB method,
for respectively conventional WC/Co SMG02/UMG04 grades, and
'WC-based' ultrafine UMG01 and nano ULTRAMANT3000 grades

Grade	SMG02	UMG04	UMG01	ULTRAMANT3000
Grain size	Submicron	Ultrafine	Ultrafine	Nano
Batch	A	A	A	A
HV5	2230 ±20	2560 ±20	2670 ±50	2820 ±60
K_{IC} (MPa.√m)	5.72 ±0.29	5.29 ±0.24	4.97 ±0.25	5.05 ±0.37

4.3.3. Palmqvist Fracture Toughness

Using indentation techniques, crack length measurements and surface preparation are the most important parameters affecting the uncertainty in fracture toughness determination.

For better accuracy, total length of cracks Σl have been determined on LOM, using a 1000x magnification. Since the Palmqvist method is also extremely sensitive to residual compressive stresses, coming from the grinding preparation step of the specimens, a long polishing time has been used in a two-step sequence, with first 3μm and then 1μm diamond suspensions on separate polishing clothes. From in-house results on many hardmetals specimens, stress-free surfaces are produced with this preparation method, as determined by residual stress measurements done by the XRD technique.

A load of 5kgf has been selected to produce cracks long enough, to test a significant volume of the microstructures, but not too long to avoid multiple fields examination, which can introduce additional summing errors. As can be seen in Table 6, the sums of crack length Σl exhibit very low scatter for the four specimens tested, as a result of well-defined cracks from HV indents, indicating homogeneous properties of specimens (microstructures and preparation). This is in good agreement with NPL's findings, indicating that the scatter in measured total crack length is diminishing with lower binder content, smaller WC grain sizes and higher hardness of the WC/Co hardmetal [9].

Table 6. Indentation fracture toughness K_{IC} (MPa.√m), calculated with the Shetty's formula (1) –load : HV5

Grade Structure	UMG01 'ultrafine'		ULTRAMANT3000 'nano'	
Batch	B	C	B	C
2a (μm)	59.6 ±0.3	59.0 ±0.5	57.5 ±0.4	56.6 ±0.6
HV5	2609 ±24	2667 ±49	2803 ±41	2891 ±58
Σl (μm)	273.0 ±1.9	265.2 ±2.7	253.6 ±3.8	250.4 ±3.3
K_{IC}	6.0	6.2	6.4	6.6

Slightly higher K_{IC} values with Palmqvist method have been determined for ULTRAMANT3000 as compared to UMG01, despite a net HV5 increase of about 200units (Table 6). Intergranular and secondary phases, though occupying a minimum volume, are thought to play a key role in the fracture toughness stability (SEVNB results) or slight increase (Palmqvist results) for this new nanostructured grade, as compared to UMG01 grade.

SEVNB and Palmqvist K_{IC} results are plotted in Figure 5, as a function of hardness. Good agreement between these two methods has been found recently [9], on 8 different WC/Co hardmetals covering the range HV30=1000-1800, comparing NPL Palmqvist data and CERATIZIT SEVNB values. For WC/Co carbides with higher hardness, or super-hard 'WC-based' materials, there is no or little literature data comparing these two methods.

In figure 5, only data published by Richter et al [10] on binderless WC carbides (with cobalt content~0%) are indicated. These ultrafine binderless grades were covering the HV10=2680-2875 range, and Palmqvist toughness values are reported, by without disclosing the formula used. Demonstration parts were also consolidated by alternative densification strategies, like Hot-Pressing or Spark Plasma Sintering, which could have induced specific properties related to the densification process and to the final microstructures. Regardless of these limitations, a reasonable agreement can be found from our data on ‘WC-based’ grades and those on these binderless WC carbides.

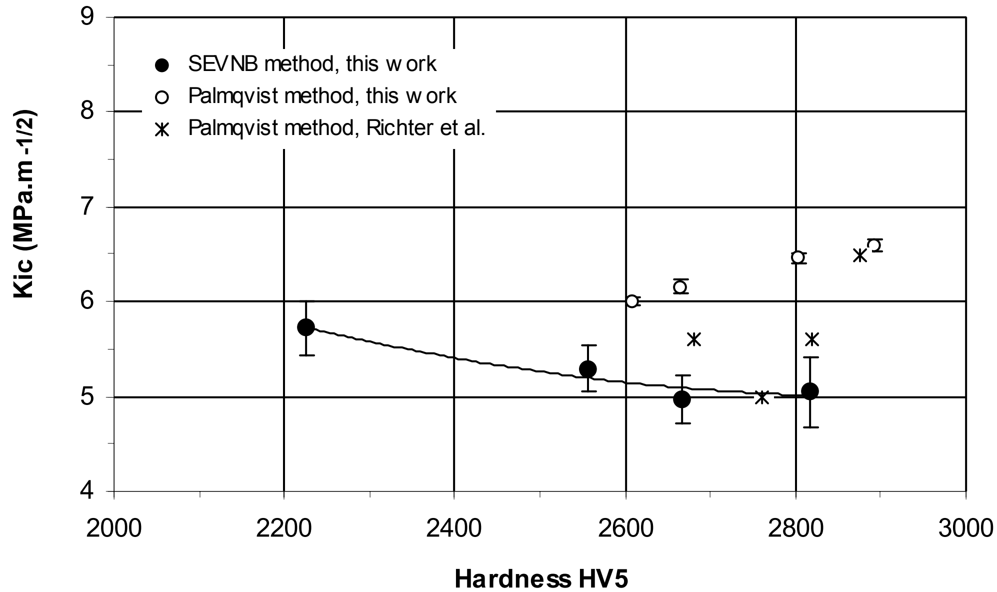

Figure 5. Fracture toughness vs hardness for super-hard ‘WC-based’ grades, developed at CERATIZIT, and results of Richter et al [10] on ‘nano’-binderless WC.

4.4. Macro-Abrasive Wear Tests

Slurry wheel abrasion tests (ASTM B611-76) have been conducted on the two ‘WC-based carbides’ ULTRAMANT3000 and UMG01, and also on conventional WC/Co submicron SMG02 grade. Experiments have been conducted on substrates, with different hardness values within their respective HV10 specifications (cf Table 4), to illustrate that the higher the hardness, the higher the measured W numbers, corresponding to increased wear resistance :

Table 7. ASTM B611-76 Abrasion Slurry Tests

Grade	SMG02	UMG01		ULTRAMANT3000	
Batch	B	D	E	D	C
HV10	2302	2622	2653	2784	2854
W (cm^{-3})	561	1278	1294	1558	1981

As can be seen in Table 7, with an hardness increase of about 200HV10 units for the substrate, abrasion wear resistance determined for the new nanostructured ULTRAMANT3000 is nearly *1.5times* greater than the previous UMG01 grade that performed already well. This increased performance should offer added value, by reducing downtimes, with fewer nozzles replacements and lower maintenance costs.

5. FIELD-TESTING

ULTRAMANT3000 AWJ nozzles are routinely produced since January 2004. Preliminary results collected from European endusers indicate superior lifetime, as compared to previous generation of AWJ nozzles made in UMG01 grade. More experiments are needed for a proper evaluation of the potential of this new nanostructured grade.

With 'mild' abrasion conditions selected by one end-user, ULTRAMANT3000 nozzles have been examined after 90 hours of testing time, cutting parameters being listed in Table 8. Abrasive flow rate was reduced from typical values of about 350-500g/min down to 80g/min for this specific application. After 90h, the final bore diameters were still far away from the maximum bore diameters where the nozzles must be replaced (~0.76x1.5time=1.14mm).

Table 8. Cutting parameters selected by one end-user

Nozzle Items	#41141-0.76
Water Pressure	Approx. 300MPa
Abrasive type	#180 (grit undisclosed)
Abrasive flow rate	80g/min
Test duration	90hours
Initial bore diameter	0.76mm
Final bore diameter	0.89mm

The 2 worn nozzles have been longitudinally cross-sectioned (cf fig.6), and surfaces of the inner bore have been examined by SEM at approx. 1mm from the exit orifice, where abrasion wear should dominate. At a magnification of 5000x, a pattern of fine and parallel grooves can be seen indicating grooving abrasion mode for the inner walls of the carbide substrate (fig.7A). At higher magnification, mild abrasion of the nano-WC grains is observed, while intergranular and secondary phases other than WC grains seem to encounter some material pull-out (cf fig.7B).

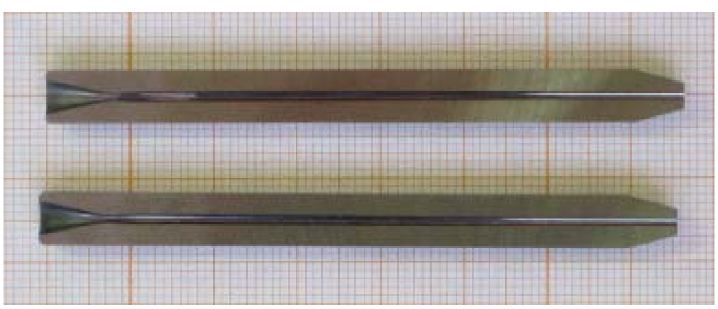

Figure 6. Cross-sections of worn ULTRAMANT3000 nozzles, tested with cutting parameters of Table 8

From these observations, further progress in abrasion resistance could be made, by decreasing first the amount and the size of intergranular and secondary phases, but also maybe by strengthening the bonds between WC grains and the small amount of intergranular and secondary phases.

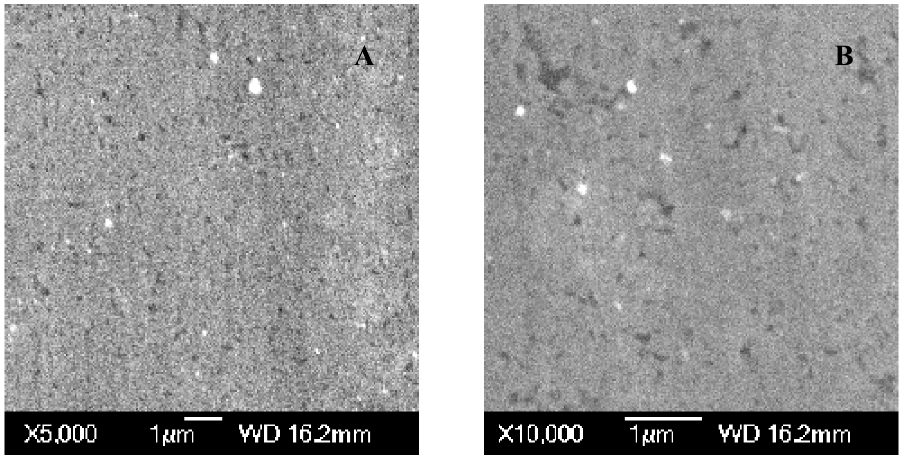

Figure 7. SEM micrographs of worn ULTRAMANT3000 nozzles
-bore surfaces examined at 1mm from the exit orifice.
white spots = submicron debris originating from the abrasive grit
in grey contrast, intergranular and secondary phases

6. CONCLUSIONS

Due to decreasing particle sizes of WC starting powders available and improved alloys compositions, AWJ nozzles with very regular microstructure and mean WC grain size of about 150nm (ECD) have been successfully manufactured using up-to-date extrusion technology and sinter-HIP densification process. These nozzles are now routinely produced under the trade name ULTRAMANT 3000, since January 2004.

Outstanding Vickers hardness, as compared to conventional WC/Co cemented carbides, more than 2800HV10 or 2900HV5, are typically measured for this new *nanostructured* 'WC-based' grade. Also remarkable is that the fracture toughness of this new grade is not further decreasing, as compared to ultrafine carbide grades with lower hardness, used for AWJ nozzles. This is of particular importance for focusing tubes submitted also to erosive wear by angular particle impacts, where material loss can be induced by brittle fracture. From erosion models by elastic-plastic fracture [11], it is shown that fracture toughness is the most important parameter determining the wear by micro-fractures. The higher the fracture toughness, the higher is the resistance to material loss induced by micro-fractures. This unique combination of extremely high hardness and good fracture toughness, as compared to hard materials such as alumina, boron carbide, SiC or TiB_2-based composites, makes ULTRAMANT3000 an ideal candidate for focusing tubes in AWJ cutting technology.

Macro-abrasive wear tests conducted at CERATIZIT have already shown the potential of this new grade, reaching *1.5times* greater abrasion wear resistance, compared to the previous ultrafine generation. Additional erosion tests with SiC or garnet are currently under progress. Extensive field-testing is also in progress in collaboration with end-users, but preliminary results collected from AWJ cutting experiments are positive, with increased lifetime reported.

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