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Wear-resistance and hardness: Are they directly related for nanostructured hard materials?

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ABSTRACT

The major challenge in the field of cemented carbides and other hard materials is to obtain their better combination of hardness, wear-resistance and fracture toughness. It is well known that the dependence of abrasion wear on fracture toughness for WC–Co cemented carbides is represented by a relatively narrow band and it is hardly possible to "break away" out from it by the use of conventional approaches based on varying the WC mean grain size and Co content. Also, it is well known that the wear-resistance of conventional cemented carbides depends mainly on their hardness. The major objective of this paper is to establish what will happen with the wear-resistance of hard materials as a result of their nanostructuring when the hardness is nearly the same as for conventional WC–Co cemented carbides. The results obtained provide clear evidence that, if one enters the region of nanostructured materials with the mean grain size of less than 10 nm, traditional wisdom indicating that the wear-resistance is directly related to the hardness appears not to be valid. In some cases of such nanostructured materials, it can be possible to achieve the dramatically improved wear-resistance compared to that of conventional WC–Co cemented carbides at nearly the same level of hardness and fracture toughness. The abovementioned is based on considering hard nanomaterials of the following four types: (1) WC–Co cemented carbides with nanograin reinforced binder, (2) near-nano WC–Co cemented carbides, (3) cemented carbides of the W–C–Cr–Si–Fe system for hard-facing having a nanostructured Fe-based binder, and (4) CVD hard materials consisting of nanostructured W_2C grains embedded in a tungsten metal binder.

1. Introduction

It is well known that the abrasion wear-resistance of conventional WC–Co cemented carbides and other hard materials depends mainly on their hardness, and the dependence is represented by a relatively narrow band [1]. In turn, the dependence of hardness on fracture toughness for WC–Co materials having different combinations of WC mean grain size and Co content is represented by a relatively narrow hyperbolic band [2]. It is hardly possible to "break away" out from the both bands by the use of conventional approaches based on varying the WC mean grain size and Co content. Therefore, the major challenge in the field of hard materials is to obtain their better combination of hardness, wear-resistance and fracture toughness; in other words, to "break away" out from the dependences relating the wear-resistance and hardness on the one hand, and the wear-resistance and fracture toughness on the other hand.

There is a general trend in the modern carbide industry to produce WC–Co materials 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 nanostructured cemented carbides with the WC mean grain size below 100 nm; numerous publications in this field are summarized in the review paper [3]. There are a great number of works in literature evaluating the possibility of fabricating nanostructured WC–Co materials from WC nanopowders (see e.g. [4–6]). However, these works did not result in obtaining fully dense cemented carbides with WC mean grain size significantly below 100 nm. All the attempts to obtain nanograined cemented carbides from WC nanopowders failed so far because of the very intensive growth of WC nanograins during sintering as a result of the high sintering activity of the nanostructured WC powders. The only industrial WC-based nanostructured materials having a full

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density produced by liquid-phase sintering are designated in literature as “near-nano” cemented carbides with the WC mean grain size slightly above 100 nm (see e.g. [7,8]). Meanwhile, it is well known that one can simultaneously improve the hardness, toughness and strength of different alloys, e.g. Al-based alloys, due to the precipitation hardening, which can be designated as “nanostructuring”, only if the mean grain size of nano-precipitates is of the order of nearly 10 nm to 20 nm or less than 10 nm (see e.g. [9]). It can be expected that, if the WC mean grain size is noticeably greater than 10 to 20 nm, decreasing the WC mean grain size of WC–Co materials would lead to their higher hardness but reduced fracture toughness, in a similar way as for conventional fine- and ultrafine-grain cemented carbides. Therefore, there should be a certain “border line” with respect to the carbide mean grain, below which the nanostructuring leads to a simultaneous increase of both hardness and fracture toughness, and above which the hardness can be increased only at the expense of fracture toughness. It is still a question mark whether the existing near-nano cemented carbides lie above or below this hypothetical “border line”, in other words, whether they are characterized by an improved combination of hardness and fracture toughness in comparison with conventional WC–Co materials. Also, the strengthening mechanism in the precipitation hardened Al-based alloys and nanostructured WC–Co cemented carbides can be different. In the first case the nano-precipitates are embedded in an Al-based matrix leading to a peculiar dislocation structure, which should play an important role. In the second case the WC–WC and WC–Co grain boundaries are expected to be very important with respect to obtaining an improved combination of hardness, toughness and strength.

There is another type of nanostructured cemented carbides, which are WC–Co materials with nanograin reinforced binder [10–13]. The microstructure of such materials comprises ultra-coarse WC grains and a Co-based binder reinforced by hard nanoparticles of nearly 3 nm in size. Tool lifetime of road-planing and mining picks with inserts or tips of such nanostructured materials is found to be dramatically prolonged. Nevertheless, there are no results in literature on the systematic examination of wear-resistance of the cemented carbides with nanograin reinforced binder in comparison with conventional WC–Co grades of similar hardness and fracture toughness.

Recently we elaborated and patented another class of nanostructured hard materials for hard-facings [14–18]. The microstructure of the novel hard-face materials comprises WC, multicomponent carbides of the Fe–W–Cr–C and Fe–Cr–Si–C systems and a special low melting point Fe-based binder containing W, Cr, Si and C. The reactivity of the binder with steels is extremely high leading to the formation of much liquid phase at the interface between steel substrates and the hard-facing obtained by the use of plasma transferred arc (PTA) welding, which results in a thick intermediate zone at the interface. The binder of the novel carbide hard-facings is enhanced by hard nano-whiskers and nano-platelets of about 20 nm to 100 nm in diameter, which are embedded in a nanostructured Fe-based binder matrix. The binder matrix consisting of a mixture of ferrite and austenite is a unique nanostructured alloy having a mean grain size of nearly 5 nm. Nevertheless, there are no results in literature on the systematic examination of wear-resistance of such nanostructured hard-face materials in comparison with conventional WC–Co cemented carbides of similar hardness and fracture toughness.

Another type of nanostructured hard materials, the structure of which is close to that of WC–Co cemented carbides, is represented by coatings with the brand name “Hardide-T” [19]. The Hardide-T coatings are nanomaterials produced by CVD, which comprise W_2C nanoparticles embedded in a tungsten metal matrix. The Hardide CVD method can produce materials with hardness in a very broad range: from 400 Vickers units up to 3500 Vickers units. The optimum wear- and erosion-resistance was achieved when the high hardness was combined with enhanced toughness. The Hardide-T type coatings, which show the best wear-resistance, have a hardness in the range of 1100–1600 Vickers units combined with enhanced toughness, crack- and impact-resistance. The coating's high hardness inhibits the micro-cutting mechanisms of wear and erosion, while its toughness, ductility, residual compressive stresses and homogeneous microstructure prevent fatigue micro-cracking/chipping and platelet mechanisms of erosion.

The Hardide coatings are typically 50 μm thick – exceptionally thick among hard CVD coatings – tough and ductile to withstand 3000 micro-strain deformations without damage. The coating is applied in a low-temperature CVD process at around 500 °C, which enables coating of a wide range of materials: stainless steel, tool steels stable at 500 °C, Ni-, Cu-, and Co-based alloys, titanium. The coating has a strong metallurgical adhesion to these substrates, with the bond strength typically exceeding 70 MPa. The gas-phase CVD process enables the uniform coating of external and internal surfaces and complex shapes, such as valves, pump cylinders ID and extrusion dies. Proven applications of the Hardide coatings include critical parts of oil drilling tools, pumps and valves operating in abrasive, erosive and corrosive environments, aircraft components, etc. Nevertheless, there are no results in literature on the systematic examination of the wear-resistance of the Hardide nanostructured materials depending on their hardness.

The major objective of this paper is to examine the wear-resistance of hard materials comprising either a nanostructured carbide phase or a nanostructured binder phase in comparison with conventional WC–Co cemented carbides having nearly the same hardness.

2. Experimental details

The cemented carbides with nanograin reinforced binder were produced according to the procedure described in Refs. [10–13]. Samples of near-nano cemented carbides with WC mean grain size of between 150 nm and 200 nm were made from the near-nano WC powder (4NP0, H.C.Starck) according to the procedure described in Ref. [7]. The near-nano carbide with 10 wt.% Co contained 1.0 wt.% chromium carbide and 0.3 wt.% vanadium carbide, and the amounts of the grain growth inhibitors were increased directly proportionally to the increase in the Co content. The microstructure and properties of the near-nano carbides are described in detail in Ref. [7]. Carbide materials of the WC–Fe–Cr–Si system in the form of hard-facing were made by the use of plasma transferred arc (PTA) welding according to the procedure described in Refs. [14–18].

Metallurgical cross-sections were made according the standard procedure for cemented carbides and examined on an optical microscope. Hardness measurements were carried out according to the DIN ISO 3878 at a load of 300 N. The indentation fracture toughness was measured by the Palmqvist method at a load of 300 N after annealing of the cross-sectional samples in a vacuum at 800 °C for 60 min according to the ISO/DIS28079. The wear-resistance was examined according to the ASTM B611-85 and ASTM G65-04 standards. TEM and HRTEM studies were carried out on the FEI Titan 80–300 instrument. Worn surfaces were examined by the use of the Philips XL30S HRSEM.

3. Results and discussion

3.1. Ultra-coarse WC–Co cemented carbides with nanograin reinforced binder

Fig. 1a shows the microstructure of the novel cemented carbides with a binder reinforced by nano-sized precipitates, which can be designated as a “nanograin reinforced binder”. It consists of large and rounded WC grains with very thick binder interlayers among them, which allows obtaining a high level of fracture toughness. The state and hardness of such thick binder interlayers are known to play the decisive role with respect to the wear-resistance of ultra-coarse cemented carbides. The binder interlayers on the surface of such ultra-coarse cemented carbides are worn out very rapidly during operation leaving unsupported WC grains, which results in the low wear-resistance and short lifetime of tools with the conventional ultra-coarse grades [13]. In order to solve this problem, the binder of the novel ultra-coarse cemented

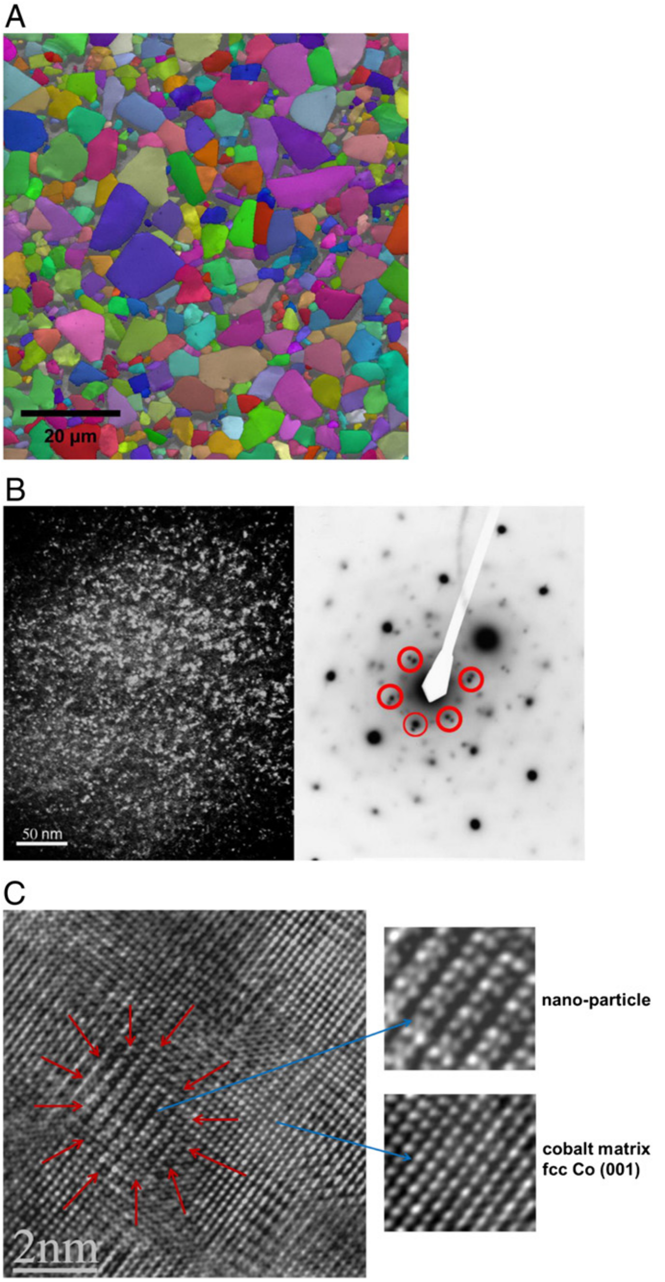

Fig. 1. Cemented carbide with nanograin reinforced binder: (a) the microstructure (an EBSD image), (b) the binder nanostructure (dark Field TEM Image from the nanoparticles in the binder and corresponding electron diffraction; the reflections from the nano-precipitates is indicated by circles), and (c) the binder nanostructure with atomic resolution (HRTEM).

carbide is reinforced by hard nanoparticles shown in Fig. 1b and c. The nanoparticles are extremely fine with mean grain size of roughly 3 nm and isolated from each other while being coherent with the cobalt binder matrix. Therefore, the binder is not embrittled as a result of the nanograin reinforcement and the carbide fracture toughness does not change. The crystal lattice of each nanoparticle is coherent with that of the Co matrix and there is no clear interface between them, which is clearly seen in Fig. 1c. The electron diffraction pattern from the binder with the nanoparticles indicates that their crystal structure corresponds to the primitive cubic crystal lattice of the Cu_3Au type. According to numerous publications on the stable W–Co–C phase diagrams summarized in Ref. [20], there is no stable W–Co–C phase with the Cu_3Au crystal lattice, so that the observed phase is metastable.

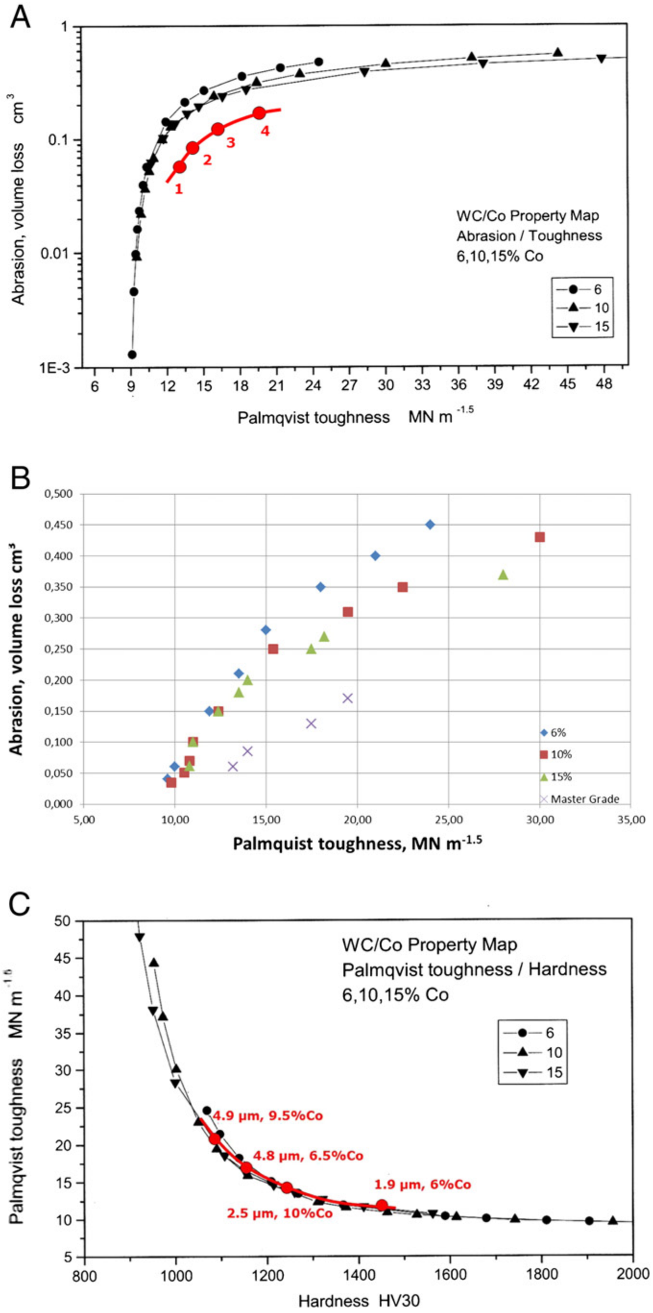

Fig. 2. Cemented carbides with nanograin reinforced binder versus conventional WC–Co grades: (a) the curve indicating the dependence of wear of the Master Grades with different combinations of WC mean grain size and Co content indicated by numbers: 1–1.9 µm, 6%Co, 2–2.5 µm, 10%Co, 3–4.8 µm, 6.5%Co, 4–4.9 µm, 9.5%Co, in comparison with the baselines for conventional WC–Co cemented carbides according to Ref. [2] (the ASTM B611 test, the logarithmic co-ordinates); (b) the same as (a) but re-constructed in the straight co-ordinates, the numbers indicate the Co contents for the conventional WC-Co cemented carbides; and (c) curves indicating the dependence of fracture toughness vs. hardness the Master Grades with different combinations of WC mean grain size and Co content in comparison with the baselines for conventional WC–Co cemented carbides according to Ref. [2].

Fig. 2 shows curves indicating dependences of the wear on the fracture toughness, and the fracture toughness on the hardness for novel cemented carbides in comparison with the baselines for conventional WC–Co cemented carbides. As it can be seen in Fig. 2a and b the wear-resistance of the novel cemented carbides with nanograin reinforce binder is dramatically improved in comparison with conventional WC–Co materials (by a factor of nearly two). As a result, it becomes possible to “break away” out from the dependence between the abrasion wear and toughness for conventional cemented carbides and achieve significantly better combinations of wear-resistance and fracture toughness. This is achieved due to only an insignificant increase in hardness of the novel carbides in comparison with the conventional cemented carbides (Fig. 2c), therefore, the dramatic improvement of wear-resistance is a result of nanostructuring the binder phase.

The novel cemented carbides with nanograin reinforced binder having a brand name "Master Grades®" are currently manufactured on a large scale, for example, several millions of road-planing picks with tips of the novel carbide grades are produced annually. Tool lifetime of the road-planing picks with the Master Grade® is prolonged by a factor of 2 to 3. As it can be seen in Fig. 3 showing worn surfaces of the novel cemented carbide after road-planing the binder phase is worn faster than WC grains during road-planing. Nevertheless, the gaps between the WC grains are relatively shallow and the WC grains do not become unsupported as in the case of the conventional ultra-coarse WC–Co grades examined in Ref. [13] resulting in the dramatically prolonged tool lifetime of the Master Grade with nanograin reinforced binder.

3.2. Near-nano WC–Co cemented carbides

Fig. 4 shows the microstructure of a near-nano carbide grade with 10 wt.% Co and WC mean grain size of roughly between 150 and 200 nm. The microstructure is very uniform with no WC grains larger than nearly 500 nm.

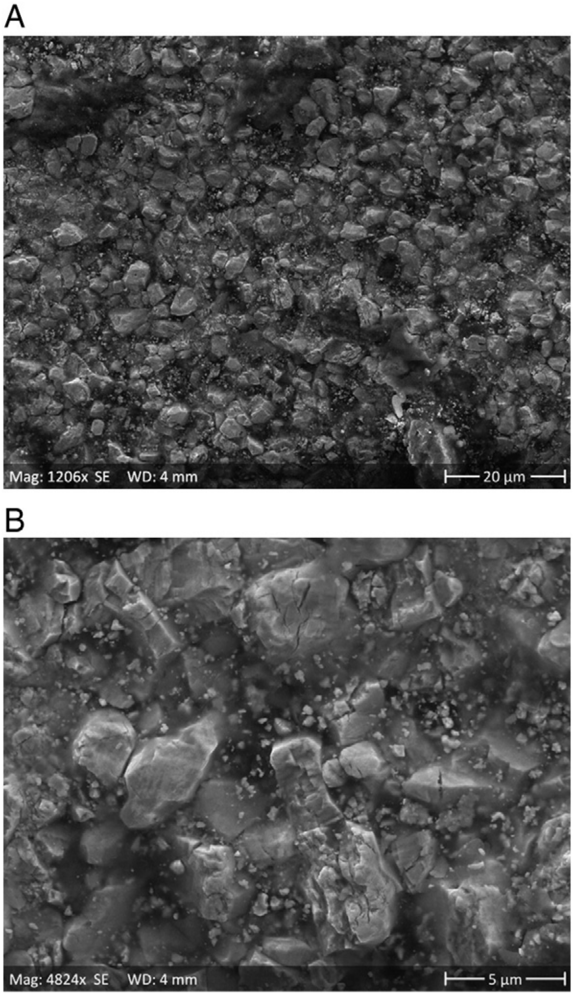

Fig. 3. Worn surfaces of the cemented carbides with nanograin reinforced binder after road-planing: (a) overview taken at low magnification, and (b) worn surface taken at high magnification.

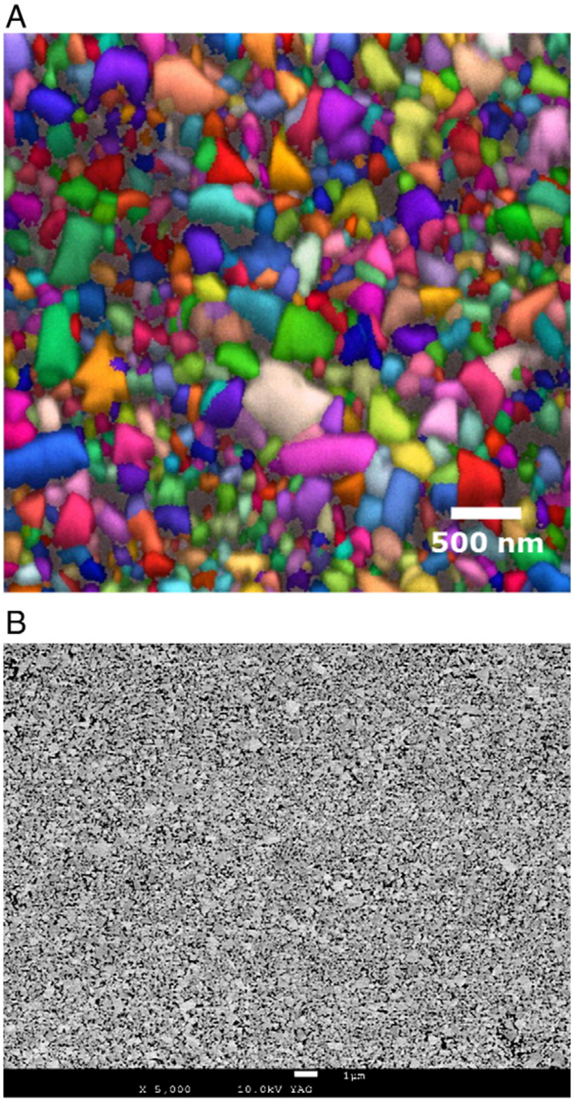

Fig. 4. Near-nano cemented carbide with 10 wt.% Co: (a) EBSD image of the microstructure, and (b) HRSEM image of the microstructure.

One can expect that the very different microstructures and Co contents of the near-nano cemented carbides and conventional coarse-grain WC–Co cemented carbides both having a moderate hardness can result in their different wear behaviors in the high-load ASTM B611 wear test. It is well known that the ASTM B611 wear test is characterized by the presence of high stresses as a result of impact of abrasive alumina particles subjected to the carbide surface by a steel wheel , which can lead to micro-fatigue phenomena on the carbide surface. Therefore, it can be expected that the hardness, fracture toughness and resistance to micro-fatigue of the near-nano cemented carbides would simultaneously play an important role in their wear behavior.

Fig. 5 shows curves indicating dependences of the wear of the near-nano carbides vs. their fracture toughness, and the fracture toughness vs. their hardness in comparison with the baselines for conventional WC–Co cemented carbides. It can be seen that the wear-resistance of the near-nano grade with 10% Co is slightly higher than that of the corresponding conventional WC–Co grade with almost the same fracture toughness. The wear-resistance of the near-nano grade with 13 wt.% Co is very similar to that of the corresponding conventional grade with the same fracture toughness. The near-nano carbides with Co contents higher than 13% are characterized by significantly worse combinations of wear-resistance and fracture toughness than those of the conventional WC–Co grades. As it can be seen in Fig. 5b the near-nano

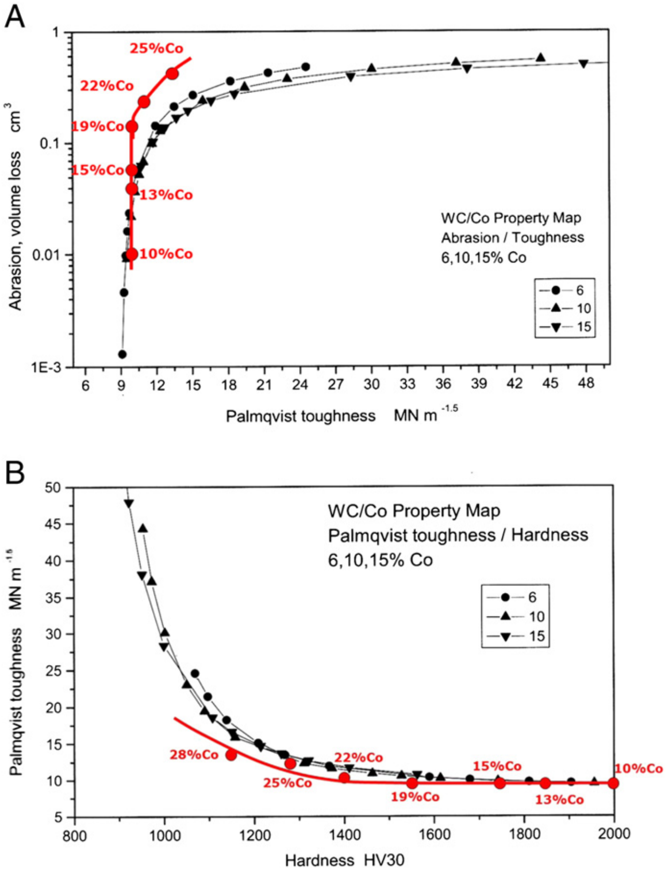

Fig. 5. Near-nano cemented carbides with different Co contents : curves indicating the dependences of (a) the wear in the ASTM B611 test vs. fracture toughness, and (b) the fracture toughness vs. hardness in comparison with baselines for conventional WC–Co cemented carbides according to Ref. [2].

carbides with more than 13 wt.% Co have also a worse combination of hardness and fracture toughness than that of the conventional WC–Co cemented carbides.

The reduced wear-resistance of the near-nano carbides with relatively high Co contents can be understood when taking into account the wear pattern of the near-nano carbide with 24 wt.% Co having a hardness of 1280 Vickers units shown in Fig. 6. The worn surface of the near-nano grade is very rough and comprises numerous traces of micro-chipping and micro-cracking. In this case, phenomena of micro-fatigue play a very important role when performing the ASTM B611 test. They lead to micro-fractures and micro-cracks on the worn surface resulting in the detachment of huge WC–Co fragments from the carbide surface. This is presumably related to the reduced fracture toughness of the near-nano grade and consequently its poor resistance to micro-fatigue. The fracture toughness and fatigue resistance of cemented carbides containing much grain growth inhibitors in some cases can be reduced in comparison with straight WC–Co grades [21]. This is caused by the fact that the grain growth inhibitors (chromium, vanadium, etc.) segregate at WC–Co interfaces and WC–WC grain boundaries usually separated by very thin Co interlayers [22,23]. Therefore, the presence of large amount of grain growth inhibitors in the near-nano carbides with high Co contents leads to their noticeably reduced fracture toughness and resistance to micro-fatigue resulting in their low wear-resistance in the high-load ASTM B611 test. In contrast to the worn surface of the near-nano carbide, the worn surface of straight WC–Co grades having nearly the same hardness but not comprising grain growth inhibitors is smooth and not characterized by micro-chipping and micro-cracking resulting in their noticeably greater wear-resistance, which is shown in Ref. [24].

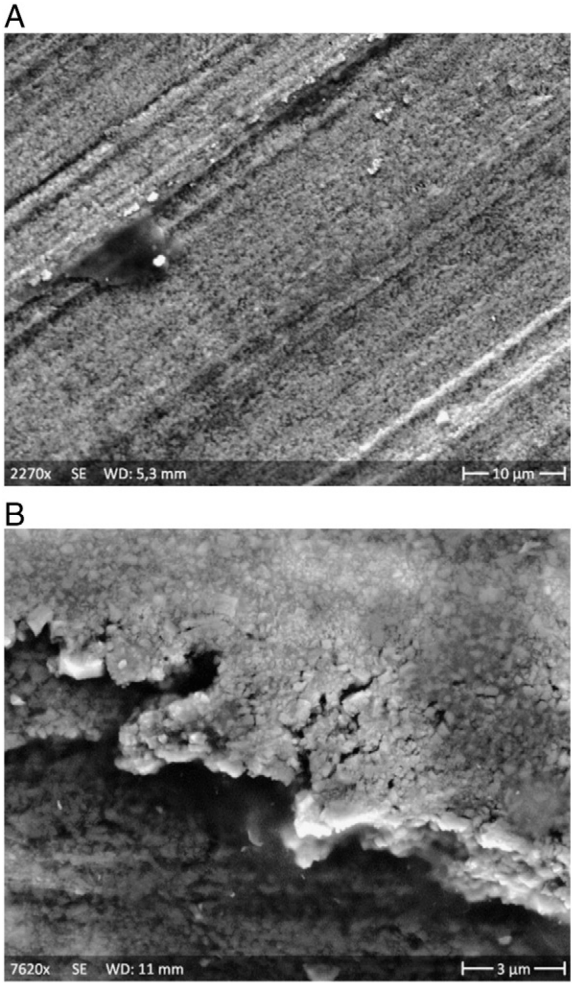

Fig. 6. Worn surfaces of near-nano cemented carbide with 24 wt.% Co and hardness of 1280 Vickers units after the ASTM B611 test: (a) overview taken at low magnification, and (b) the same as in (a) but taken at high magnification.

Therefore, the reduced wear-resistance of the high-Co near-nano grades is related to their lower fractures toughness at the same hardness being compared with the corresponding straight coarse-grain WC–Co grades. Thus, the necessity of adding high amounts of grain growth inhibitors to suppress the grain growth in the near-nano grades with high Co contents leads to their reduced fracture toughness, resistance to micro-fatigue and consequently decreased wear-resistance. Also, the WC mean grain size of the near-nano carbides presumably lies above the hypothetical “border line” with respect to the possibility of simultaneous increasing both the hardness and fracture toughness due to nanostructuring. Therefore, nanostructuring the carbide phase of WC–Co materials can potentially result in their simultaneously improved hardness, wear-resistance and fracture toughness only if the WC mean grain size would be well below 100 nm, predominantly below 10 to 20 nm. Presently, obtaining such nanostructured cemented carbides is hardly possible by the powder metallurgy route, so that fundamentally novel approaches to the fabrication of nanostructured WC–Co materials are needed.

3.3. Nanostructured carbide hard-facing of the WC–Fe–Cr–Si system

Fig. 7 shows the microstructure of novel carbide hard-face materials of the WC–Fe–Cr–Si system with a low melting point. The microstructure of the hard-facing shown in Fig. 7a and b comprises WC grains, grains of mixed carbide $(Cr, Fe)_7C_3$ and dendritic formations of the η-phases (Fe_3W_3C, $Fe_{6.8}W_{20.4}C_{6.8}$ and Fe_6W_6C) containing also some

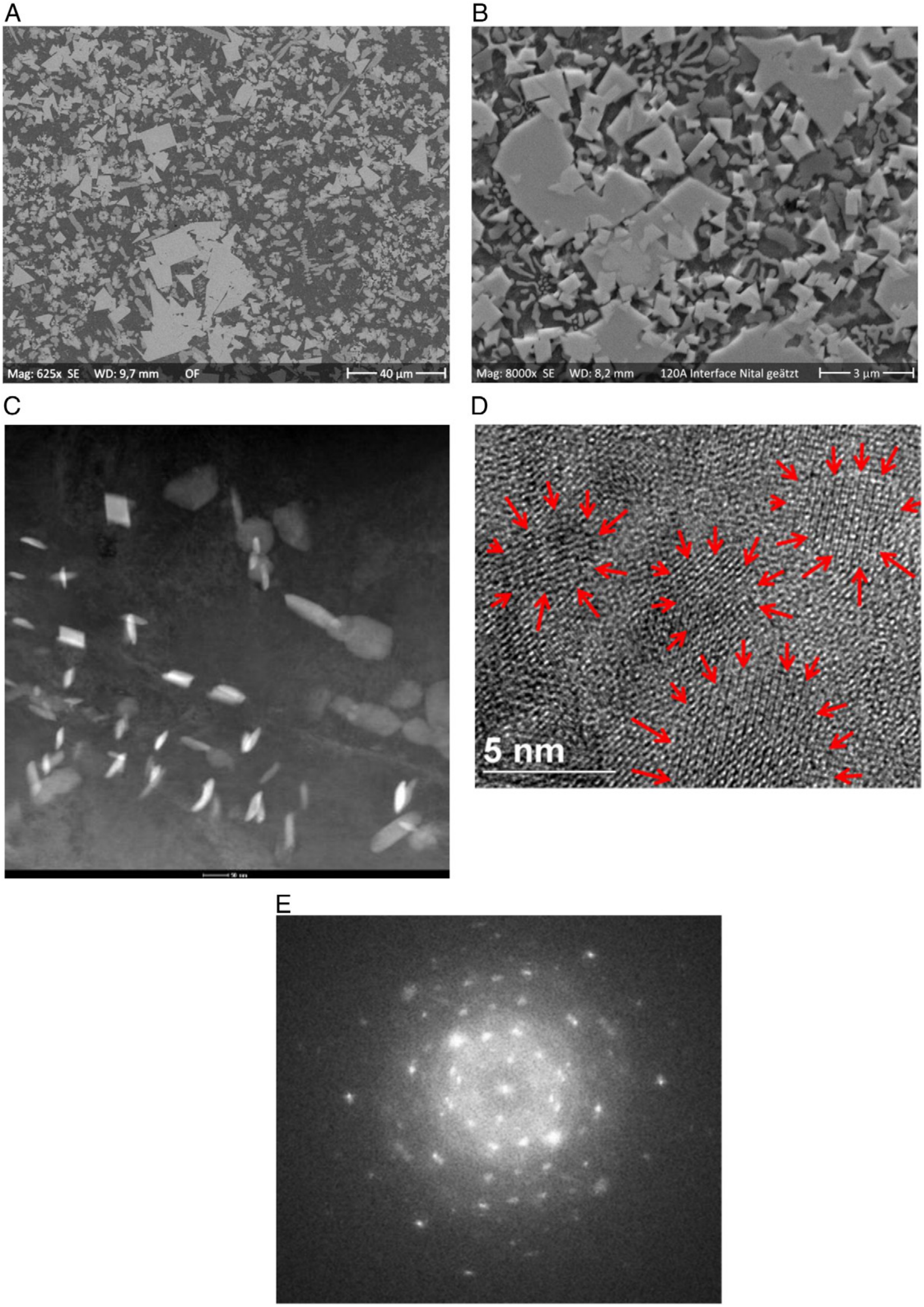

Fig. 7. Cemented carbides of the WC–Fe–Cr–Si system for hard-facing: (a) an overview of the microstructure at low magnification (HRSEM), (b) the microstructure at high magnification (HRSEM), (c) the binder nanostructure (TEM), (d) the structure of the binder matrix with atomic resolution (HRTEM, fast Fourier transformation of the binder matrix area), the nanograins are indicated by arrows, and (e) electron diffraction pattern from the binder matrix.

silicon and chromium. All the carbide grains are embedded in a Fe-based binder. The binder comprises nanoparticles in the form of nanoplatelets and nano-whiskers of the η-phases shown in Fig. 7c, which are roughly 20 to 100 nm in diameter. The binder matrix consists of a mixture of ferrite and austenite containing dissolved tungsten, chromium, silicon and carbon. As it can be seen in Fig. 7d the binder matrix is nanostructured with particle sizes below 10 nm. The electron diffraction pattern from the binder matrix shown in Fig. 7e clearly indicates that it contains no or very little amorphous phase. The nano-hardness of the binder was found to be nearly 11 GPa.

Fig. 8 shows results of the ASTM G65 test of the carbide hard-facing in comparison with conventional WC–Co grades with different Co contents. Due to the nanostructured binder, the wear-resistance of the hard-facing with hardness of about 10.5 GPa is higher than that of the WC–8%Co carbide grade with hardness of 12.5 GPa and noticeably greater than that of the WC–10% Co grade with hardness of 12 GPa. Therefore, the binder nanostructuring ensures the dramatic improvement in wear-resistance at moderate hardness. The increase in wear-resistance of the hard-facing in comparison with conventional WC–Co materials as a result of nanostructuring is equivalent to the difference in Co contents for conventional cemented carbides of roughly 5 wt.% Co. This is a very significant difference corresponding to roughly 200 to 250 Vickers units for conventional WC–Co materials.

Fig. 9 shows worn surfaces of the carbide hard-facing and the WC–10% Co cemented carbides after the ASTM G65 test. It can be seen in Fig. 9a that the wear rates of the carbide grains having a light-gray color and the binder having a dark-gray color on the surface of the hard-facing are comparable, so that there is no predominant abrasive wear of the binder phase. As a result of that, the wear-resistance of the carbide hard-facing is exceptionally high at moderate hardness due to the nanostructured binder matrix enhanced by the nano-whiskers and nano-plates. In contrast to that, the Co binder on the wear surface of the conventional WC–Co grade shown in Fig. 9b is selectively worn out leaving unsupported WC grains, which can be easily cracked, destroyed and detached from the carbide surface resulting in the high wear rate.

3.4. Nanostructured CVD W_2C–W materials Hardide-T

The Hardide coatings represent a group of nanostructured materials comprising W_2C nanograins embedded in a tungsten metal matrix produced by chemical vapor deposition (CVD). The presence of W_2C nanograins was established by TEM studies elsewhere [19]. Fig. 10a shows a metallurgical cross-section of the Hardide-T coating and Fig. 10b shows the Hardide coating surface “as deposited”. The coating has a thickness of 60 μm, hardness of 12.5 GPa, a pore-free columnar structure and follows the substrate morphology. Fig. 10c is a HRTEM image of the coating showing a W_2C nano-particle of roughly 2 to 4 nm in size (highlighted with arrows) embedded in the tungsten metal matrix. Good alignment of crystal lattices of the two phases is characteristic for coherent precipitates. W_2C nanoparticles similar to that indicated by the arrows are uniformly and densely distributed in the matrix.

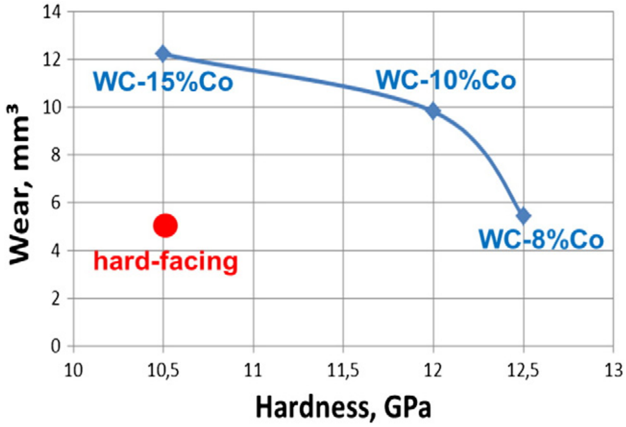

Fig. 8. Wear of the WC–Fe–Cr–Si cemented carbide for hard-facing in the ASTM G65 test in comparison with conventional WC–Co mining grades with different Co contents.

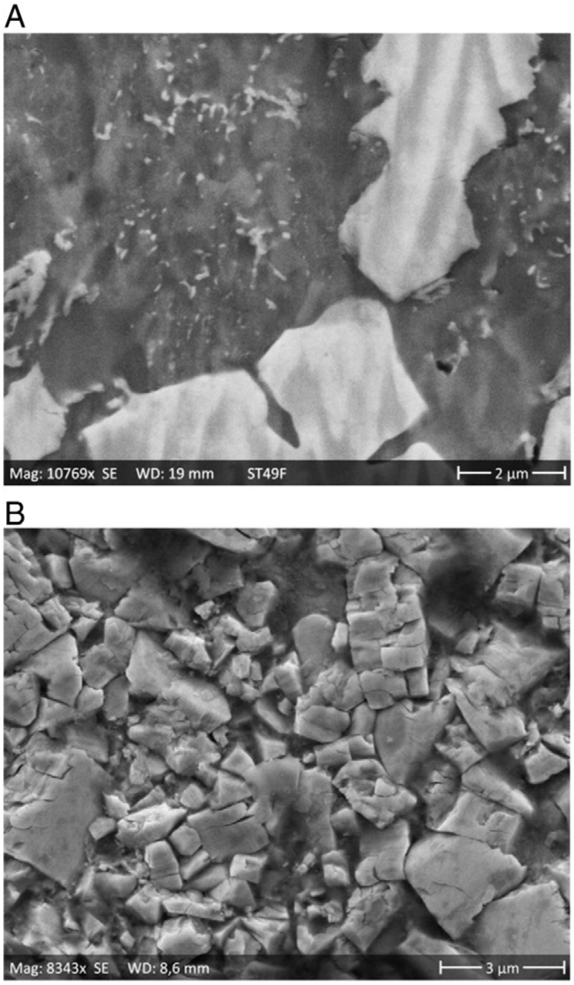

Fig. 9. Worn surfaces after the ASTM G65 test: (a) the WC–Fe–Cr–Si carbide hard-facing and (b) conventional WC–10% Co carbide grade.

Fig. 11 shows the results of the ASTM G65-E wear test and the B611 wear test performed by use of silica particles instead of alumina particles at a reduced number of revolutions (30 revs.) in order that the coating is not worn through during the test. Three samples of the Hardide-T coatings with different hardness values were examined in the wear tests. The overall increase of wear-resistance with increasing the hardness in both tests is as expected, especially when taking into account that the hardness of the abrasive particles used in both tests (silica sand) is close to 10–11 GPa. In these tests the performance of the Hardide-T coating with hardness of roughly 14.5 GPa was comparable with that of the carbide grade WC–6 wt.%Co having nearly the same hardness. It should be noted that the share of the tungsten carbide phase in the Hardide-T coating is lower than 50 vol.%, which is significantly less than in the WC–6 wt.%Co grade characterized by the WC volume share of nearly 90%. Therefore, it can be expected that if the volume percentage of the tungsten carbide phase in the Hardide-T coating were similar to that of the WC–Co grade, its hardness and consequently wear-resistance would be significantly greater than those of this grade. Nevertheless, it is hardly possible to compare the wear-resistance and other mechanical properties of the WC–Co and the W_2C–W materials, as the tungsten metal binder of the Hardide-T coatings is noticeably harder

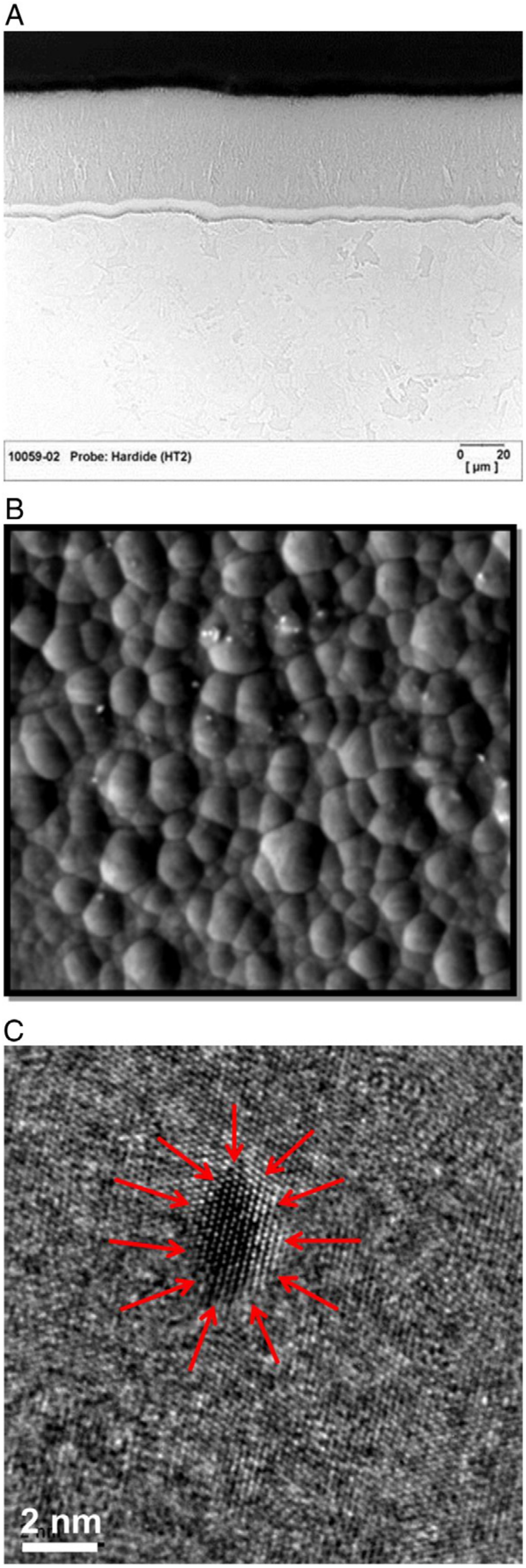

Fig. 10. Nanostructured CVD W2C-W materials Hardide-T: (a) the microstructure, (b) surface morphology, and (c) structure with atomic resolution (HRTEM).

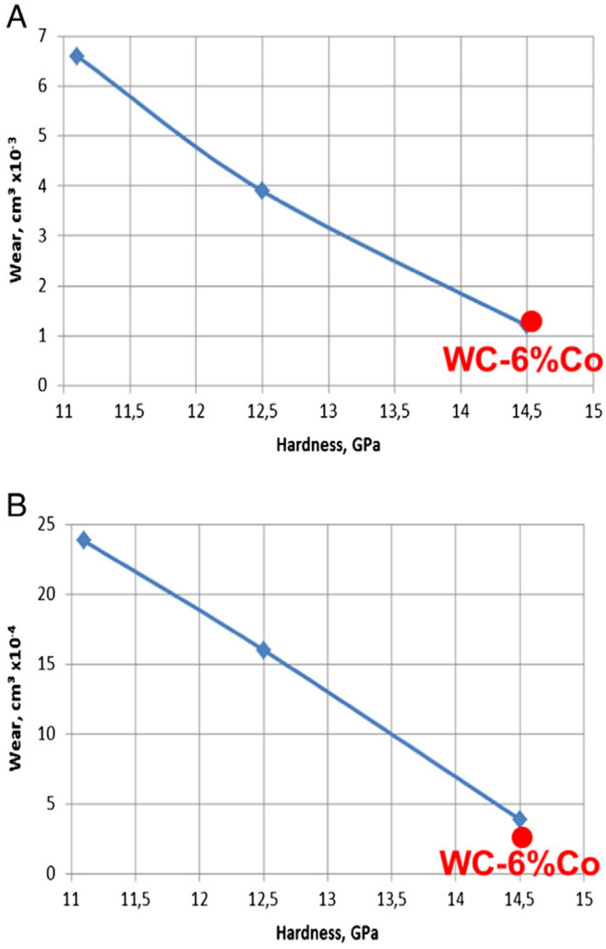

Fig. 11. Wear of Hardide-T with different values of hardness in comparison with the mining WC–6%Co carbide grade: (a) in the ASTM G65-E Test, and (b) low cycle ASTM B611 Test carried out by use of sand particles at 30 rev.

and less ductile than the Co binder of conventional WC–Co cemented carbides.

Fig. 12 shows worn surface of the Hardide-T coating in comparison with the WC–Co grade after the ASTM G65-E test. As one can see, in the case of the WC–Co cemented carbide the wear mechanism includes the predominant wear of the binder phase, which leaves WC grains unsupported. As a result, they are subjected to micro-cracking and abrasive wear. In contrast to that, as expected, the worn surface of the Hardide-T coating is very smooth and uniform without any traces of selective wear of the tungsten metal binder.

4. Conclusions

The wear-resistance of hard materials with either the nanostructured binder phase or the nanostructured carbide phase was examined in the ASTM B611 and ASTM G65 wear tests and compared with that of conventional WC–Co cemented carbides having nearly the same hardness.

The wear-resistance of WC–Co ultra-coarse grades is dramatically improved due to the nanograin reinforcement of the binder phase by nanoparticles with the mean grain size of nearly 3 nm in comparison with conventional WC–Co cemented carbides of nearly the same hardness.

The wear-resistance of near-nano cemented carbides is slightly better than that of corresponding conventional WC–Co materials only at relatively low Co contents and high hardness values. The near-nano carbides with high Co contents and moderate hardness are characterized

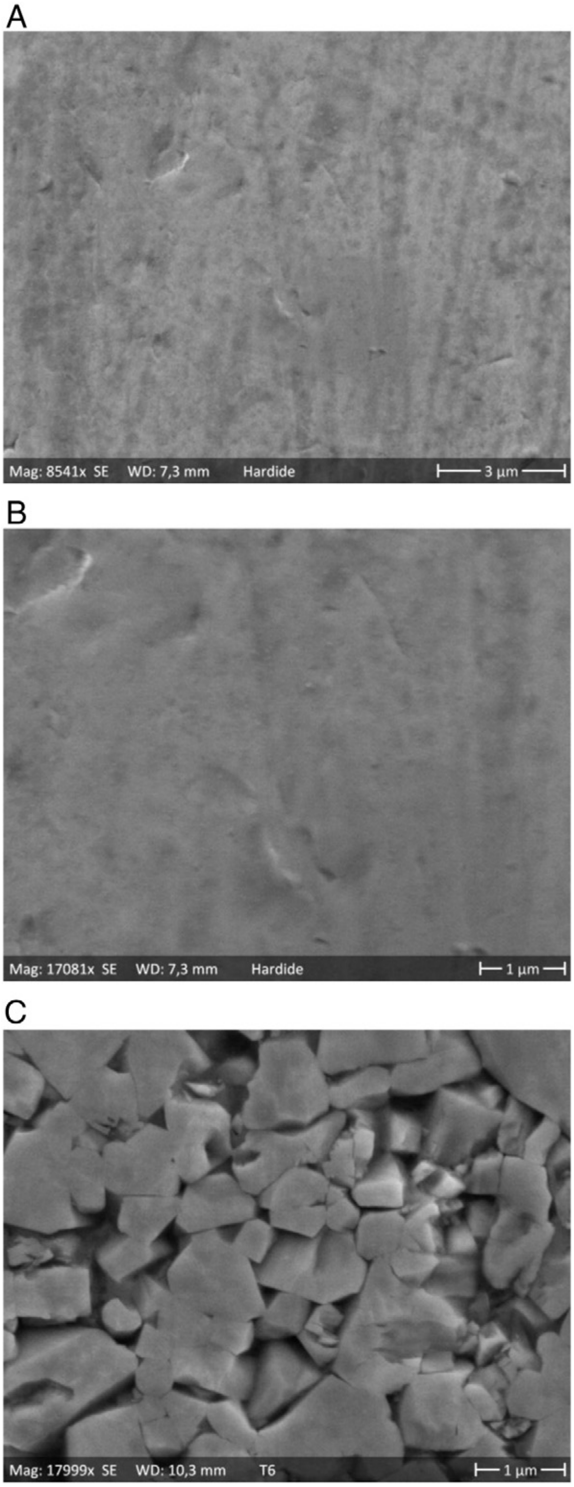

Fig. 12. Worn surfaces after the ASTM G65 test, procedure E: (a) and (b) the Hardide sample having a hardness of nearly 14.5 GPa, and (c) the WC–6%Co carbide grade having a hardness of about 14.5 GPa.

by an inferior combination of hardness, wear-resistance and fracture toughness as compared to that of conventional straight WC–Co grades. The WC mean grain size of the near-nano carbides presumably lies above the hypothetical “border line” with respect to the possibility of simultaneous increasing both the hardness and fracture toughness due to nanostructuring.

The wear-resistance of carbide hard-face materials of the WC–Fe–Cr–Si system with the nanostructured binder matrix enhanced by hard nano-plates and nano-whiskers is significantly greater than that of the conventional WC–Co cemented carbide having nearly the same hardness. This is presumably a result of both the binder nano-enhancement and the nanostructured Fe-based binder matrix having a mean grain size of nearly 5 nm.

The wear-resistance of the nanostructured CVD Hardide-T coating comprising W_2C nanoparticles embedded in the tungsten metal binder is close to that of the WC–Co grade having nearly the same hardness. It is hardly possible to compare the wear-resistance and other mechanical properties of the WC–Co and the W_2C–W materials, as the tungsten metal binder of the Hardide-T coating is noticeably harder and less ductile than the Co binder of conventional WC–Co cemented carbides.

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References

[1] Gee MG, Gant A, Roebuck B. Wear mechanisms in abrasion and erosion of WC/Co and related materials. Wear 2007;263:137–48.
[2] Roebuck B, Gee MG, Morrell R. Hardmetals — microstructural design, testing and property maps. In: Kneringer G, Rödhammer P, Wildner H, editors. Proceedings of the 15th International Plansee Seminar, vol.4. ; 2001. p. 245–66 [Reutte].
[3] Fang Z, Wang X, Ryu T, Hwang KS, Sohn HY. Synthesis, sintering and mechanical properties of nanocrystalline cemented tungsten carbide — a review. Int J Refract Met Hard Mater 2009;27:288–99.
[4] Shao G, Duan X-L, Xie J, Yu X, Zhang W, Yuan R. Sintering of nanocrystalline WC–Co composite powder. Rev Adv Mater Sci 2003;5:281–6.
[5] Goren-Muginstein G, Berger S, Rosen A. Sintering study of nanocrystalline tungsten carbide powder. Nanostruct Mater 1998;10:795–804.
[6] Arato P, Bartha L, Porat R, Berger S, Rosen A. Solid or liquid phase sintering of nanocrystalline WC/Co hardmetals. Nanostruct Mater 1998;10:245–55.
[7] Konyashin I, Ries B, Lachmann F. Near-nano WC–Co hardmetals: will they substitute conventional coarse-grained mining grades? Int J Refract Met Hard Mater 2010;28:489–97.
[8] Eiling A, Caspers B, Gille G, Gries B. Nanoskalige Hartmetalle mit Fe-basierten Bindern. In: Kolaska H, editor. Pulvermetallurgie: Neue Anforderungen – Neue Produkte – Neue Verfahren, Fachverband Pulvermetallurgie; 2008. p. 91–106.
[9] Hornbogen E. Precipitation hardening — the oldest nanotechnology. Metall 2001;9:522–6.
[10] Konyashin I., Cooper R. & Ries B. Cemented Carbide in Particular for Cutting Stone, Concrete and Asphalt. German Patent 10258537, 2006.
[11] Konyashin I, Cooper R, Ries B. Cemented carbide in particular for cutting stone, concrete and, asphalt; 2004 [EP1520056].
[12] Konyashin I, Ries B, Lachmann F. Cemented carbide material; 2012 [WO2012/130851].
[13] Konyashin I, Schäfer F, Cooper R, et al. Novel ultra-coarse hardmetal grades with reinforced binder for mining and construction. Int J Refract Met Hard Mater 2005;23:225–32.
[14] Konyashin I, Ries B, Lachmann F. Iron–metal carbide polycrystalline material for hardfacing, bodies comprising same, tools comprising same and method for making same; 2013 [WO 2013178552].
[15] Konyashin I, Ries B, Lachmann F. Constructions comprising polycrystalline material, tools comprising same, and method for making same; 2013 [WO 2013178550].
[16] Konyashin I, Ries B, Lachmann F. Constructions comprising polycrystalline material, tools comprising same, and method for making same; 2013 [WO 2013/178554].
[17] Konyashin I, Ries B, Lachmann F. Hardfacing structure containing (M, Cr)7C3 and (M, Cr)23C6 on a steel substrate; 2010 [GB2010–6365].
[18] Konyashin I, Ries B, Lachmann F, Schäfer K. Hard face structure, body comprising same and method for making same, GB2010-11583; 2010.
[19] Zhuk Y. Hardide: advanced nanostructured CVD coating. Int J Microstruct Mater Prop 2007;2(1):90–8.
[20] Fernandes CM, Senos AMR. Cemented carbide phase diagrams: a review. Int J Refract Met Hard Mater 2011;29:405–18.
[21] Konyashin I. Cemented carbides for mining, construction and wear parts. In: Sarin V, editor. Comprehensive Hard Materials. Elsevier Science and Technology; 2014.
[22] Lay S, Hamar-Thibault S, Lackner A. Location of VC in VC, Cr3C2 codoped WC–Co cermets by HRTEM and EELS. Int J Refract Met Hard Mater 2002;20:61–9.
[23] Weidow J, Andrén H-O. Grain and phase boundary segregation in WC–Co with TiC, ZrC, NbC or TaC additions. Int J Refract Met Hard Mater 2011;29:38–43.
[24] Konyashin I, Ries B. Wear damage of cemented carbides with different combinations of WC mean grain size and Co content. Part I: ASTM wear tests. Int J Refract Met Hard Mater 2014;46:12–9.