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PII: S0263-4368(19)30471-8

DOI: <https://doi.org/10.1016/j.ijrmhm.2019.105050>

Article Number: 105050

Reference: RMHM 105050

To appear in: *International Journal of Refractory Metals and Hard Materials*

Received date: 5 July 2019

Revised date: 5 August 2019

Accepted date: 5 August 2019

Please cite this article as: I. El Azhari, J. García, F. Soldera, et al., Contact damage investigation of CVD carbonitride hard coatings deposited on cemented carbides, *International Journal of Refractory Metals and Hard Materials*, <https://doi.org/10.1016/j.ijrmhm.2019.105050>

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Contact damage investigation of CVD carbonitride hard coatings deposited on cemented carbides

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Abstract

The evolution of damage induced as contact load is increased has been investigated on single- and multilayered coated cemented carbides by means of spherical indentation. The main objective of the study was to assess the effect of the intermediate wear-resistant carbonitride layer on the contact damage resistance of industrial milling (multilayered) inserts. This was approached by evaluating systems consisting of a single carbonitride layer of different chemical nature: novel Zr(C,N) and conventional Ti(C,N) chemical vapor deposition (CVD) coatings. Deformation and damage phenomena were characterized using a wide range of advanced techniques: confocal laser scanning microscopy, scanning electron microscopy, focused ion beam and X-ray synchrotron. Zr(C,N) coated systems are found to exhibit a higher mechanical integrity than Ti(C,N) counterparts. Main reasons behind are the relatively different thermal residual stresses generated during CVD cooling, as a result of the dissimilar coefficient of thermal expansion between the coating and the substrate, as well as the intrinsic cohesive strength of the studied coatings. Such different mechanical response was also discerned to affect the interaction between cracking and layer assemblage in multilayer coated specimens. It then supports the beneficial effect of using Zr(C,N) as the intermediate wear-resistant layer toward enhanced performance of industrial milling inserts.

Keywords: Contact damage, Ti(C,N) Zr(C,N) CVD coatings, Residual stresses, X-ray synchrotron, WC-Co

1. Introduction

WC-Co cemented carbides, also commonly referred to as hardmetals, are successful composite materials used in demanding applications like metal cutting and forming. For cutting applications, tool life and performance are significantly improved by using coatings as external protective layers, deposited by either chemical vapor (CVD) or physical vapor (PVD) deposition routes [1,2]. Wear resistant coatings are generally based on transition metal carbides, nitrides or carbonitrides, because of their hybrid ceramic and metal-like properties. This combination of characteristics has attracted considerable attention [3,4]; and thus, literature focused on development and application of these films is quite extensive (e.g. Refs. [1,5–7]). However, brittleness of these hard coatings is still an issue, and addressing this problem is a subject of high interest. In this regard, a recently developed $\text{Zr(C,N)/Al}_2\text{O}_3$ multilayer CVD coated milling insert has shown prolonged tool life in comparison to that exhibited by the well-established $\text{Ti(C,N)/Al}_2\text{O}_3$ coated inserts [8]. Aiming to get an in-depth understanding of such distinct response, a testing campaign has been launched to assess the effective influence of the carbonitride (CN) layer on the thermo-mechanical behavior of the coated tool. It has included X-ray synchrotron measurement of residual stresses developed under thermal cycling [8] as well as micromechanical characterization of polycrystalline Ti(C,N) and Zr(C,N) coatings [9,10]. In this regard, although theoretical and experimental studies dealing with mechanical properties of zirconium-base coatings are quite limited compared to titanium-based counterparts, there is a consensus that Zr(C,N) is a promising material in highly demanding applications [4,11,12].

The objective of the present study is to document and analyze the damage

scenario resulting from contact loading on wear-resistant CVD hard coatings deposited on a hardmetal substrate. Referred damage is introduced in a controlled manner by means of spherical indentation. In contrast to sharp-like indenters, the use of a blunt indenter permits the delivery of concentrated stresses over a small area of specimen surface, such that damage evolution with increasing applied load may be assessed. Such experimental approach has proven to be successful in the evaluation of contact damage phenomena in hard and brittle bulk materials, such as ceramics [13], cemented carbides [14] and even polycrystalline diamond [15], as well as in coating-substrate systems, mainly PVD-coated hardmetals and tool steels [16–20]. Following this approach, spherical indentation experiments were conducted on specimens coated with CVD carbonitride layers of different chemical nature: Ti(C,N) and Zr(C,N). They were followed by extensive and detailed optical and scanning electron microscopy inspection of damage scenario in top- and cross-section views, i.e. at both surface and subsurface levels. Finally, findings on single-layered specimens are invoked to rationalize and understand damage features observed on industrial milling inserts (effective multilayered samples) when subjected to a similar testing protocol.

2. Materials and methods

2.1 Tested Samples

The study was focused on coating/substrate systems consisting of single carbonitride [Ti(C,N)-s and Zr(C,N)-s] layers deposited onto a fine-grained WC-6wt%Co industrial grade used as substrate [2]. Films were deposited in a CVD hot wall reactor using metal chloride, acetonitrile and hydrogen reactant at temperatures between 885 and 930 °C (moderate temperature CVD process, MT-CVD). Differences between the two single-layer coated specimens studied are limited to the chemical nature of the carbonitride wear resistant layer, i.e. either Ti(C,N) or Zr(C,N). Schematic outlines of layer assemblage for the specimens investigated are given in Fig. 1, and corresponding thicknesses are listed in Table 1. Aiming to explore the practical relevance of this study, the investigation was extended to include testing of industrial milling cutting inserts. These specimens represent more complex multilayer [Ti(C,N)-m and Zr(C,N)-m] coating-substrate systems (details and corresponding layer assemblage outlines are also given in Table 1 and Fig. 1, respectively) in which an intermediate wear resistant carbonitride layer - similar to the ones tested here in single-layer coated specimens - is known to play a key role on the effective performance of the cutting tool under service conditions [8]. In this regard, it should be noticed that the thickness of single-layer variants was aimed to be close to the total thickness of the multilayer ones, i.e. 5-6 microns. It guarantees that similar coating thickness / spherical indenter radius ratios are involved during contact load tests (to be described below). However, it also implies that analysis of induced damage under contact loading should be limited to direct comparison between specimens with same layer assemblage, either single- or multilayer. Main reasons behind this statement are that both effective

load-bearing and residual stress state within the carbonitride layer depend on its particular thickness, this being different in single- and multilayer assemblages which is about 5 and 3 microns, respectively.

Fig. 1: Layer assemblage outline for the coating/substrate systems studied: a. Single-layer carbonitride [(C,N)-s] coated cemented carbide, including thin TiN interlayer (yellow) deposited on the substrate, prior to CN coating deposition. b. Multilayer [(C,N)-m] coated cemented carbide where in addition to referred TiN layer, a Ti(C,N,O) interlayer (dark blue) is deposited on the CN layer, prior to Al_2O_3 deposition.

Table 1: List of coated samples, and different corresponding layer assemblage, investigated.

Sample reference	TiN (0.3 μm)	CN Layer / thickness (μm)	Ti(C,N,O) (0.6 μm)	$\alpha\text{-Al}_2\text{O}_3$ (3 μm)
Ti(C,N)-m	✓	Ti(C,N) / 3 μm	✓	✓
Zr(C,N)-m	✓	Zr(C,N) / 3 μm	✓	✓
Ti(C,N)-s	✓	Ti(C,N) / 5 μm		
Zr(C,N)-s	✓	Zr(C,N) / 5 μm		

2.2 Testing procedure

Contact loading tests of coated systems were carried out by means of spherical indentation. They were conducted using a servo-hydraulic testing machine (Instron 8500) and a hardmetal indenter with a curvature radius (r_{sph}) of 1.25 mm. Monotonic loads were applied using a trapezoidal waveform. Contact was initiated by applying a low preload (10 N), followed by load increase with a rate of 10 N/s (ramp) until reaching the selected maximum level. After holding maximum applied load during 20 s, the indenter was quickly unloaded. Maximum applied load ranged from 600 to 2400 N. Mechanical tests were conducted on specimens exhibiting two different surface topography conditions. One corresponded to “as-deposited”, i.e. surface exhibiting topography and roughness directly resulting from the coating deposition process. The other one is referred to as “polished”, i.e. the surface was previously subjected to gentle

polishing with a 0.02 μm alumina suspension. This post-coating mechanical-like treatment was made attempting to enhance contact damage inspection by reducing the original roughness - of the “as-deposited” layer - that could hinder damage examination.

2.3 Characterization techniques

Residual imprints were characterized, in terms of dimensions and induced damage, by means of confocal laser scanning microscopy - CLSM (Olympus OLS4100). In order to assess the contact area during indentation, a sputtered gold film (about few nm in thickness) was deposited on the coated specimens before contact load testing [17]. Damage and cracking features at the subsurface were observed on cross-sections prepared using a Helios Nanolab 600 dual beam focused ion beam (FIB) / scanning electron microscopy (SEM) unit.

2.4 Residual stress measurements

Residual stresses were measured by means of X-ray diffraction, using energy-dispersive synchrotron diffraction. Measurement were performed at the Material Science Beamline EDDI (Energy Dispersive Diffraction) of the Helmholtz-Zentrum at the storage ring BESSY in Berlin, Germany [21]. The target was to measure and analyze the residual stresses in single-layered coatings. The $\sin^2\psi$ method was used to determine residual stress values, on the basis of its numerical stability and insensitivity to experimental uncertainties.

3. Results and discussion

3.1 Single-layer coated cemented carbides: *Ti(C,N)-s* and *Zr(C,N)-s*

3.1.1 Contact damage

The induced damage was first evaluated directly at the surface, i.e. from a top-view perspective using both CLSM and SEM. In general, as maximum applied load increases, irreversible deformation of the coated system is observed through circumferential cracks at the coating surface. They were already discerned at the smallest load level applied, i.e. 600 N, for both single-layer coated specimens (Fig. 2). These cracks are induced by the tensile radial stresses and strains which increase with distance from the impression center [22], and reach maximum values near the contact edge area with the indenter [22–24]. Furthermore, radial cracks outside the imprint were also observed as an additional damage characteristic. However, different from the circular ones, these radial fissures emerge at quite different load levels, depending on the chemical nature of the carbonitride layer, i.e. 800 N for the *Ti(C,N)-s* specimen and barely at 2400 N for the *Zr(C,N)-s* one. They result from tangential tensions that develop at the periphery of the contact [25,26] at load levels higher than those usually required for promoting circumferential cracks. As imposed load increased, density and sharpness of cracks, particularly of the circumferential ones, were also higher (Fig. 2). Although clear circular-like cracks were revealed for both coatings, cracking path was more continuous for *Zr(C,N)-s* specimens than for *Ti(C,N)-s* ones, the latter exhibiting a rather disrupted aspect. This is illustrated in the closer view of induced damage shown in Fig. 3.

Fig. 2: Residual imprint and cracking damage evolution with increasing loads for Ti(C,N)-s and Zr(C,N)-s specimens.

Fig. 3 . Circumferential cracks induced after spherical indentation (with an applied load of 2200 N):
a. choppy-like path (arrows), due to interaction with CVD cooling cracks network, in Ti(C,N)-s specimen. b. Continuous path, in absence of any CVD cooling cracks, in Zr(C,N)-s sample.

Within above framework, it may be stated that film cracking is governed by load transfer from the plastically deformed substrate into the coating, together with the effective fracture strength of the latter, i.e. that resulting from the compromising balance among intrinsic hardness (which is comparable between the two coatings [27]), residual stress state and mechanical integrity related to potential pre-existing cracking features. These two aspects will now be discussed.

3.1.2 Cracking-network induced after CVD cooling

As it was referred above, contact loading tests were conducted on surfaces corresponding to both “as-deposited” and “polished” conditions. As expected, mechanical response was not different in both cases. However, the used testing protocol allowed us not only to visualize the damage induced after imposing load, but also to inspect surface condition of carbonitride layers before mechanical testing. Regarding the latter, it permitted to reveal a peculiar network of cracks homogeneously

spread over the entire surface for Ti(C,N)-s specimen (Fig. 4a). This clearly was not the case for polished surface of Zr(C,N)-s specimen (Fig. 4b), which points out the cracking as an intrinsic result of final cooling during CVD process that follows deposition of the corresponding coatings.

Fig. 4 a. Cracking network induced during CVD cooling observed for Ti(C,N)-s specimen after polishing. b. Absence of cooling cracks network for Zr(C,N)-s sample.

Both carbonitride single layers deposited in this study exhibit a coefficient of thermal expansion (CTE) larger than that of the used hardmetal substrate (Table 2). As a consequence, coatings experience larger contractions than the substrate during cooling down after deposition. However, as a result of their corresponding dimensions, the layer has to follow the deformation of the substrate, resulting then on effective tensile loading of the coating [28]. Under high temperature deposition conditions (around 900°C), the generated tensile stresses may exceed the coating strength, which would result in generation of a cooling cracking network that relieve the stresses [28–30]. Absence of CVD cooling cracks on the surface of “polished” Zr(C,N)-s specimen should then be attributed to the lower CTE of the layer, as compared to the

one of Ti(C,N)-s sample. Therefore, CTE mismatch (with respect to the substrate) is lower in the former, and consequently the generated tensile stresses are reduced. Attention must then be drawn to the fact that Zr(C,N) exhibits the lowest CTE among all the carbonitrides of group IV [4].

An estimated value of the thermal stresses generated in the coating may be obtained according to [31]:

$$\sigma = (E_c / (1 - \nu_c)) * (\alpha_c - \alpha_s) * \Delta T \quad (1)$$

where E_c , ν_c and α_c are Young's modulus, Poisson's ratio and CTE of the coating, respectively; α_s is CTE of the substrate and ΔT is the difference between room and deposition temperatures. Inserting the corresponding parameters (Table 2) within equation (1), thermal stress values of 1025 MPa and 1877 MPa are obtained for Zr(C,N)-s and Ti(C,N)-s specimens, respectively. Residual stresses measured by synchrotron analysis revealed notably lower mean values for Zr(C,N)-s sample (560 ± 40 MPa) and more noticeably for Ti(C,N)-s one (465 ± 30 MPa), for which the measured value is about 4 times lower than the estimated one. A plausible explanation is that stresses are relaxed after extensive cracking and formation of cooling cracks network for Ti(C,N)-s sample. Accordingly, for Zr(C,N)-s specimens, stress relaxation without extensive cracking would not be expected, considering that stresses are retained as long as the fracture strength is not reached [32]. Then, lower measured tensile stresses could be attributed to relaxation through non-elastic or plastic deformation [30]. However, this assumption should be ruled out since relaxation of around 400 MPa through namely plastic deformation appears to be unrealistic. The remaining presumption is the existence of compressive intrinsic residual stresses, which developed during deposition of the coating and prior to cooling down. For CVD

thin films, possible origins of such stresses are defect incorporation into the films during evaporation, formation of non-equilibrium structures, grain boundary relaxation, etc. [30,33]. Following above ideas, the existence of prior intrinsic stresses cannot be discarded even for Ti(C,N)-s specimen. Nevertheless, a theoretical evaluation of these stresses is rather complex [33], and is out of the scope of this study.

Tensile residual stresses and cracking network resulting from CVD cooling are then aspects that may be invoked for understanding previous findings. On one hand, existence of tensile residual stresses should be responsible, at least partly, for the relatively low levels of applied load required for inducing circumferential cracking in both coated specimens. The fact that Zr(C,N)-s specimens do not show a higher cracking resistance than Ti(C,N)-s ones, as it could be expected from the relatively different calculated residual tensile stresses developed during deposition in both cases, may be rationalized by stress relief effects resulting from cracks emerging after CVD cooling stage in the latter. On the other hand, the referred CVD cooling cracking network must be directly associated with the quite early radial cracking exhibited by the Ti(C,N)-coated specimens. In this regard, it clearly affects cracking scenario resulting from both radial and circumferential stresses induced during contact load tests. Within this context, it may be postulated that bumpy crack path shown in Fig. 3a for Ti(C,N)-s specimen is indeed a consequence of the referred interaction. It reflects crack emergence from the existing CVD crack network (where cracks become thicker) and extension through effective fragmented units of the flawed layer, yielding even a visual impression of crack deflection phenomenon. As this combined action cannot exist in Zr(C,N)-s specimens, mainly because the absence of cracking event after CVD cooling stage, contact-induced fissures are discerned to follow a continuous path for these coated samples (Fig. 3b).

Table 2: Mechanical and average thermal properties of CN coatings. * Stoichiometry is subjected to slight variations. For more information, please refer to a recent work by the authors [10]. **Sandvik Coromant database.

Component	E modulus (GPa)	Poisson's ratio	CTE ($10^{-6} K^{-1}$)	Deposition temperature ($^{\circ}C$)
Ti(C_{0.5}*,N_{0.5}*)	463 [27]	0.193 [27]	9.2 [34]	885
Zr(C_{0.5}*,N_{0.5}*)	405 [27]	0.177 [27]	7.7 [34]	930
Substrate**	626	0.22	5.4	-

3.1.3 Cracking mechanisms

Contact damage was also assessed at the subsurface level by means of cross-section inspection. It was done on FIB-milled trenches perpendicular to circular cracks. Through-thickness cracks, nucleating at the surface and propagating down into the substrate, are evidenced in both cases (Fig. 5 a,b). However, crack path appears to be dissimilar: intergranular for Ti(C,N)-s specimens and transgranular for Zr(C,N)-s ones. This experimental fact is further supported by detailed in-plane SEM images of circumferential cracks taken on the surface of “as deposited” samples (Fig. 5 c,d). They have permitted to evidence that cracks propagate almost exclusively along the grain boundaries in the case of Ti(C,N)-s samples, whereas they mainly follow transgranular paths in Zr(C,N)-s ones. These results are in a complete agreement with findings previously reported by the authors regarding uniaxial compression response of micropillars milled out of same coatings studied here. There, it was evidenced that Ti(C,N) micropillars also fail exclusively along the grain boundaries, opposite to the more transgranular failure discerned for the Zr(C,N) ones [9]. This behavior was

correlated to segregation of chlorine along the grain boundaries for the former, which is detrimental for the cohesive strength along the grain boundaries [10]. As a summary, the higher resistance exhibited by the Zr(C,N)-s samples may be rationalized on the basis of higher strain energy dissipation for inducing irreversible deformation and/or damage, as compared to the Ti(C,N)-s one. For the latter, the intrinsic low cohesive strength at the grain boundaries together with the residual stress state (induced during CVD cooling) results in an extensive intergranular cracking network that affected the structural integrity of the Ti(C,N)-s coated system.

Fig. 5: a./b. Cross sections at circumferential cracks (located at the edge of residual imprints) induced by spherical indentation under an applied load of 2200N for Ti(C,N)-s and Zr(C,N)-s samples, respectively. c./d. In plane SEM images of referred circumferential cracks for Ti(C,N)-s and Zr(C,N)-s specimens, respectively.

3.2 Multilayer coated cemented carbide: *Ti(C,N)-m* and *Zr(C,N)-m*

3.2.1 Contact damage

Multilayer coated specimens (corresponding to industrial milling inserts) were also subjected to contact loading, following testing and characterization protocols similar to the ones described above for single-layer coated systems. In general, related findings to those described for *Ti(C,N)-s* and *Zr(C,N)-s* samples were evidenced. On the one hand, as applied load was increased, circular cracks nucleated and developed at the edges of residual impressions. However, radial cracks were not discerned, at least up to highest applied load used in this study, i.e. 2400 N. On the other hand, relatively different crack paths, depending on the chemical nature of the - now - intermediate carbonitride layer involved, were discerned: nearly continuous and rather disrupted for *Zr(C,N)-m* and *Ti(C,N)-m* samples, respectively (Fig. 6). Regarding this result, cross sections for each system were performed to check whether the observed damage in Fig. 6 was resolved at the same depth level. Alumina thickness after polishing was found to be comparable, which pointed out that qualitative differences in cracking paths correspond to almost similar depth level (down from the surface). Thus, these differences may be directly ascribed to the distinct intermediate carbonitride layer, since it is the only difference existing between layer assemblages of multilayered specimens studied [*Ti(C,N)-m* and *Zr(C,N)-m*].

Fig. 6 Comparison of induced damage at the edges of residual imprints, revealed after polishing, for a. Ti(C,N)-m and b. Zr(C,N)-m. Applied load was 2400 N in both cases. Imprints were gently polished (after performing the test) to remove surface roughness hindering damage features. Observed surface corresponds to top Al_2O_3 layer.

Inspection of FIB-milled cross-sections perpendicular to circular cracks permitted to have more insight. As shown in Fig. 7, several through-thickness cracks are evidenced. They are connected with some of the multiple small fissures discerned at the outer alumina layer. These cracks are observed to run down, following a straight path, until reaching the substrate. Density of microcracks is clearly higher in the alumina top layer than in the intermediate carbonitride ones.

Fig. 7 Cross sections at circumferential cracks (located at the edge of residual imprints) induced by spherical indentation under an applied load of 2200N (as-deposited samples): **a.** Ti(C,N)-m and **b.** Zr(C,N)-m. Numerical designation in micrographs corresponds to different layers, as follows: 1 - α -Al₂O₃; 2 - Ti(C,N,O); 3a - Ti(C,N); 3b - Zr(C,N); 4 - TiN; 5 - WC-Co substrate.

3.2.2 Structural integrity of multilayer assemblage

A comparison between cracking scenario for single-layer and multilayer coated specimens is not simple. The presence of the external alpha-alumina (α -Al₂O₃) layer implies several effects. Among them, it should be highlighted that alpha-alumina exhibits higher hardness and brittleness than both CN coatings. It is noticed in Fig. 7, where multiple fine cracks are induced within the alumina as a result of spherical indentation. Furthermore, alumina top layer also presents CVD-related cracks nucleated during cooling from deposition temperature. Density and magnitude of this pre-existing cracking scenario would be directly dependent on effective tensile residual stresses induced within coatings as a result of the dissimilar CTE between the substrate and the deposited multilayers. From this viewpoint, cross-section inspection of non-tested “as-deposited” specimens (Fig. 8) indicates that it might be less developed for coated specimens involving an intermediate Zr(C,N) layer. This statement is based on the observation that cracks nucleated at the alumina surface

film either do not develop into the intermediate Zr(C,N) layer or get blunted when crossing it. This is clearly not the case for Ti(C,N)-m sample. Hence, relative differences between CTEs of intermediate CN layers and the substrate, which is lower for Zr(C,N), may significantly reduce tensile stresses that drive cracks to propagate down throughout the multilayer assemblage. As a consequence, mechanical integrity gets preserved for coatings including Zr(C,N) as intermediate layer. This experimental fact could then be recalled for explaining, at least partly, the different performance evaluated for industrial milling inserts as a function of the chemical nature of the used intermediate carbonitride layer.

Fig. 8 FIB cross section displaying propagation (or not) of pre-existing cracks at the Al_2O_3 top layer (induced during cooling after CVD) into intermediate CN ones for a. Ti(C,N)-m and b. Zr(C,N)-m specimens. The referred cracks appear to be stopped at the intermediate layer for Zr(C,N)-m specimen. Dashed arrow shows direction of propagation.

5. Conclusions

Damage induced by spherical indentation on single- and multilayered coated

cemented carbides has been studied. The more complex multilayer systems included an intermediate wear resistant carbonitride layer, similar to the ones tested here in single-layer coated specimens. The main variable under consideration is the chemical nature of the referred CN layer: Ti(C,N) or Zr(C,N). Film cracking under contact loading is governed by load transfer from the plastically deformed substrate into the coating, together with the effective fracture strength of the latter. Within this study, contact damage is assessed to depend upon the compromising balance between surface integrity (resulting from CVD process) and residual stress state, both of them linked to relative differences in CTE between coating and substrate. In this regard, in contrast to Zr(C,N)-s, Ti(C,N)-s is observed to develop a peculiar cooling cracks network fragmenting the carbonitride layer into small islands, hence damaging its structural integrity. Additionally, despite the different length scale, these contact damage tests are in a complete agreement with previous micromechanical tests in terms of crack propagation path which is intergranular for Ti(C,N)-s and mainly transgranular for Zr(C,N)-s. Such higher mechanical integrity together with higher cohesive strength at the grain boundaries may be recalled for rationalizing the enhanced performance reported for industrial milling cutting inserts containing an intermediate Zr(C,N) layer.

Acknowledgment

Dr. Jeanette Persson (AB Sandvik Coromant R&D) is acknowledged for producing the coating system layers. Dr. Fernando García Marro (CIEFMA/UPC, Barcelona), Kim Albo Selma (UPC, Barcelona) and Dr. Trifon Todorov (UPC, Barcelona) are deeply acknowledged for their assistance during contact damage testing. Dr. Christoph Pauly (Saarland university) is nicely thanked for the discussion. Ing. Mohamed Gharafi (formerly Cadi Ayyad

university, Marrakesh) is thanked for finite element modeling attempts. The European Commission is acknowledged for funding through the projects: Erasmus Mundus Doctoral Programme DocMASE, RISE Project CREATE-Network (No 644013) and EFRE project AME-Lab (European Regional Development Fund C/4-EFRE-13/2009/Br). AB Sandvik Coromant is acknowledged for the partial financial support of the PhD thesis (Idriss El Azhari). German Academic Exchange Service (DAAD) and “GradUS global” program are thanked for the financial support to participate in the ICSHM11 conference.

References

- [1] K.-D. Bouzakis, N. Michailidis, G. Skordaris, E. Bouzakis, D. Biermann, R. M'Saoubi, Cutting with coated tools: Coating technologies, characterization methods and performance optimization, *CIRP Ann.* 61 (2012) 703–723. doi:10.1016/j.cirp.2012.05.006.
- [2] J. García, V. Collado Ciprés, A. Blomqvist, B. Kaplan, Cemented carbide microstructures: a review, *Int. J. Refract. Met. Hard Mater.* 80 (2019) 40–68. doi:10.1016/j.ijrmhm.2018.12.004.
- [3] L. Toth, *Transition Metal Carbides and Nitrides*, 1st ed., Academic Press, 1971.
- [4] W. Lengauer, *Transition Metal Carbides, Nitrides, and Carbonitrides*, in: R. Riedel (Ed.), *Handb. Ceram. Hard Mater.*, Wiley-VCH Verlag GmbH, Weinheim, Germany, 2000: pp. 202–252. doi:10.1002/9783527618217.ch7.
- [5] A.T. Santhanam, Application of transition metal carbides and nitrides in industrial tools, in: S.T. Oyama (Ed.), *Chem. Transit. Met. Carbides Nitrides*, Springer Netherlands, Dordrecht, 1996: pp. 28–52. doi:10.1007/978-94-009-1565-7_2.
- [6] S. Söderberg, M. Sjöstrand, B. Ljungberg, Advances in coating technology for metal cutting tools, *Met. Powder Rep.* 56 (2001) 24–30. doi:10.1016/S0026-0657(01)80174-0.
- [7] K. Bobzin, High-performance coatings for cutting tools, *CIRP J. Manuf. Sci. Technol.* 18 (2017) 1–9. doi:10.1016/j.cirpj.2016.11.004.
- [8] J. García, M.F. Moreno, J. Östby, J. Persson, H.C. Pinto, Design of coated cemented carbides with improved comb crack resistance, in: *Proc. 19th Plansee Semin.*, Reutte, Austria, 2017.
- [9] I. El Azhari, J. Garcia, M. Zamanzade, F. Soldera, C. Pauly, L. Llanes, F. Mücklich,

- Investigations on micro-mechanical properties of polycrystalline Ti(C,N) and Zr(C,N) coatings, *Acta Mater.* 149 (2018) 364–376. doi:10.1016/j.actamat.2018.02.053.
- [10] I. El Azhari, J. Barrirero, J. García, F. Soldera, L. Llanes, F. Mücklich, Atom Probe Tomography investigations on grain boundary segregation in polycrystalline Ti(C,N) and Zr(C,N) CVD coatings, *Scr. Mater.* 162 (2019) 335–340. doi:10.1016/j.scriptamat.2018.11.041.
- [11] E. Silva, M. Rebelo de Figueiredo, R. Franz, R. Escobar Galindo, C. Palacio, A. Espinosa, S. Calderon V., C. Mitterer, S. Carvalho, Structure–property relations in ZrCN coatings for tribological applications, *Surf. Coat. Technol.* 205 (2010) 2134–2141. doi:10.1016/j.surfcoat.2010.08.126.
- [12] J. Kim, Y.J. Suh, Temperature- and pressure-dependent elastic properties, thermal expansion ratios, and minimum thermal conductivities of ZrC, ZrN, and Zr(C_{0.5}N_{0.5}), *Ceram. Int.* 43 (2017) 12968–12974. doi:10.1016/j.ceramint.2017.06.195.
- [13] B.R. Lawn, Indentation of Ceramics with Spheres: A Century after Hertz, *J. Am. Ceram. Soc.* 81 (1998) 1977–1994. doi:10.1111/j.1151-2916.1998.tb02580.x.
- [14] A. Góez, D. Coureaux, A. Ingebrand, B. Reig, E. Tarrés, A. Mestra, A. Mateo, E. Jiménez-Piqué, L. Llanes, Contact damage and residual strength in hardmetals, *Int. J. Refract. Met. Hard Mater.* 30 (2012) 121–127. doi:10.1016/j.ijrmhm.2011.07.013.
- [15] F. García-Marro, A. Mestra, V. Kanyanta, K. Maweja, S. Ozbayraktar, L. Llanes, Contact damage and residual strength in polycrystalline diamond (PCD), *Diam. Relat. Mater.* 65 (2016) 131–136. doi:10.1016/j.diamond.2016.03.004.
- [16] E. Tarrés, G. Ramírez, Y. Gaillard, E. Jiménez-Piqué, L. Llanes, Contact fatigue behavior of PVD-coated hardmetals, *Int. J. Refract. Met. Hard Mater.* 27 (2009) 323–331. doi:10.1016/j.ijrmhm.2008.05.003.
- [17] G. Ramírez, A. Mestra, B. Casas, I. Valls, R. Martínez, R. Bueno, A. Góez, A. Mateo, L. Llanes, Influence of substrate microstructure on the contact fatigue strength of coated cold-work tool steels, *Surf. Coat. Technol.* 206 (2012) 3069–3081. doi:10.1016/j.surfcoat.2011.12.012.
- [18] J.J. Roa, E. Jiménez-Piqué, R. Martínez, G. Ramírez, J.M. Tarragó, R. Rodríguez, L. Llanes, Contact damage and fracture micromechanisms of multilayered TiN/CrN coatings at micro- and nano-length scales, *Thin Solid Films.* 571 (2014) 308–315. doi:10.1016/j.tsf.2014.04.018.
- [19] J. Yang, F. García Marro, T. Trifonov, M. Odén, M.P. Johansson-Jõesaar, L. Llanes, Contact damage resistance of TiN-coated hardmetals: Beneficial effects associated with substrate grinding, *Surf. Coat. Technol.* 275 (2015) 133–141. doi:10.1016/j.surfcoat.2015.05.028.
- [20] G. Ramírez, E. Jiménez-Piqué, A. Mestra, M. Vilaseca, D. Casellas, L. Llanes, A comparative study of the contact fatigue behavior and associated damage micromechanisms of TiN- and WC:H-coated cold-work tool steel, *Tribol. Int.* 88 (2015) 263–270. doi:10.1016/j.triboint.2015.03.036.
- [21] Ch. Genzel, I.A. Denks, J. Gibmeier, M. Klaus, G. Wagener, The materials science synchrotron beamline EDDI for energy-dispersive diffraction analysis, *Nucl.*

- Instrum. Methods Phys. Res. Sect. Accel. Spectrometers Detect. Assoc. Equip. 578 (2007) 23–33. doi:10.1016/j.nima.2007.05.209.
- [22] J.S. Wang, Y. Sugimura, A.G. Evans, W.K. Tredway, The mechanical performance of DLC films on steel substrates, *Thin Solid Films*. 325 (1998) 163–174. doi:10.1016/S0040-6090(98)00418-0.
- [23] A. Abdul-Baqi, E. Van der Giessen, Numerical analysis of indentation-induced cracking of brittle coatings on ductile substrates, *Int. J. Solids Struct.* 39 (2002) 1427–1442. doi:10.1016/S0020-7683(01)00280-3.
- [24] M. Kot, W. Rakowski, J.M. Lackner, Ł. Major, Analysis of spherical indentations of coating-substrate systems: Experiments and finite element modeling, *Mater. Des.* 43 (2013) 99–111. doi:10.1016/j.matdes.2012.06.040.
- [25] C.J. Studman, J.E. Field, The indentation of hard metals: the role of residual stresses, *J. Mater. Sci.* 12 (1977) 215–218. doi:10.1007/BF00566260.
- [26] F.B. Abudaia, J.T. Evans, B.A. Shaw, Spherical indentation fatigue cracking, *Mater. Sci. Eng. A*. 391 (2005) 181–187. doi:10.1016/j.msea.2004.08.068.
- [27] Q. Yang, W. Lengauer, T. Koch, M. Scheerer, I. Smid, Hardness and elastic properties of Ti (C x N 1- x), Zr (C x N 1- x) and Hf (C x N 1- x), *J. Alloys Compd.* 309 (2000) L5–L9. doi:10.1016/S0925-8388(00)01057-4.
- [28] H. Chien, C. Diaz-Jimenez, G.S. Rohrer, Z. Ban, P. Prichard, Y. Liu, The influence of residual thermal stresses on the mechanical properties of multilayer α -Al₂O₃/TiC_xN_{1-x} coatings on WC/Co cutting tools, *Surf. Coat. Technol.* 215 (2013) 119–126. doi:10.1016/j.surfcoat.2012.07.088.
- [29] C. Bjormander, CVD deposition and characterization of coloured Al₂O₃/ZrO₂ multilayers, *Surf. Coat. Technol.* 201 (2006) 4032–4036. doi:10.1016/j.surfcoat.2006.08.035.
- [30] J. García, H. Pinto, E. Ramos-Moore, C. Espinoza, J. Östby, R. Coelho, In-situ high temperature stress analysis of Ti(C,N) coatings on functionally graded cemented carbides by energy dispersive synchrotron X-ray diffraction, *Int. J. Refract. Met. Hard Mater.* 56 (2016) 27–34. doi:10.1016/j.ijrmhm.2015.12.001.
- [31] C. Gao, Z. Zhao, X. Li, Modeling of thermal stresses in elastic multilayer coating systems, *J. Appl. Phys.* 117 (2015) 055305. doi:10.1063/1.4907572.
- [32] M. Gassner, N. Schalk, M. Tkadletz, C. Czettel, C. Mitterer, Thermal crack network on CVD TiCN/ α -Al₂O₃ coated cemented carbide cutting tools, *Int. J. Refract. Met. Hard Mater.* 81 (2019) 1–6. doi:10.1016/j.ijrmhm.2019.02.006.
- [33] M. Birkholz, C. Genzel, Residual Stress Analysis, in: *Thin Film Anal. X-Ray Scatt.*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, FRG, 2006: pp. 239–295. doi:10.1002/3527607595.ch6.
- [34] K. Aigner, W. Lengauer, D. Rafaja, P. Ettmayer, Lattice parameters and thermal expansion of Ti(C_xN_{1-x}), Zr(C_xN_{1-x}), Hf(C_xN_{1-x}) and TiN_{1-x} from 298 to 1473 K as investigated by high-temperature X-ray diffraction, *J. Alloys Compd.* 215 (1994) 121–126. doi:10.1016/0925-8388(94)90828-1.

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Highlights:

- Zr(C,N) coated systems are found to exhibit a higher mechanical integrity than Ti(C,N).
- Higher residual stresses are relaxed through extensive cracking for Ti(C,N).
- Crack propagation path is intergranular for Ti(C,N) and mainly transgranular for Zr(C,N).
- Latter result is in agreement with previous experiments performed at the micro-scale.