Atom Probe Tomography investigations on grain boundary segregation in polycrystalline Ti(C,N) and Zr(C,N) CVD coatings.

Idriss El Azhari ^{a,b,c*}, Jenifer Barrirero ^{a,c}, José García ^d, Flavio Soldera ^{a,c}, Luis Llanes ^b, Frank Mücklich ^{a,c}

- ^a Functional Materials, Department of Materials Science and Engineering, Saarland University, Campus D 3.3, D-66123 Saarbrücken, Germany
- ^b Materials Science and Metallurgical Department (CIEFMA), Barcelona East School of Engineering (EEBE), Universitat Politècnica de Catalunya, 08019, Barcelona, Spain
- ^c Material Engineering Center Saarland (MECS), D-66125 Saarbrücken
- ^d Sandvik Coromant R&D, SE-126 80, Stockholm, Sweden

Abstract:

Atom Probe Tomography (APT) was used to obtain a direct evidence of Chlorine segregation and Cobalt diffusion at the grain boundaries (GBs) of polycrystalline coatings deposited by moderate temperature chemical vapor deposition (MT-CVD) on a WC-Co cemented carbide substrate. Reasons behind segregations are discussed, and its effects are correlated to the micromechanical properties of Ti(C,N) and Zr(C,N). It is concluded that chlorine segregation is a relevant factor for explaining the low cohesive strength at the GBs of Ti(C,N) leading to intergranular failure during micro-compression testing, while its absence in Zr(C,N) along with Co diffusion contribute to grain boundary strengthening.

Keywords

CVD polycrystalline coatings, Atom Probe Tomography, Grain boundary segregation, Chlorine, Cobalt

Characterization of microstructure in terms of orientation, texture and interfaces is fundamental for understanding the physical properties and behavior of polycrystalline materials. Interfaces or grain boundaries (GBs) play a decisive role in controlling the overall mechanical properties of fine-grained materials [1]. Classical example is the empirical Hall-Petch law, which predicts the evolution of hardness as a function of grain size. Nowadays, concepts like GB engineering and even GB segregation engineering are emerging due to the observations that solutes or impurities tune greatly the structure, phase state and atomic bonding [2]. Regarding mechanical properties, segregation at the interfaces might reduce or enhance cohesion and bonding strength at GBs [2]. Within this context, the present study is a sequel to a recently published work [3], in which micromechanical properties of MT-CVD Ti(C,N) and Zr(C,N) coatings were studied by means of micropillar compression. A relevant finding of such work was that the brittle behavior of Ti(C,N) is dominated by low cohesive strength along the grain boundaries and pure columnar crack propagation, while Zr(C,N) coatings attested of a better cohesive strength and inter/transgranular failure. One plausible cause for such distinct behavior could be segregation of impurities at interfaces. For low temperature CVD processes, chlorine contamination is a concern [4–21], which stems from the widely used metal chloride as a precursor in CVD reactions (e.g. TiCl_4 is the most widely used inorganic precursor employed in the CVD of titanium-containing materials (TiN, TiC, TiO_2 , Ti(C,N)) [22]). However, most authors have reported that chlorine is incorporated into the lattice [4,5,7,9–11,13,19,23], rather than to interfaces and no direct evidence has been

provided. Therefore, APT is performed on Ti(C,N) and Zr(C,N) coatings to explore if segregation is occurring at GBs and discuss which effect this segregation could have on the mechanical properties of these coatings.

Ti(C_{0.5},N_{0.5}) and Zr(C_{0.5},N_{0.5}) were deposited by MT-CVD process on a WC-6wt%Co substrate at a constant temperature of 885 and 930 °C, respectively, in a hot wall reactor using TiCl₄, CH₃CN and H₂ as gas precursors. The thickness of the coating was 5±0.2 µm. A TiN starting interlayer of 0.3±0.02 µm was previously deposited to promote the nucleation of the carbonitride coating and to improve adhesion to the substrate. Prior to the preparation of APT samples, an embedded cross-section of the deposited coatings was mirror polished with 0.02 µm alumina suspension as the final step. Afterwards, APT sample preparation was conducted in a dual-beam focused ion beam / scanning electron microscopy workstation (FIB / SEM) Helios NanoLab 600™ (FEI). Specimens were extracted from a cross section view at the middle distance between the substrate and the top surface of the coating by the lift-out technique described in [24]. An electron beam induced Pt-capping layer was first deposited to protect the sample from gallium (Ga) implantation. After the lift-out and thinning of the samples, a low energy milling at 2 kV was performed to minimize Ga induced damage. Between 6 to 8 specimens were prepared and measured from each lift-out. Laser Pulsed APT was performed in a LEAP™ 3000XR (CAMECA) at a repetition rate of 200 kHz, a specimen temperature of about 60 K, a pressure lower than 1 x 10⁻¹⁰ Torr (1.33 x 10⁻⁸ Pa) and a laser pulse energy of 0.5 nJ. The evaporation rate of the specimen was 5 atoms per 1000 pulses. Datasets were reconstructed and analysed with the IVAS™3.6.14 software (CAMECA) based on the voltage curves. The evaporation field was estimated to be 40 V/nm for the Ti(C,N) specimens and 45 V/nm for Zr(C,N). This estimation was done with the help of the Kingham curves for Ti and Zr [25]. All specimens were reconstructed with an image compression factor of 1.65 and a k-factor of 3.3 [26].

In total, five APT datasets of the Ti(C,N) coating and four datasets of the Zr(C,N) coating were analysed. Two datasets for each coating presented GBs, while the rest of the reconstructions showed homogeneous in-grain composition. All compositions presented in Table 1 were obtained after elemental decomposition analysis and background subtraction in IVAS software. Due to the high amount of molecular ions and multiple events during detection of carbides, the C content in the Ti(C,N) coating was corrected using two methods introduced in literature: ^{13}C -method [27] and 24Da peak correction [28]. For the Zr(C,N) coating, no loss at the ^{12}C peak was observed and no correction at the 24Da peak was necessary. Table 1 presents a weighted average of the in-grain composition of five APT specimens of Ti(C,N) and three specimens of Zr(C,N). The in-grain composition was calculated using the whole dataset for APT specimens with no GBs and in cubic regions of interest in specimens with GBs. The average compositions in the Co-rich and Cl-rich boundaries (Table 1) were measured inside 1 at.% Co and 1 at.% Cl iso-concentration surfaces for all specimens with GBs. The open source software Blender 2.76 with the open access plug-in AtomBlend were used for the images presented in this work.

Fig. 1 shows an APT reconstruction inside a Ti(C,N) grain of the polycrystalline CVD coatings. The dataset shows a homogenous distribution of Ti, C and N; thus, an absence of clustering between TiC and TiN compounds. This demonstrates the complete miscibility between the three elements in the lattice. Such result is consistent with first principles calculation of the formation energy of $\text{Ti}(\text{C}_x\text{N}_{1-x})$ [29]. In addition, impurities like oxygen O, chlorine Cl and cobalt Co are present at very low concentration (<200 ppm especially for Cl and Co, further details are in Table 1). However, in Fig. 2 it is evidenced that segregation of Co and Cl takes place at the GBs in the polycrystalline Ti(C,N). Co and Cl show interlocked and demixed regions with an average concentration of around 2.2 at.% for each element (Table 1). Different perspectives of this co-segregation and demixing are presented in Fig. 2 (b). Two concentration profiles crossing Co and Cl rich regions were calculated in cylindrical regions of interest and are presented in Fig. 2 (c) and (d), respectively. The sampling of the

concentration profiles was adjusted to minimize statistical error using a fixed number of counts per sampling block.

Similar to Ti(C,N), a homogeneous distribution of Zr, C and N was confirmed inside the grains of the Zr(C,N) coating. This is also in accordance with the first principle calculations of formation energy for Zr(C_xN_{1-x}) [30]. Moreover, along with Ti, impurities of Cl and Co are detected with very low concentration.

The APT reconstruction of Zr(C,N) with GBs in Fig. 3 shows , in contrast to Ti(C,N), segregation of homogeneously distributed Co without Cl. Different perspectives of this homogeneous Co segregation are shown in Fig. 3 (b), and concentration profiles crossing selected regions are displayed in Fig. 3 (c) and (d). Table 1 summarizes the weighted average concentration in the grains and at the boundary for the analyzed specimens. The concentrations are consistent with the predicted Tm_{0.5}(C_{0.25}N_{0.25}) (Tm: Ti/Zr) that results from the use of acetonitrile (CH₃CN) as a CVD precursor and delivers constant C/N ratio [31]. The deviation of N content with respect to the expected stoichiometry can be related to the deposition conditions, presence of vacancies, as well as possible local compositional variations between the individual grains. Furthermore, a slight underestimation of N of 1-2 at.% cannot be excluded when using APT due to the high amount of multiple events during detection [32]. Existence of Ti impurities in Zr(C,N) can come either from the residual TiCl₄ (or sub-chloride) during prior TiN deposition or from dissolved Ti in the diffused Co. The latter assumption is discarded by considering that solubility of TiN in cobalt is very limited [33] and by the comparison of Ti compositions in the bulk and at the interfaces of Zr(C,N) (Table 1).

Chlorine contamination related to CVD processes, using metal chloride precursors, is well known and documented for Low Temperature (LT) CVD processes; like Plasma Assisted (PA) [4–13,23,34] and Low Pressure (LP) CVD [12,14–21]. However, its effects on MT-CVD process are underestimated or overlooked, given that chlorine content decreases considerably with higher temperatures and at MT-CVD temperature deposition range (700~950°C) the Cl concentration is very low. As an example, it was reported for TiN

deposited by LP-CVD that the chlorine content is decreasing from 7.2% at the deposition temperature of 450 °C down to 0.15% at 850 °C [20]. In this investigation, comparison between the Ti(C,N) and Zr(C,N) is key in understanding the segregation of chlorine and its resulting effect. This is possible since both coatings have similar B1 lattice structure and comparable physical properties [35,36], and share the same simplified CVD reaction deposition [37,38]:

where T_m is the transition metal Ti or Zr.

For Ti(C,N) PA-CVD, Kim et al. has shown that the chlorine content decreased largely with an increase of the temperature [6], and generally there is a consensus that the main parameter controlling the chlorine contamination in LT-CVD processes using metal chloride is the temperature [5,6,10,13–17,20,21,23,34]. Some authors even controlled the chlorine contamination by changing only the temperature, while keeping the other parameters constant [13,23,34]. This might be not only related to the effect of the thermal decomposition of the metal chloride, but also to the crucial role of the reductant H_2 (equation (1)) or hydrogen source in general. On the one hand, it was stated that without H_2 gas in the CVD chamber, the deposition in PA-CVD processes is not possible [4], and the thermal decomposition of the $TiCl_4$ to titanium subchlorides ($TiCl_3$, $TiCl_2$ and $TiCl$) is poor even at high temperatures (e.g. at ~1700 °C, decomposition of $TiCl_4$ does not exceed 10%) [22]. On the other hand, post-annealing treatment with hydrogen source (H_2 or NH_3) was proposed as a solution to reduce the chlorine contamination for TiN coating [19,18,17]. With the increase of temperature, HCl production is kinetically promoted as the reaction rate follows Arrhenius behavior [22]. As a result, active chlorine (which can be reabsorbed on interfaces of the growing film) is more desorbed and converted to highly stable HCl [22] which is the most stable form of chlorine [8]. Subsequently, the residual chlorine is cleaned from the system by improving formation of the stable HCl gas that will be evacuated afterwards.

1 In this study, deposition of Zr(C,N) is conducted at 45°C higher than Ti(C,N) since ZrCl₄ is
2 more stable than TiCl₄ and requires higher activation energy to reach similar deposition rate
3 as for the Ti(C,N). Therefore, it is suggested that the absence of chlorine segregation in the
4 Zr(C,N) and its lower concentration inside the grain is due to higher temperature deposition,
5 along with the lower metal chloride partial pressure [6], which is in this study two times lower
6 for Zr(C,N) compared to Ti(C,N). All APT specimens obtained for this study showed
7 consistent results with no Cl segregation at the GB of Zr(C,N). Despite the small number of
8 analyzed GBs, it is considered that they are representative of the polycrystalline coating,
9 since under the used parameters, the CVD deposition is uniform [39]. Therefore, the
10 reactions (during deposition) and diffusion (during cooling step) that could lead to Cl
11 segregation are considered rather homogeneous. Besides, the Zr(C,N) APT specimens show
12 multiple triple junctions (Fig. 3). Triple junctions are high energy boundaries with a high
13 number of vacancies and high diffusivity which would be the most energetically favorable
14 sites for segregation to occur [40]. The absence of Cl segregation at these triple junctions is
15 a strong evidence of the general absence of Cl at GBs in this coating.

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34 Determining the chemical state or form of segregated chlorine at the GBs based on
35 the APT is not a trivial question and beyond the capabilities of the technique. For TiN
36 deposited through PA-CVD, it was proposed that the Cl is incorporated into the lattice
37 structure forming a solid solution with Ti and N [4,5,7,9–11,13,19,23]. Stoiber et al. added
38 that when chlorine exceeds the limit of solubility in the TiN lattice (3.2 at.%), it segregates
39 afterwards at the GBs [23]; whereas Buiting et al. suggested that for LP-CVD TiN, chlorine is
40 preferentially segregated at the GBs [15,16]. These conclusions were based on general
41 correlations, e.g. the expansion of the lattice parameter with higher chlorine, decrease of N
42 content with higher Cl contamination, relaxation of residual stresses, evolution of chlorine
43 profiles content with change in grain size. However, in both cases no direct evidence was
44 provided. In this study, Table 1 shows that there is nearly no solubility of Cl in Ti(C,N) (as the
45 concentration is estimated about 200 ppm inside the grain) and the chlorine is rather
46 segregated at the GBs up to 2.2 at.%. Additionally, Ti(C,N) has a finer grain size than

Zr(C,N) [3] which is consistent with the role of chlorine in refinement of the microstructure [6,10,23]. Then, it is suggested that chlorine acts as an impurity, which is adsorbed on the crystal facets during film growth and segregates, yielding finally smaller grain sizes. Hence, chlorine can be considered as a structure forming factor during the film growth [23,41]. Additionally, concentration profile crossing chlorine rich region in Fig. 2 (d) displays a slight drop in C and N content with an increase of Ti content and the average values in Table 1 reveal that Titanium concentration is decreasing in the Co rich regions while it remains stable (or increases fractionally) in the Cl rich regions. This could be an indication that the chlorine (or active chlorine as mentioned earlier) may exist in the form of Titanium subchlorides, which was already supported by previous works [8,14,16]. Additionally, for $Ti_{1-x}Al_xN$, it was also concluded that chlorine originates mainly from incomplete dissociation of the metal chloride $AlCl_3$ [8,12,21].

Comparison of the micromechanical properties for both coating from micro-compression tests is not an easy task [3], taking into account, beside their similarities, their differences in grain size, in the transition metal phase and microstructure. Nevertheless, the property that is contrasted in this study is the specific inter-columnar cracking for Ti(C,N) which can be caused either by the reduced dislocation activation at room temperature or lower cohesive strength at the GBs [3]. The APT investigations have provided support to the previous speculations about segregation of impurities as a potential cause of the GB brittleness for Ti(C,N), as given by its specific intergranular fracture during micro-compression tests (Fig. 4). However, Co segregates also in Zr(C,N) GBs which has better cohesive strength than Ti(C,N) and shows instead of a pure intercolumnar cracking rather a mixed trans/intergranular crack propagation mode [3]. Then, what is the impact of both Cl and Co elements on the strength at the GBs?

Usually, segregation of chemical elements at GBs promotes embrittlement of the material. However, it was reported for particular cases that it can have a beneficial reverse effect of enhancing the ductility [42–45]. Accordingly, two approaches were established to

understand this **contradictory** effect of impurities, either through the analysis of the effects of segregated elements on the electronic structure at the GB [46] or with calculation of the segregation energy [47]. Both methods require first principles calculations and analysis, which is out of the scope of the present study. Nevertheless, chlorine, with its intrinsic high electronegativity, would **definitely** have a dramatic negative effect on the interfacial cohesion and electronic structure between adjacent atoms at the GBs. The role of chlorine has been highlighted in the GB embrittlement of Ni-based superalloys [48] and sintered Titanium dioxide (TiO₂) [49] which leads to intergranular fracture. For the LT-CVD titanium based coating, it is agreed on the deterioration of mechanical properties with the increase of chlorine content, i.e. decrease in hardness [5–12,23] and in adhesion to the substrate [6,8,10–12].

Diffusion of WC-Co substrate elements in the coating during CVD deposition has been already reported [50,51]. In this study, cobalt diffuses from the substrate to the coating crossing the TiN interlayer through the interfaces and segregates at GBs thereafter with concentrations of 2.77 at% and 2.25 at% for Zr(C,N) and Ti(C,N) respectively. Very low concentrations at the bulk have been resolved: 600 ppm and 300 ppm for Ti(C,N) and Zr(C,N) respectively. These results are aligned with earlier work of Akiyama et al. on a similar Ti(C,N) coating [51]. As for the absence of tungsten (W) in both coatings, it is related to the higher mobility of Co compared to W [51]. It might be expected that segregation of cobalt will have a negative effect on the mechanical properties **e**specially at higher temperatures, where these coatings are expected to perform efficiently when low melting phases form at the interface, leading to the drop of high-temperature strength [52]. Still, it was reported that diffusion and segregation of elements (at the GBs) from the WC-Co substrate during the deposition enhances the adhesion to the substrate and wear resistance [50,51]. This may indicate that Co might have a strengthening effect on the interfaces, an assumption which is proved through first principles electron-structure calculations on the interface adhesion of Co/Ti(C,N) by Dudiy et al. [53]. The author, explained the development of a strong Co-C(N) metal modified covalent bond at the interface which is even stronger than the bulk bonding

1 between Ti-C(N) [53]. Considering the close physical properties between Ti(C,N) and
2 Zr(C,N), similar effects for Zr(C,N) might be expected. Since both coatings have similar
3 amount of Co segregating at the boundaries, it can be pointed out that one relevant factor
4 contributing to the low cohesive strength and enhanced intergranular fracture of Ti(C,N), in
5 comparison to Zr(C,N), is the segregation of chlorine at the GBs. Chlorine co-segregates
6 alongside with cobalt and alters its homogeneous distribution at the boundaries (Fig. 2 (b)).

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14 Based on the combination of APT characterization and assessment of micro-
15 mechanical response, the following conclusions can be summarized:

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19 - Even at high deposition temperature of 885 °C for Ti(C,N) on a WC-Co substrate,
20 chlorine segregates at GBs along with cobalt with demixing Cl and Co rich zones.
21 Cl is suggested to stem from the Titanium subchlorides, which adsorbs and
22 segregates at the interfaces during crystal growth resulting in a finer
23 microstructure.
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31 - Zr(C,N) exhibited only Co segregation at the GBs which diffused from the
32 substrate during CVD deposition. It is proposed that Co is enhancing the GB
33 strength or at least not harmful toward it.
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41 - Absence of Cl segregation in Zr(C,N) is attributed to the higher deposition
42 temperature and lower metal chloride partial pressure.
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46 - Chlorine segregation might be one of the factors contributing to the low cohesive
47 strength at the GBs of Ti(C,N), which results in the specific intergranular fracture
48 behavior evidenced under uniaxial compression of micropillars.
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References:

- [1] H. Gleiter, Prog. Mater. Sci. 33 (1989) 223–315.
- [2] D. Raabe, M. Herbig, S. Sandlöbes, Y. Li, D. Tytko, M. Kuzmina, D. Ponge, P.-P. Choi, Curr. Opin. Solid State Mater. Sci. 18 (2014) 253–261.
- [3] I. El Azhari, J. Garcia, M. Zamanzade, F. Soldera, C. Pauly, L. Llanes, F. Mücklich, Acta Mater. 149 (2018) 364–376.
- [4] S. Li, W. Huang, H. Yang, Z. Wang, Plasma Chem. Plasma Process. 4 (1984) 147–161.
- [5] T. Arai, H. Fujita, K. Oguri, Thin Solid Films 165 (1988) 139–148.
- [6] S.B. Kim, S.K. Choi, S.S. Chun, K.H. Kim, J. Vac. Sci. Technol. Vac. Surf. Films 9 (1991) 2174–2179.
- [7] K.-T. Rie, A. Gebauer, J. Woehle, Surf. Coat. Technol. 60 (1993) 385–388.
- [8] K.H. Kim, S.H. Lee, Thin Solid Films 283 (1996) 165–170.
- [9] K.-T. Rie, A. Gebauer, J. Wöhle, Surf. Coat. Technol. 86 (1996) 498–506.
- [10] B. Arnold, I. Endler, Microchim. Acta 125 (1997) 83–87.
- [11] K. Wetzig, I. Endler, Microchim. Acta 125 (1997) 121–125.
- [12] S. Anderbouhr, V. Ghetta, E. Blanquet, C. Chabrol, F. Schuster, C. Bernard, R. Madar, Surf. Coat. Technol. 115 (1999) 103–110.
- [13] K. Kawata, H. Sugimura, O. Takai, Thin Solid Films 407 (2002) 38–44.
- [14] S.R. Kurtz, R.G. Gordon, Thin Solid Films 140 (1986) 277–290.
- [15] M.J. Buiting, A.H. Reader, MRS Online Proc. Libr. Arch. 168 (1989).
- [16] M.J. Buiting, A.F. Otterloo, A.H. Montree, J. Electrochem. Soc. 138 (1991) 500–505.
- [17] N. Yokoyama, J. Electrochem. Soc. 138 (1991) 190.
- [18] R.I. Hegde, R.W. Fiordalice, P.J. Tobin, Appl. Phys. Lett. 62 (1993) 2326–2328.

- [19] R. Leutenecker, B. Fröschle, U. Cao-Minh, P. Ramm, *Thin Solid Films* 270 (1995) 621–626.
- [20] N. Ramanuja, R.A. Levy, S.N. Dharmadhikari, E. Ramos, C.W. Pearce, S.C. Menasian, P.C. Schamberger, C.C. Collins, *Mater. Lett.* 57 (2002) 261–269.
- [21] J. Wagner, V. Edlmayr, M. Penoy, C. Michotte, C. Mitterer, M. Kathrein, *Int. J. Refract. Met. Hard Mater.* 26 (2008) 563–568.
- [22] F. Teyssandier, *J. Electrochem. Soc.* 145 (1998) 2167.
- [23] M. Stoiber, E. Badisch, C. Lugmair, C. Mitterer, *Surf. Coat. Technol.* 163–164 (2002) 451–456.
- [24] K. Thompson, D. Lawrence, D.J. Larson, J.D. Olson, T.F. Kelly, B. Gorman, *Ultramicroscopy* 107 (2007) 131–139.
- [25] D.R. Kingham, *Surf. Sci.* 116 (1982) 273–301.
- [26] P. Bas, A. Bostel, B. Deconihout, D. Blavette, *Appl. Surf. Sci.* 87–88 (1995) 298–304.
- [27] M. Thuvander, J. Weidow, J. Angseryd, L.K.L. Falk, F. Liu, M. Sonestedt, K. Stiller, H.-O. Andrén, *Ultramicroscopy* 111 (2011) 604–608.
- [28] J. Angseryd, F. Liu, H.-O. Andrén, S.S.A. Gerstl, M. Thuvander, *Ultramicroscopy* 111 (2011) 609–614.
- [29] V.I. Ivashchenko, P.E.A. Turchi, L.A. Ivashchenko, P.L. Skrynskii, *Metall. Mater. Trans. A* 37 (2006) 3391–3396.
- [30] V.I. Ivashchenko, P.E.A. Turchi, V.I. Shevchenko, *J. Phys. Condens. Matter* 21 (2009) 395503.
- [31] Z.-J. Liu, P. Leicht, Y.-X. Liu, Z.-K. Liu, *Surf. Coat. Technol.* 201 (2006) 2818–2821.
- [32] I. Povstugar, P.-P. Choi, D. Tytko, J.-P. Ahn, D. Raabe, *Acta Mater.* 61 (2013) 7534–7542.
- [33] P. Ettmayer, H. Kolaska, W. Lengauer, K. Dreyer, *Int. J. Refract. Met. Hard Mater.* 13 (1995) 343–351.
- [34] E. Badisch, C. Mitterer, P.H. Mayrhofer, G. Mori, R.J. Bakker, J. Brenner, H. Störi, *Thin Solid Films* 460 (2004) 125–132.
- [35] W. Lengauer, in: R. Riedel (Ed.), *Handb. Ceram. Hard Mater.*, Wiley-VCH Verlag GmbH, Weinheim, Germany, 2000, pp. 202–252.
- [36] Q. Yang, W. Lengauer, T. Koch, M. Scheerer, I. Smid, *J. Alloys Compd.* 309 (2000) L5–L9.
- [37] H.O. Pierson, in: *Handb. Chem. Vap. Depos. CVD*, 2nd ed., Park Ridge: Noyes Publications, USA, 1999, pp. 231–259.

- [38] S. Kudapa, K. Narasimhan, P. Boppana, W.C. Russell, *Surf. Coat. Technol.* 120 (1999) 259–264.
- [39] C. Mitterer, in: V.K. Sarin, L. Llanes, D. Mari (Eds.), *Compr. Hard Mater. - Vol. 2 Ceram.*, Elsevier, Amsterdam, 2014, pp. 449–468.
- [40] P. Stender, Z. Balogh, G. Schmitz, *Phys. Rev. B* 83 (2011).
- [41] P.. Barna, M. Adamik, *Thin Solid Films* 317 (1998) 27–33.
- [42] K. Aoki, O. Izumi, *J. Jpn. Inst. Met.* 43 (1979) 1190–1196.
- [43] C.L. White, R.E. Clausing, L. Heatherly, *Metall. Trans. A* 10 (1979) 683–691.
- [44] C.. Liu, C.. White, J.. Horton, *Acta Metall.* 33 (1985) 213–229.
- [45] T. Takasugi, O. Izumi, N. Masahashi, *Acta Metall.* 33 (1985) 1259–1269.
- [46] M.E. Eberhart, D.D. Vvedensky, *Phys. Rev. Lett.* 58 (1987) 61.
- [47] J.R. Rice, J.-S. Wang, *Mater. Sci. Eng. A* 107 (1989) 23–40.
- [48] D.A. Woodford, R.H. Bricknell, *Scr. Metall.* 17 (1983) 1341–1344.
- [49] R. Dittmann, E. Wintermantel, T. Graule, *J. Eur. Ceram. Soc.* 33 (2013) 3257–3264.
- [50] S. Takatsu, K. Shibuki, *Thin Solid Films* 127 (1985) 283–292.
- [51] K. Akiyama, E. Nakamura, I. Suzuki, T. Oshika, A. Nishiyama, Y. Sawada, *Surf. Coat. Technol.* 94 (1997) 328–332.
- [52] A.P. Katz, H.A. Lipsitt, T. Mah, M.G. Mendiratta, *J. Mater. Sci.* 18 (1983) 1983–1992.
- [53] S.V. Dudiy, B.I. Lundqvist, *Phys. Rev. B* 64 (2001).

Table 1: Atomic percentage for different areas in Ti(C,N) and Zr(C,N).

	Compostion at. %	Ti	Zr	C	N	Co	O	Cl
Ti(C,N)	In the grain	51.55 ± 0.06	-	26.22 ± 0.05	22.00 ± 0.04	0.06 ± 0.01	0.16 ± 0.01	0.02 ± 0.01
	Co rich region at the boundary	48.59 ± 0.15	-	27.12 ± 0.13	21.40 ± 0.18	2.25 ± 0.06	0.16 ± 0.01	0.49 ± 0.03
	Cl rich region at the boundary	51.66 ± 0.43	-	24.46 ± 0.24	20.96 ± 0.20	0.39 ± 0.06	0.24 ± 0.01	2.28 ± 0.11
Zr(C,N)	In the grain	0.11 ± 0.01	49.74 ± 0.06	28.51 ± 0.04	21.60 ± 0.03	0.03 ± 0.01	-	0.01 ± 0.01
	Co rich region at the boundary	0.08 ± 0.01	49.09 ± 0.10	24.50 ± 0.06	23.55 ± 0.05	2.77 ± 0.03	-	0.01 ± 0.01

Fig. 1: Atomic maps inside a grain in Ti(C,N) coating. Homogeneous distribution of Ti, N and C.

Fig. 2: (a) Atomic map of a GB in Ti(C,N) containing Co and Cl segregation (b) Isolated Co and Cl segregations at the GB - Two 90° rotated views are presented for clarity. Sections of cylinder c and d crossing Co rich and Cl rich are shown respectively. The segregation highlights the demixing of Co and Cl. (c) Concentration profile across a Co rich region at the boundary corresponding to cylinder c. (d) Concentration profile across a Cl rich region corresponding to cylinder d. These concentration profiles are calculated in cylindrical regions of interest with a direction perpendicular to the GBs. The sampling of the concentration profiles was adjusted to minimize statistical error using a fixed number of counts per sampling block.

Fig. 3: (a) Atomic map of Co segregation at the GBs in $\text{Zr}(\text{C},\text{N})$. (b) Isolated Co segregation at the GBs in two different perspectives for clarity. (c,d) Concentration profiles across the Co segregation at the GBs according to cylindrical regions of interests indicated by the arrows in (a).

Fig. 4: Top view post compression images of (a) $\text{Ti}(\text{C},\text{N})$ and (b) $\text{Zr}(\text{C},\text{N})$ micropillars. While $\text{Zr}(\text{C},\text{N})$ shows indefinite crack propagation, $\text{Ti}(\text{C},\text{N})$ fails at the GBs showing low cohesive strength leading to intercolumnar failure. (For more details refer to [3]).