Empowering PVD for corrosion protection

TiMgGdN coatings with game-changing corrosion performance: A genuine competitor to electroplated chromium

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1 Introduction

PVD technology is currently only relevant when corrosion is of minor importance in the application. For components under complex corrosive and tribological stress, electroplating and chemical coating technologies are the state-of-the-art [1]. However, these generally have lower hardnesses and thus reduced wear resistance compared to PVD coatings. Due to the use of aggressive chemicals, electroplating and chemical coating technologies are subject to high environmental protection requirements and REACH restrictions. In addition to higher coating costs, environmental aspects are already driving the market towards the search for new and innovative coating alternatives. This is where PVD technology comes into focus.

Although PVD coating systems are considered state-of-the-art in cutting technology, their potential in many applications, such as in the areas of forming, engineering industry, energy generation and mobility, is currently not being fully exploited due to the unsatisfactory corrosion behavior of PVD-coated steels. Therefore, there is a high economic and technological interest on the part of users in the development of PVD coatings that, in addition to their superior tribological properties, also achieve simultaneous corrosion protection for unalloyed and low-alloyed quenched and tempered steels, despite their reduced coating thickness.

The unsatisfactory corrosion behavior of PVD coatings is to a large extend caused by process-related growth defects such as pinholes or macroparticles („droplets") [2]. Typical PVD hard coatings based on TiN or CrN typically exhibit a nobler behavior compared to unalloyed and low-alloyed steels and therefore accelerate galvanic corrosion due to the high anodic current density
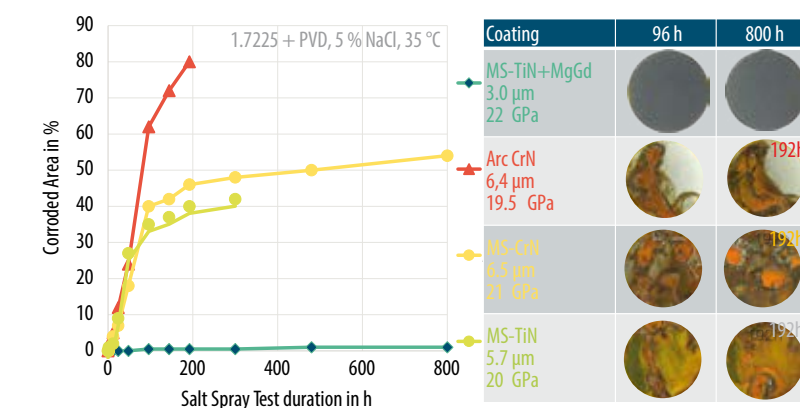
FIGURE 1: Salt spray test corrosion benchmark proves the outstanding corrosion performance of TiN+MgGd. MS: DC magnetron sputtered, Arc: Arc evaporated.

present at defects [3]. The driving force for galvanic corrosion is determined by the difference in corrosion potentials between the coating and the substrate (**Fig. 2**).

Research activities aimed at improving the corrosion protection properties of PVD hard nitride coatings have primarily focused on optimizing the coating architecture and reducing defects, such as through multilayers [2, 5]. The use of HiPIMS (High Power Impulse Magnetron Sputtering) technology results in denser coatings with good adhesion due to the high ionization and thus an improvement in corrosion properties [6]. Similar results are achieved by nanostructuring, e.g. by adding Si to increase the nucleation density and limit crystal growth [7].

Nevertheless, the improvements achieved with these strategies only allow a inhibition of the corrosion, but not effective and permanent corrosion protection.

Therefore, in applications that are subject to both tribological and corro-

SUMMARY

A novel, monolithic DC-magnetron sputtered TiN+MgGd coating, only 3 to 5 µm thick, effectively protects steel substrates from corrosion. This achievement is due to alloying of TiN with MgGd, which not only maintains the renowned wear resistance of TiN coatings, but potentially improves it through optimized deposition parameters.

The key to the enhanced corrosion resistance lies in the addition of magnesium (Mg) and gadolinium (Gd). It reduces the coating's free corrosion potential, thereby mitigating the driving force for galvanic corrosion between coating and substrate. Moreover, at specific Mg to Gd ratios, a cathodic protection effect can be observed. Crucially, the presence of Gd is essential for this performance. It imparts hydrophobicity to the coating surface, reinforces a passivating layer and significantly enhances defect tolerance.

This discovery paves the way for a sustainable alternative to electroplated chromium or combined electroplating and PVD, offering superior corrosion protection with minimal coating thickness.

sive stress, typical hard chrome coatings with a thickness of 15 µm to 30 µm are still mainly used. Health and environmental considerations as well as an increased consumer awareness are causing the industry to rethink alternative coatings to the application to chromium (VI), which is why PVD coatings are already being used successfully today, e.g. for the coating of bolts for timing chains, precision bearings, piston rings or valve train components in the engine sector [8]. However, corrosion plays no role or a subordinate role there, which severely limits the further increase in the application depth of PVD coatings.

At the Center for Structural Materials at the Technical University of Darmstadt, the binary coating system TiN was optimized in terms of corrosion properties by alloying with Mg-Gd in the projects IGF 19124N and IGF 20706N of the industrial joint research association IGF, which were supervised by the European Research Society for Thin Films e.V. (EFDS). With the developed strategy, a corrosion resistance of more than 800 h in the salt spray test was achieved for TiN+MgGd coatings [9–11].

2 Experimental

2.1 Coating deposition

The coatings were deposited using DC magnetron sputtering in an industrial coating unit (Cemecon CC800/9). Powder metallurgy targets (500 mm x 88 mm) manufactured by Plansee Composite Materials were used (**Fig. 3**). These targets exhibited a homogenous distribution of the constituent elements (Ti, Mg, and Gd). Therefore, the pristine powders, with a grain size below 45 µm, were spark plasma sintered at 500 °C at a pressure of 30 MPa. Energy-dispersive X-ray spectroscopy (EDX) confirmed the homogeneous distribution of all elements within the target. Due to limited availability, only one TiMgGd target was used. The target faced the opposite side of the substrate with a fixed machine table configuration. The Ti:MgGd ratio for the coating was determined from previous studies using multi-component targets. For comparison, TiN+Mg coatings were also deposited using a powder metallurgical TiMg target with the same Ti:Mg ratio as the TiMgGd target. The deposition parameters are summarized in table 1.

2.2 Substrate Materials

Circular steel blanks (Ø 24 mm x 7.9 mm) were machined from 100Cr6 (1.3505), 42CrMo4 (1.7225), and 16MnCr5 (1.7131) rods and then subjected to heat treatments. 100Cr6 and 42CrMo4 underwent a quenching and tempering, while the 16MnCr5 was case hardened. Grinding and polishing steps generated three surface roughness conditions: polished (Rz < 0.05 µm), fine grinded (0.2 µm < Rz < 0.5 µm) and coarse grinded (Rz > 1.5 µm).

FIGURE 2: Electrochemical series of metals: Open circuit corrosion potential of TiN and CrN in comparison to several metals (cf. [4]).

FIGURE 3: Novel powder metallurgic TiMgGd Target (top) and coating deposition (bottom).

ZUSAMMENFASSUNG

PVD für den Korrosionsschutz – TiMgGdN-Beschichtungen mit bahnbrechender Korrosionsleistung: Ein echter Konkurrent für galvanisch abgeschiedenes Chrom

Die an der TU Darmstadt entwickelte TiN+MgGd-Schicht ermöglicht einen für PVD-Schichten einzigartigen Korrosionsschutz. Die Schutzwirkung wird bereits in dem für PVD-üblichen Schichtdickenbereich zwischen 3 µm und 5 µm erzielt. Gleichzeitig wurde die für PVD-TiN bekannte Verschleißbeständigkeit aufrechterhalten, bzw. durch Anpassung der Beschichtungsparameter verbessert.

Die Legierung von Magnesium (Mg) und Gadolinium (Gd) zu TiN verringert das freie Korrosionspotential der Beschichtung und reduziert damit die Triebkraft für die galvanische Korrosion zwischen Beschichtung und Substrat an Fehlstellen. Bei einem bestimmten Verhältnis von Mg zu Gd wurde ein kathodischer Schutzeffekt beobachtet. Gd ist für die Korrosionsbeständigkeit unerlässlich, da es die Oberfläche der Beschichtung hydrophob macht, eine stabile Passivschicht bildet und die Fehlstellentoleranz deutlich erhöht.

Damit existiert erstmals ein PVD-Schichtsystem als konkurrenzfähige und nachhaltige Alternative zu galvanischen und chemischen Beschichtungen.
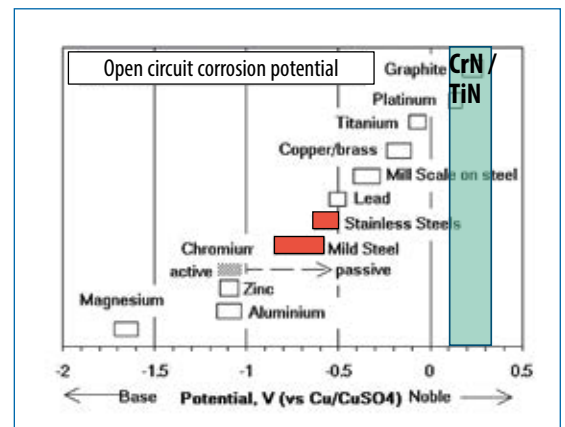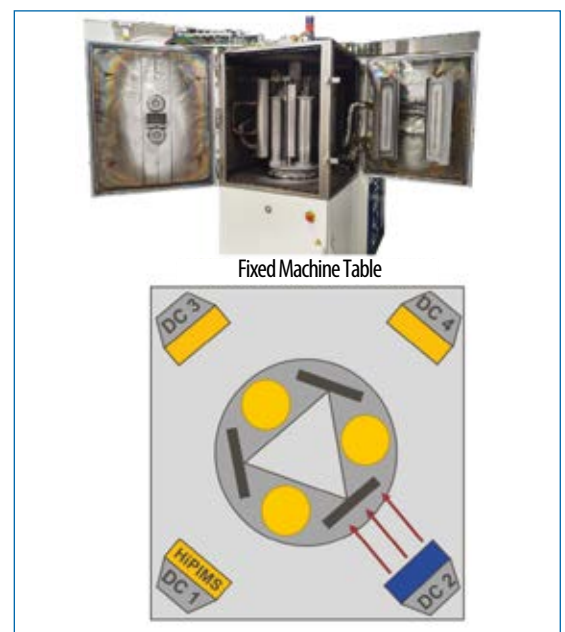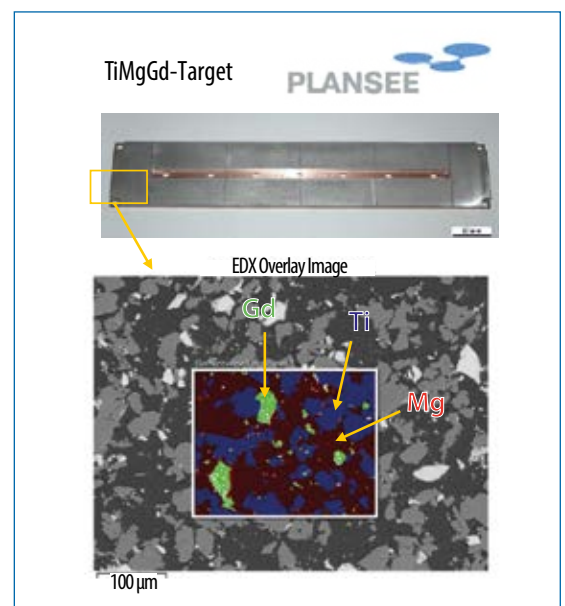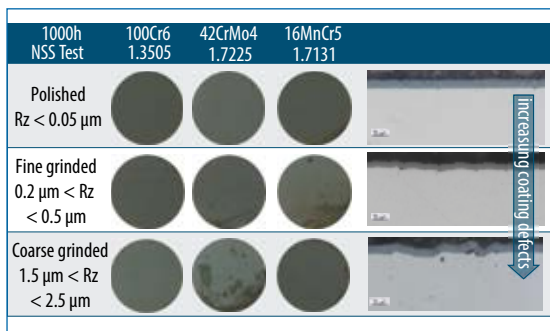
FIGURE 4: Influence of substrate material and roughness on the corrosion properties of 5µm thick TiN+MgGd coatings.
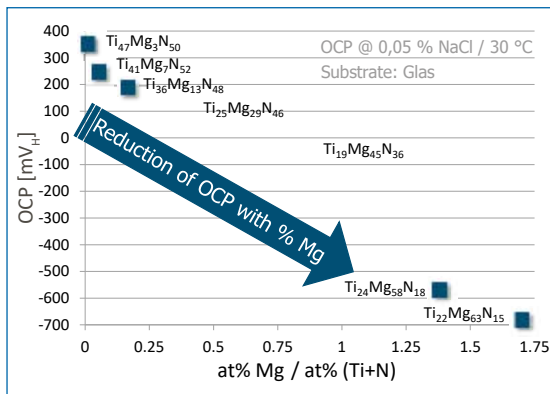

FIGURE 5: Reduction of the open circuit potential (OCP) by alloying TiN with Mg.

2.3 Corrosion Testing

The specimens were subjected to the neutral salt spray test (SST: 5 % NaCl mist, 35 °C) according to DIN EN ISO 9227 for a maximum duration of 1000 hours. Periodically, the specimens were removed, evaluated for corrosion attack using image analysis, and then returned to the chamber.

3   Results

The corrosion protection potential of TiN+MgGd coatings was demonstrated through a benchmark comparison test against DC (direct current) magnetron-sputtered TiN and CrN and arc-evaporated CrN (**Fig. 1**). As substrate material, polished 100Cr6 specimens were used. All benchmark coatings were deposited in industry-standard processes provided by partners, except for TiN+MgGd. While the benchmark coatings have thicknesses between 5.7 µm and 6.5 µm (roughly twice the thickness of the 3 µm TiN+MgGd coating), the hardness of all coatings are within a narrow range between 19.5 and 22 GPa, indicating similar wear resistance. The adhesion of the indus-

trial coatings, tested by scratch testing, was found to be significantly higher than that of TiN+MgGd due to application of industrial pre-treatment processes.

Despite their larger thickness, the benchmark PVD coatings exhibited inferior performance in the salt spray test compared to the TiN+MgGd coating. This unsatisfactory performance is attributed to galvanic corrosion between the coatings and the less noble steel substrate. **Fig. 2** illustrates the open circuit potential difference between the coating and the substrate, which creates a driving force for galvanic corrosion. Once initiated, the corrosion kinetics increase due to high anodic current densities at defect sites.

In contrast, the TiN+MgGd coating shows superior salt spray test performance, exhibiting minimal macroscopic corrosion attack even after 800 hours of exposure.

Both the coating type and the substrate's microstructure and roughness influence corrosion performance (**Fig. 4**). Polished specimens, regardless of the substrate material, showed no signs of corrosion after 1000 hours of salt spray testing. However, with increasing surface roughness, particularly the 16MnCr5 steel exhibits minor corrosion spots. Despite these minimal occurrences, the corrosion performance of all substrates with the TiN+MgGd coating remains superior to that observed with TiN and CrN coatings (**Fig. 1**).

Increased substrate roughness generally elevates the risk of coating defects, potentially allowing the electrolyte to penetrate the substrate at these locations. Additionally, the amount of impurities within the substrate material can impact its corrosion behavior. Specimens created from rod material may contain inclusions on the coated sur-

face. These inclusions further increase the risk of coating defects like pinholes. Moreover, inclusions often possess different electrochemical properties compared to the surrounding steel matrix, promoting localized galvanic corrosion at these sites. The prevalence of inclusions is directly proportional to the steel's sulfur content, as sulfur (S) and manganese (Mn) form longitudinal MnS inclusions. Accordingly, 100Cr6 exhibits the lowest amount of MnS, while 16MnCr5 has the highest.

In conclusion, the investigation of surface roughness and material purity demonstrates that a 5 µm thick TiN+MgGd coating can effectively protect even grinded surfaces from corrosion.

To explain the superior corrosion performance of the TiN+MgGd coatings, a fundamental coating analysis was performed, and two effects were derived, which are designated by the authors as the Mg- and the Gd-effect [11, 12].

3.1 Mg-Effect

Alloying TiN with Mg maintains the TiN lattice structure due to the substitution of Mg for Ti at Ti sites. While magnesium itself requires corrosion protection due to its low nobility, its addition to TiN significantly reduces the open circuit potential (OCP) of the entire coating as the Mg content increases (**Fig. 5**). The variation of the Mg content is achieved by employing multi-component targets with a flexible arrangement of Ti and Mg segments. The impact of Mg alloying on OCP is substantial: $Ti_{47}Mg_3N_{50}$ exhibits a relatively noble OCP of approximately +360 mVH (referenced to the standard hydrogen electrode), while the higher Mg content coating $Ti_{24}Mg_{58}N18$ has a significantly lower OCP of only -660 mVH. This decrease of OCP reduces the susceptibility to galvanic corrosion between the coating

MF etching	Pressure	BIAS	Anode current	Duration
	400 mPa	200 V	20 A	1 h
Deposition	**Target power**	**Booster voltage**	**BIAS voltage**	**Deposition mode**
	2 kW	90 V	-100 V	DC
	Deposition pressure	**Deposition temperature**	**N$_2$ / Ar-ratio**	**Substrate Rotation**
	400 mPa	< 200 °C	0.25	Off

TABLE 1: Typical deposition parameters for TiN+MgGd.

and the substrate. Similar observations were made during potentiodynamic tests of coated steel specimens, where the coating's OCP even fell below that of the steel, suggesting the possibility of a cathodic protection effect.

3.2 Gd-Effect

Gadolinium (Gd) plays a crucial role in enhancing the corrosion protection performance of TiN+MgGd coatings through three key mechanisms:

1. Surface hydrophobization: Gd influences surface energy, leading to hydrophobicity, hindering the penetration of corrosive media to the underlying steel even through coating defects. Contact angle measurements demonstrate a substantial increase in hydrophobicity, with TiN+Mg coatings exhibiting contact angles between 87° and 89°, compared to 110° and 117° for TiN+MgGd coatings.

2. Enhanced defect tolerance: Despite the presence of pinholes and droplets on the surface, no macroscopic corrosion is observed. Scanning electron microscopy (SEM) analysis of specimens after 1000 hours of salt spray testing reveals that corrosion products effectively seal coating defects (**Fig. 6**), significantly slowing down the corrosion kinetics. This effect is evident on both polished and grinded surfaces. However, isolated active corrosion sites are occasionally observed, as exemplary shown in **Fig. 6d** for the medium-roughness specimen. These sites are comparable in size to those „disarmed" by corrosion products. One possible explanation is the coincidence of a MnS inclusion and a coating defect, triggering localized corrosion due to the complex electrochemical interaction between coating, substrate, and inclusion.
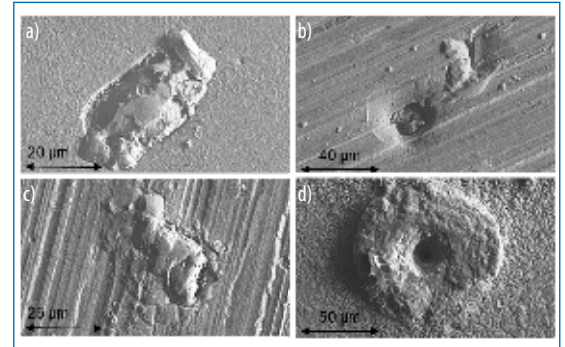
3. Formation of a stable passivation layer: X-ray photoelectron spectroscopy (XPS) analysis of TiN+MgGd and TiN+Mg before and after the 1000-hour salt spray test demonstrates the superior stability of Gd-containing coatings. Without gadolinium, the surface chemistry changes significantly after the salt spray test (**Fig. 7**). This is indicated by a decrease in Mg-Mg and Mg-N bonds, while Mg-OH increases. Additionally, a decrease in Ti-Ti bonds and an increase in Ti-O suggest oxidation of metallic Mg to Mg-OH. Furthermore, the metasta-ble Mg-N decomposes to Mg-OH at the coating surface in a corrosive environment. The chance in surface chemistry is also evident by the color change of TiN+Mg after the salt spray test.

In contrast, TiN+MgGd exhibits excellent chemical stability under salt spray conditions (**Fig. 8**). No change in binding energies or surface appearance is observed before and after the test. This outstanding behavior is attributed to the formation of gadolinium oxides. These oxides are known for their superior thermodynamic stability compared to oxides and hydroxides of Ti or Mg [13]. Consequently, they form an extremely stable passivation layer with minimal water and acid solubility.

Glow discharge optical emission spectroscopy (GD-OES) depth profile analysis confirms this observation. **Fig. 9** shows that without Gd, TiN+Mg coatings undergo chemical decomposition in a corrosive environment. The results indicate magnesium release alongside surface oxidation, likely occurring along the grain boundaries of the columnar PVD-coating microstructure.
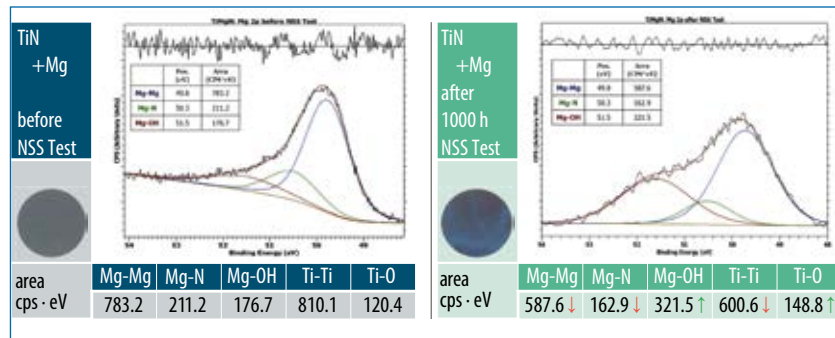
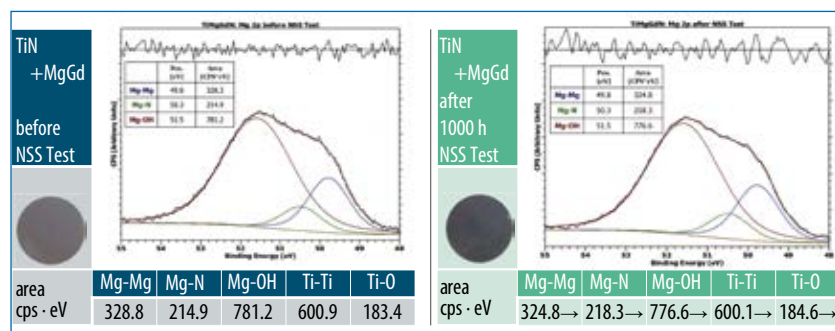Wear performance was evaluated using oscillating pin-on-disk tests conducted with an SRV 3 tribometer (**Fig. 10**). Wear resistance was defined as the maximum load the PVD coating on the 100Cr6 substrate (60 HRC) could withstand under the test parameters without experiencing coating failure.

Optimizing the deposition parameters allows tailoring the TiN+MgGd coating properties to prioritize either wear resistance (+V) or corrosion resistance (+K). Notably, achieving a balance between both properties is also possible. While optimizing for wear performance can lead to a slight decrease in corrosion resistance, even wear-optimized TiN+MgGd coatings still outperform TiN and CrN in the salt spray test, which lack any inherent corrosion protection.

FIGURE 6: SEM analysis of corrosion sites of 5.3 µm TiN+MgGd coated 1.3505 steel after 1000 h salt spray test: a) polished Rz < 0.05 µm, b) and d) grinded 0.2 µm < Rz < 0.5 µm, c) grinded 1.5 µm < Rz < 2.5 µm.

area cps · eV	Mg-Mg	Mg-N	Mg-OH	Ti-Ti	Ti-O
TiN+Mg before NSS Test	783.2	211.2	176.7	810.1	120.4
TiN+Mg after 1000 h NSS Test	587.6 ↓	162.9 ↓	321.5 ↑	600.6 ↓	148.8 ↑

FIGURE 7: XPS Analysis of the Mg 2p Peak of TiN+Mg before (left) and after (right) 1000 h salt spray test.

area cps · eV	Mg-Mg	Mg-N	Mg-OH	Ti-Ti	Ti-O
TiN+MgGd before NSS Test	328.8	214.9	781.2	600.9	183.4
TiN+MgGd after 1000 h NSS Test	324.8 →	218.3 →	776.6 →	600.1 →	184.6 →

FIGURE 8: XPS Analysis of the Mg 2p Peak of TiN+MgGd before (left) and after (right) 1000 h salt spray test prove chemical stability of the surface passivation layer .

4 Conclusion and Outlook

The research presented demonstrates a significant improvement in corrosion protection for low-alloy steels achieved by a novel MgGd alloying concept applied to binary TiN coatings. This enhancement is attributed to the synergistic effects of Mg and Gd. Magnesium addition reduces the free corrosion potential of the coating, mitigating the driving force for galvanic corrosion between the coating and substrate. Gadolinium exhibits multifaceted contributions: it promotes hydrophobicity, hindering electrolyte penetration through defects. Furthermore, Gd enhances the defect tolerance by facilitating the sealing of pinholes by corrosion products, thereby stopping further corrosion at these sites. Finally, Gd is crucial for ensuring the chemical stability of the coating under corrosive environments. This is achieved through the formation of dense and stable passivation layers rich in gadolinium oxide. The knowledge regarding the corrosion mechanisms provide a basis for the targeted corrosion optimization of other commercially available PVD coatings like CrN, ZrN, or TiAlN. This opens new avenues for market expansion and applications where the potential of functionally tailored, individualized PVD coatings remains underexploited due to prevailing corrosion limitations.
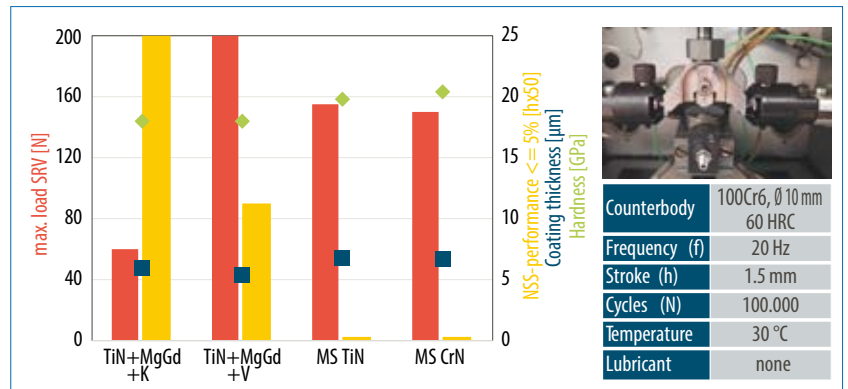
Acknowledgement

References

[1] C.H. Hsu et al.: Surface and Coatings Technology 231 (2013) 380–384.

[2] P. Panjan et al.: Coatings 9 (2019) 511.
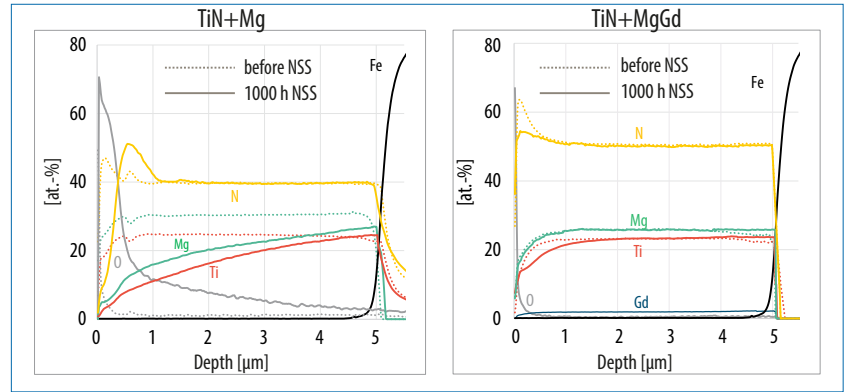
FIGURE 9: GD-OES depth profiles of TiN+Mg (left) and TiN+MgGd (right) before and after the salt spray test prove chemical stability of TiN+MgGd.

FIGURE 10: Wear performance. Substrate material 100Cr5 (13505). +K: coating optimized for corrosion, +V: coating optimized for wear performance.

[3] X. Xu et al.: Surface and Coatings Technology 411 (2021) 126997.

[4] E. Roos et al.: Korrosion. In: Werkstoffkunde für Ingenieure, Springer Vieweg (2022) p. 8.

[5] J. Creus et al.: Surface and Coatings Technology 130 (2000) 224–232.

[6] W.-D. Münz: Vakuum in Forschung und Praxis 19 (2007) 12–17.

[7] W. Tillmann, M. Dildrop: Surface and Coatings Technology 321 (2017) 448–454.

[8] Schaeffler Technologies AG & Co. KG: Technische Produktinformation TPI 186, Herzogenaurach, 2020.

[9] H. Hoche et al.: Surface and Coatings Technology 391 (2020) 125659.

[10] T. Ulrich et al.: Surface and Coatings Technology 422 (2021) 127496.

[11] T. Ulrich et al.: Surface and Coatings Technology 474 (2023) 130093.

[12] H. Hoche et al.: Surface and Coatings Technology 376 (2019) 74–83.

[13] S.-H. Jeon et al.: Corrosion Science 75 (2013) 367–375..

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