Improved corrosion resistance of cathodic arc evaporated Al$_{0.7}$Cr$_{0.3-x}$V$_x$N coatings in NaCl-rich media


A. Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria
B. Department of Physics and Astronomy, Uppsala University, 75120 Uppsala, SE, Sweden
C. Oerlikon Balzers, Oerlikon Surface Solutions AG, 9496 Balders, Liechtenstein
D. Plansee Composite Materials GmbH, D-86983 Lechbruck am See, Germany
E. Institute of Materials Science and Technology, TU Wien, A-1060 Wien, Austria

1. Introduction

One of the biggest drawbacks regarding the application of corrosion protective PVD coatings on bulk materials (e.g. steels) is the presence of open porosities. Pores or defect sites (e.g. embedded macroparticles, porosity due to highly orientated columnar growth, pin holes, etc.) allow the corrosive medium to travel unhindered to the coating/substrate interface and generate galvanic couples [1–3]. Depending on the materials that make up this galvanic cell, coatings may either act as the anodic element (providing sacrificial protection) [4], or act as the cathodic element, in which anodic dissolution and pitting of the substrate material ensues [5]. For the latter case, which pertains to most ceramic protective coatings, the coating itself remains inert, whereas the steel underneath suffers detrimental corrosion [6–11].

In recent years, a great number of strategies have been pursued to minimize the open-porosity values in protective PVD coatings and limit the probability of the electrolyte to make contact with less noble substrates. Whether this is achieved by: i) increasing the coating thickness [12–14], ii) incorporating a dense interlayer between the substrate and coating (interlayer designs) [6,15,16], iii) disrupting the columnar growth orientation by means of multilayer architectures [17–20], or iv) by refining the coating morphology altogether through alloying routes [21], all approaches aim to obstruct fast-track diffusion pathways between the electrolyte and the substrate in order to improve the corrosion behavior of the system.

Following a doping strategy, this study provides novel insights into the positive impact that V-doping imparts on the corrosion behavior of cathodic arc evaporated AlCrN thin films in NaCl-rich media. An Al$_{0.7}$Cr$_{0.3}$N$_x$ chemistry was chosen as the base system, whereupon chromium was progressively substituted with vanadium. In a series of Al$_{0.7}$Cr$_{0.3-x}$V$_x$N depositions, with vanadium contents ranging from x = 0–22.3 at% on the metal sublattice, two strategies are being pursued: i) improving the corrosion behavior solely by means of vanadium-doping, and ii) further improving the corrosion resistance of the Al$_{0.7}$Cr$_{0.3}$-V$_x$N series through an annealing step and consequent development of a vanadium-rich top-oxide scale. Thus, the first part of this study will focus on the effect of vanadium content in the as-deposited state, by considering changes in microstructure and crystal phase composition, while the second part will provide a detailed investigation on the oxide scale formation and diffusion mechanisms of the annealed samples.

2. Experimental methods

All coatings were deposited in an industrial scale deposition system.
(INNOVA, Oerlikon Balzers, Liechtenstein) by cathodic arc evaporation. Al\textsubscript{0.7}Cr\textsubscript{0.3-x}V\textsubscript{x}N targets were powder-metallurgically manufactured by Plansee Composite Materials GmbH and used for all coating variants. Steel foil with 0.05 mm thickness, and low-alloy steel discs (90MnCrV8) were utilized as substrates. Whereas the steel-foil was solely appropriated for as-deposited characterization purposes (e.g. analysis of the coatings morphology via fracture cross-section, coating thickness measurements and crystal-phase investigations by X-ray diffraction), the coated steel discs were exclusively used for electrochemical-corrosion experiments and post-corrosion analysis. All substrates were ultrasonically cleaned in acetone and ethanol before they were mounted into the deposition chamber. With a base pressure of \( \Delta P < 5.0 \times 10^{-4} \) Pa, the substrates were further cleaned for 25 min by an argon plasma etching procedure (Oerlikon Surface Solutions AG).

All arc evaporated coatings were deposited in a pure N\textsubscript{2} atmosphere at 3.5 Pa, with a DC-bias of up to \(-100\) V at 480 °C. Regarding the corrosion behavior, all coatings were grown to a thickness ~5 µm for optimal comparison.

2.1. Gradient coating procedure

Fig. 1 shows the schematic of the deposition chamber equipped with six arc-sources. A total of 11 Al\textsubscript{0.7}Cr\textsubscript{0.3-x}V\textsubscript{x}N coatings with varying V-content were deposited (designated P0-P10, by using several target compositions: Al\textsubscript{0.7}Cr\textsubscript{0.3}, Al\textsubscript{0.8}Cr\textsubscript{0.2}V\textsubscript{0.1}, Al\textsubscript{0.7}Cr\textsubscript{0.15}V\textsubscript{0.15} and Al\textsubscript{0.7}Cr\textsubscript{0.1}V\textsubscript{0.2} at%.

P0 designates the Al\textsubscript{0.7}Cr\textsubscript{0.3}V\textsubscript{x}N base coating with the lowest V-content (0 at% V). The deposition system was equipped with four Al\textsubscript{0.7}Cr\textsubscript{0.3} targets and operated with a two-fold substrate rotation, as shown in Fig. 1a. Depending on the V content of each target, together with the relative distance of the substrates to each of the two respective arc-sources, a slightly different coating composition was obtained.

P1-P9 represent Al\textsubscript{0.7}Cr\textsubscript{0.3-x}V\textsubscript{x}N coatings with varying V-contents that come from a stationary deposition mode (no substrate rotation). Three substrates were placed between two adjacent arc sources, equipped with different target compositions, as shown in Fig. 1b. Depending on the V content of each target, together with the relative distance of the substrates to each of the two respective arc-sources, a slightly different coating composition was obtained.

P10 denotes the Al\textsubscript{0.7}Cr\textsubscript{0.3}V\textsubscript{x}N coating with the highest V-content. The deposition system was equipped with four Al\textsubscript{0.7}Cr\textsubscript{0.1}V\textsubscript{0.2} targets and operated with a two-fold substrate rotation (Fig. 1c).

2.2. Annealing experiments in air

Isothermal annealing experiments were conducted in air at 700 °C. For each treatment, the chamber furnace (Medlin & Naber GesmbH, Vienna, Austria) was preheated to 700 °C and let equilibrate for a minimum of 12 h. All temperature profiles were monitored using a Naber Temperature TP1 processor in conjunction with a mounted type K thermocouple. The coated samples were then placed into the preheated chamber and annealed isothermally for 3 h.

2.3. Characterization of as-deposited and annealed coatings

For studying the morphology of the coatings (coating thickness, surface texture, and the integrity of the substrate-coating interfaces), a Zeiss Sigma 500 VP high-resolution field emission gun scanning electron microscope (FEGSEM) was used. With an acceleration voltage, ranging between 3 kV and 7 kV, characterization of coating thickness and
Coating morphology were performed on fracture cross sections of coated steel-foil substrates. Equipped with an EDAX Octane elect system, energy dispersive X-ray spectroscopy (EDX) was utilized for quantitative elemental investigations. Complementary to the EDX measurements, Time-of-Flight Heavy Ion Elastic Recoil Detection Analysis (ToF-HIERDA) was employed. All measurements were performed at the 5 MV 15SDH-2 Pelletron tandem accelerator at Uppsala University [22] employing $^{127}$I$^{8+}$ projectiles with a primary energy of 36 MeV with an incident angle of 67.5° with respect to the surface normal and a recoil detection angle of 45° with respect to the incident beam direction. Elemental composition depth profiles were determined using the CONTES software package [23] with the total systematic and statistical uncertainties estimated to be below 5% of the deduced value for the major constituents. For a more detailed description of the analytical set-up, we refer the reader to Storm et. al. [24].

For a more detailed investigation of the coating morphologies, Fig. 3: SEM micrographs showing fracture cross-sections of as-deposited Al$\text{}_0.7$Cr$\text{}_0.3$V$\text{}_x$N with varying vanadium contents (P0 to P10). Their respective vanadium contents (at% on the metal sublattice) are presented above.

Fig. 4: TEM investigations highlighting grain-refinement, as a consequence of V-doping. a-c feature bright-field images of as-deposited cross sections of the Al$\text{}_0.7$Cr$\text{}_0.3$N, Al$\text{}_0.7$Cr$\text{}_0.19$V$_{0.11}$N and Al$\text{}_0.7$Cr$\text{}_0.08$V$_{0.22}$N coatings, respectively. Further SAED and HR-TEM images render information about the crystallinity, as well as manifestation of grain-boundaries that comprise the coating matrix.
transmission electron microscopy (TEM, FEI TECNAI F20, equipped with a field emission gun and operated at an accelerating voltage of 200 kV) was conducted. Bright field (BF) imaging was utilized to learn more about the microstructure, crystallinity, and texture. For the preparation of the TEM lamellas, a standard lift-out procedure during focused-ion beam etching (FIB) milling was utilized (Scios 2 DualBeam system, ThermoFisher Scientific).

For crystallographic investigations, Bragg-Brentano X-ray diffraction (BBHD) was utilized, using a PANalytical Xpert Pro MPD system equipped with a Cu-Kα radiation source (wave length $\lambda = 1.54$ Å).

Electrochemically corroded samples were embedded in a conductive polymer-matrix, their cross-sections ground and polished, and analyzed via SEM and EDX. Accordingly, pit-formations, coating-substrate adherence, and fast-track diffusion routes of the electrolyte were examined.

2.4. Electrochemical corrosion experiments

Linear potentiodynamic polarization experiments were performed using a three-electrode set-up. With a saturated Ag/AgCl reference electrode (SSC), a Pt-counter electrode (CE) and the coated steel sample as working electrode (WE), the electrochemical experiments were conducted in a 0.1 M NaCl solution. Each sample was mounted into a press-fit corrosion cell, which accommodated a sample contact area of $1.58 \text{ cm}^2$. All samples were left to equilibrate for 20 min, after which the corrosion potential ($E_{\text{corr.}}$) was measured. Once the measured potential drops below a time derivative limit ($\frac{dE}{dt} = 1 \times 10^{-6} \text{ V/s}$), the recorded potentials from the last 5 s was averaged and taken as $E_{\text{corr.}}$. The linear sweep voltammetry (LSV) measurements were started cathodically at $E_{\text{corr.}} = 300 \text{ mV}$ and swept into the anodic region with a sweep-rate of.

Fig. 5: XRD spectra of the as-deposited arc evaporated Al$_{0.7}$Cr$_{0.3-x}$V$_x$N coatings with increasing V-contents (at% V on the metal sublattice). Reference patterns were taken from Ref. [25–27].

Fig. 6: Electrochemical investigations of as-deposited Al$_{0.7}$Cr$_{0.3-x}$V$_x$N coatings with varying vanadium-content (at% V on metal sublattice): a) Shows the original Tafel-plots measured in 0.1 M NaCl-solution, from which b) polarization resistance and open porosity values were calculated.
1 mV/s up to +1.2 VSSC. With a current-density cut-off value set to 1 mA/cm², the electrochemical tests were controlled and monitored by a potentiostat (Autolab PGSTAT302N, Metrohm).

2.5. Deductions based on polarisation measurements

Since protective coatings are prone to coating defects or open porosities, the measured galvanic current densities of the coated steel samples will depend on the contact ratio of the electrolyte and the coating/substrate surfaces. In other words, when the electrolyte is brought in contact with a “porous” coating surface, part of the electrolyte will contact the coating and part of the substrate material beneath, generating a galvanic couple.

From the Tafel-plots, the cathodic and anodic Tafel-slopes (βc and βa), as well as corrosion current density values (i corr) and corrosion potential (Ecorr) were extrapolated (see Fig. 2). By using the Stern-Geary Equation (see Eq. 1), the polarization resistance (Rρ) could be calculated for the uncoated substrate, as well as all Al0.7Cr0.3+VxN coated samples.

\[
\text{Stern–Geary Equation} (R_\rho) = \frac{\beta_c \times \beta_a}{2.33 \times i_{corr} (\beta_c + \beta_a)} \quad (1)
\]

Finally, according to the following relation (Eq. 2), the porosity of the coating was calculated:

\[
P = \left( \frac{R_{\rho(\text{substrate})}}{R_{\rho(\text{coating})}} \right) \times 10^{- \frac{i_{corr} (\beta_c + \beta_a)}{i_{corr} (\beta_c + \beta_a)}} \quad (2)
\]

where P denotes the open porosity of the coating, \( R_{\rho(\text{substrate})} \) is the polarization resistance of the uncoated substrate material, \( R_{\rho(\text{coating})} \) is the polarization resistance of the coated substrate, \( \Delta E_{\text{corr}} \) refers to the difference in the corrosion potential between the uncoated and coated substrate, and \( \beta_0(\text{substrate}) \) to the anodic Tafel-slope of the bare substrate – also see Fig. 2.

Lastly, by combining the corrosion current density (i corr) with Faraday’s Law (see Eq. 3), the corrosion rate (CR) may be calculated (see Eq. 4).

\[
W = \frac{A_w \times Q}{z} \quad (3)
\]

where W is the mass material removed, \( A_w \) is the atomic weight of the sample, Q is the total charge passed through the system and z is the number of electrons transferred in the reaction.

\[
CR = \frac{W \times A_s}{\rho} \quad (4)
\]

where \( A_s \) is the exposed surface area and \( \rho \) is the density of the material.

### 3. Results and discussion

#### 3.1. Microstructure and composition analysis

The as-deposited microstructures of all Al0.7Cr0.3+VxN coatings are shown in Fig. 3. The fracture cross section labeled P0 represents the as-deposited microstructure of the base system Al0.7Cr0.3+N with 0 at% vanadium. We would like to point out that this coating does not come from a stationary deposition run, but instead was deposited in a conventional manner with rotation and four identical target compositions. P1 to P9, on the other hand, do originate from the stationary gradient deposition and are numbered according to the arrangement within the chamber (revisit Fig. 1). P10 represents the microstructure of the coating with the highest V-content and was also deposited with substrate rotation and four identical Al0.7Cr0.3+V0.2 targets mounted within the deposition chamber. Above the cross-sectional SEM images the corresponding V-contents are plotted (at% on the metal sublattice, determined by EDX and verified by ERDA). For a complete overview of the chemical compositions, we refer to Appendix A.

First observations of the as-deposited microstructures indicate a gradual grain-refinement with increasing vanadium content. While a distinct columnar growth morphology exists for chemistries \( \leq 10.7 \) at% of V on the metal sublattice (P0-P3), a reduction in the column sizes can be noticed for contents \( \geq 10.7 \) but \( \leq 15.0 \) at% (P4, 5 and 7). From 15.0 at% upwards, the microstructure transitions into a coarse grained microstructure (P6 and P8) after which a featureless morphology predominates (P9 and P10).

TEM investigations further substantiate these observations. Fig. 4 shows the bright-field cross-sections of the as-deposited coatings P0, P7 and P10 with V-contents of 0, 11.6 and 22.3 at%, respectively (at% V on metal sublattice). Standing in good agreement with the previously shown SEM images, the effect of grain-refinement is clearly visible as the vanadium content increases. An initial refinement of the columnar structure is observed between P0 and P7, after which a featureless morphology develops. Selected area electron diffractograms (SAED), as well as high resolution TEM (HR-TEM) images were collected near the coating surfaces, to provide localized information about the coatings’ crystallinity. Starting with the Al0.7Cr0.3+N coating with 0 at% V-content (P0), the SAED(00) provides a diffraction pattern with distinct diffraction dots, which is indicative of a crystalline morphology. The respective HR-TEM(00) image features a well-defined column-boundary, which would, in case of a subsequent corrosion experiment, offer a preferential diffusion path for chloride species. Such fast track diffusion pathways for chloride species have been investigated in a previous study [1], and deemed to be a significant draw-back in effectively providing corrosion protection. As vanadium is substituted for chromium, first to 11.6 at% (P7) and then further to 22.3 at% V-content (P10), the SAED features...
smeared diffraction dots (SAED), or even a ring-like diffraction pattern (SAEDc). Together with the respective HR-TEM images (HR-TEMb and HR-TEMc), which indicate narrowing of distinct column boundaries, both HR-TEM and SAED analysis point out that the microstructure transitions into a more nanocrystalline structure with a discontinuous columnar arrangement (highlighted by the x in the HR-TEMc image of Fig. 4).

3.2. Structural evolution in relation to V-content

Fig. 5 features X-ray diffractograms and peak-patterns for the as-deposited Al0.7Cr0.3–xVxN samples P0 to P10. Analogous to Fig. 3, the vanadium contents and chamber locations are listed next to each diffractogram with increasing V-content from bottom to top.

The Al0.7Cr0.3N base system with no vanadium content (P0) features a face-centered-cubic (fcc) crystal structure and exhibits a single-phase Cr(Al)N solid solution with mixed [111]/[200] growth orientations. As chromium is replaced by vanadium in the AlCrN-base-system, the crystal lattice is able to maintain the fcc-Cr(Al)V,N solid solution up to a vanadium content of 6.4 at% on the metal sublattice (P1 = 5.1 at% V and P2 = 6.4 at% V). However, as more vanadium is added (P3 = 8.1 at%), the solubility limit for Al in the fcc-Cr(Al)V,N structure is reached, and the formation of the wurzite-Al(Cr,V)N phase is favored. Consequently, from P4 (10.7 at% V) to P9 (17.4 at% V), a dual-phase, consisting of the fcc-Cr(Al,V,N) and w-type Al(Cr,V)N phases make up the coating structures. While we identify the onset for the formation of w-Al(Cr,V)N at a V-content of about 8.1 at% (Fig. 5, P3) and the formation of a dual-phase crystal structure thereafter (Fig. 5, P4 to P10), we can relate the competitive growth orientations between the w-Al(Cr,V)N and fcc-Cr(Al,V,N) to the gradual grain-refinement first observed at P4 (Fig. 3).

Based on this, we propose that the nucleation of the competitive w-Al(Cr,V)N phase with increasing V-content inhibits the growth of the opposing fcc-Cr(Al,V,N) crystallites.

Also interesting is the maximum phase-fraction of the w-type Al(Cr,V,N) to fcc-Cr(Al,V,N) peaking at 15 at% V (P6), after which the fcc-Cr(Al,V,N) or rather fcc-V(Al,Cr)N phase is again stabilized and the w-type Al(Cr,V,N) phase recedes. This observation is solely made upon the intensity-evolution of the predominant w-AlN 002 reflex.

3.3. Electrochemical corrosion properties

Tafel-plots of the bare 90MnCrV8 alloy (low alloy steel) and as-deposited Al0.7Cr0.3–xVxN coated samples are shown in Fig. 6a. Tafel-extrapolations were made manually with no additional software package for data analysis. From the intersection of the anodic and cathodic Tafel-branches the corrosion currents (i_{corr}) and corrosion potentials (E_{corr}) have been determined for all samples (listed in Table 1).

3.4. Current density vs. V-content

Firstly, the corrosion currents (i_{corr}) and passivation currents (i_{pass}) that were measured decrease significantly with increasing vanadium-to-chromium-ratio. Whereas quite similar i_{corr} values were obtained for the uncoated alloy and the Al0.7Cr0.3N-coated samples with 0 at% V-content (3.17 × 10^{-6} and 3.32 × 10^{-6} A/cm^2, respectively), a gradual reduction of the corrosion current densities was measured in accordance with the substitution of chromium with vanadium. In more detail, for a V-content of 5.1 at% on the metal sublattice (P1), i_{corr} determined to be 1.23 × 10^{-6} A/cm^2, whereas for V-contents of 11.6 and 22.3 at% (P7 and P10), the measured i_{corr} values decreased to 6.01 × 10^{-7} and 9.81 × 10^{-8} A/cm^2, respectively.

3.5. Corrosion potential vs. V-content

Secondly, a significant positive shift of the E_{corr} can be observed from the uncoated alloy (low alloy steel = −569 mV_{SSC}) to all Al0.7Cr0.3–xVxN coated samples (P0 = −354 mV_{SSC}), which indicates a reduced anodic activity of the coated sample over the bare alloy. Further positive shifting of the E_{corr} is measured as the vanadium-to-chromium-ratio increases for the Al0.7Cr0.3–xVxN coatings. The most noble E_{corr} is therefore obtained by the coating with 22.3 at% V on the metal sublattice (P10 = −148 mV_{SSC}). At this point, we again would like to point...
Corrosion Science 221 (2023) 111376

3.6. Open Porosity vs V-content

When considering that porosities and fast track diffusion sites along incoherent grain boundaries contribute to a more anodically active galvanic couple (coating/alloy), control over the open porosity of protective coatings is of great importance [1]. Therefore, we would like to put the aforementioned electrochemical data in context with the open porosity values (Eqs.1–2). Fig. 6b shows a bar chart visualizing the correlation between the V-content the open porosity (P_{open}) and the polarization resistance (R_{p}) of all as-deposited coatings. Standing in good agreement with the SEM and TEM analysis, a gradual decrease in the open porosity rate (P_{open}) is observed with increasing V-content. Naturally, with less contact area between the electrolyte and the substrate alloy, the polarization resistance of the coating/substrate couple increases with increasing V-content. All values are also listed in Table 1.

3.7. Isothermal annealing of Al_{0.7}Cr_{0.3–x}V_{x}N coatings

Now that the microstructure, open porosity, and corrosion behavior have been thoroughly discussed in light of the vanadium content in the Al_{0.7}Cr_{0.3–x}V_{x}N coatings, we wish to further investigate the corrosion resistance of their respective annealed states. With the goal to develop a vanadium-rich top-oxide scale — intended to function as an additional sealing barrier and to minimize fast-track diffusion junctions to the coating-substrate interface — we first investigated the oxidation behavior of the annealed coatings. Fig. 7 shows the Bragg-Brentano X-ray diffractograms for Al_{0.7}Cr_{0.3–x}V_{x}N samples P0 to P10, that have been annealed isothermally at 700 °C for 3 h in air. As 700 °C is well below the phase transition temperature of fcc-AlN to w-Al(O,Cr,N) (>900 °C) for the Al_{0.7}Cr_{0.3}N system, we can assume that the overall phase-stability of the Al_{0.7}Cr_{0.3–x}V_{x}N remains stable throughout the annealing treatment [28]. Moreover, 700 °C also falls well below the oxidation temperature of the fcc-Al_{0.7}Cr_{0.3}N system, where temperatures of > 900 °C have been reported necessary for producing Cr_{2}O_{3} and Al_{2}O_{3} scales [29]. We therefore expect a distinct vanadium threshold content, where predominatly vanadium-oxides form upon annealing at 700 °C.

Analogous to the XRD analysis of the as-deposited coatings (Fig. 5), the vanadium contents (at% V on metal sublattice) are listed next to each diffractogram with increasing V-content from bottom to top, together with their respective deposition chamber positions. A reduced corridor of diffraction angles was chosen for the illustration, as i) most of the oxides, (Cr_{2}O_{3}, Al_{2}O_{3}, VO, V_{0}O_{2n+1}, V_{0}O_{2n-1}, V_{0}O_{2n}) feature their prominent Bragg diffractions between 15 and 30 degrees, and ii) any diffraction reflexes larger than 30 ° would overlap with the fcc-Cr(Al,V)N and w-Al(Cr,V)N peaks [25–27,30–36]. Evident from the diffractograms in Fig. 7, no oxide peak was detected for any of the annealed Al_{0.7}Cr_{0.3–x}V_{x}N coatings with a V-content up to 8.1 at% (P0 to P3). At a V-content of 10.7 at%, however, first indications of oxidation are noticeable (P4). A similar V-threshold has been reported by Tillmann et al., observing an oxidation onset at 10.7 at% V, however, with slightly different Al and Cr metal ratios [37]. At V-contents of 11.6 at% and higher, significant oxidation of the coating surfaces is measured with the most prominent Bragg-reflexes identified as a mixed anorthic-AlVO_{4} and orthorhombic-V_{3}O_{5} scale.

This sudden onset of the mixed V-oxide evolution is also observed by SEM-analysis. Fig. 8a shows combined top-view images of the as-deposited (bottom half) and its respective annealed coating surfaces (top-half) for all vanadium containing Al_{0.7}Cr_{0.3–x}V_{x}N coated samples. Standing in good agreement with the XRD measurements, a distinct onset of a developing surface-oxide is seen for the sample P4 (10.7 at% V.

Fig. 8. : SEM top-view images of Al_{0.7}Cr_{0.3–x}V_{x}N coatings with varying V-contents (at% V on metal sublattice): a) shows combined images consisting of as-deposited (bottom) and annealed states (top, 700 °C for 3 h in air). b) features selected annealed coating surfaces at lower magnification.

out that the measured E_{corr} for all coated samples are mixed potentials between the coating and substrate material, owed to open porosities and coating defects.

Now that the microstructure, open porosity, and corrosion behavior have been thoroughly discussed in light of the vanadium content in the Al_{0.7}Cr_{0.3–x}V_{x}N coatings, we wish to further investigate the corrosion resistance of their respective annealed states. With the goal to develop a vanadium-rich top-oxide scale — intended to function as an additional sealing barrier and to minimize fast-track diffusion junctions to the coating-substrate interface — we first investigated the oxidation behavior of the annealed coatings. Fig. 7 shows the Bragg-Brentano X-ray diffractograms for Al_{0.7}Cr_{0.3–x}V_{x}N samples P0 to P10, that have been annealed isothermally at 700 °C for 3 h in air. As 700 °C is well below

the phase transition temperature of fcc-AlN to w-Al(O,Cr,N) (>900 °C) for the Al_{0.7}Cr_{0.3}N system, we can assume that the overall phase-stability of the Al_{0.7}Cr_{0.3–x}V_{x}N remains stable throughout the annealing treatment [28]. Moreover, 700 °C also falls well below the oxidation temperature of the fcc-Al_{0.7}Cr_{0.3}N system, where temperatures of > 900 °C have been reported necessary for producing Cr_{2}O_{3} and Al_{2}O_{3} scales [29]. We therefore expect a distinct vanadium threshold content, where predominatly vanadium-oxides form upon annealing at 700 °C.

Analogous to the XRD analysis of the as-deposited coatings (Fig. 5), the vanadium contents (at% V on metal sublattice) are listed next to each diffractogram with increasing V-content from bottom to top, together with their respective deposition chamber positions. A reduced corridor of diffraction angles was chosen for the illustration, as i) most of the oxides, (Cr_{2}O_{3}, Al_{2}O_{3}, VO, V_{0}O_{2n+1}, V_{0}O_{2n-1}, V_{0}O_{2n}) feature their prominent Bragg diffractions between 15 and 30 degrees, and ii) any diffraction reflexes larger than 30 ° would overlap with the fcc-Cr(Al,V)N and w-Al(Cr,V)N peaks [25–27,30–36]. Evident from the diffractograms in Fig. 7, no oxide peak was detected for any of the annealed Al_{0.7}Cr_{0.3–x}V_{x}N coatings with a V-content up to 8.1 at% (P0 to P3). At a V-content of 10.7 at%, however, first indications of oxidation are noticeable (P4). A similar V-threshold has been reported by Tillmann et al., observing an oxidation onset at 10.7 at% V, however, with slightly different Al and Cr metal ratios [37]. At V-contents of 11.6 at% and higher, significant oxidation of the coating surfaces is measured with the most prominent Bragg-reflexes identified as a mixed anorthic-AlVO_{4} and orthorhombic-V_{3}O_{5} scale.

This sudden onset of the mixed V-oxide evolution is also observed by SEM-analysis. Fig. 8a shows combined top-view images of the as-deposited (bottom half) and its respective annealed coating surfaces (top-half) for all vanadium containing Al_{0.7}Cr_{0.3–x}V_{x}N coated samples. Standing in good agreement with the XRD measurements, a distinct onset of a developing surface-oxide is seen for the sample P4 (10.7 at% V.
on metal sublattice), where nucleation-islands of vanadium-oxides stud the coating surface. At slightly higher vanadium-concentrations (11.6 at% V on metal sublattice), a converging of the nucleation islands results in a more pronounced oxide scale, which develops thicker and even higher V-contents (15.0 at% and 17.4 at% V on metal sublattice for P6 and P9, respectively), larger oxide islands develop, which converge of vanadium-oxide patches evolve at a V-content of 13.5 at% (P5). At even higher V-contents (15.0 at% and 17.4 at% V on metal sublattice for P6 and P9, respectively), larger oxide islands develop, which converge to fully cover the coating surface. This is the case for P10 (22.3 at% V on metal sublattice), where a continuous and crystalline vanadium oxide scale has developed on top of the coating.

3.8. Electrochemical investigations of annealed Al0.7Cr0.3−xVxN-coated samples

LSV measurements of the annealed samples were conducted in an identical manner to the electrochemical investigations of the as-deposited Al0.7Cr0.3−xVxN coated samples. Fig. 9a shows the Tafel-plots of the isothermally annealed Al0.7Cr0.3−xVxN coated samples, as well as the bare alloy (not annealed). As the V-content of the coatings increases, a shifting of the Ecorr into more positive potentials is observed, accompanied by an anew decreasing in the corrosion currents (i corr). Tafel-extrapolations again provide the electrochemical parameters, such as cathodic and anodic Tafel-slopes (βc and βa, respectively), corrosion current densities (i corr) and corrosion potentials (Ecorr), that were then used for calculating the coatings’ porosities (according to Eq. 1 and Eq. 2). The porosity values for all as-deposited and annealed Al0.7Cr0.3−xVxN samples are plotted in Fig. 9b, with the intention to better illustrate the improved values between the as-deposited and annealed states, as well as to further highlight the beneficial effect of the V-content. A summary of the extrapolated electrochemical values, as well as the calculated values, such as polarization resistance and open porosities are also listed in Table 2.

Lastly, corrosion rates of the as-deposited, as well as annealed coated steel samples were calculated. As there are no indications of dissolution or oxidation processes of the coating material, it is expected that the current densities measured during the electrochemical experiments must come from the low alloy steel substrate (dissolution of iron). In this case, together with Faraday’s Law, the mass-loss of the substrate was calculated by correlating the corrosion currents (i corr) with the dissolution of iron (Eq. 3 and Eq. 4). Fig. 10 shows the individual corrosion rates (mg/cm² per year) for each Al0.7Cr0.3−xVxN-steel couple. Evident is the gradual reduction in mass-loss with increasing V-content within the coatings and an even further reduction in the corrosion rate for the annealed series. With the exception of the as-deposited Al0.7Cr0.3N coating (P0, 0 at% V), all Al0.7Cr0.3−xVxN coated steel samples exhibit reduced corrosion rates over the uncoated steel substrate.

Reason for this slightly increased corrosion rate of the Al0.7Cr0.3N coated samples, despite the intended protective character of the coating, is the galvanic couple that forms when the electrolyte makes contact with both, the coating matrix and the steel substrate. The more noble coating surface thereby acts as the cathode, whereas the steel-substrate adopts the role of the anode. Due to the vastly larger contact area made between the coating surface (large cathode) compared to the small contact area made between the diffused electrolyte and the steel alloy (small localized anode), accelerated oxidation occurs. As vanadium quite drastically refines the morphology of the Al0.7Cr0.3−xVxN system, it yields fewer porosities (direct diffusion pathways) for the NaCl-electrolyte to reach the coating-substrate interface. Accordingly, with fewer contact area between the electrolyte and the steel substrate, lower corrosion currents (corrosion rates) are generated. We therefore see a strong correlation between the open-porosity values and the calculated corrosion rates of the Al0.7Cr0.3−xVxN-steel couples.

3.9. Vanadium-oxide scale investigation by TEM

To further answer why the annealed Al0.7Cr0.3−xVxN sample with the highest V-content (P10 w. 22.3 at% V) performs best in light of its corrosion resistance, additional TEM analysis have been conducted. Here, the aim was to verify the crystal-structures that have been identified by XRD measurements in earlier sections, as well as to take a closer look at the diffusion profiles that evolved during the annealing process. For this, SAEDs together with TEM bright-field images of the coating’s surface near region provide localized information about the crystal structure and crystallinity. Shown in Fig. 11a is a bright-field TEM image, which highlights three distinctly different morphologies: a crystalline top-oxide, a nanocrystalline oxygen enriched band underneath, and the pristine coating matrix at the bottom (as found in the as-deposited state).
Table 2

Electrochemical properties of annealed $\text{Al}_x\text{Cr}_{0.3-}x\text{V}_x\text{N}$ coated low-alloy steel substrates in 0.1 M NaCl solution. $E_{\text{corr}}$, corrosion potential; $I_{\text{pass}}$, passive current density; $I_{\text{corr}}$, corrosion current density; $\beta_a$, cathodic Tafel-slope; $\beta_p$, anodic Tafel-slope; $R_p$, polarization resistance; $P_{\text{por}}$, open porosity deduced from $R_p$.

<table>
<thead>
<tr>
<th>Material</th>
<th>V-content (at%)</th>
<th>$E_{\text{corr}}$ (mV)</th>
<th>$I_{\text{pass}}$ (A/cm$^2$)</th>
<th>$I_{\text{corr}}$ (A/cm$^2$)</th>
<th>$\beta_a$ (mV/dec)</th>
<th>$\beta_p$ (mV/dec)</th>
<th>$R_p$ (k$\Omega\times$cm$^2$)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Al}<em>0\text{Cr}</em>{0.3-}x\text{V}_x\text{N}$ annealed at 700 °C for 3 h</td>
<td>0 (p%v)</td>
<td>-291</td>
<td>$2.61 \times 10^{-4}$</td>
<td>$4.39 \times 10^{-6}$</td>
<td>127.6</td>
<td>67.2</td>
<td>43.1</td>
<td>6.34 $\times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>5.1 (p%v)</td>
<td>-269</td>
<td>$2.23 \times 10^{-5}$</td>
<td>$3.60 \times 10^{-7}$</td>
<td>86.1</td>
<td>86.5</td>
<td>51.1</td>
<td>2.75 $\times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>6.4 (p%v)</td>
<td>-248</td>
<td>$8.80 \times 10^{-6}$</td>
<td>$8.99 \times 10^{-7}$</td>
<td>108.0</td>
<td>127.8</td>
<td>27.9</td>
<td>2.70 $\times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>8.1 (p%v)</td>
<td>-242</td>
<td>$5.96 \times 10^{-6}$</td>
<td>$2.45 \times 10^{-7}$</td>
<td>93.4</td>
<td>61.8</td>
<td>65.2</td>
<td>9.66 $\times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>10.7 (p%v)</td>
<td>-233</td>
<td>$7.54 \times 10^{-6}$</td>
<td>$3.31 \times 10^{-8}$</td>
<td>117.4</td>
<td>43.1</td>
<td>408.9</td>
<td>1.18 $\times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>11.6 (p%v)</td>
<td>-210</td>
<td>$6.79 \times 10^{-7}$</td>
<td>$2.30 \times 10^{-8}$</td>
<td>128.4</td>
<td>102.1</td>
<td>1132.0</td>
<td>2.13 $\times 10^{-5}$</td>
</tr>
<tr>
<td></td>
<td>13.5 (p%v)</td>
<td>-194</td>
<td>$1.72 \times 10^{-7}$</td>
<td>$9.15 \times 10^{-9}$</td>
<td>92.9</td>
<td>65.1</td>
<td>1794.4</td>
<td>8.34 $\times 10^{-7}$</td>
</tr>
<tr>
<td></td>
<td>15.0 (p%v)</td>
<td>-203</td>
<td>$4.90 \times 10^{-6}$</td>
<td>$8.58 \times 10^{-9}$</td>
<td>74.2</td>
<td>66.3</td>
<td>1751.5</td>
<td>1.12 $\times 10^{-5}$</td>
</tr>
<tr>
<td></td>
<td>15.6 (p%v)</td>
<td>-147</td>
<td>$1.40 \times 10^{-7}$</td>
<td>$1.60 \times 10^{-8}$</td>
<td>111.5</td>
<td>124.8</td>
<td>1580.9</td>
<td>2.32 $\times 10^{-8}$</td>
</tr>
<tr>
<td></td>
<td>17.4 (p%v)</td>
<td>-95</td>
<td>$5.26 \times 10^{-8}$</td>
<td>$8.18 \times 10^{-9}$</td>
<td>181.8</td>
<td>283.3</td>
<td>5813.9</td>
<td>1.33 $\times 10^{-7}$</td>
</tr>
<tr>
<td></td>
<td>22.3 (p%v)</td>
<td>-47</td>
<td>$1.61 \times 10^{-8}$</td>
<td>$1.59 \times 10^{-9}$</td>
<td>129.2</td>
<td>206.6</td>
<td>21,511.0</td>
<td>1.50 $\times 10^{-9}$</td>
</tr>
</tbody>
</table>

Fig. 10: Comparison of the corrosion rates of as-deposited $\text{Al}_x\text{Cr}_{0.3-}x\text{V}_x\text{N}$ coated and annealed $\text{Al}_x\text{Cr}_{0.3-}x\text{V}_x\text{N}$ coated low-alloy steel substrates with varying V-contents (at% V on metal sublattice).

Starting with the top-oxide, single-crystalline domains are detected, as is evident from the spot-pattern of the SAEDs in Fig. 11b. Indexing of the pattern renders a triclinic (anorhctic) structure of the AIVO$$_4$$-oxide with the space group P$$_T$$, which stands in excellent agreement with the findings from the XRD measurements and results from Franz et. al. [38,39].

Moving below the granular top-oxide, the SAEDs in Fig. 11c features a combination of an amorphous material with a characteristic halo-ring pattern, as well as a nanostructured polycrystalline matrix, with typical smeared diffraction rings that appear further away from the primary beam. The decomposition of the original polycrystalline matrix to a semi-amorphous morphology can be attributed to the oxidation process during annealing, where oxygen inward diffusion is accompanied by simultaneous dissipation of nitrogen. By integrating the SAEDs ring-pattern and plotting it over the reciprocal of the lattice-spacing, an intensity plot with broadened but still defined peaks is generated, which is shown in Fig. 11f. Again, we can deduce that the broadened peaks convey an amorphous character of the coating matrix, whereas more defined [200] and [220] reflexes of the fcc-CrN crystal structure suggest residue fragments of the original coating structure. The fact that only fcc-CrN residues appear in the intensity plot suggests a faster degradation mechanism of the hexagonal phase fraction, which greatly affects the diffusion of oxygen and other alloyed elements, such as vanadium. Lastly, SAEDs and SAEDs are intended to show the pristinal dual fcc-Cr (Al,V)N and w-type Al(Cr,V)N phases. Furthermore, they reveal significant differences in the crystallinity of the coating morphology that is in close proximity of the oxygen-diffusion front (SAEDs) and the morphology that is further away (SAEDs). Evident from SAEDs in Fig. 11d and Fig. 11e, similar diffraction rings are obtained, whose integration in Fig. 11f also show close to identical intensity plots and, as expected, render the correct n-spacings for the fcc-Cr(Al,V)N and w-Al (Cr,V)N crystal structures. We therefore conclude that there is a sharp oxygen diffusion front, with little to no lattice distortion after.

3.10. Description of diffusion mechanisms

Next, the diffusion mechanisms are investigated in more detail. In accordance with the TEM analysis in Fig. 11, the same region of the annealed sample is chosen. First, we would like to direct the reader’s attention to a top view SEM image in Fig. 12a and emphasize that the entire coating surface is homogeneously studded with a highly crystal residue fragments of the original coating structure. The fact that only defined [200] and SAEDs suggest an amorphous character of the coating matrix, whereas more defined [200] and [220] reflexes of the fcc-CrN crystal structure suggest residue fragments of the original coating structure. The fact that only fcc-CrN residues appear in the intensity plot suggests a faster degradation mechanism of the hexagonal phase fraction, which greatly affects the diffusion of oxygen and other alloyed elements, such as vanadium. Lastly, SAEDs and SAEDs are intended to show the pristinal dual fcc-Cr (Al,V)N and w-type Al(Cr,V)N phases. Furthermore, they reveal significant differences in the crystallinity of the coating morphology that is in close proximity of the oxygen-diffusion front (SAEDs) and the morphology that is further away (SAEDs). Evident from SAEDs in Fig. 11d and Fig. 11e, similar diffraction rings are obtained, whose integration in Fig. 11f also show close to identical intensity plots and, as expected, render the correct n-spacings for the fcc-Cr(Al,V)N and w-Al (Cr,V)N crystal structures. We therefore conclude that there is a sharp oxygen diffusion front, with little to no lattice distortion after.
crystalline AlVO which results from an outward diffusion of vanadium in order to form a coating matrix underneath. Also evident is a vanadium depletion layer, recorded. This coincides with the understanding that there is a sharp interface between the oxidized coating and the remaining pristine coating morphology. Moreover, a distinct vanadium depletion layer is shown. Standing in good agreement with the findings from the line-scan, the presence of the depletion layer suggests an outward directed diffusion of vanadium for the formation of the AlVO-oxide. Chromium also indicates outward directed diffusion, however only to a marginal degree. As Cr does not participate in the formation of a top oxide, it instead concentrates at the grain-boundaries of the AlVO-4-crystallites as shown in Fig. 12 c, as well as EDX map of 12d. Lastly, aluminum shows little migration across the oxygen/nitrogen diffusion-front. This observation suggests that sufficient aluminum is originally present for the formation of the AlVO4-top oxide, with no chemical gradient that will instigate further Al diffusion to the surface.

3.11. Overview of electrochemical parameters of various coating systems

Lastly, we wish to place the corrosion resistance of the presented Al0.7Cr0.3.30.22N coatings into context with other material-systems deposited by this research group. Fig. 13 shows an overview of \( I_{\text{corr}} \) vs. \( E_{\text{corr}} \) values of various coating materials deposited on low alloy steel (90MnCrV8) that have been electrochemically tested in an identical electrolyte through the coating. In a series of 10 Al0.7Cr0.3.30.22N coatings with varying V-contents, ranging from 5.1 to 22.3 at% on the metal sublattice, each raise in the V-fraction lowered the corrosion currents noticeably, and resulted in a positive shift of the respective corrosion potential. Using the Stern-Geary equation together with the assumption that the coating material remains inert throughout the electrochemical experiment (only the steel substrate accounts for the anodic current), an approximation revealed a significant decline in the coatings' open porosity 

![Fig. 11. TEM investigations highlighting the oxidation behavior of Al0.7Cr0.3.30.22N coating isothermally annealed at 700 °C in air for 3 h. a) shows a bright-field image, highlighting the most prominent structural features, as well as the positions of SAED(a-d) measurements. (b-e) show the SAED-patterns that originate from the positions labeled in sub-figure (a). f) features the integrated ring-patterns from SAED(b-d).](image-url)

4. Conclusion

To improve the corrosion resistance of cathodic arc evaporated AlCrN-based coatings in NaCl-rich media, this study has provided two effective approaches: i) a doping-strategy with vanadium, and ii) an annealing strategy at 700 °C in air for 3 h.

In a deposition series of Al0.7Cr0.3.3-VxN coatings, a direct correlation was found between the V-content, the coatings' crystallinity, and their corrosion current densities during electrochemical investigation. With increasing vanadium fractions, more refined coating morphologies were obtained, as well as lower current densities during the corrosion experiments. We propose that the reason for the progressive grain refinement is attributed to the nucleation of the favorable w-Al(Cr,V)N phase at higher vanadium contents, which inhibits the growth of the opposing fcc-Cr(Al,V)N crystallites. As a result, diffusion paths from the coating surface to the coating-substrate interface become increasingly branched, as more grain boundaries impede the migration of the electrolyte through the coating. In a series of 10 Al0.7Cr0.3.3-VxN coatings with varying V-contents, ranging from 5.1 to 22.3 at% on the metal sublattice, each raise in the V-fraction lowered the corrosion currents noticeably, and resulted in a positive shift of the respective corrosion potential. Using the Stern-Geary equation together with the assumption that the coating material remains inert throughout the electrochemical experiment (only the steel substrate accounts for the anodic current), an approximation of the coatings' open porosity was made [3]. Appropriately, the approximation revealed a significant decline in the coatings' porosity values, which is a result of the observed grain-refinement due to
increasing V-fractions.

Moreover, a second series of Al$_{0.7}$Cr$_{0.3}$V$_{x}$N coatings with V-contents ranging from 5.1 to 22.3 at% on the metal sublattice was annealed at 700 °C for 3 h in air and electrochemically tested in a 0.1 M NaCl-solution. For all annealed samples, significant shifting of the $E_{\text{corr}}$ into more positive potentials was measured, accompanied by an anew decreasing in the corrosion currents ($i_{\text{corr}}$). Compared with the electrochemical values from the doping strategy, further improvement was obtained through the additional annealing step at 700 °C. We attribute this enhanced corrosion resistance to the formation of a ~1 µm thick AlVO$_4$-top oxide, followed by a ~0.5 µm thick oxygen-enriched (vanadium depleted) nanocrystalline layer underneath. We propose that this combination of top-oxide formation and formation of a near amorphous oxygen enriched layer below, drastically reduces the open-porosity rates of the coating structure as a whole and renders improved corrosion protection.

CRediT authorship contribution statement

O. E. H. and H. R. conceived the research. O. E. H. conducted the coating depositions, as well as the electrochemical corrosion tests. P. K. prepared the TEM lamellas, whereas T. W. conducted the TEM measurements. E. N. and D. P. conducted the ToF-HIERDA measurements. O. H. and P. P. supported the research by providing indispensable funding, while L. S., J. R., and S. K. assisted the research with their thematic expertise. H. R. also provided funding acquisition and oversaw the research as supervisor. Finally, all authors have contributed in revising and approving the final version of the manuscript.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Oliver E. Hudak reports financial support was provided by Christian Doppler Research Association.

Data Availability

Data will be made available on request.

Fig. 12: EDX investigations highlighting the diffusion behavior of the Al$_{0.7}$Cr$_{0.08}$V$_{0.22}$N coating isothermally annealed at 700 °C in air for 3 h. a) shows a top-view SEM image of the crystalline top-oxide. b) features a STEM cross-section image of the top-most section of the annealed coating with the most prominent features labeled. c) displays an EDX-line scan that belongs to the segment shown sub-figure (b). d) displays EDX-maps, originating from the same segment as shown in sub-figures (b and c).
Table A1
Overview showing the chemical compositions of the as-deposited $\text{Al}_{0.7}\text{Cr}_{0.3}\text{V}_{x}\text{N}$ coatings. All listed values reflect EDX measurements that have been corrected according to ERDA measurements. Accordingly, ERDA values from samples P4 and P10, with compositions equivalent to $\text{Al}_{0.32}\text{Cr}_{0.19}\text{V}_{0.49}$, provided the correction standard.

<table>
<thead>
<tr>
<th>sample</th>
<th>V-content (at%)</th>
<th>Al-content (at%)</th>
<th>Cr-content (at%)</th>
<th>N-content (at%)</th>
<th>impurities (Oxygen) (at%)</th>
<th>Al-content on metal sublattice (at%)</th>
<th>Cr-content on metal sublattice (at%)</th>
<th>V-content on metal sublattice (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P0</td>
<td>0.0</td>
<td>32.8</td>
<td>14.9</td>
<td>48.9</td>
<td>3.5</td>
<td>68.8</td>
<td>31.2</td>
<td>0.0</td>
</tr>
<tr>
<td>P1</td>
<td>2.7</td>
<td>34.7</td>
<td>15.9</td>
<td>45.5</td>
<td>1.2</td>
<td>65.1</td>
<td>29.8</td>
<td>5.1</td>
</tr>
<tr>
<td>P2</td>
<td>3.2</td>
<td>32.5</td>
<td>14.5</td>
<td>47.2</td>
<td>2.5</td>
<td>64.7</td>
<td>28.9</td>
<td>6.4</td>
</tr>
<tr>
<td>P3</td>
<td>4.0</td>
<td>32.7</td>
<td>13.2</td>
<td>47.4</td>
<td>2.6</td>
<td>65.5</td>
<td>26.4</td>
<td>8.1</td>
</tr>
<tr>
<td>P4</td>
<td>5.2</td>
<td>32.4</td>
<td>10.9</td>
<td>48.2</td>
<td>3.2</td>
<td>66.8</td>
<td>22.5</td>
<td>10.7</td>
</tr>
<tr>
<td>P5</td>
<td>7.2</td>
<td>31.9</td>
<td>9.1</td>
<td>48.4</td>
<td>3.3</td>
<td>66.1</td>
<td>18.9</td>
<td>15.0</td>
</tr>
<tr>
<td>P6</td>
<td>6.6</td>
<td>31.4</td>
<td>10.6</td>
<td>48.2</td>
<td>3.2</td>
<td>64.7</td>
<td>21.8</td>
<td>13.5</td>
</tr>
<tr>
<td>P7</td>
<td>5.6</td>
<td>31.4</td>
<td>11.2</td>
<td>48.4</td>
<td>3.3</td>
<td>65.1</td>
<td>23.3</td>
<td>11.6</td>
</tr>
<tr>
<td>P8</td>
<td>7.6</td>
<td>30.5</td>
<td>10.4</td>
<td>48.3</td>
<td>3.3</td>
<td>63.3</td>
<td>21.4</td>
<td>15.6</td>
</tr>
<tr>
<td>P9</td>
<td>8.4</td>
<td>30.7</td>
<td>9.4</td>
<td>48.2</td>
<td>3.2</td>
<td>63.3</td>
<td>19.4</td>
<td>17.4</td>
</tr>
<tr>
<td>P10</td>
<td>10.6</td>
<td>30.3</td>
<td>6.5</td>
<td>48.9</td>
<td>3.7</td>
<td>63.9</td>
<td>13.8</td>
<td>22.3</td>
</tr>
</tbody>
</table>

Table A2
Overview of deposition parameters, as well as electrochemical parameters ($I_{\text{corr}}$ and $E_{\text{corr}}$) measured in 0.1 M NaCl solution, pertaining to Fig. 13.

<table>
<thead>
<tr>
<th>sample</th>
<th>deposition technique</th>
<th>$T_{\text{dep}}$ (C)</th>
<th>$P_{\text{dep}}$ (Pa)</th>
<th>atmosphere</th>
<th>bias (V)</th>
<th>$I_{\text{corr}}$ (A)</th>
<th>ref.</th>
<th>$E_{\text{corr}}$ (mV)</th>
<th>$I_{\text{corr}}$ (A/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{AlCrN}$</td>
<td>cae</td>
<td>480</td>
<td>3.5</td>
<td>N$_2$</td>
<td>$\geq -100$</td>
<td>-148</td>
<td>[1]</td>
<td>-375</td>
<td>$2.57 \times 10^{-6}$</td>
</tr>
<tr>
<td>$\text{AlCrVN}$</td>
<td>cae</td>
<td>480</td>
<td>3.5</td>
<td>N$_2$</td>
<td>$\geq -100$</td>
<td>-47</td>
<td>[1]</td>
<td>-375</td>
<td>$1.03 \times 10^{-7}$</td>
</tr>
<tr>
<td>$\text{CrN}$</td>
<td>cae</td>
<td>480</td>
<td>3.5</td>
<td>N$_2$</td>
<td>$\geq -100$</td>
<td>-47</td>
<td>[1]</td>
<td>-375</td>
<td>$1.59 \times 10^{-8}$</td>
</tr>
<tr>
<td>$\text{TiN}$</td>
<td>cae</td>
<td>500</td>
<td>3.5</td>
<td>N$_2$</td>
<td>-80</td>
<td>150</td>
<td>[40]</td>
<td>-384</td>
<td>$9.57 \times 10^{-7}$</td>
</tr>
<tr>
<td>$\text{TiAIN}$</td>
<td>cae</td>
<td>500</td>
<td>0.8</td>
<td>N$_2$</td>
<td>-80</td>
<td>160</td>
<td>[40]</td>
<td>-385</td>
<td>$9.89 \times 10^{-8}$</td>
</tr>
<tr>
<td>s-$\text{CrSiB}_2$</td>
<td>cae</td>
<td>500</td>
<td>3.0-3.2</td>
<td>N$_2$</td>
<td>-40 to -80</td>
<td>200</td>
<td>[40,41]</td>
<td>-314</td>
<td>$2.12 \times 10^{-7}$</td>
</tr>
<tr>
<td>$\text{AlCrN}$</td>
<td>sputtering</td>
<td>500</td>
<td>1.3</td>
<td>Ar/N$_2$</td>
<td>-160</td>
<td>-94</td>
<td>[1]</td>
<td>-398</td>
<td>$1.54 \times 10^{-8}$</td>
</tr>
<tr>
<td>$\text{y-TiAl}$</td>
<td>sputtering</td>
<td>$\leq 300$</td>
<td>0.4</td>
<td>Ar</td>
<td>-50</td>
<td>-</td>
<td>[42]</td>
<td>-464</td>
<td>$1.65 \times 10^{-7}$</td>
</tr>
<tr>
<td>$\text{HfSiB}_2$</td>
<td>sputtering</td>
<td>550</td>
<td>0.56</td>
<td>Ar</td>
<td>-40</td>
<td>0.4</td>
<td>[43]</td>
<td>-560</td>
<td>$4.11 \times 10^{-8}$</td>
</tr>
<tr>
<td>$\text{TiB}_2$-based</td>
<td>sputtering</td>
<td>550</td>
<td>0.4</td>
<td>Ar</td>
<td>-50</td>
<td>0.4</td>
<td>[44]</td>
<td>-543</td>
<td>$5.29 \times 10^{-8}$</td>
</tr>
<tr>
<td>$\text{CrSiB}_2$</td>
<td>sputtering</td>
<td>550</td>
<td>0.7</td>
<td>Ar</td>
<td>-40</td>
<td>0.4</td>
<td>[45]</td>
<td>-407</td>
<td>$1.50 \times 10^{-8}$</td>
</tr>
<tr>
<td>$\text{CrSi}_2$</td>
<td>sputtering</td>
<td>400</td>
<td>0.4</td>
<td>Ar</td>
<td>-50</td>
<td>0.4</td>
<td>[43]</td>
<td>-375</td>
<td>$7.24 \times 10^{-7}$</td>
</tr>
</tbody>
</table>
Acknowledgments

The financial support by the Austrian Federal Ministry for Digital and Economic Affairs, the National Foundation for Research, Technology and Development and the Christian Doppler Research Association is gratefully acknowledged (Christian Doppler Laboratory "Surface Engineering of high-performance Components"). We also thank for the financial support of Plansee SE, Plansee Composite Materials GmbH, and Oerlikon Balzers, Oerlikon Surface Solutions AG. In addition, we want to thank the X-ray center (XRC) of TU Wien for beam time as well as the electron microscopy center - USTEM TU Wien - for providing the SEM and TEM facilities. The authors acknowledge TU Wien library for financial support through its Open Access Funding Program.

Appendix

See Table A1 and A2.

References

[6] O.E. Hudak et al., The financial support by the Austrian Federal Ministry for Digital and Economic Affairs, the National Foundation for Research, Technology and Development and the Christian Doppler Research Association is gratefully acknowledged (Christian Doppler Laboratory "Surface Engineering of high-performance Components"). We also thank for the financial support of Plansee SE, Plansee Composite Materials GmbH, and Oerlikon Balzers, Oerlikon Surface Solutions AG. In addition, we want to thank the X-ray center (XRC) of TU Wien for beam time as well as the electron microscopy center - USTEM TU Wien - for providing the SEM and TEM facilities. The authors acknowledge TU Wien library for financial support through its Open Access Funding Program.

Appendix

See Table A1 and A2.

References

[6] O.E. Hudak et al., The financial support by the Austrian Federal Ministry for Digital and Economic Affairs, the National Foundation for Research, Technology and Development and the Christian Doppler Research Association is gratefully acknowledged (Christian Doppler Laboratory "Surface Engineering of high-performance Components"). We also thank for the financial support of Plansee SE, Plansee Composite Materials GmbH, and Oerlikon Balzers, Oerlikon Surface Solutions AG. In addition, we want to thank the X-ray center (XRC) of TU Wien for beam time as well as the electron microscopy center - USTEM TU Wien - for providing the SEM and TEM facilities. The authors acknowledge TU Wien library for financial support through its Open Access Funding Program.

Appendix

See Table A1 and A2.

References

[6] O.E. Hudak et al., The financial support by the Austrian Federal Ministry for Digital and Economic Affairs, the National Foundation for Research, Technology and Development and the Christian Doppler Research Association is gratefully acknowledged (Christian Doppler Laboratory "Surface Engineering of high-performance Components"). We also thank for the financial support of Plansee SE, Plansee Composite Materials GmbH, and Oerlikon Balzers, Oerlikon Surface Solutions AG. In addition, we want to thank the X-ray center (XRC) of TU Wien for beam time as well as the electron microscopy center - USTEM TU Wien - for providing the SEM and TEM facilities. The authors acknowledge TU Wien library for financial support through its Open Access Funding Program.