1. Introduction

The present study aims to determine the effect of Al on the corrosion resistance of nanostructured TiAlN coating deposited using a pulsed direct current plasma-assisted chemical vapor deposition (Pulsed-DC PACVD) technique. The nanostructured TiAlN coatings were synthesized with different Al-content values of by distinct precursor TiCl₄-AlClperiences, which showed that the deposited coating has a high corrosion resistance.

Also, a few advanced techniques such as plasma-assisted chemical vapor deposition (PACVD) and cathodic arc physical vapor deposition (Arc-PVD) have been adopted to deposit nanostructured coatings at low temperatures. According to the industrial requirements for the treatment of complicated geometry dies, the PACVD technique is a suitable method for deposition of TiAlN coating in 3.5 wt% NaCl solution. The results indicated that the polarization curves revealed more improved than the TiN and TiAlN coated samples, which showed that the TiAlN coated samples had an exceptionally high polarization resistance compared to the substrate and other coatings.

Also, a nanostructured TiAlN coating formed a dense, protective layer to protect the coating and its substrate from corrosion. The number of TiCl₄-to-TiCl₄ has improved the lifecycles of the coatings such as TiAlN, TiN, TiAlN(1) and TiAlN(3) coatings, whereas the Al content increases due to the solid solution effect. The Ti and Al atoms diffuse into the structure of the TiAlN coating, therefore, the resulted TiAlN coating is increased compared to TiN coating. As a result and due to the solid solution effect, there is a possibility that the hardness value will increase. On the other hand, the tribological properties of the coating will be changed by deformation of the coating's microstructure. Also, a nanostructured TiAlN coating forms a dense passive layer to protect the coating and its substrate from corrosion. The number of AlCl₃-to-TiCl₄ has improved the lifecycles of the coatings such as TiAlN, TiN, TiAlN(1) and TiAlN(3) coatings, whereas the Al content increases due to the solid solution effect. The Ti and Al atoms diffuse into the structure of the TiAlN coating, therefore, the resulted TiAlN coating is increased compared to TiN coating. As a result and due to the solid solution effect, there is a possibility that the hardness value will increase. On the other hand, the tribological properties of the coating will be changed by deformation of the coating's microstructure.
addition, the deposited coating polarization resistance is the highest value that agrees with the results 
obtained from the curves of Tafel polarization at the 
30% duty cycle. However, no activity was seen in the 
correlation between the electrochemical behavior and 
Al content of a nanostructured TiAIN coating depos-
ited by the PACVD method. In this study, therefore, the 
effect of AlCl₃/TiCl₄ precursor ratios on the microstruc-
tural and electrochemical behavior of nanostructured 
TiAIN coatings is investigated.

2. Experimental procedures

2.1. Substrate preparation and coating deposition

As a hot-work tool steel, AISI H11 (DIN 1.2343) including 4.7 at% chromium and 1 at% vanadium in the composition was utilized as the substrate. The samples were prepared in the form of bars measuring Ø 20 × 10 mm and Ø 50 × 10 mm. They were then exposed to quenching and tempering as appropriate heat treatment. A suitable microstructure was acquired by heating for 0.5 h at 1050°C, cooling in especial oil, and heating for 30 min at 550°C [11]. The specimens were nitried in a vacuum chamber using the plasma nitride (PN) process for 4 h at 485°C. The PN process was applied in an atmosphere containing 75 vol. % of hydrogen and 25 vol. % of nitrogen gas. The detailed parameters of the PN process are reported in Table 1.

For this purpose, a nanostructured TiN coating was first applied to the substrates as a buffer layer for about 1-h due to the assisting adhesion of a nanostructured TiAIN coating [9], followed by deposition of a nanostructured TiAIN coating for 150 min. Both coatings were continuously applied using the pulsed mode of the direct current PACVD technique (Plasmamanavar Co., Iran). Table 1 lists the parameters of the coating deposition in detail. The TiCl₄ and AlCl₃ materials as precursors were fed into the chamber reactor utilizing a quantity of carrier gas (e.g. H₂ gas). The TiCl₄ and AlCl₃ tanks were maintained around the boiling temperatures of 40°C and 170°C, respectively. In the present research, various ratios of AlCl₃/TiCl₄ (1, 2 and 3) were applied. A schematic of the PACVD process is illustrated in the Figure 1.

In this study, the plasma nitride-treated specimens were introduced as TiAIN with a nanostructured TiN/ TiAIN layer. The specimens were characterized with a field emission scanning electron microscope (FE-
SEM, ZEISS S4800), by X-ray diffraction (XRD, N8 
Bruker) utilizing Cu-Kα radiation at a scan speed of 0.02° 2θ/sec in the normal mode, and by electron 
probe micro-analysis (EPMA, CAMECA SX100) for deter-
mining the Cl content and Knoop micro-hardness indenter with a load of 25 g at ambient temperature.

2.2. Corrosion testing

The corrosion behavior of the substrates with TiN and 
TiAIN nanostructured coatings was investigated by 
electrochemical corrosion tests in a 3.5 wt. % NaCl 
solution. For this purpose, the corrosive medium was 
maintained at 25 ± 1°C. Electrochemical testing of all 
samples was carried out using a three-electrode flat 
cell, µAutolab Type III/FRA2 system controlled by com-
puter. The substrates and TiAIN specimens, an “Ag/ 
AgCl” in 3.0 M KCl, and Pt wire were utilized as working 
electrodes and counter and reference electrodes. The 
polarization tests started after 3600 s stabilization of 
the specimens in an “open-circuit condition” in order 
to reach a stable potential. The measurements were 
taken at a 1 mV/s scan rate over a potential ranging 
from ~ 0.25 V (vs. Ecorr) up to +800 mVAg/AgCl. Also, the 
electrochemical impedance spectroscopy (EIS) mea-
surements were carried out under “open-circuit condi-
tions” at a step rate of 10 point/decade in the applied 
frequency range of 100 kHz to 10 mHz by employing 
an alternating amplitude of 10 mV.

3. Results and discussion

3.1. Microstructure of nanostructured TiAIN 
coating

According to the precursor ratio, the composition sto-
ichiometry of Ti₁₋ₓAlₓN coatings obtained Ti₀.₈₁Al₀.₁₉N,
Ti$_{0.73}$Al$_{0.27}$N, and Ti$_{0.63}$Al$_{0.37}$N for AlCl$_3$:TiCl$_4$ ratios of 1, 2, and 3, respectively.

**Figure 2** depicts the XRD patterns of the nanos- tructured TiAlN coatings using the determined pre-cursor ratios shown in Table 1. The TiAlN coatings were grown with a strong (200) preferred orientation of the typical B1 (NaCl structure). The structural properties of the coatings in the different composition stoichiometry of Ti$_{1-x}$Al$_x$N coatings are various. That is because of the distinction between the atomic radii of aluminum ($R_{Al} = 0.143$ nm) and titanium ($R_{Ti} = 0.146$ nm). Figure 2 illustrates that the XRD patterns of the coatings removed toward higher angles with increases in the Al content as the AlCl$_3$/TiCl$_4$ ratios increased. This relocation was caused by an increases in the Al content in the composition of TiAIN coatings. According to the Bragg’s equation, the diffraction angle is increased by decreasing the d-value (inter-planar distance), because the Al atomic radius is smaller than that of Ti. Therefore, the lattice parameters of the coatings with different precursor ratios changed to affect the mechanical properties. In the Bragg’s equation, the wavelength and order of reflection are 1.5404 Å and 1, respectively. **Figure 3** presents the amount of the lattice parameters in the various coatings that are listed in detail in Table 2.

The full width at half maximum (FWHM) value for each sample was calculated from XRD graphs, after which the crystallite size of the films was measured by Scherer’s formula (relation (1)) [8]:

$$D = \frac{0.94 \times \lambda}{(\beta^2 - \beta_0^2)^{0.5} \cdot \cos \theta}$$  

(1)
where $D$ shows the crystallite size, $\beta$ reveals the FWHM of the diffraction peak (radian), $\beta_i$ depicts the peak broadened due to micro-strain, $\lambda$ shows the wavelength of the incident Cu-K$_{\alpha}$ X-ray and $\theta$ reveals the diffraction angle. Since the crystallite size is inversely proportional to FWHM, the larger the FWHM value, the smaller the crystallite size. Thus, the (200) peak of the XRD pattern of the TiAlN(3) coating is a somewhat wider than the others, which implies that the grain size of the TiAlN(3) sample is the smallest. The measured crystallite size of the coatings was calculated at 15–20 nm, as shown in the graph in Figure 3. It is shown that the crystallite size decreases with increases in the precursor ratio, because the Al content assists in developing a solid solution as an obstacle to the grain growth. Therefore, the crystallite size is obviously decreased by increasing the AlCl$_3$ content in the deposition process. Moreover, Figure 4 exhibits SEM images (a, c, and f) of TiAlN coatings under different conditions that clearly display the calculated nano-grain size. Moreover, according to Figure 4(b,d,e), despite the fact that the thicknesses of all the TiAIN coatings are about 3 µm, the types of growth displayed by the coatings are different. It is noteworthy that the equiaxed growth value of the TiAIN (2) coating is higher than that of the other coatings.

### 3.2. Mechanical properties of TiAIN nanostructured coatings

Figure 5 shows micro-hardness values for TiAIN coatings in different AlCl$_3$/TiCl$_4$ ratios, TiN coating, and an untreated specimen. For hardness evaluation, the suitable force (25 gr) was used depending on the thickness of the coating. Figure 4(b,d,e) shows that the thickness of the TiAIN(2) coating is about 3 µm. The results indicate that TiAIN coatings are significantly harder than the TiN nanostructured coating due to a solid solution of Al in the TiN coating [12]. But in the TiAIN samples, the hardness value verifies the different precursor ratios. There are some main effects to point out: (i) an interplanar spacing effect, (ii) a grain size effect and (iii) a chlorine content effect. Based on this investigation, effects (i) and (ii) enhance the hardness of the TiAIN nanostructured coatings but effect (iii) diminishes the properties. In the TiAIN(3) sample, effect (iii) is the predominant effect related to hardness.

Improvement of the hardness of the TiAIN coatings with different Al contents can be attributed to a reduction in the interatomic distance of the TiAlN structure. Since the Al atomic radius is smaller than that of Ti, it can be inferred that the interplanar spacing is reduced by adding Al content [5]. In addition, according to relation (2), the inter-planer distance ($d$) is related to the covalent energy ($E_h$) [4]:

$$E_h = Kd^{-2.5}$$

(2)

the enhancement value of the hardness is therefore ascribed to increases in the covalent energy value in the TiAIN nanostructured coatings. This indicates that TiAIN(3) would have the best mechanical properties when considering only the effect (ii). Figure 2(a) illustrates the changes in the grain size of TiAIN coatings in different AlCl$_3$/TiCl$_4$ ratios. According to the Hall–Petch relation [13], the hardness value increases with decreases in the grain size due to the strengthening of the grain boundary. Therefore, it is predicted that the hardness value increased continuously based on the experimental results, and that the hardness value

### Table 2. Details of the calculation of lattice parameter of TiN and TiAIN coatings.

|       | TiN | TiAIN(1) | TiAIN(2) | TiAIN(3) |
|-------|-----|----------|----------|----------|
| Diffraction Angle (2$\theta$) | 42.7 | 43.35    | 43.46    | 43.57    |
| Lattice Parameters (Å)       | 4.23 | 4.17     | 4.16     | 4.15     |

### Figure 3. Crystallite size and lattice parameters of TiAIN nanostructured coatings with different AlCl$_3$/TiCl$_4$ ratios.
of the coating diminished after a determined precursor ratio was reached due to proliferation of the chlorine content. The high hardness value is observed to be about 2820 HV for the TiAlN (2) sample.

The hardness value is improved by increasing the AlCl$_3$/TiCl$_4$ ratio up to 2, but the significant properties are debilitated after feeding a higher ratio of the precursor into the chamber. Figure 5 shows that chlorine content is added by increasing the ratio of the precursor. The chlorine as a disturbing element is gathered in the grain boundary. It decreases the mechanical properties, probably because the Cl element functions as a sliding board for the grains of the TiAlN nanostructured coating. It was previously shown that, in addition to the Cl content, the oxide content has the same effect on the deterioration of the mechanical properties of coatings [14]. Also, according to EPMA data, the stoichiometric of the TiAlN coatings attained Ti$_{0.81}$Al$_{0.19}$N, Ti$_{0.73}$Al$_{0.27}$N, and Ti$_{0.63}$Al$_{0.37}$N for TiAlN(1), TiAlN(2), and TiAlN(3), respectively.

### 3.3. Electrochemical measurements

Figure 6 depicts an evaluation of the open-circuit potential changes with exposure time in 3.5 wt. % NaCl solution for the substrate and TiN and TiAlN nanostructured coatings. It can be observed that the open-circuit potential values of the substrate and coatings varied slightly with increases in the exposure time after 1800 s, which demonstrates the proper surface conditions. A study by Elmkhah et al. [10] has shown that the open-circuit potential values of nanostructured TiAlN coatings deposited by the pulsed-DC PACVD technique were stabilized after 1800 s of immersion in the test solution. As seen in Figure 6, the stable open-circuit potential values of the TiN and

![Figure 4](image.png)

Figure 4. SEM images of the morphologies and cross-sections for different coatings: (a,b) TiAIN-1 coating, (c,d) TiAIN-2 coating, and (e,f) TiAIN-3 coating.
TiAlN nanostructured coatings are more positive than that of the substrate specimen, a result consistent with the reported results in the references [10].

The polarization curves of the substrate and the TiN and TiAlN nanostructured coatings in the test solution are shown clearly in Figure 7. An identical shape is shown for all of the curves, with a distinct Tafel behavior, the linear variation of the potential was seen as a function of the current density observed in all the situations. Similar potentiodynamic polarization plots are seen in 3.5 wt. % NaCl solution for nanostructured TiAlN coatings deposited by the pulsed-DC PACVD technique [10] and for TiN coatings deposited by the high-power impulse magnetron sputtering and direct-current magnetron sputtering methods [15]. As can be seen in Figure 7, the potentiodynamic polarization plots show that the passive behavior of the TiAlN(2) nanostructured coating improved more than that of the TiN, TiAlN(1) and TiAlN(3) coatings. Also, the these curves show that the TiAlN(2) nanostructured coating has an exceptional polarization resistance that is considered much higher in comparison to the substrate and TiN, TiAlN(1) and TiAlN(3) coatings. Therefore, a better passive film must have been formed on the surface of the TiAlN(2) nanostructured coating. The variations in corrosion current density ($i_{corr}$) and corrosion potential ($E_{corr}$) of all the samples in a 3.5 wt. % NaCl solution are presented in Table 3. The corrosion current density was calculated using Tafel extrapolation of the linear part for the cathodic branch back to $E_{corr}$ (with an accuracy of over 95%) [16]. As can be seen, the TiAlN(2) nanostructured coating shown the least corrosion current density compared with the substrate and other coatings.

Figure 8 indicates the Nyquist and Bode plots of the substrate and TiN and TiAlN nanostructured coatings in the test solution. All the Nyquist plots show imperfect semicircles. As the largest semicircle belongs to the
TiAlN (2) nanostructured coating, this coating has the highest total resistance. In order to emulate the EIS plots of the substrate and TiN & TiAlN nanostructured coatings in 3.5 wt. % NaCl solution, the equivalent electrical circuits (EECs) depicted in Figure 9(a, b) were used, respectively [10]. These EECs provided the best fitting with the EIS data of the substrate and TiN & TiAlN nanostructured coatings, as shown in Figure 8. In EEC with a one-time constant (Figure 9(a)), \(Q_{dl}\) is the constant phase element (CPE) of the double layer, \(R_{ct}\) is the charge-transfer resistance, and \(R_S\) stands for the solution resistance. Also, in EEC with two-time constants (Figure 9(b)), \(Q_{coat}\) shows the CPE of the coating, \(R_{pore}\) stands for the pore resistance, \(Q_{dl}\) shows the CPE of the double layer, and \(R_{ct}\) depicts the charge-transfer resistance [10,17,18]. The impedance function of a CPE \((Q)\) can be expressed as Equation (3) [19]:

\[
Z_Q = Y_Q^{-1} (j\omega)^{-n}
\]

where \(Y_Q\) reveals the \(Q\) constant, \(\omega\) shows the angular frequency, and \(n\) is a parameter related to surface roughness. Factor \(n\) (defined as a \(Q\) power) lies between 0.5 and 1.0 [20]. Therefore, the capacitance associated with \(Q\) can be calculated as Equation (4) [21]:

\[
C = \left[ Y_Q R_S^{(1-n)} \right]^{-1-n}
\]

The variations of the pore and charge-transfer resistances in addition to the coating and double-layer capacitances of the substrate and TiN and TiAlN nanostructured coatings in 3.5 wt. % NaCl solution are illustrated in Table 4. As can be seen, the TiAlN (2) nanostructured coating depicts the highest pore and charge-transfer resistances in comparison to other samples. Therefore, the calculated amount of polarization resistance \((= R_{pore} + R_{ct})\) is the highest for this nanostructured coating which shows the lowest corrosion current density. Moreover, it can be seen that the value of the double-layer capacitance for the TiAlN(2) nanostructured coating is the lowest, which depicts the lowest dissolution rate of the passive film and therefore the best passive behavior of this coating [22].

Generally, it was observed that the amount of chlorine in the coating increased with the relative chloride concentration. The best mechanical coating properties were found in TiAlN (2) nanostructured coating, which was formed using an AlCl\(_3\)-to-TiCl\(_4\) precursor ratio of 2:1. When a greater amount of the AlCl\(_3\) precursor was added, the mechanical properties were diminished as a result of the excessive increase in the chlorine concentration in the TiAlN (2) nanostructured coating. A similar trend was observed for the corrosion behavior by varying the composition of the TiAlN coatings. First, the corrosion resistance of the TiN coating is better than that of the uncoated substrate. Second, the corrosion resistance of the TiN coating was improved by increasing the content of Al as the solid solution. Increasing the precursor ratio (increasing the aluminum content) raised the corrosion resistance up to a value of 2:1 for AlCl\(_3\):TiCl\(_4\) ratio. Thus, the maximum corrosion resistance was achieved in the TiAlN (2) coating. With a further increase in the precursor ratio, however, the corrosion resistance was reduced. It seems that an excessive increase in chlorine in the chemical composition of the coating might lead to a decrease in the corrosion resistance.
Figure 8. (a) Nyquist and (b, c) Bode plots of the substrate and TiN and TiAlN nanostructured coatings in 3.5 wt. % NaCl solution.

Figure 9. Best equivalent electrical circuits used for modeling the experimental impedance data: (a) substrate and (b) TiN and TiAlN nanostructured coatings.

Table 4. Extracted data from electrical equivalent circuits.

|                | Substrate | TiN   | TiAIN(1) | TiAIN(2) | TiAIN(3) |
|----------------|-----------|-------|----------|----------|----------|
| $R_s$/kΩ.cm$^{-2}$ | 0.31      | 0.29  | 0.31     | 0.30     | 0.29     |
| $R_{ct}$/kΩ.cm$^{-2}$ | 1.72      | 9.48  | 12.96    | 44.28    | 11.34    |
| $C_{dl}$/µF.cm$^{-2}$ | 217.5     | 310.2 | 199.8    | 46.7     | 153.1    |
| $n_{dl}$          | 0.731     | 0.755 | 0.764    | 0.865    | 0.778    |
| $R_{pore}$/kΩ.cm$^{-2}$ | –         | 0.03  | 0.45     | 20.81    | 1.62     |
| $C_{coat}$/µF.cm$^{-2}$ | –         | 342.5 | 226.1    | 49.8     | 262.5    |
| $n_{coat}$        | –         | 0.650 | 0.685    | 0.681    | 0.646    |
4. Conclusion
In this study, the TiCl₄ precursor was used to deposit the TiN coating, but both the TiCl₄ and AlCl₃ precursors were used for the deposition of the TiAlN coating. The mechanical properties of TiAlN nanostructured coatings is improved by increasing the precursor ratio of AlCl₃/TiCl₄ up to 2, because it increases the solid solution hardening and reduces the crystallite size effects. The mechanical properties were diminished by further increases in the precursor ratio. This caused an increase in the amount of Cl-content in the stoichiometry of the coatings. In this case, the Cl element probably functions as a sliding board for the grains of the coating. Therefore, a AlCl₃/TiCl₄ ratio of 2 is appropriate for achieving the highest hardness in a TiAIN (2) sample, i.e., 2820 HK. Polarization and impedance spectroscopy curves reveal, moreover, that TiAIN (2) nanostructured coatings have exceptionally high polarization resistance compared to the substrate and other coatings.

Disclosure statement
No potential conflict of interest was reported by the authors.

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