Corrosion resistance of PVD hard coatings for tribological engineering applications

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Abstract. The present paper focuses on corrosion resistance of hard coatings deposited on tool steel via Physical Vapour Deposition (PVD) process. Three coating types were investigated – TiN, TiCN and DLC/TiAlN. An immersion corrosion test was performed on the PVD coated tool steels in accordance to ASTM G31 standard. With immersion corrosion test in aggressive media of 3.5% NaCl solution at ambient temperature of 33°C and exposure duration of up to 72 hours, the presence of the PVD coatings on the tool steel surface have improved the corrosion resistance of the tool steel surfaces. The results showed that the DLC/TiAlN coated tool steel has the highest corrosion resistance with corrosion rate of 36.58 mm/year, followed by TiCN and TiN coatings with corrosion rate of 42.10mm/year and 96.86 mm/year, respectively. The uncoated tool steel exhibits the lowest corrosion resistance of 140.61 mm/year. The present study suggests that the DLC coating deposited on SKD11 tool steel substrate has better stability than that of TiCN- and TiN-coated surfaces because the DLC can prevent the corrosion more efficiently than TiCN and TiN.

1. Introduction

Metal forming is an effective means of producing thousands of workpiece components. However, it does not come without the manufacturing challenge. A highly localized pressure of the long-term sliding surfaces between tool/workpiece contacts can cause mechanical stress, wear and corrosion problems on the tool surfaces, and thus calling for the need of coatings with high hardness and corrosion resistance. Physical Vapour Deposition (PVD) hard coating deposited onto tool steel substrate is one of the common methods to protect the tool steel substrate from surface damage, thereby prolong its lifetime in producing good product quality. A great number of hard coatings are available and they have been used in the industry for protecting the tool steel surface, such as TiN, CrN, TiAlN [1], AlCrN [2], TiC and TiCN [3,4].

Recently, Diamond-like Carbon (DLC) coating has gained acceptance in various industries, for example, automotive, medical, and tooling components, owing to its several attractive properties, including their low friction coefficient, high hardness, good corrosion resistance, good wear resistance, and protection of the tool steel surface. These properties make the DLC coating is suitable for many tribological applications in mechanical systems, such as valve train tappets, gears, and piston pins [5,6]. Unfortunately, depositing single DLC coating layer onto the tool steel surface alone is insufficient, since the single-layer DLC coating can easily be delaminated and shorten the tool lifetime [7,8]. Thereby, the single-layer DLC coating is impractical to protect the tool steel surface from severe wear and surface damage. As a result, this early coating failure could expose the tool steel substrate to corrosive environments, which expedite the corrosion behaviour of the tool steel substrate and reduce...
the lifetime of the tool. Introducing multi-layer coatings onto the substrate tool [9,10] had shown that the multilayer coatings were able to add the degree of freedom in tailoring the coatings’ property [11,12], but little information is available on the corrosion behaviour issues of the coating.

Even if the tool surfaces are coated with excellent protective hard coatings, the surface damage causing a slightly deeper scratches and the peel-off of the coating during metal forming operation could be one of the main factors contributing to corrosion, that generates a pathway for corrosive materials to reach out and react with the tool steel substrate [13] [14]. Therefore, the present paper examines the corrosion resistance of the hard tool coatings in aggressive media of NaCl solution. The investigated DLC/TiAlN coating will be studied and compared with the two commercially industrial hard coating, TiCN and TiN, for metal forming applications.

2. Materials and method

2.1. Materials

The tool steel material is a cold work tool steel SKD11 with high C and Cr contents that was alloyed with Mn, Mo, P, S, Si, and V. The tool steels were through-hardened, tempered to 60 HRC, and subsequently polished to a smooth surface roughness before the coating was applied. Table 1 presents the mechanical properties and the compositions of the tool steel used in the experiments.

| Components | Composition | Density $\rho$ (g/cm$^3$) | Poisson ratio $\nu$ | Elastic modulus $E$ (GPa) |
|------------|-------------|----------------------------|-------------------|--------------------------|
| Tool steel (AISI D2) | 1.4% C, 0.6% Mn, 11% Cr, 0.03% P, 0.03% S, 0.04% Si, 0.8% Mo, 0.2% V | 7.58 | 0.3 | 210 |

2.2. Coating

Two commercially available hard coatings, TiCN and TiN, and a new coating, a double-layer a-C:H type DLC/TiAlN, were selected and deposited on the tool steel substrates, see Figure 1. Their corrosion resistance were compared with the uncoated tool steel. The investigated coating films shown in Figure 1 was deposited onto the tool steel substrate (SKD11, with a surface hardness of 60 HRC) via a Physical Vapour Deposition (PVD) process. The tool steel roughness after coating was the same as before $\sim Ra = 0.02 - 0.1 \mu m$. The mechanical properties and surface characteristics of the coatings are presented in Table 2, where the uncertainty values represent the observed variations in the investigated areas.

![Figure 1: Structure of hard coatings deposited onto the tool steel SKD11 for the experiments.](image-url)

| Coating | Thickness (µm) | Hardness (HV) | Roughness $Ra$ (µm) |
|---------|----------------|---------------|---------------------|
| DLC/TiAlN | 4 ± 0.2 | 3,000 | 0.026 |
| TiCN | 4 ± 0.3 | 3,000 | 0.089 |
| TiN | 4 ± 0.2 | 2,000 | 0.092 |
2.3. Immersion corrosion test

Immersion corrosion test was performed to determine the corrosion resistance of the test specimens coated with the hard coatings according to ASTM G31 standard [15]. As seen in Figure 2, the scratches were made on the test specimen before the corrosion test to generate high porosity surface that serve as a pathway for corrosive materials to reach out to the SKD11 tool steel substrate. The materials and apparatus needed for the immersion corrosion test are shown in Figure 3. The test solution used in this immersion corrosion test was sodium chloride solution with concentration of 3.5% out of 100 mL distilled water. The experiments were carried out up to 72 hours in an oven with temperature of 45 ºC [16][17]. The mass of each specimen was measured before and after the experiments using analytical balance meter.

With assumption that a localized or an internal corrosion is not present before the experiments, the average corrosion rate in accordance to ASTM G31 is given in the following formula:

\[
\text{Corrosion rate} = \frac{KW}{ATD}
\]  

where, \( K \) is constant value (unit) to express corrosion rate \( 8.76 \times 10^4 \) mm/year [15], \( T \) is time of exposure in hours, \( A \) is area in cm\(^2\), \( W \) is mass loss in g and \( D \) is density in g/cm\(^3\).

![Figure 2: Scratches made on the test specimen by a 200 µm stylus tip made of diamond.](image)

![Figure 3: Test materials and apparatus needed for the corrosion test.](image)

3. Results and discussion

After 72 hours of immersion corrosion experiments on all four test specimens, including the three tool steel SKD11 substrates that were coated with TiN, TiCN and DLC/TiAlN, it can be seen that the corrosion has took place in some of the test specimens. As expected, the uncoated tool steel exposed to the immersion solution containing 3.5% NaCl has the highest mass and corrosion rate in comparison to the coated test specimens. This is because of no protective barrier against the corrosion agents on the uncoated tool steel. Therefore, the corrosive agents and substances like NaCl can easily reacted to the uncoated tool steel surfaces, causing it to degrade within a short period of time and exhibits more...
surface damage in comparison to the coated tool steel specimens. In the case of the tool steels coated with different hard coatings, TiCN tends to be corroded more easily compared to the other coatings. Among all coatings, DLC/TiAlN has the highest corrosion resistance. The double-layer DLC/TiAlN enhanced the corrosion behaviour of the coating and acted as an excellent protective coating against NaCl even there is some scratches present on the test specimen. As seen in Figure 5, pitting corrosion appeared on the side of scratch track. The location or area that pitting corrosion is more likely to occur is somewhere around crack or pores, which in this case, caused by the scratches made before the immersion corrosion test. It can also be observed that the pits most likely to grow downward, deep inside the scratch surface area. The observations on each test specimen after the experiments suggests that the DLC/TiAlN coating deposited on SKD11 tool steel substrate has better stability than that of TiCN- and TiN-coated surfaces. This indicates that the DLC can prevent the corrosion more efficiently than TiCN and TiN.

Figure 4: Measurements of mass loss (left) and corrosion rate (right) of each test specimen after the experiments.

Figure 5: Corrosion occurred on each test specimen after the experiments.

4. Conclusion
PVD hard coating is becoming an emerging alternative for the metal forming industry to produce large quantity of high quality metal components with improved performance in a more eco-friendly and safe way. In the present work, three PVD hard coatings were characterized in terms of corrosion behaviour. The DLC/TiAlN PVD coating showed the best compromise between good corrosion resistance, making it a promising choice for specific applications in metal forming. It is worth noting that the DLC/TiAlN PVD coating studied in the present work was in the form of a double layer with a thickness comparable to penetration depth. Despite this, its performance was quite encouraging and could be further improved with increasing thickness. In applications where high-localized loads and creeps are expected, it is preferable, as in the case of forming of advanced high strength steels, to choose double layer over multilayer PVD coating to avoid delamination. The same situation is valid for corrosion resistance, where the fragility of the layer can lead to cracks and consequently to localized attacks with a worsening of the protective properties, especially in aggressive environments.
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