

PLASMA NITRIDING AND PAPVD HARD COATING: A CRITICAL OVERVIEW OF DUPLEX COATING PROCESSING

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It has already been reported that duplex coatings, consisting of plasma nitriding of steel substrates and subsequent deposition of hard coatings by PAPVD (Plasma-Assisted Physical Vapour Deposition), can improve both wear and contact fatigue resistance and also the load support capability of steel substrates. However, the adhesion at the coating/substrate interface can be strongly affected by the presence of a compound layer, which can be produced during the plasma nitriding step. This compound layer can destabilise during coating deposition; its destabilisation would lead duplex coatings to exhibit poor adhesion. The aim of this work was to produce well-adherent PAPVD duplex coatings on AISI H13 steel substrates for tribological applications. In the first stage, duplex TiN coatings have been used to investigate the problem of compound layer destabilisation. An intermediate treatment consisting of cooling down the samples in vacuum and carrying out an Ar plasma-etching step has been developed. This treatment allows the production of duplex coatings with good adhesion strength by successfully avoiding compound layer destabilisation. It also elucidates a systematic approach to produce duplex coatings which are compound-layer-free, by removing this iron nitride layer through an Ar sputtering mechanism. The same adhesion strength was measured for duplex TiN coatings with nitrided cases consisting of mono-phase ϵ compound layer + diffusion zone and for duplex TiN coatings with nitrided cases consisting of a diffusion zone only. In the second stage, non-duplex and duplex (Ti,Al)N and Cr-N coatings were prepared and characterised by X-ray diffraction (XRD), glow discharge optical emission spectroscopy (GDOES), surface profilometry, nanoindentation and Knoop hardness measurements, scratch tests and scanning electron microscopy (SEM). The corrosion response of duplex (Ti,Al)N and Cr-N coatings and that of the uncoated substrate was also investigated using potentiodynamic tests. The corrosion results indicated that both duplex coatings improved the corrosion resistance of a hardened AISI H13 steel substrate, with the duplex Cr-N coating exhibiting the best corrosion response. The wear resistance of duplex and non-duplex (Ti,Al)N, Cr-N and TiN coatings was evaluated by micro-abrasive wear tests. Impact tests were also carried out to investigate their resistance to dynamic loading. Duplex (Ti,Al)N coatings exhibited the best wear resistance in micro-abrasive wear tests. The results obtained in such tests suggested the occurrence of abrasive wear by plastic deformation, with the hardest coatings displaying the lowest wear rates. The highest wear rates were recorded for duplex and non-duplex Cr-N coatings. However, a duplex Cr-N coating exhibited the best performance in impact tests using a tungsten carbide ball. The duplex Cr-N coating displayed the lowest elastic modulus among all tested coatings, which could be attributed to a small presence of an α -Cr metallic phase. This coated system also showed the smallest difference between the substrate and coating elastic moduli. For the duplex-coated systems, compressive subsurface stresses due to a nitriding treatment in conjunction to compressive stresses in the film (produced by the ion plating technique) probably lowered the magnitude of the tensile stresses in the affected zone. The better impact resistance obtained for duplex coatings in comparison to their non-duplex counterparts seems to be supported by such statement. The ambivalent behaviours exhibited by duplex (Ti,Al)N and Cr-N coatings in different tribological tests reveal the important role of selecting the most adequate coating for a given tribological application.

Keywords: PAPVD coatings, plasma nitriding, load-bearing capacity, elasticity property mismatch, micro-abrasive wear testing, impact testing.

1. INTRODUCTION

1.1. PAPVD duplex coating development

Failure of a hard coating/soft substrate system under many tribological conditions is rarely promoted by conventional wear. Instead, the tribological failure is often caused by debonding of the coating from the substrate (adhesive failure), fracture of the coating

(cohesive failure) or even by subsurface fracture (substrate failure). The effects of coating thickness and substrate properties on the initiation and development of the plastic zone, and also on the load-bearing capacity of a coating/substrate system, are extremely important aspects which should be considered when analysing the fracture behaviour of these systems. Duplex treatments consisting of a plasma nitrided

layer followed by a PAPVD hard coating have been developed in recent years to specifically improve the coating/substrate performance and, therefore, the lifetime of coated-components by changing the substrate properties. A combined treatment consisting of plasma nitriding followed by PAPVD deposition was invented by Berghaus in the early 1930's [1-3]. Since then many duplex coatings have been produced by means of a two-stage process: substrates are first plasma nitrided in a nitriding plant (conventional diode plasma nitriding) and subsequently coated in a PAPVD equipment. In the early 1980's, Korhonen and Sirvio [4] showed that it was possible to achieve a plasma-assisted nitriding treatment in a standard low-pressure PAPVD equipment. In 1983, a duplex treatment consisting of low-pressure plasma nitriding followed by an ion-plated TiN coating was sequentially produced in a PAPVD plant [5].

Finite element analyses of plastic deformation of TiN-coated systems, under normal contact with a rigid sphere [6], indicated that yielding of the coating was initiated at a higher load as the coating thickness and/or substrate yield strength were increased. Plastic deformation was mainly concentrated on the substrate and hardly occurred in the coating when this one was relatively thin and/or the substrate was relatively soft. As the coating thickness was increased and/or the substrate yield strength became higher, plastic deformation in the coating was more evident and the plastic zone in the substrate, at the interface, was smaller. Therefore, a high load-bearing capacity was achieved under these conditions. In this work [6], the load-bearing capacity was defined as the minimum load at which plastic deformation occurred in the coating/substrate system. The results clearly indicated that this parameter not only depended on coating thickness but also on both mechanical and physical properties of the substrate. Plots of the threshold load between elastic and elastic-plastic contact as a function of the coating thickness, for three specific TiN/substrate combinations, with different substrate materials possessing increasing mechanical strength (Al, Ti and HSS), were used to determine the absolute load-bearing capacity of a coating/substrate system. An index parameter, defined as the load ratio between the threshold load obtained for a given coating/substrate system and the threshold load obtained for the uncoated substrate, was also plotted as a function of the coating thickness. From this plot, it was possible to conclude that the critical thickness above which the coating gave rise to the load-bearing capacity was dependent on the substrate material; the stronger the substrate, the higher the coating thickness. Since a nitrided subsurface can increase the load-bearing capacity of coating systems, the development of duplex coatings was technologically triggered in order to improve the performance of thin PAPVD coatings by increasing the substrate hardness. A plasma nitriding treatment prior to coating deposition is an attractive alternative to changes in coating thickness, since substantial increases in this parameter adversely affect the coating/substrate adhesion. Thicker coatings are expected to have higher residual stresses and a

weaker coating/substrate adhesion will usually result in such systems.

2. RESULTS

2.1. TiN coating systems

Duplex TiN coatings were deposited on AISI H13 steel substrates (composition: 0.35% C, 5.00% Cr, 1.00% V, 1.50% Mo) in order to investigate the problem of compound layer destabilisation. A non-duplex TiN was also produced for comparison. Details regarding process parameters for the plasma nitriding step, coating deposition and intermediate treatment can be found elsewhere [13-14]. Duplex and non-duplex TiN coatings were subjected to Knoop microhardness measurements and scratch tests. Further information on these test parameters can be found in references [13-14]. Table I summarises the TiN coating systems that were produced.

Table I: Summary of TiN coating systems under investigation

| Coating/substrate system | Knoop hardness (kg mm ⁻²)/substrate | Compound layer structure |
|----------------------------|---|---|
| Duplex TiN1 (D TiN 1) | Annealed/370 ^a | Mono-phase ϵ (Fe ₂₋₃ N) |
| Non-duplex TiN1 (ND TiN 1) | Hardened/830 | ----- |
| Duplex TiN2 (D TiN 2) | Hardened/830 | Mono-phase ϵ (Fe ₂₋₃ N) |
| Duplex TiN3 (D TiN 3) | Hardened/830 | None |

^a After carrying out a plasma nitriding in an annealed AISI H13 steel for 120 min, the substrate Knoop hardness was increased to ~1200 kg mm⁻².

Table II: Summary of Knoop microhardness and scratch test results carried out in the TiN coating systems

| TiN coating system | Knoop hardness (kg mm ⁻²) | Scratch adhesion critical loads | |
|--------------------|---------------------------------------|---------------------------------|---------------------|
| | | L _{C1} (N) | L _{C2} (N) |
| D TiN 1 | 2433 ± 10 | 48 ± 2 | >188 |
| ND TiN 1 | 2935 ± 80 | 25.7 ± 3.2 | 52.3 ± 2.9 |
| D TiN 2 | 2999 ± 40 | 37.7 ± 3.3 | 152.8 ± 9.3 |
| D TiN 3 | ----- | 37.5 ± 3.8 | 150.5 ± 7.1 |

Results from Knoop microhardness and scratch tests, which are shown in Table II, indicated that:

(1) A plasma nitriding treatment prior to coating deposition substantially increased the substrate hardness. By carrying out a duplex treatment on annealed AISI H13 steel substrates, a 6-fold increase in surface hardness was achieved. (2) The duplex treatment increased the load support for the hard TiN coating and, as a result, higher adhesion critical loads were recorded for the duplex TiN coatings in comparison to the non-duplex TiN coating. (3) The same adhesion strength was measured for duplex TiN coatings with nitrided cases consisting of mono-phase ϵ compound layer + diffusion zone and for duplex TiN coatings with nitrided cases consisting of a diffusion zone only. (4) It seems that the presence of a

compound layer is not detrimental for achieving good adhesion strength on duplex coatings. If compound layer destabilisation is avoided, well-adherent duplex coatings can be produced.

2.2. Tribological response of duplex and non-duplex (Ti,Al)N, TiN and Cr-N coatings in micro-abrasive wear and impact tests

Non-duplex and duplex (Ti,Al)N, TiN and Cr-N coatings (plasma nitriding + PAPVD coating) were deposited onto hardened AISI H13 steel substrates by ion plating using electron beam evaporation. The duplex specimens were plasma nitrided and PVD-coated in a continuous process. Further details regarding plasma nitriding, coating deposition and characterisation can be found in references [13,15]. The micro-abrasive [13,16] and impact [13,17] wear responses of these coatings were evaluated and they could be related to some key properties, such as hardness and the difference between the coating and substrate elastic moduli (elastic property mismatch) [18]. The major results obtained from micro-abrasive wear are shown in Tables III.

Table III: Micro-abrasive wear test results: coating and substrate wear coefficients (k_c and k_s)

| Specimen | k_c and C.I. (95%) ($\times 10^{-13} \text{ m}^3 \text{ N}^{-1} \text{ m}^{-1}$) | | k_s and C.I. (95%) ($\times 10^{-13} \text{ m}^3 \text{ N}^{-1} \text{ m}^{-1}$) | |
|---------------------|---|-------------|---|-------------|
| Non-duplex (Ti,Al)N | 2.36 | 2.20-2.55 | 9.62 | 8.22-11.61] |
| Duplex (Ti,Al)N | 1.44 | 1.34-1.54 | 8.84 | 8.63- 9.07 |
| Non-duplex TiN | 7.27 | 7.15-7.39 | 9.65 | 9.54-9.76 |
| Duplex TiN | 3.86 | 3.81-3.90 | 8.75 | 8.46-9.05 |
| Non-duplex Cr-N | 27.79 | 22.13-38.09 | 9.84 | 9.58-10.12 |
| Duplex Cr-N | 18.11 | 16.63-19.86 | 9.53 | 9.39-9.68 |
| Uncoated substrate | ----- | ----- | 9.40 | 9.00-9.82 |

In terms of micro-abrasive wear resistance, all coating systems, except for both duplex and non-duplex Cr-N coatings, exhibited higher micro-abrasive wear resistance than the uncoated substrate. The duplex (Ti,Al)N showed the highest micro-abrasive resistance (lowest k_c wear coefficient), followed by the non-duplex (Ti,Al)N, duplex TiN, non-duplex TiN, duplex Cr-N and non-duplex Cr-N. Although the duplex treatment provides an improvement in terms of abrasive wear (the duplex-treated samples showed higher micro-abrasive wear resistance in comparison to their non-duplex counterparts), the choice of the PAPVD coating still plays an important role in terms of improving the micro-abrasive wear resistance. For instance, a non-duplex (Ti,Al)N coating exhibited a higher micro-abrasive wear resistance than a duplex TiN coating. Both duplex and non-duplex Cr-N displayed the lowest wear resistances to abrasion. Their non-favourable performance in terms of micro-abrasive wear could be attributed to their relatively lower hardness (in comparison to that of the other

coatings and to the SiC particles) in combination with a 2.0-2.5 μm film thickness, which made these coatings prone to be penetrated by the SiC particles (4-5 μm in size), with subsequent coating delamination [16]. The coating wear coefficients (k_c) were found to decrease with increasing coating hardness for the same sort of abrasive, indicating a mechanism of abrasive wear by plastic deformation [16]. Such mechanism was also confirmed by SEM inspection of the wear craters [16]. The coating hardness (H) and modified elastic modulus (E'), which were measured by nanoindentation [18], are shown in Table V. A direct correlation between hardness and micro-abrasive wear resistance could be established, with the hardest coating displayed the lowest wear rates [18].

In terms of impact wear resistance, the best performance was achieved by the duplex Cr-N coating, which exhibited only cohesive failures even after 5×10^4 impacts (Table IV). Compared to duplex (Ti,Al)N and TiN coatings, the duplex Cr-N coating demonstrated a greater ability to follow substrate deformation, showing comparatively less cohesive failures [13,17]. In general terms, the duplex treatment increased the impact wear resistance of non-duplex (Ti,Al)N, TiN and Cr-N coatings [13,17]. The nitrided case seemed to have minimised substrate deformation under the hard PVD coating so that fewer cohesive failures occurred in the duplex coatings. Conversely, all non-duplex coatings exhibited adhesive failures after a certain number of impacts. The worst performance in terms of impact wear was achieved by the non-duplex TiN coating and, after 5×10^4 impacts, a large number of adhesion failures could be observed [13,17]. For the duplex-coated systems, compressive subsurface stresses due to a nitriding treatment in conjunction to compressive stresses in the film (produced by the ion plating technique) certainly lowered the magnitude of the tensile stresses in the affected zone. This explains the better impact resistance of duplex coatings in comparison to their non-duplex counterparts. A direct correlation between impact wear performance and elastic property mismatch (Table V) could be established [18], with the duplex Cr-N coating, having the smallest difference between coating and substrate elastic, exhibiting the best impact wear response. Conversely, the non-duplex TiN coating, which displayed the highest elastic property mismatch, was outperformed by all other coatings in impact tests. The smallest elastic property achieved by the duplex Cr-N coating results from a lower coating elastic modulus, which could be attributed to a small presence of an α -Cr metallic phase [15,18], and from a higher substrate elastic modulus, which was increased after the plasma nitriding treatment. By comparing two different tribological tests (micro-abrasive wear and impact tests), it can be easily noticed that different PAPVD coatings provided different responses. Thus, wear mechanisms (i.e., wear by plastic deformation or by brittle fracture) and test conditions should be previously evaluated in order to select a suitable coating for a given tribological application.

Table V: Average values of H and E' (modified E) for duplex and non-duplex coating systems. The elastic property mismatch is also shown.

| Specimen | E' _{average} (GPa) | H _{average} (GPa) |
|---------------------------|-----------------------------|----------------------------|
| Non-duplex (Ti,Al)N | 362 ± 13 | 36.5 ± 2.5 |
| Duplex (Ti,Al)N | 388 ± 15 | 37.5 ± 2.3 |
| Non-duplex TiN | 411 ± 8 | 33.3 ± 2.1 |
| Duplex TiN | 371 ± 8 | 31.2 ± 1.2 |
| Non-duplex Cr-N | 323 ± 11 | 34.5 ± 2.8 |
| Duplex Cr-N | 281 ± 6 | 27.4 ± 2.0 |
| H13 steel substrate | 229 ± 5 | 9.0 ± 0.2 |
| Plasma nitrided substrate | 243 ± 5 | 17.2 ± 1.2 |

The major conclusions regarding the tribological response of PAPVD coatings are:

1. Duplex treatments consisting of plasma nitriding followed by PAPVD deposition are effective in improving both micro-abrasive and impact wear resistance of non-duplex PAPVD coatings and uncoated AISI H13 steel substrate.

2. In terms of abrasive wear mainly caused by plastic deformation, the most important parameter to improve the wear resistance of PAPVD coated systems is a higher coating (and subsurface) hardness in comparison to that of the abrasive. Thus, duplex PAPVD coatings are expected to provide a superior performance in tribological contacts where wear is mainly caused by abrasive particles and material removal takes place by a plastic deformation mechanism.

3. In terms of impact wear, an important parameter in the tribological response is the elastic property mismatch (i.e., the difference between coating and substrate elastic moduli). The smaller this difference, the higher the impact wear resistance is. Therefore, duplex PAPVD coatings are promising coatings to be used under dynamic load conditions, since the plasma nitriding treatment increases the substrate elastic modulus and coatings with low elastic modulus can be produced by properly controlling PAPVD deposition parameters. Another advantage of duplex coatings in such tribological contacts is the presence of subsurface compressive stresses, which allied to compressive residual stresses in PAPVD coatings, helps in lowering the magnitude of the tensile stresses in the affected zone.

3. CONCLUSIONS

This paper aimed at highlighting the beneficial aspects of a duplex treatment consisting of plasma nitriding followed by PAPVD hard coating. The challenges in terms of duplex coating processing were also discussed and directions in order to produce well-adherent coatings (and then overcome problems regarding compound layer destabilisation during PAPVD deposition) were also given. The advantages of using a sequential duplex treatment in a PAPVD plant were also highlighted. For this particular process, an intermediate treatment consisting of cooling down the samples in vacuum and carrying out an Ar plasma-etching step, was also developed in order to provide duplex coatings with good adhesion strength. This was achieved by successfully avoiding compound layer

destabilisation. The intermediate treatment also allowed the production of duplex coatings that were compound-layer-free, by removing this iron nitride layer through an Ar sputtering mechanism. Moreover, it was shown that the presence of a mono-phase ϵ -Fe₂-₃N compound layer was not detrimental to the coating/substrate adhesion, if process parameters were carefully controlled to avoid its destabilisation. In general terms, benefits from a sequential duplex treatment were achieved in terms of increasing the load support for PAPVD hard coatings and, thus, the load-bearing capacity of the system. Duplex coatings also showed a superior performance than their non-duplex counterparts and hardened AISI H13 steel substrate in micro-abrasive and impact wear tests, indicating that the former coatings are more suitable to be used in such tribological applications.

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