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Improvement of the Corrosion Resistance of PVD Hard Coating/Substrate Systems - Recent Developments -

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Abstract

Hard coatings play a continuously increasing role in the field of tribology as well as for decorative applications. In both areas they are often also exposed to corrosive media. While especially hard nitride coatings show a high corrosion resistance for themselves, hard coating/substrate systems may suffer from a severe corrosion attack due to the defects in the coating structure (pores, pinholes) resulting from the PVD-typical film morphology. While a huge number of investigations cover the tribological properties, only limited studies deal with the corrosion behaviour of coating substrate systems and attempts are made to improve their corrosion resistance. The present paper shortly describes the corrosion mechanisms and reports characteristic examples of the system behaviour. Special emphasis is laid on recent investigations to improve the corrosion resistance by alloying, interlayers or multilayered coating structures.

Key words : Hard Coating, Corrosion

1. Introduction

Because of their tribological performance hard coatings are most often used to reduce wear and friction. This application results in a drastic increase of the life time of parts and tools. Due to their attractive and variable colours they are also frequently used for decorative applications like watch cases, eyeglass frames, door plates and sanitary parts¹⁻⁵). In the latter cases the gold- or brass-like colours of TiN and ZrN or the grey, dark-blue or black

colours of TiC, (Ti, Al)N or C films are the base of developments in design and technology. They, furthermore, exhibit good biological compatibility, the base for their use as coatings for prostheses or medical instruments⁶⁻⁸). Many of these applications are also connected with corrosive attack, e.g. by technical reagents or corrosive gaseous or liquid environments. This may reduce the lifetime of coated parts drastically, even if the coating materials themselves are characterised by a high corrosion resistance.

Vapour-deposited coatings mostly are chara-

cterised by pores and pinholes through which a corrosion attack on the (most often less noble) substrate material takes place. The following survey will give examples on the effects of processes and process parameters as well as on possibilities to improve the corrosion resistance especially also reporting more recent literature.

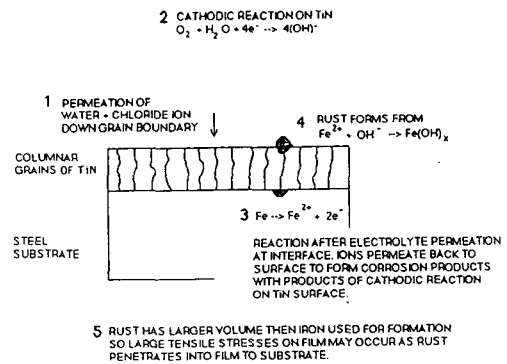
2. Corrosion and corrosion-tests

Corrosion is defined as "attack on a material by its reaction with the environment and the resulting deterioration of the materials properties"^{9, 10}. Most often it is related to an electrochemical reaction with a liquid or gaseous medium.

Concerning corrosion, generally a distinction has to be made between a homogeneous attack of the complete surface area and a local corrosion attack. This means for coating/substrate systems that either the total area of the coatings is attacked (as in the case of so-called sacrificial coatings) or the substrate is locally corroded at damaged areas, depending on the nobility ratio of coating and substrate material. As already mentioned, hard coatings mostly form the more noble component and the substrate material or another less noble interlayer will face the corrosive attack, i.e. galvanic corrosion. The reactions are schematically illustrated in Fig. 1 for a TiN coating on steel in an electrolyte ($H_2O + NaCl$). Water and Cl^- ions penetrate through pores and the iron of the steel-based material is dissolved and Fe^{2+} ions diffuse towards the coating surface forming rust by the reaction with OH^- ions. Voids are formed underneath the coating¹¹. This corrosion type is also observed with brass or zinc substrate materials.

The pores and pinholes known from the structure zone models exhibit a remarkable density. A strong increase of the pore density with decreasing film thickness is observed. A similar, but lower defect density has also been found in PACVD coatings. Fig. 2 illustrates this marked increase in defect density with decreasing film thickness¹². The pinhole area for $0.1 \mu m$ magnetron-sputtered TiN was calculated to 3% ¹³.

The corrosion behaviour is studied on one



Schematic diagram of the proposed corrosion model for coated materials.

Fig. 1 Corrosion of hard coating/substrate systems (schematically)

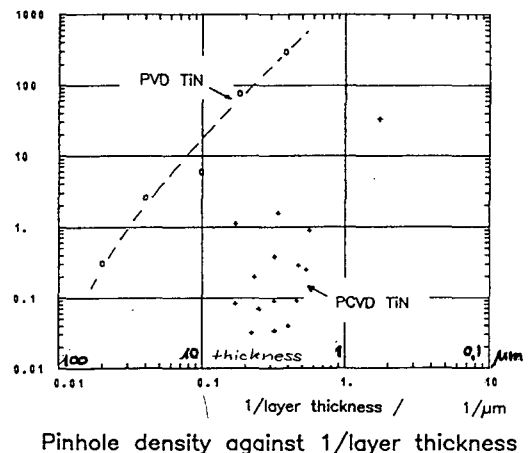


Fig. 2 Pinhole density as a function of coating thickness¹².

hand by application-oriented so-called short-time test representing the exposure to a specific gaseous climate or a liquid (salt spray test, Kesternich test, immersion tests, etc.) with subsequent qualitative or semi-quantitative evaluation of the corrosion damage. On the other hand electrochemical tests in corrosive media yield specific data on the behaviour of the system¹⁴⁻¹⁶. The advantage of the latter methods is that only the kinetics is changed and not the mechanism itself. In the following the corrosion behaviour of the coating/substrate systems shall especially be characterised by current density-potential measurements. Earlier literature on hard coating/substrate systems is summarised in¹⁶.

3. Corrosion studies with hard-coated parts

The above-mentioned relations are illustrated in Table 1 reporting corrosion potentials E_{corr} and corrosion current densities I_{corr} for some TiN and ZrN coatings¹⁷. All samples with hard coatings on glass show positive E_{corr} values, those of ZrN being lower than those of TiN. The nitride coatings on steel substrates show almost

the same (negative) values given by the steel substrate. The corrosion current is strongly increased, too, when compared with coating/glass systems. This reflects the high contribution of the substrate corrosion to the total corrosion process.

The effect of the coating thickness is, as an example, illustrated for PACVD-TiN coatings in Fig. 3¹⁸. Only thicknesses higher than about $14\mu\text{m}$ guarantee a satisfying corrosion resistance. The I-U curves for coatings $< 5\mu\text{m}$ thick

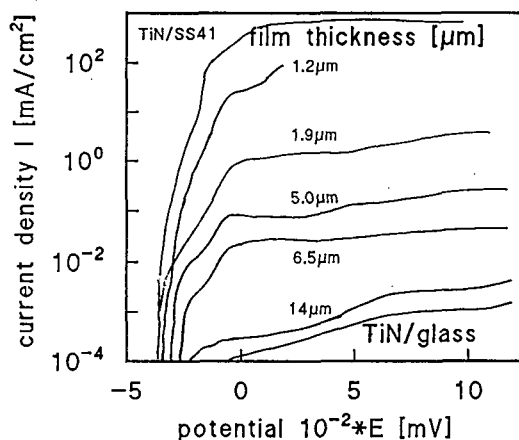


Fig. 3 Effect of coating thickness on I-U curves for PACVD-TiN in HCl 18.

Table. 1

Process	System	Electrolyte	E_{corr} [mV]	I_{corr} [$\mu\text{A}/\text{cm}^2$]
Activated react. evaporation	TiC/glass	1 N HCl	+ 200	0.15
	Ti/glass	--" --	- 610	6
Sputtering	TiN/glass	0.1 N H ₂ SO ₄	+ 270	0.0055
	TiN/C45	--" --	- 380	3.5
	C45	--" --	- 440	2600
PVD	TiN/glass	0.1 N H ₂ SO ₄	+ 240	0.01
	C45	--" --	- 440	2600
Sputtering	ZrN/glass	0.1 N H ₂ SO ₄	+ 50	0.01
	ZrN/C45	--" --	- 450	1
PVD	ZrN/glass	0.1 N H ₂ SO ₄	+ 110	0.01

give only a partial corrosion resistance. Such thicknesses, however, are in the range of practical applications, especially decorative coatings most often are in the range of $1\mu\text{m}$. The strong increase of the pinhole defect density was recently proved for very thin magnetron-sputtered TiN coatings on SUS304 steel. The decreasing current density can easily be seen in Fig. 4¹³⁾.

The total character of the I-U curves, of course, strongly depends on the substrate material, as this is in contact with the corrosive medium through the coating defect (see e.g.^{16, 48)}.

The effect of the PVD process and its actual parameters can easily be described by the influence of these parameter values and the process characteristics. All means which lead to the deposition of denser coating structures improve the corrosion resistance of the system. E.g., a $3\mu\text{m}$ thick PVD-TiN coating exhibits a very similar behaviour as a $7\text{--}8\mu\text{m}$ CVD-TiN coating (Fig. 5)¹⁹⁾. Especially the substrate temperature affects the coating morphology in accordance with the structure zone models of Movchan and De-

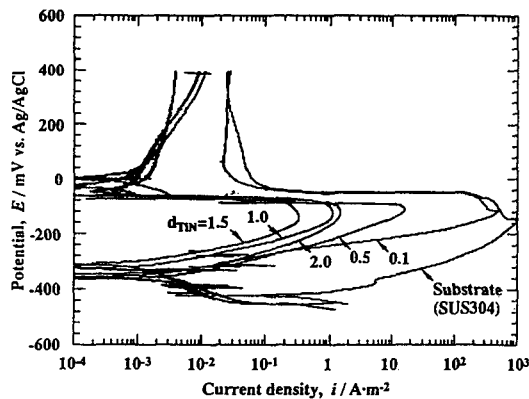


Fig. 4 Effect of coating thickness on I-U curves for magnetron-sputtered TiN on SUS304 steel 13.

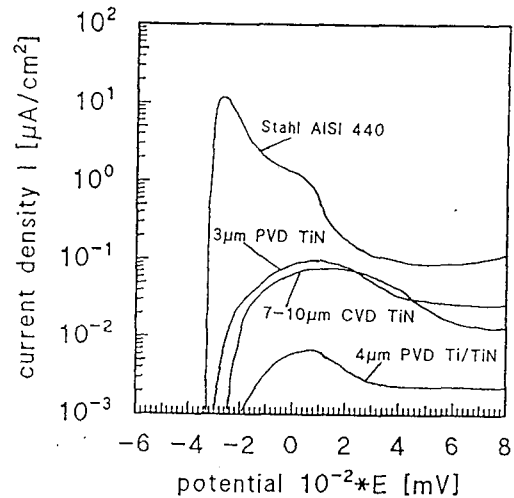


Fig. 5 I-U curves for PVD- and CVDTiN 19.

mchisin²⁰⁾ and Thornton²¹⁾. The I-U curves of ion-plated TiN (hollow cathode arc discharge evaporation) on ball bearing steel shows a strong decrease of the current density with increasing substrate temperature (Fig. 6)²²⁾. Similarly, an ion plating process results in a denser structure of PVD coatings when compared with vacuum evaporation²³⁾. Such an improvement with respect to the corrosion current density by applying PVD processes which are characterised by a higher percentage of ions is also demonstrated by BN coatings on Al substrates when deposited by ion beam assisted deposition (IBAD) and sputtering, respectively²⁴⁾. An other factor influencing the corrosion behaviour of coating substrate systems is the plasma power density, an increase of which reduces E_{corr} , I_{corr} and the corrosion current density²⁵⁾. Obviously this is caused by a change in the chemical composition of the coatings. The influence of the nitriding process was recently studied by comparing for (A) solid Ti, (B) sputtered Ti

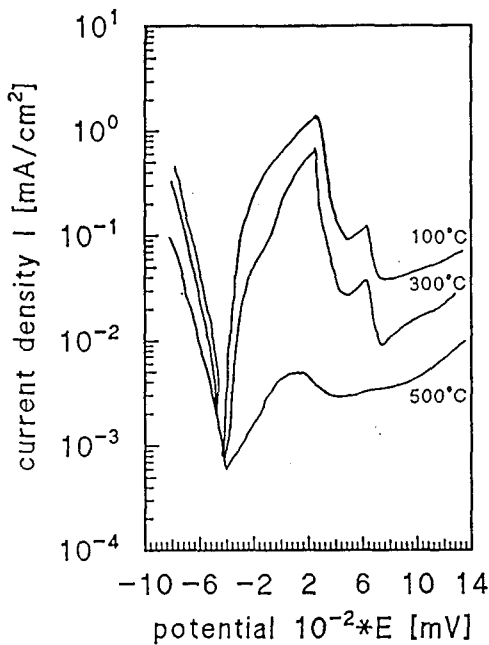


Fig. 6 Effect of substrate temperature on I-U curves of ion-plated TiN in 1 N H₂SO₄. 22.Fig

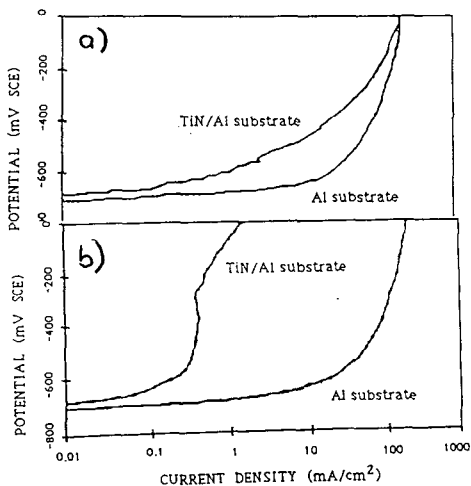


Fig. 7 TiN on Al substrates of different roughness resulting in complete and incomplete coverage 27.

coatings, (C) nitrated solid Ti, (E) nitrated Ti coatings and (F) reactively sputtered TiN coat-

ings. The I-U curves in 3% NaCl solution show a slight increase of the current density in the order A through D, but the sputtered TiN films are quite close to the uncoated AISI substrate material²⁶⁾.

The surface roughness of the part to be coated also significantly influences the corrosion behaviour of the system. A higher substrate surface roughness results in a less complete coverage of the substrate with the coating material because of shadowing effects during the PVD film growth. This is illustrated in Fig. 7 for TiN on aluminium²⁷⁾. A reduced number of coating defects with decreasing surface roughness was also observed for CrN on steel²⁸⁾.

A large number of investigations discuss the effect of alloying additives in binary (nitride) coatings. This effect can be based on a "chemical" interaction increasing the corrosion potential of the coating material. There is, however, also a "physical" effect, i.e. denser and more fine-grained coatings are formed. As examples, the following studies shall be cited: (Ti, Pd)N²⁹⁾, (Ti, Si)N³⁰⁾, (Ti, Cr)N^{31-33, 39)} or (Ti, Y)N³⁴⁾. In the case of (Ti, Al)N the Al-rich coatings, however, show a slightly increased porosity and, hence, a worse corrosion behaviour³⁵⁾. This was recently proved by³⁶⁾ with magnetron-sputtered TiN and (Ti, Al)N coatings. In contrast, electrochemical impedance measurements showed the best behaviour of Ti_{1-x}Al_xN film prepared by dynamic ion beam mixing for x=0.3³⁷⁾.

The addition of nonmetallic elements is well-known for carbonitrides, e.g. a systematic variation of the N/C ratio in the order TiN→TiC results in an increase of the corrosion current with decreasing N content³⁸⁾. Similar studies

were also made for Cr(C, N) coatings⁴⁰. Zr(B, N) coatings on steel exhibit a slight decrease of the current density and a somewhat improved corrosion resistance compared with ZrB coatings⁴¹. A number of M-B-N coatings was deposited on alumina yielding the polarisation curves of the coating material themselves in 5 N H₂SO₄ (Ti-Si-B-N, Ti-Si-C-N, Ti-C-N, Ti-Al-C-N)⁴².

4. Improvement of the corrosion behaviour by interlayers and multilayers

As illustrated in the above chapter, the corrosion attack on hard-coated parts can be reduced by a denser coating structure resulting from well-known and well-defined variations of the vapour deposition process and its parameters. Another possibility for an improvement of the corrosion resistance is the deposition of interlayers and/or multilayered coatings. Such interlayers may be deposited by physical or electrochemical processes (PVD, ECD). Some examples will be given in the following.

4.1 PVD interlayers

The deposition of PVD interlayers of metals more noble than the substrate material can reduce the corrosion attack. Such solutions are well-known from electroplated multilayer systems. Additionally, the number of pores and pinholes can be reduced, when new coating structures of the hard coatings are formed on the top of the interlayer. Marked improvements are, e. g. found for 4 μ m thick Ti/TiN-PVD coatings when compared with 3 μ m PVD-TiN¹⁹. Similar results are reported for Ti/TiN on iron substra-

tes⁴³. The benefit of the Ti layer is additionally attributed to its passivation. Other promising PVD-interlayers are PVD-Ni or PVD-Cr⁴⁴. Very recently Cr, CrN or Cr/CrN are used as barrier layers against dezincification of Cu alloys during the corrosion reaction⁴⁵.

A marked improvement also results from an intermediate plasma etching of the PVD-TiN hard coating. Such a process additionally supports the new formation of nuclei, reducing the throughpores in the Ti/TiN layer system. Fig. 8 illustrates this effect showing the I-U curves of sputtered TiN coatings with a Ti interlayer with and without intermediate sputter etching together with the brass substrate and TiN on glass⁴⁶

4.2 PVD multilayers

The above-mentioned reduction of the corrosion attack by an interlayer can even be improved by the deposition with a "pulsed" N₂

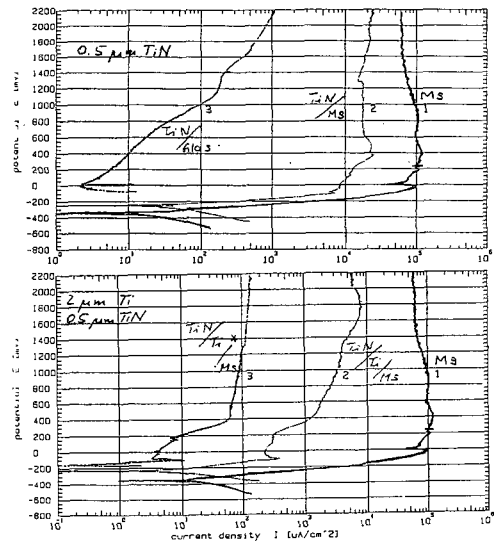


Fig. 8 Effect of intermediate plasma etching after Ti interlayer deposition in 0.8M NaCl solution 46.

flow during the triode sputtering process yielding layers richer and poorer in their nitrogen content. Especially successful seemed layer sequences of ϵ -Ti₂N and TiN on C45 steel. Zr/ZrN multilayers did not show an improvement when compared with a ZrN coating⁴⁷. Other studies with Ti/TiN, Zr/ZrN, Hf/HfN and Nb/NbN multilayered coatings deposited by magnetron sputtering and electron beam evaporation show marked improvements⁴⁸. More recently, the following systems have been studied to some extent: Ti/TiN^{49, 53}, Cr/CrN^{53, 54} and TiN/C⁵⁵. The number of multilayer sequences varies from 3 to several hundreds for total coating thicknesses of few microns. The reduced corrosion current density of $3 \times$ (Ti/TiN) sputtered film (in 1 M H₂SO₄) is counter-balanced by a subsequent deformation of the steel samples caused by defect formation during the deformation process⁴⁸.

Multilayered coatings with superlattice structures seem also to be promising for the improvement of the corrosion resistance but are not yet studied with this respect.

4.3 ECD interlayers

Especially in the field of decorative hard coatings, electrochemically deposited interlayers represent the state-of-the-art. The substrate materials coated with ECD-Ni or ECD-Ni-Pd interlayers are brass, German silver, zinc die cast as well as steel⁵⁶⁻⁶³. These ECD coatings show a lower porosity when compared with PVD coatings. In most cases, however, they are thicker (5-20 μ m) than the usual decorative PVD hard coatings ($\leq 1 \mu$ m). An advantage of the ECD coatings is also the tailoring of the sur-

face morphology. A certain disadvantage is the need of two deposition processes ("wet" electroplating and "dry" PVD). Furthermore, structural changes and partial evaporation of interlayer components may occur during the subsequent PVD coating processes due to its elevated substrate temperatures. In principle, however, it makes sense to divide the functions of a coating substrate system into an easy workable substrate (brass), a corrosion resistant (and structurally designed) interlayer (Ni), a wear-resistant decorative hard coating (TiN, ZrN, (Ti, Al)N) and, in part, a sputtered gold finish for increased lustre. In the following examples the discussion of such a system behaviour shall be restricted to the I-U curves, even if a variety of tests are applied especially the application-related so-called shorttime test (salt spray etc.)

The decrease of the corrosion current density of a brass substrate by a 10 μ m thick ECD-Ni interlayer and an additional 1 μ m thick sputtered TiN coating is shown in Fig. 9. It can be seen that the effect of the Ni interlayer is even more improved by the TiN top layer⁶⁴. Similar effects are also found for electroless Ni-P interlayers^{65, 66}. Also the following combinations are

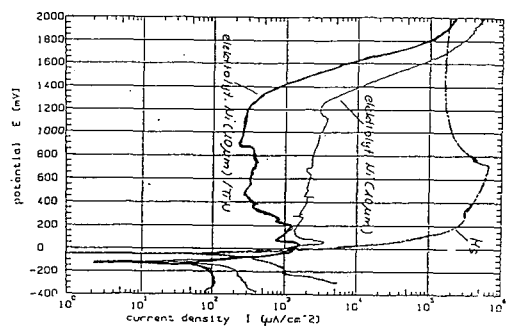


Fig. 9 Effect of an ECD-Ni interlayer on the I-U curves of TiN-coated brass substrates in 0.8M NaCl solution⁶⁴.

commercially used: Sn-Ni(ECD)/Zr(PVD)⁶⁷, in part with an additional Ni(ECD underlayer instead of the Zr interlayer⁶⁸). Other layer series are semibright Ni(ECD)/bright Ni(ECD plus Sn-Ni(ECD))⁶⁹ or Pd-Ni(ECD)⁷⁰ interlayers followed by ZrN with or without a Zr interlayer. Because of possible allergic reactions, when Ni-containing products are in close contact to the human skin, attempts were made to replace Ni by Cu-Sn-Zn ECD interlayers⁶⁴. The substrate temperatures have, however, to be kept low because of possible evaporation of interlayer components during the PVD process.

For machine parts, also ECD-Cr interlayers are studied besides Ni. In such cases, the combination of CrN/Cr has been proved to be better than TiN/Cr, as can be seen from the I-U curves in Fig. 10³⁴. The final selection of the PVD-ECD combination will be made on the basis of the actual need with respect to friction, wear and corrosive environment. A further important factor is how interlayers affect the adhesion of the hard coatings and how they meet shear stresses. This has additionally to be studied and adapted to the general requirements.

The corrosion behaviour of hard coating/sub-

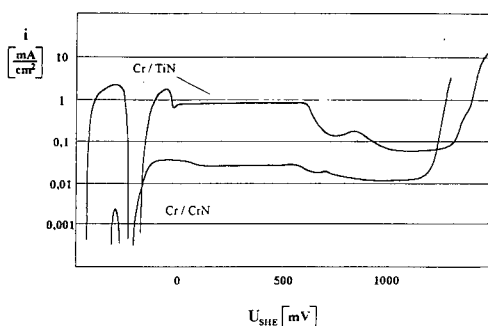


Fig. 10 TiN and CrN on ECD-Cr interlayers in 1 N H_2SO_4 34.

strate systems shall finally be characterised by two microstructures. Fig. 11 shows the corrosion attack on (a) a brass sample coated with ECD-Ni and a thin (not visible) TiN coating¹⁴, and (b) a Cr interlayer with a TiN and CrN top coating, respectively^{34, 71}.

4.4 Substrate pretreatment

A substrate pretreatment by plasma nitriding is increasingly used to increase the load bearing properties of the steel substrate material (duplex coatings). Only recently nitrided and hardcoated parts are also studied with respect to their corrosion behaviour⁷²⁻⁷⁴. Both processes applied separately yield an improved corrosion resistance, which is further increased for duplex treatment (Fig. 12)⁷². A positive effect of duplex coating was also found for PVD-deposited TiN, CrN and (Ti, Al)N coatings on prenitrided

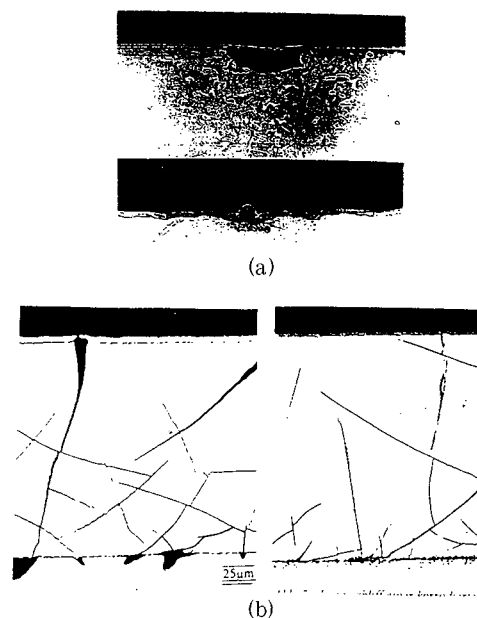


Fig. 11 Microstructure of corroded hard coating/substrate systems. (a) TiN/ECD-Ni/brass 14, (b) TiN and CrN/ECD-Cr/steel 34.

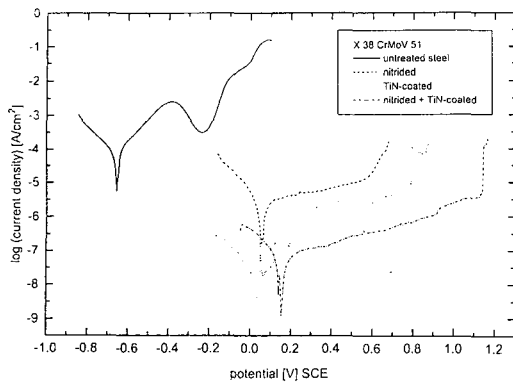


Fig. 12 I-U curves of nitrided, coated and duplex-coated samples 72.

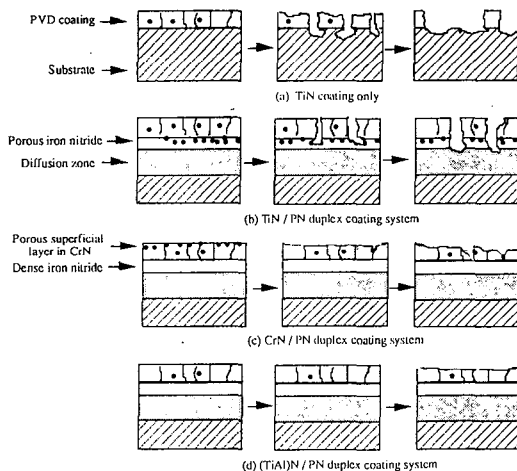


Fig. 13 Schematic illustration of the corrosion process in copated, nitrided and duplex-coated samples 68.

EN40B steel in 3.5% NaCl solution⁷⁴). The corrosion mechanisms explaining the increasing improvement by duplex coatings is schematically illustrated in Fig. 13⁶⁸).

5. Recent developments

The recent investigations on the corrosion behaviour of hard coating substrate systems and

its improvement cover all the facts mentioned above, i.e.:

- i. Variation of the coating thickness and process parameters,
- ii. Addition of third or fourth elements ("alloying"),
- iii. Interlayers by ECD and/or PVD,
- iv. Multilayers and
- v. Duplex coating.

All corrosion studies are difficult to compare because of the different test condition. This especially holds for the solutions in electrochemical tests.

6. Conclusions

The corrosion behaviour of a material or a composite generally is a system effect based on the properties of the part and the medium interacting with its surface. Hard coating/substrate systems are normally characterised by the following facts:

- Hard coating materials normally are relatively noble.
- In most cases the hard coatings are relatively thin and show pores and pinholes.
- The corrosive medium can penetrate through the defects reacting with the substrate material and causing galvanic corrosion.

An improvement of the corrosion resistance of hard-coated parts can be obtained by the following measures:

- Increased hard coating thickness
- Lower substrate roughness
- Denser coating morphology by suitable processes and process parameters including inter-

mediate ion etching.

- "Alloying" of the hard coatings.
- PVD interlayer(s) including intermediate ion etching.
- PVD multilayers.
- ECD interlayer(s).
- Duplex coatings

The recent development and investigations mainly base on the factors given and the additional investigation of duplex coatings (plasma nitriding plus PVD coating):

The hard coating/substrate system has to be specifically selected according to the technical need of substrate, coating and environment.

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