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PVD multi-layer hard coatings — Composition, structure and properties

Revêtements durs multicouches déposés par PVD — Composition, structure et propriétés

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Foreword

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This document was prepared by Technical Committee ISO/TC 107, *Metallic and other inorganic coatings*, SC 9, *Physical vapor deposition coatings*.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

Multi-layer hard coatings by physical vapor deposition (PVD), which possess high coating-substrate adhesion, high hardness and good wear resistance, are widely applied on tools and machine parts to improve their service life. Based on the chemical compositions, the mainstream PVD multi-layer hard coatings in the market involve transition metal nitrides and carbides, such as Ti/TiN, TiN/CrN, CrN/AlCrN, TiC/TiCN and CrAlN/AlCrTiSiN. To date, there has been no standard to qualify the composition, structure and properties of these multi-layer hard coatings, which has limited their further development.

This document defines the measurement and evaluation of the composition, microstructure, surface quality, thickness, hardness and tribological properties (such as friction and wear performance) of multi-layer hard coatings. The methods are for the purpose of coating development. Where standards for quality assurance in production exist, they are referred to in this document.

PVD multi-layer hard coatings — Composition, structure and properties

1 Scope

This document specifies the evaluation standard of the composition, structure and properties of multi-layer hard coatings by common physical vapor deposition (PVD), indicating a vacuum deposition method that produces a material source by evaporation, sputtering or related non-chemical ways.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 4545-1, *Metallic materials — Knoop hardness test — Part 1: Test method*

ISO 6507-1, *Metallic materials — Vickers hardness test — Part 1: Test method*

ISO 9220, *Metallic coatings — Measurement of coating thickness — Scanning electron microscope method*

ISO 14577-1, *Metallic materials — Instrumented indentation test for hardness and materials parameters — Part 1: Test method*

ISO 20808, *Fine ceramics (advanced ceramics, advanced technical ceramics) — Determination of friction and wear characteristics of monolithic ceramics by ball-on-disc method*

ISO 26423, *Fine ceramics (advanced ceramics, advanced technical ceramics) — Determination of coating thickness by crater-grinding method*

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

4 Samples for composition, structure and properties evaluation

Samples for the composition, structure and properties evaluation should be coated in the same batch as the products requiring the composition, structure and properties evaluation. The samples should be polished to a mirror finish (R_{pk} < 0,05 µm) before being coated and cleaned using ultrasonic agitation, which immerses them in the correct solution to remove hydrocarbons and other surface contaminants.

5 Testing of composition, structure and properties

5.1 Testing of chemical composition

The chemical composition of PVD multi-layer hard coatings is decided by many factors, including the composition of the evaporator source, the energy density of incident atoms/ions, the deposition pressure and the bias voltage. Various elements in the evaporator source can segregate during deposition, which results in different contents in the coatings. Testing methods that can be used to characterize the chemical compositions of PVD multi-layer hard coatings are energy dispersive spectrometer (EDS), electron probe micro analysis (EPMA), X-ray photoelectron spectrometer (XPS), auger electron spectrometer (AES), secondary ion mass spectrometry (SIMS), X-ray fluorescence (XRF) and glow discharge optical emission spectroscopy (GDOES). The details are shown in Table 1.

Table 1 — Testing methods of chemical compositions of PVD multi-layer hard coatings

Testing method	Surface area		Cross-sectional area		Maps and line scans
	Metal elements	B, C, N and O elements	Metal elements	B, C, N and O elements	
EDS	Recommended (excluding Li and Be)	Recommended (excluding B and C)	Recommended (monolayer thickness more than 100 nm)	Recommended (excluding B and C)	Recommended
EPMA	Recommended	Recommended	Recommended	Recommended	Recommended
XPS	Recommended	Recommended	Recommended (only by etching)	Recommended (only by etching)	Recommended (destructive)
AES	Recommended	Recommended	Preferably recommended	Preferably recommended	Recommended
SIMS	Preferably recommended	Preferably recommended	Preferably recommended	Preferably recommended	Recommended (destructive)
XRF	Recommended	—	—	—	—
GDOES	Preferably recommended	Preferably recommended	Preferably recommended (only by etching)	Preferably recommended (only by etching)	Recommended (destructive)

5.2 Testing of layer structure

Different structures of PVD hard coatings observed by electron microscope, including columnar crystal, equiaxed crystal and amorphous, lead to different grain or crystallite types, boundary energy and texture, which influence their hardness, internal stress, toughness and adhesion. Therefore, structure testing is essential for coating evaluation.

PVD multi-layer hard coatings can be defined in two classes. The first class comprises several different layers consecutively, including the adhesive layer, transition layer, hard core layer and/or surface adaptive layer for lubrication, hydrophobicity, electroconductivity, etc, as shown in Figure 1 a). The other class comprises two kinds of layers, in which every two adjacent layers constitute a unit and the thickness is called the "modulation period" ($\Lambda = \lambda_A + \lambda_B$; λ_A and λ_B are the thickness of the A layer and B layer, respectively). It is called "nano-layered coating" when Λ is less than 100 nm or "super-lattice coating", as shown in Figure 1 b).

Methods such as SIMS, scanning electron microscope (SEM) and transmission electron microscope (TEM) are able to detect and confirm the layer structure of coatings. Detailed information about analysing the layer structure by TEM is given in Annex A.

a) Several different layers

b) Periodic structure

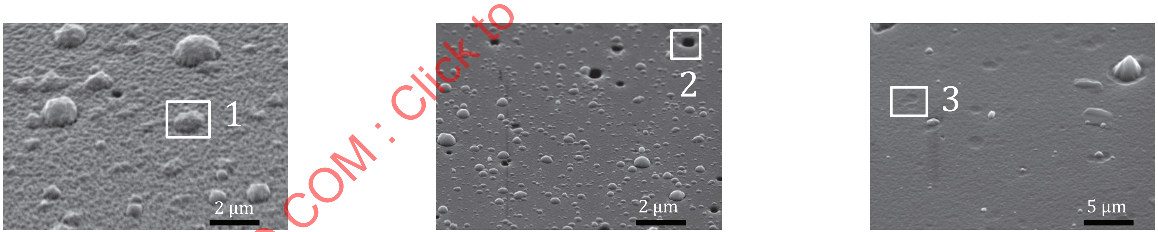
Key

1	adhesive layer	4	modulation layer A
2	transition layer	5	A layer
3	hard core layer	6	B layer

Figure 1 — Typical cross-section structures of PVD multi-layer hard coatings

5.3 Testing of surface deficiency

Droplets often occur in PVD hard coating processes. In addition, defects such as pinholes and shallow craters can form on the coating surface for some PVD techniques. Figure 2 shows the droplets, pinholes and shallow craters for arc ion plated coatings. The droplets are mainly from unreacted metal particles. The pinholes are from the shrinking of grain or crystallites during the coating growth. The shallow craters are from a spallation of the droplets.



a) b) c)

Key

1 droplet

2 pinhole

3 shallow crater

Figure 2 — Droplets and defects on the surface of arc ion plated coatings

These droplets and defects affect the mechanical properties, such as hardness, friction and wear of hard coatings, further influencing their service performance. Therefore, it is necessary to calculate the deficiency rate on the coating surface.

Surface deficiency analysis can be applied to evaluate the surface quality of coatings. Deficiency rate is defined as the percentage of the area composed of droplets, pinholes and shallow craters divided by the total observing area. A lower deficiency rate means better surface quality. A maximum value of 10 % for the deficiency rate should be an acceptable performance of polished coatings.

The steps to calculate the surface deficiency rate are as follows.

a) The surface of coatings should be polished to reach an invariable value of roughness. The polishing process is finished when the relative error of the polished coating is less than 10 %.

b) Prepare at least two specimens or small products, and ultrasonically clean the surface by acetone or alcohol for 5 min.

c) Observe the surface by SEM images. Take five images with ×1 000 magnifications for each sample. All images should be taken under the same parameters (pixels, colour, brightness, contrast and sharpness) and in second electron mode.

d) The useless information in the selected images should be deleted and the images adjusted to greyscale.

e) The selected images are analysed using an image processing software, which can automatically pick up the deficiency rate.

f) Calculate the average value of the deficiency rate of the 10 images.

When adjusting the greyscale of the image, and the colour and brightness contrast between the deficiency and background for each image, the same parameter should be selected in order to avoid errors caused by human error or fraud.

An example of a surface deficiency rate calculation is given in Annex B.

5.4 Testing of thickness

The ball crater-grinding method shall be adopted to measure the thickness of PVD multi-layer hard coatings in accordance with ISO 26423. For the precise thickness measurement of the coatings, an electron microscope (SEM or TEM) is preferred, especially TEM for each thin layer. The observation steps of SEM specimen shall be in accordance with ISO 9220 for metallic substrates. In the case of cermet and ceramic substrates, the specimen of electron microscope should be fractured for cross-section rather than being polished.

5.5 Testing of properties

5.5.1 Hardness

5.5.1.1 General

The hardness value of the coatings depends on the shape of the indenter and the calculation methods. The hardness of the coatings can be measured by nano-indentation testing (see 5.5.1.2) and static indentation (microhardness) testing (see 5.5.1.3). The nano-indentation test method is used to avoid the influence of substrate on the hardness of thin coatings. The method requires higher surface quality for coated specimens, which means the deficiency rate should be less than 3 % and the surface roughness (R_{pk}) less than 0,1 µm. The microhardness testing method, including the Vickers and Knoop tests, is widely used and easily performed in industrial production. All specimens should be polished before testing.

5.5.1.2 Nano-indentation test

The principle of this test is to calculate the hardness according to the force-depth curve by continuously recording the force exerted and the depth of an indenter pushing into the surface of a test piece or work piece. The testing steps shall be in accordance with ISO 14577-1. A diamond indenter should be adopted for the hardness measurement of PVD hard coatings.

For the multi-layer hard coatings, the following considerations should be taken into account.

a) Indentations should be performed at least three-times distance than their indentation diameter away from interfaces or free surfaces. The minimum distance between each indentation should be at least five times larger than the indentation diameter.

b) To avoid unwanted interactions of surface defects during indentation, the hardness values should be obtained at an indentation depth range of approximately 50 nm to 200 nm from the surface.

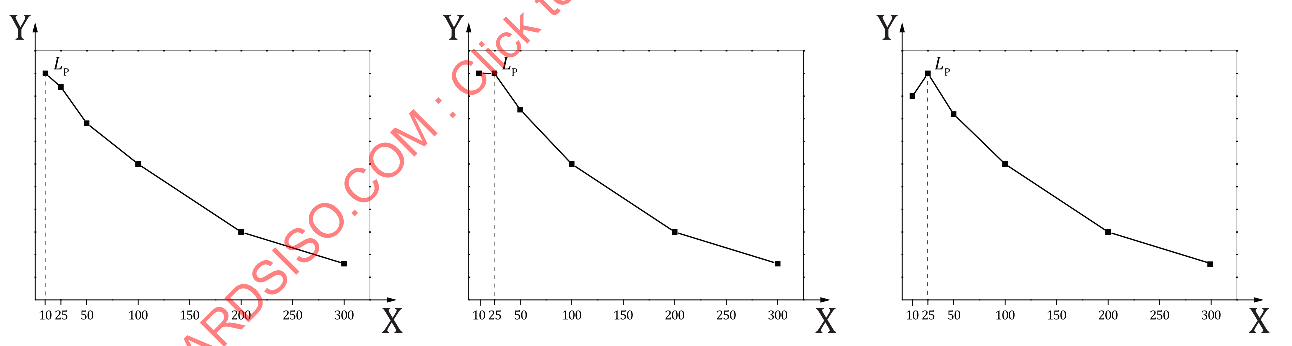
5.5.1.3 Microhardness test

There are two types of microhardness indenters: a square base, pyramid-shaped diamond indenter for the Vickers test and a narrow, rhombus-shaped diamond indenter for the Knoop test. Microhardness values of the hard coatings are affected significantly by the coating thickness, substrate hardness, surface roughness and defects. The microhardness of a coating can be determined only if the indentation depth is less than 1/10 of the coating thickness.

For the multi-layer hard coatings, the following considerations should be taken into account.

a) Since the Knoop indentation is shallower than the Vickers at the same load, the Knoop microhardness test is suitable to coatings with thickness of more than 2 µm. The Vickers microhardness test can be adopted for thicknesses higher than 4 µm.

b) The microhardness indenter shall be used to obtain a hardness of composite (coating and substrate) materials at 10 gf, 25 gf, 50 gf, 100 gf, 200 gf and 300 gf loads in accordance with ISO 4545-1 and ISO 6507-1. The hardness values are then potted against the loads in the range of approximately 10 gf to 300 gf. There are three kinds of hardness distribution, as shown in Figure 3. The loading value, L_p, is defined as the correct load for microhardness measurement, avoiding the influence of indentation size effect. Therefore, the average value, as the hardness of multi-layer hard coatings, should be calculated by five indentations at the testing condition of L_p.



a) A linear correlation between the hardness and load **b) The measured hardness value keeping constant at loads of 10 gf and 25 gf** **c) The measured hardness value exhibiting the maximum value at a load of 25 gf**

Key

X load, in gf

Y hardness, in HK/HV

L_p loading value

Figure 3 — The determination of L_p at three kinds of hardness distribution

The substrate effect is obvious for a thin coating with low hardness, and the coating hardness should be accepted at a load of 10 gf, as shown in Figure 3 a). There is no substrate effect at the low load (below 25 gf) for an ultra-hard and thick coating, and the measured hardness at a load of 25 gf should be defined as the coating hardness, as shown in Figure 3 b). When the coating surface exhibits a high roughness and deficiency rate, the measured hardness at a load of 10 gf is affected greatly by surface quality, resulting in lower hardness than the actual value. In order to avoid the effects of surface quality and substrate, the maximum value obtained at a load of 25 gf should be accepted, as shown in Figure 3 c).

5.5.2 Friction and wear

Friction and wear properties of multi-layer hard coatings determine their performances in industrial applications. Considering the small thickness of hard coatings, the ball-on-disk (BOD) test shall be applied to characterize their tribological properties in accordance with ISO 20808. The test at room temperature shall be carried out. The test at high temperatures should be set depending on the service environment of PVD coatings.

For the multi-layer hard coatings, the following considerations should be taken into account.

a) Wear counterparts: The choice of wear counterparts should be considered depending on the working conditions. They should possess enough hardness to produce apparent wear tracks on the coating surface. The recommended diameter of the sphere is 6 mm.

b) Applied load: 1 N, 5 N and 10 N, depending on the coating thickness and hardness.

   1) Apply a load of 1 N when the coating thickness is less than 2 µm or the coating hardness is less than 1 800 HK.

   2) Apply a load of 5 N when the coating thickness is between 2 µm to 5 µm or the coating hardness is between 1 800 HK to 2 800 HK.

   3) Apply a load of 10 N when the coating thickness is more than 5 µm or the coating hardness is more than 2 800 HK.

c) Sliding speed: 0,1 m/s. The diameter of the sliding circle should be more than 3 mm.

d) Sliding distance: approximately 180 m to 720 m.