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Carbon based films — Classification and designations

Films à base de carbone — Classification et désignations

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Foreword

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This document was prepared by ISO/TC 107, *Metallic and other inorganic coatings*.

Introduction

Carbon based films are applied as a coating to modify the surface properties of parts or to synthesize the carbon material. The applications cover machine elements, tools, optics, electronics, medical engineering, microsystem technology, electrochemistry, acoustics, decoration and many more. Carbon based films exist as many different types, which differ significantly in their properties. It is therefore important to choose the right film type for a given application.

The aim of this document is to provide a consistent classification that covers all carbon based film types. Furthermore, the classified film types are named with a system of consistent designations. This enables both providers and users to compare different carbon based films on common nomenclature.

Carbon based films — Classification and designations

1 Scope

This document specifies classification, designations and short names for carbon based films. These are films in which carbon is the predominant constituent part and which are deposited by physical vapour deposition (PVD) or chemical vapour deposition (CVD) process. This includes amorphous carbon-based films, also called diamond-like carbon films (DLC), as well as CVD diamond films, graphite and polymer-like films.

This document is applicable to those films which are produced on an industrial scale. Additional carbon based films are under development.

This document refers to the material of carbon based films. It does not refer to the entire coating that can consist of a main functional layer with additional layers below or on top.

A layer can change in composition and/or material property over its thickness. Such layers are called gradient layers. The definitions in this document refer to non-gradient layers.

A carbon based film can include other elements like hydrogen, metal elements or others. Metal constituents can be included as metal carbides. Films with additional elements are only covered by this document if carbon is the predominant constituent part. Carbon incorporated as carbide, as can be present in metal-containing amorphous carbon films (a-C:Me, a-C:H:Me), does not count to this amount.

This document does not apply to the class of carbon materials such as fullerenes, carbon nanotubes and graphene.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

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

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

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

3.1
substrate
workpiece upon which deposition is to take place

3.2
nanocrystalline
polycrystalline form with a crystallite size in the range of 1 nm to 500 nm, measured on the growth side of the film

3.3
microcrystalline
polycrystalline form with a crystallite size in the range of 0,5 µm to 10 µm, measured on the growth side of the film

4 Abbreviated terms

PVD physical vapour deposition

CVD chemical vapour deposition

5 Deposition

Many different PVD and CVD methods are used to deposit carbon based films. The properties of a carbon film type may differ depending on the deposition method. A list of common deposition methods is given in Annex A.

6 Classification

6.1 General

The classification of carbon based films is based on the material composition.

6.2 Main carbon film groups

Carbon based films are subdivided into the following main groups according to their chemical bonding state:

— **polymer-like carbon films**, where the carbon atoms are linked in chain formations, with crosslinks between the chains, and which contain a high amount of hydrogen (polymer-like);

— **amorphous carbon films**, where the carbon atoms are in a random, cross-linked arrangement (amorphous);

— **crystalline carbon films**, which are characterized by a regular arrangement of the carbon atoms, such that crystals are formed, subdivided into:

  — **diamond films**, where the carbon atoms are arranged in the diamond crystal lattice, and

  — **graphite films**, where the carbon atoms are arranged in the graphite crystal lattice.

Polymer-like carbon films may also be called plasma-polymer films.

The group of amorphous carbon films are also called diamond-like carbon films (DLC films).

From the main groups, further film types are classified according to the criteria described in 6.3.

6.3 Classification criteria

6.3.1 General

For the classification, the following properties and criteria are used:

— crystallinity;

— ratio of sp^2 to sp^3 of CC bonds;

— hydrogen content;

— content of additional elements.

Methods for the characterization of these properties are given in Annex B.

6.3.2 Crystallinity

Carbon based films are non-crystalline (e.g. amorphous, polymer-like) or crystalline. If crystalline, they can vary in relation to their lattice type (diamond lattice, graphite lattice) and the crystallite size (nanocrystalline, microcrystalline).

6.3.3 Ratio of CC sp^2 to sp^3 hybridization

The carbon atoms of the applied carbon film are able to form different hybridization states (sp^3, sp^2 and sp^1). Depending on the ratio of the different hybridization states, a different ratio of C-C-, C=C- and C≡C-bonds is realized. The ratio of CC sp^2 to sp^3 bonds of the carbon film types differs significantly.

6.3.4 Hydrogen content

Hydrogen may be present in carbon based films up to several 10 atomic %.

6.3.5 Content of additional elements

Besides hydrogen, carbon based films may contain additional elements like metals (e.g. W, Ti) or doping elements (e.g. Si, O, N, F, B), to modify the properties. Films with additional elements are only covered by this document if carbon is the predominant constituent part. Carbon incorporated as carbide, as it may be present in a-C:Me or a-C:H:Me, does not count to this amount.

6.4 Coating architecture

6.4.1 Monolayer

A carbon based film can consist of one single layer. Diamond films, for example, are usually deposited as monolayer with no additional layers below or on top.

6.4.2 Multilayer

If a coating is prepared by subsequent layers of different compositions, it should be designated as "multilayer". All layers shall be taken into account for a full description of a coating. Amorphous carbon films for example, are usually deposited as multilayer coatings.

6.4.3 Gradient layers

A layer may change in composition and/or material property over its thickness. Such layers are called gradient layers. Amorphous carbon films, for example, are often deposited as gradient layers. A gradient composition is not included in the definitions of this document.

6.5 Classification table

Table 1 shows the classification of carbon based films according to the criteria listed above, the film designations and the short names.

Table 1 — Classification of carbon film types

Main group	Polymer-like carbon films	Amorphous carbon films (diamond-like carbon, DLC)							Crystalline carbon films			
									Diamond films			Graphite films
Doping, additional elements		Hydrogen-free			Hydrogenated				Undoped		Doped	Undoped
				Modified with metal			Modified					
							With metal	With non-metal				
Chemical bonding state	Polymer-like	amorphous							Nanocrystalline	Microcrystalline	Microcrystalline or nanocrystalline	Crystalline
Predominating CC bond type	sp^2 or sp^3, linear bond	sp^2	sp^3	sp^2	sp^2	sp^3	sp^2	sp^2	sp^3	sp^3	sp^3	sp^2
Designation	Polymer-like carbon film	Hydrogen-free amorphous carbon film	Tetrahedral hydrogen-free amorphous carbon film	Metal-containing hydrogen-free amorphous carbon film	Hydrogenated amorphous carbon film	Tetrahedral hydrogenated amorphous carbon film	Metal-containing hydrogenated amorphous carbon film	Modified hydrogenated amorphous carbon film	Nanocrystalline CVD diamond film	Microcrystalline CVD diamond film	Doped CVD diamond film	Graphite film
Short name	–	a-C	ta-C	a-C:Me (Me = W, Ti…)	a-C:H	ta-C:H	a-C:H:Me (Me = W, Ti,…)	a-C:H:X (X = Si, O, N, F, B,…)	–	–	–	–

7 Polymer-like carbon films

Polymer-like carbon films are similar to polymers in terms of composition and film properties. They may contain more than 40 atom % hydrogen. They may also contain other additional elements. Polymer-like carbon films can appear in a huge variety; this is outside the scope of this document.

8 Amorphous carbon films

The group of amorphous carbon films is subdivided into seven film types. The following naming convention applies.

— The film designation contains “amorphous carbon film”, short name “a-C”.

— If the amount of hydrogen is almost zero, the term “hydrogen-free” is added preceding the film designation. No letter is added to the short name.

— If a substantial amount of hydrogen is incorporated, the term “hydrogenated” is added preceding the film designation. The letter “H” is added succeeding the short name, connected with a double-dot with the letter “C".

— If a substantial amount of metal elements is incorporated, the term “metal-containing” is added preceding the film designation. The metal element symbol is added as last part to the short name, connected with a double-dot. If the metal element shall not be given, the letters “Me” can be used alternatively.

— If a substantial amount of other non-metallic elements is incorporated, the term “modified” is added preceding the film designation. The element symbol (“X” in Table 1) is added as last part to the short name, connected with a double-dot.

— If the predominating CC bond is sp^3 hybridized, the term “tetrahedral” is added preceding the film designation. The letter “t” is added preceding to the short name.

Table 2 lists the film designations and short names of the seven types of amorphous carbon films.

Table 2 — Film designation and short names of amorphous carbon films

Film designation	Short name
Hydrogen-free amorphous carbon film	a-C
Tetrahedral hydrogen-free amorphous carbon film	ta-C
Metal-containing hydrogen-free amorphous carbon film	a-C:Me
Hydrogenated amorphous carbon film	a-C:H
Tetrahedral hydrogenated amorphous carbon film	ta-C:H
Metal-containing hydrogenated amorphous carbon film	a-C:H:Me
Modified hydrogenated amorphous carbon film	a-C:H:[X]
X: element symbol	

Amorphous carbon films often contain a significant amount of hydrogen. In the so-called hydrogen-free amorphous carbon films, no hydrogen is intentionally added during the deposition process. Nevertheless, these films may contain a very small amount of hydrogen, which can be incorporated unintentionally.

The hardness and wear resistance of amorphous carbon films depend mainly on two factors:

— The higher the content of CC sp^3 hybridizations, the harder the film is;

— The higher the hydrogen content, the softer the film is.

Both factors depend on each other.

Metal elements may be incorporated in amorphous carbon films as doping or as carbides. The carbide parts have a crystalline composition, which is surrounded by the amorphous carbon matrix.

9 Diamond films

Diamond films can be deposited only by CVD, not by PVD. They contain almost 100 % sp^3 hybridized CC bonds. They may contain a very small amount of hydrogen or other elements. Diamond films are used as thin-film coating or freestanding. To achieve freestanding CVD diamond, a CVD diamond film with a high film thickness is deposited (thick-film). Afterwards, the substrate is removed so that the diamond is left freestanding with a usual thickness between 300 µm and 2 000 µm.

The thin-film diamond can be doped or undoped. Undoped diamond thin-film is offered as nanocrystalline or as microcrystalline version. In addition, multilayers are offered that combine several nano- and microcrystalline layers.

Table 3 lists the film designations and short names of the three types of diamond films.

Table 3 — Film designation and short names of diamond films

Film designation	Short name
Nanocrystalline CVD diamond film	(no short name)
Microcrystalline CVD diamond film	(no short name)
Doped CVD diamond film	(no short name)

10 Graphite films

Graphite films are crystalline and predominately contain sp^2 hybridized carbon atoms. They may contain a very small amount of hydrogen or other elements. A subtype of graphite films is graphene, which can be deposited as a film by CVD.

Annex A
(informative)

Deposition methods

A.1 General

These deposition methods are used to deposit carbon based films. The list is not exhaustive. Carbon based films can also be deposited by a combination of methods.

A.2 PVD methods

A.2.1 Sputtering

— magnetron sputtering

— reactive magnetron sputtering

A.2.2 Evaporation

— unfiltered arc evaporation

— filtered arc evaporation

— pulsed laser deposition (PLD)

A.3 CVD methods

— hot-filament activated CVD

— plasma-activated CVD

— atomic layer deposition (ALD)

Annex B
(informative)

Characterization methods

B.1 General

To separate the different carbon film types, the following analysis methods can be used. Different methods for one parameter may give different results.

B.2 Crystallinity

B.2.1 Crystal or amorphous structure

— X-ray diffraction (XRD)

— TEM

B.2.2 Polymer-like structure

— infrared (IR) spectroscopy

— Raman spectroscopy

— nuclear magnetic resonance spectroscopy (NMR)

B.2.3 Crystallite size

— X-ray diffraction (XRD)

— TEM

— SEM

B.3 Ratio of sp^2 to sp^3 hybridized CC bonds

— UV Raman spectroscopy

— electron energy loss spectroscopy (EELS)

— nuclear magnetic resonance spectroscopy (NMR)

— X-ray absorption near edge structure (XANES)

— Near-edge X-ray absorption fine structures (NEXAFS)

— X-ray photo-electron spectroscopy (XPS)

B.4 Content of hydrogen

— elastic recoil detection analysis (ERDA) / Rutherford backscattering spectrometry (RBS)

— secondary ion mass spectrometry (SIMS)