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Carbon-based protective coatings

by JÖRG PATSCHEIDER

Abstract

The use of protective coatings applied on valuable objects against detrimental influences from the environment is a concern both in museum applications and in all-day life. The protection of restored surfaces can often be achieved by sealing with waxes while surfaces exposed to mechanical erosion have to be shielded from excessive wear by thin hard coatings. The present article describes briefly the nature of carbon-based protective coatings, their deposition techniques, their fields of applications and which of the described classes of coatings may be useful for restorers.

Introduction

The protection of surfaces exposed to various kinds of harmful influences has been a concern since ancient times. The use of lacquers, varnishes and glazes since early Mesopotamian cultures are early examples of protective coatings where the hardness combined with the optical properties (transmission and scattering of light) improve the final "product" in terms of durability and visual appearance. These concepts are still used in modern technologies using thin films which combine high hardness, chemical stability, specific colours, electrical and many other properties to form a compound material. This then allows the separate optimisation of the base material like its weight or shape on one side and of the properties of the surface, namely the coating on the other side. The thickness of such films varies in a wide range, they can be as thin as a few nanometer (a millionth of a millimetre) on computer hard disks or several millimetres thick for heavy duty ceramic coatings. Most of these coatings are deposited using plasma assisted processes in order to enable the chemical reaction necessary to form the films from gaseous precursors¹⁻⁴. Films deposited by low pressure plasma techniques have typically a thickness in the range of a few tenths of a micrometer (thousandth of a millimetre) to less than ten micrometers. The plasma processes applied to synthesize thin film coatings are closely related to the plasmas which are used for the restoration of ancient objects recovered from soils.

Carbon Coatings

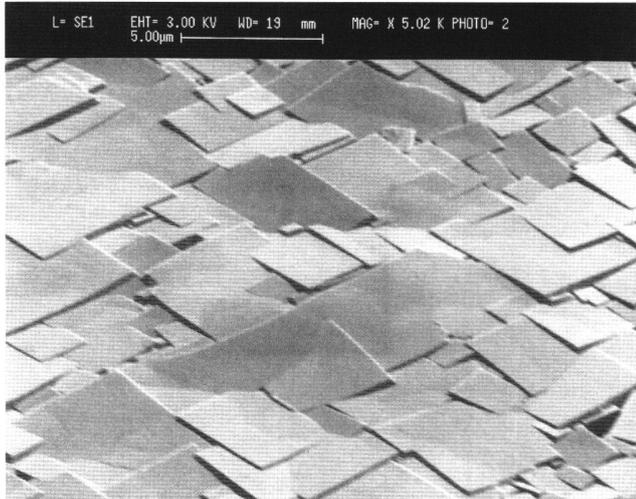
In absence of abrasive forces waxes can often provide sufficient protection of restored surfaces of metallic objects by

their sealing action. However, surfaces exposed to mechanical and thermochemical erosion, as they occur e.g. in drilling and chipping tools, have to be shielded from excessive wear by thin hard coatings. Carbon-based thin films are a whole group of protection layers fulfilling these requirements. The chemistry of carbon is, owing to its two hybridisation states, one of the most various of all elements. Condensed carbon atoms with their possibility to form three or four chemical bonds to their neighbouring atoms can form various kinds of networks ranging from long-chained aliphatic polymers with very few links between the carbon-carbon chains to diamond with the highest possible interconnection between the carbon atoms. The properties of thin films of carbon materials can vary, according to the nature and density of their chemical bonds, from soft and high flexibility to extreme hardness and rigidity. Consequently there is a variety of thin films consisting mainly of carbon which have found applications in different industrial areas. Carbon coatings can be divided into three main groups according to their different constitution:

Polymeric coatings

Polymeric coatings consist of carbon and hydrogen (sometimes plus oxygen and/or halogens) where the carbon atoms are more or less loosely linked. Polymer coatings can be synthesized either by conventional chemical methods starting from liquids or by deposition from gaseous hydrocarbon precursors using a glow discharge plasma⁵⁻⁷. Polyethylene-type of polymers for example are a class of materials with interesting diffusion barrier properties. They contain only saturated carbon-carbon bonds (sp³-carbon) with high contents of chemically bonded hydrogen; they are very soft due to the low degree of cross-linking (i.e. two- and three-dimensional interconnections between carbon-carbon groups). Polymeric coatings can be deposited on nearly any base material at temperatures below 100 °C. The chemistry of polymer coatings can be specifically altered e.g. by introducing polar groups (ketones, esters etc.) in apolar matrices or water-repellent groups (e.g. CF₂) and thus match the barrier requirements for a specific application. Polymeric thin films are therefore of potential interest to the community of restoration specialists seeking coatings to prevent or at least slow down further corrosion of restored objects. The fact that plasma polymers can be deposited directly after the final plasma treatment in the same reactor without exposing the objects

to air makes them interesting as sealing coatings deposited as a last step in the plasma treatment. An often mentioned requirement for protection treatments in restoration of objects is the reversibility of the treatment. Plasma-deposited polymer coatings can fulfil these demands to a large extent since they can be removed by hydrogen plasma etching procedures.



friction coefficient, often used as protective coatings in order to minimize friction. Their excellent chemical stability recommends the use in chemically aggressive environments as well as for surgical applications⁹. In contrast to many other hard coatings available on the market DLC can be deposited at temperatures as low as 50 °C. Good adhesion of these coatings is obtained on smooth surfaces,

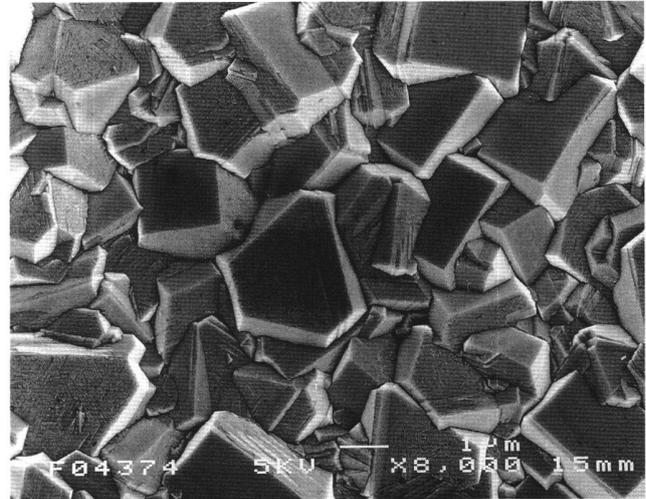


Fig. 1: Coatings made from synthetic diamond.

a) The well oriented diamond film was deposited by microwave plasma chemical vapor deposition on silicon with a specific bias pre-treatment. Such morphologies are required for optical and electronic applications.

b) The randomly oriented diamond film was grown by hot filament plasma chemical vapor deposition on molybdenum. Such films can be deposited on large surfaces.

Though these coatings provide protection against humidity they will not retain their barrier properties for very long times (e.g. twenty or hundred years). Polymers undergo increased cross-linking processes which consist of breaking bonds and building new carbon-carbon bonds. A macroscopic consequence is the embrittlement of polymers and thus the loss of barrier properties.

sometimes with the help of interlayers¹⁰; however, on coarse surfaces as they are found on freshly restored objects adhesion problems may occur due to the considerable mechanical stresses found in DLC. In addition large pores or even a complete lack of coating may occur. DLC is therefore not recommended as a protective layer against corrosion on historic metal objects.

Diamond-like carbon coatings

Diamond-like carbon coatings (DLC, a-C:H) is a group of carbon-based materials which can be synthesized only in form of thin films by ion-assisted processes⁸. They are characterised by a high degree of cross-linking with considerable internal stresses which results in both high hardness and high elasticity. In contrast to polyethylene, additional graphite domains in DLC make this material black. By adjusting the energy of the ions impinging on the growing surface, the character of DLC can be tuned from polymer-like, rather soft thin films to highly strained elastic coatings of very high hardness. DLC films are, due to their low

Diamond

Diamond is the hardest material known to man and it is therefore evident to use it as a superhard coating. The outstanding properties of diamond (hardness, optical transparency, high heat conductivity, electrically insulating, chemically inertness) open a wide range of actual and potential applications of diamond thin films. They are used where ordinary coatings cannot do the job. This is the case e.g. in space application where diamond-based gas sensors are used or as tips for scanning force microscopes. While the deposition of polymers and DLC poses virtually no practical problems, the synthesis of diamond coatings has

not been possible but for the last fifteen years. The two most important methods to synthesize diamond films are *hot filament chemical vapour deposition* (HFCVD) and *microwave plasma chemical vapour deposition* (MWCVD). The latter is a method utilizing plasmas comparable to the ones used in the equipment of the Swiss National Museum in Zurich. However, the wavelength is about hundred times smaller and the volume over which the plasma can be homogeneous is accordingly smaller. The advantages like high degree of excitation and the possibility of zero bias are mandatory for the deposition of high quality diamond films, which can be deposited on flat areas of less than 10 cm in diameter.

One of the main problems to overcome in diamond deposition is the nucleation, the initial stage of growth on nanometric diamond particles¹. The generation of these diamond nuclei is the crucial step which decides whether the growing diamond layer consists of highly oriented particles with flat and smooth surfaces or if a coarse polycrystalline randomly oriented film is formed. (Fig. 1). Electronic applications need diamond films with a minimum of grain boundaries and maximum purity while wear reduction for cutting tools can be achieved with randomly oriented diamond films. The procedures to promote the nucleation of diamond films comprise seeding with diamond particles¹², conditioning with organic matter¹³ and bias pre-treatment^{14,15}.

The temperature to deposit good quality diamond has been lowered from 900 °C to less than 400 °C recently¹⁶. This improvement makes diamond coatings very attractive for

the protection of steel tool surfaces. However, with respect to the severe temperature restrictions imposed in the restoration of metal objects, thin diamond films will not be suitable as protective carbon coating for the conservation of restored metallic objects.

Summary

Carbon-based coatings which may contain additional elements like hydrogen and oxygen have found widespread use in industrial applications for protection against wear and chemical attack. However, most of these coatings of a few micrometers thickness are applied on smooth surfaces. The topography of such surfaces are in sharp contrast to the ones usually encountered on historic objects. The highest potential for application in museums work lies in the group of the polymeric coatings where important properties like wetting, diffusion, colour, elasticity and so on can be adjusted by choosing the right starting materials and the appropriate process parameters.

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