Characterization of ANTACON diamond-like carbon and ta-C coatings with low internal stresses by nanoindentation

Relevant for: Nanoindentation, DLC coatings

By combining the laser deposition process with the laser tempering process, ANTACON GmbH from Mittweida (DE) has succeeded in producing extremely hard DLC coatings with low internal stresses. With the help of Anton Paar's nanoindentation test devices, the mechanical properties of these coatings could be quantitatively analyzed and indentation hardness up to 61GPa were measured.

1 Manufacturing of ANTACON's high-performance coatings

1.1 Motivation

In the industrial environment, economic losses occur due to wear and tear, which causes direct and/or indirect costs. Significant factors here are, for example, cost-intensive new acquisitions, necessary overhauls, production downtimes and maintenance costs. The annual economic loss is estimated at approx. 2 – 7 % of GDP in Germany alone. In addition to economic aspects, ecological factors are playing an important role in the manufacturing companies. For example, about 23 % of global energy consumption is due to tribological (frictional) contacts. The introduction of advanced tribological technologies can reduce global CO_2 emissions by up to 1,460 million tons CO_2-equivalent in the short term [KHOL]. The ANTACON company is a pioneer in innovation and development of new clean tribological technologies, thereby contributing to a more sustainable economy.

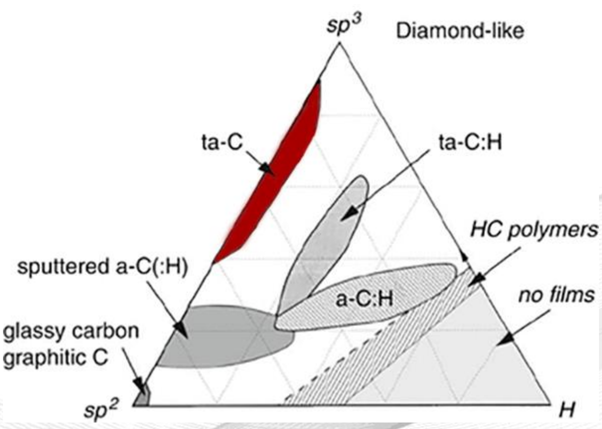


Figure 1: The classification of DLC layer types, the three corners correspond respectively to diamond (sp^3-hybridised), graphite (sp^2-hybridised), and hydrogen content (H). [JROB]

Due to supply chains that have become uncertain and constantly rising raw material costs as a result of disruptive events, industry has a great need for reliable tools and machine components that increase process reliability in production chains and minimize downtimes together with replacement costs. It is common that the main cost driver is not the worn tool itself, but rather the resulting production downtime during the tool exchange or an excessive amount of scrap during production using the worn tool. The user benefits both directly and indirectly from the use of super-hard high-performance tribological coatings and thus achieves a competitive advantage in this competitive market. For example, an automotive supplier can significantly extend the service life of its tools and components through the use of application-specific ANTACON coatings, thereby significantly reducing its costs.

1.2 Manufacturing of stress-free DLC coatings

The hardness of ceramic protective coatings or thin films is measured using instrumented indentation method and it is expressed as H_{IT} with values generally reported in the GPa range. Conventional wear resistant coatings often have hardness lower than 25 GPa. Using special processes however, it is possible to produce carbon-based coatings that have structure and properties similar to diamond. Such coatings are called diamond-like carbon (DLC) and have been used in industrial applications for many years.

A particular representative of DLC coatings is tetrahedrally amorphously bonded hydrogen-free carbon (ta-C). Its classification is shown in the ternary phase diagram (cf. Figure 1). Its outstanding properties, such as high hardness, wear and corrosion resistance and low friction are due to over 60 % high fraction of sp^3-hybridised carbon.

However, due to many challenges in the production of ta-C coatings, they are often only produced with maximum hardness ~45 GPa and a maximum layer thickness of ~1.5 µm. The main reason for this is the high compressive residual stresses that builds up during the deposition process. Since layer hardness and layer residual stresses correlate with each other, a compromise between layer hardness and the resulting layer residual stresses and the maximum possible layer thickness must be made. Otherwise, high residual stresses of superhard DLC coatings lead to premature delamination and mechanical instability already at layer thickness below 1 µm, which severely limits their use.

This problem could be solved by the innovation of ANTACON GmbH. ANTACON uses a patented technology that allows series production of superhard, stress-free ta-C coatings with stable mechanical properties. Figure 2 clearly shows the proof by means of Rockwell penetration testing. The imprint in the ANTACON stress-free ta-C coating (cf. Figure 2, bottom) does not exhibit any clod-like delamination of large radial extent compared to the conventional ta-C coating (cf. Figure 2, top). The special deposition procedure for stress-free wear protective ta-C coatings from ANTACON is unique worldwide.

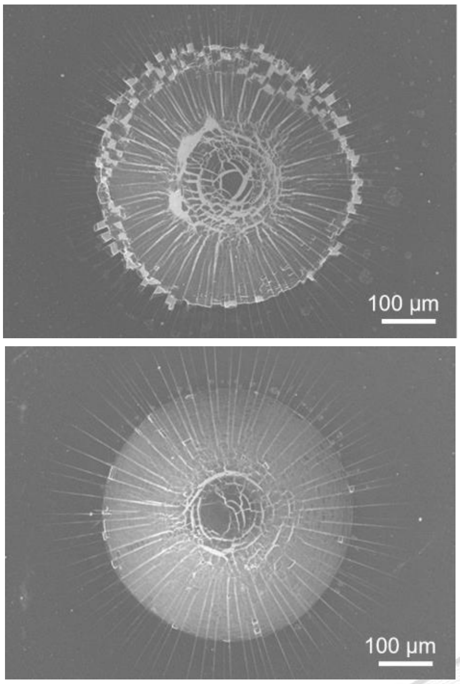


Figure 2: Comparison of Rockwell penetration tests according to DIN 4856 of 1 µm ta-C coated 100Cr6 steel, top: conventional ta-C coating with high layer residual stresses, bottom: stress-free ta-C coating from ANTACON.

The main properties of these ta-C coatings and their deposition process are listed in Table 1. In addition, these coatings

- Extreme coating hardness (> 60 GPa) without internal stresses,
- No limits on the coating thickness,
- Excellent mechanical stability and adhesion,
- Chemical inertness and biocompatibility.
- No distortion or hardness decrease in temperature-sensitive materials ($T_{Process}$ < 90 °C)

Table 1: Overview of the main properties of ta-C from ANTACON.

Layer properties of ANTACON ta-C	
Material:	C
Structure:	amorphous
Hardness H_{IT} [GPa]:	up to 70
Residual layer stresses [GPa]:	approx. 0.1
Maximum layer thickness [µm]:	any
Coefficient of friction µ (dry vs. steel)	0.1
Average roughness Ra [µm]:	< 0.1
Deposition temperature [°C]:	< 90
Max. application temperature in air [°C]:	< 500

Figure 3 shows a schematic representation of the combined laser pulse deposition and annealing process for the production of ANTACON ta-C coatings in vacuum. First, a laser beam (ablation laser) is focused on the target (source of the layer-forming particles) and generates a directed particle stream that moves in the direction of the substrate to be coated. During the layer deposition, another laser is used to anneal the growing layer. This allows production of stress-free ta-C coatings of any thickness with extremely high hardness and high mechanical load-bearing capacity.

1.3 Applications of superhard ta-C coatings

ANTACON ta-C coatings can be used for increasing of the service life of tools and components by up to ten times compared to common wear resistant coatings. With the significant increase of service life, ANTACON's coating solutions therefore improve energy and resource efficiency as well as the process reliability of many tribological systems.

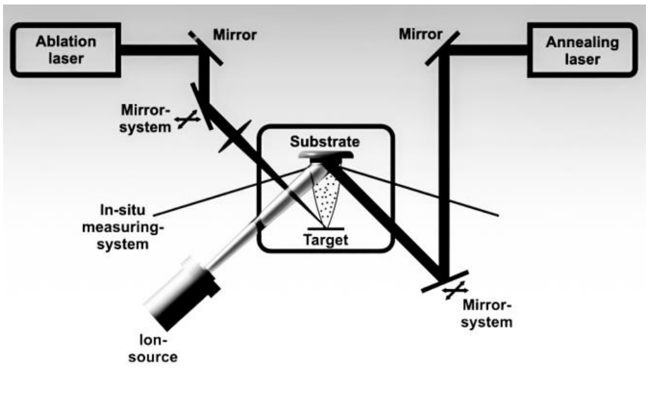


Figure 3: Schematic illustration of the combined deposition and relaxation process.

ANTACON's ta-C coatings such as sTAC60® ($H_{IT} \geq 60$ GPa) are most interesting for users who want to significantly improve wear resistance of their components where the conventional DLC coatings do not offer sufficient protection. Typical examples include coatings of oil-filled test probes as well as the stamping of duplex steel but the main application is on the finishing of heavily stressed products such as tools and machine components. By minimizing additional work such as reworking, regeneration and logistics, the process costs are significantly reduced.

In addition to increasing service life and minimizing friction, superhard ta-C coatings find applications as anti-adhesion or barrier coatings. In general, the spectrum of applications ranges from the market segments of the automotive industry, machinery, tool production, microelectronics, medical technology and plastics processing to aerospace technology and food and pharmaceutical industry.

2 Coating characterization with Anton Paar nanoindentation devices

New developments of materials, coatings and multilayer systems require a precise analysis of the characteristic material properties on the nanoscale range. Naniondentation (instrumented indentation testing according to ISO 14577) can be used to characterization of mechanical properties of coatings and thin films. The main results are hardness (H_{IT}) and elastic modulus (E_{IT}). In the instrumented indentation test, load and indentation depth are continuously applied and measured in a material by means of a loading and unloading process using a three-sided diamond indenter. The aim is to determine the elasto-plastic properties, whereby the indentation hardness H_{IT} is a parameter that describes the permanent deformation and elastic modulus E_{IT} the ability to deform elastically.

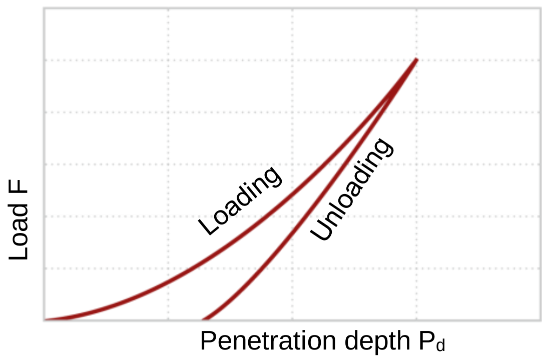
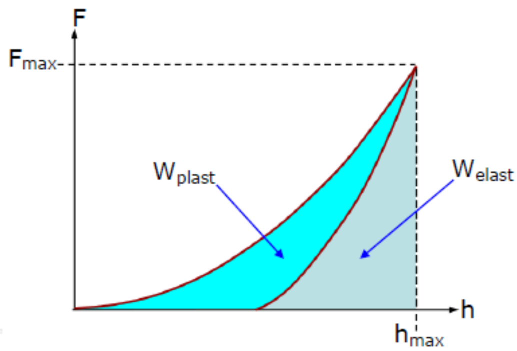


Figure 4: Schematic illustration of the indentation curve for instrumented indentation testing.

2.1 Instrumented indentation testing

Instrumented indentation testing is a method that allows the determination of localized mechanical material properties. The technology is suitable for both bulk materials and coatings. During the indentation test, the test load and indentation depth of the test specimen are continuously recorded over the entire loading and unloading period. The result is the load-penetration depth curve (see Figure 4). Hardness and elastic modulus are determined using the Oliver&Pharr method [OLPH]. In addition to elastic modulus and hardness, other values such as elastic and plastic indentation energy W_{elast} and W_{plast} as well as η_{IT} ratio can be determined from nanoindentation tests.



$$\eta_{IT} = \frac{W_{elast}}{W_{elast} + W_{plast}} \cdot 100$$

Figure 5: Illustration of the calculation of the penetration work.

Most often Berkovich indenter (three-sided pyramid) is used but other geometries (spherical, Vickers) can be used [FICR].

The ultra-high resolution Anton Paar UNHT³ nanoindenter with true force and depth sensors is suitable to investigate mechanical properties of very thin and very hard materials such as the ta-C coatings.

The UNHT³ features patented surface reference technology: a reference probe monitors the surface position of the sample while the diamond indenter performs the measurements. This eliminates problems with thermal drift and instrument stiffness and allows a wide range of penetration depths (from a few nm up to 100 µm) and test loads (from a few µN up to 100 mN).

Figure 6: The UNHT³ ultra-nanoindentation device with the patented surface referencing.

2.2 Measurement procedure

The test parameters were chosen according to preliminary investigation on similar coatings. The following parameters were used:

- Maximum load: 20 mN
- Load and unload duration: 30 seconds
- Hold time at constant load: 20 seconds

Five measurements with a spacing of 20 µm were done.

2.3 Results and comparison with conventional DLC coatings

The measured curves of the ta-C layer of ANTACON are shown in Figure 7. The shape of the curves shows that a very hard material was measured, since loading and unloading curves have approximately the same shape – which is confirmation of mostly elastic deformation with little plastic deformation. The maximum penetration depth was approximately 130 nm and the following hardness, elastic modulus and η_{IT} ratio of the ANTACON ta-C were obtained:

- $H_{IT ta\text{-}C}$ = 61.5 GPa ± 5.9 GPa
- $E_{IT ta\text{-}C}$ = 630.4 GPa ± 82.4 GPa
- $\eta_{IT ta\text{-}C}$ = 97 % ± 3 %

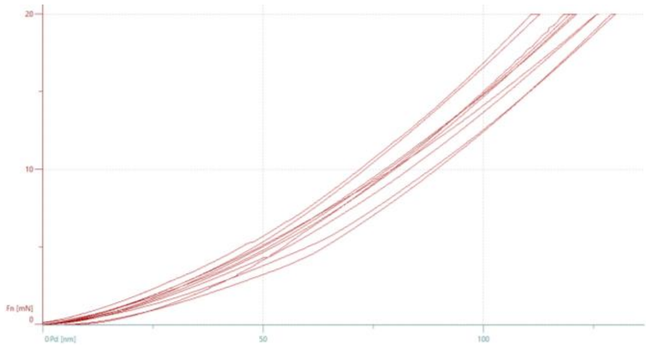


Figure 7: Force-penetration curves of the five measurements.

For a better understanding of H_{IT} and E_{IT}, the values were compared with conventional DLC layers, measured with the same instrument:

- $H_{IT DLC}$ = 26.5 GPa ± 0.5 GPa
- $E_{IT DLC}$ = 214.8 GPa ± 2.5 GPa
- $\eta_{IT DLC}$ = 72 % ± 1 %

This comparison clearly shows that the ANTACON ta-C coatings exhibit significantly higher hardness and elastic modulus as well as higher elasticity than conventional DLC coatings.

2.4 Summary

Mechanical properties of the ANTACON stress-free superhard ta-C coating were investigated with instrumented indentation test. The measurement results show that the hardness of the newly developed DLC coatings is more than twice as high as that of conventionally produced DLC coatings. Other characteristic values such as modulus of elasticity and wear resistance were also foundd to be significantly higher than those of conventional DLC coatings. ANTACON's superhard ta-C coatings can therefore significantly increase the service life of components in terms of wear resistance in tribological systems.

3 References

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