Hard coatings:
state-of-the-art and applications

,

INTRODUCTION

Hardness values of some bulk materials (GPa):

Diamond	80-100
Cubic BN	50
Si_3N_4	17
Steels	2
FCC metals	~1

Coatings: 1-10 μm thick layers
20-50 GPa hardness

Hardness: **TiN: 27 GPa**, **CN_x: 20 GPa**, **DLC: 20-25 GPa**

Other properties:

friction coef. (<0.2, ideal: 0.01),
wear (mass/time),
elasticity (10%), in some cases 50-80%
thoughness,
plasticity,
thermal stability (1000°C),
enviromental stability (water, vacuum, oxygen)

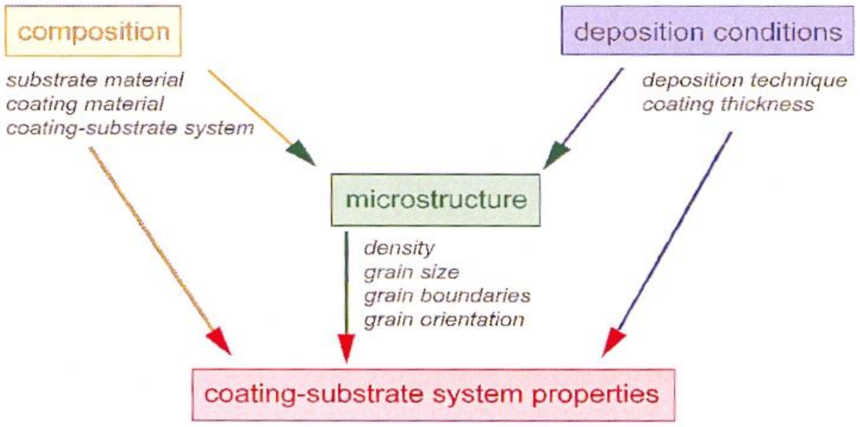


Figure 2 *Main factors influencing the properties of the coating-substrate system (redrawn after Holleck [Holl 1986]).*

Table 1 *Classification of hard coatings according to the character of the dominating chemical bonding present in the constituting material (after H. Holleck [Holl 1986]).*

MAINLY METALLIC	MAINLY COVALENT	MAINLY IONIC (CERAMIC)
borides carbides of transition metals nitrides	borides carbides of Al, Si & B nitrides	oxides of Al, Zr, Ti, Be
TiB_2 TiC TiN WC CrN	SiC SiN AlN BN	Al_2O_3 ZrO_2 BeO

Another commonly used classification of hard coatings is according to the element forming the ceramic with the transition metallic elements:

- nitrides (*Me*-***N***)
- borides (*Me*-***B***)
- carbides (*Me*-***C***)

I. *Hard PVD ceramic coatings –*

Single metal nitride PVD coatings e.g. TiN, CrN, ZrN

The first generation of hard PVD coatings were single metal nitrides such as TiN, CrN and ZrN. They have been exploited commercially since the middle of the 80's in cutting applications because of their higher hardness compared to high speed steel and cemented carbide and for decorative purposes because of their attractive appearance. TiN has a distinctive yellow-gold colour, CrN looks unsurprisingly like chrome and ZrN has a green-gold colour. ZrCN is used to simulate gold in decorative applications such as watch cases.

These PVD coatings are still available and in many applications are the best option.

However their temperature resistance is insufficient for applications such as high speed machining. TiN for example decomposes at 450 °C.

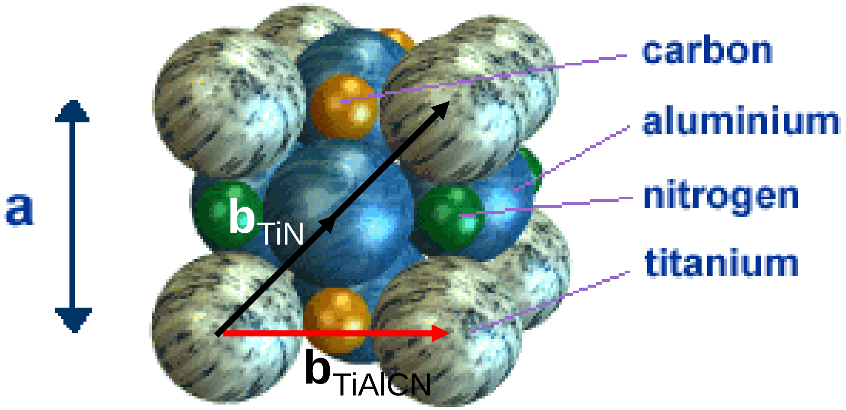
Therefore the next step in the development of hard PVD coatings was the improvement of the temperature resistance to make the coatings more suitable for applications such as high speed machining and general high temperature wear protection.

A standard TiN coating has hardness of 25-30 GPa

II: *Hard PVD ceramic coatings –* **Alloy coatings improve oxidation resistance, e.g. TiAlN**

This improvement in temperature resistance was achieved by introducing other elements such as Cr, Al or Y, as well as C into the TiN lattice.

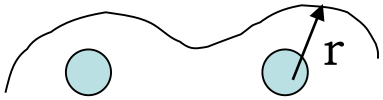
Ordered alloys
Disordered alloys



a = lattice parameter

$$\boxed{r=Gb/\tau}$$

G; shear modulus
b; Burgers vector
τ; shear stress



http://www.pvd-coatings.co.uk/

Material	**Hardness GPa**
TiN	**27**
$Ti_{0.5}Al_{0.5}N$	**28**
TiAlVN	**30**
$Ti_{0.75}Al_{0.25}N$	**31**

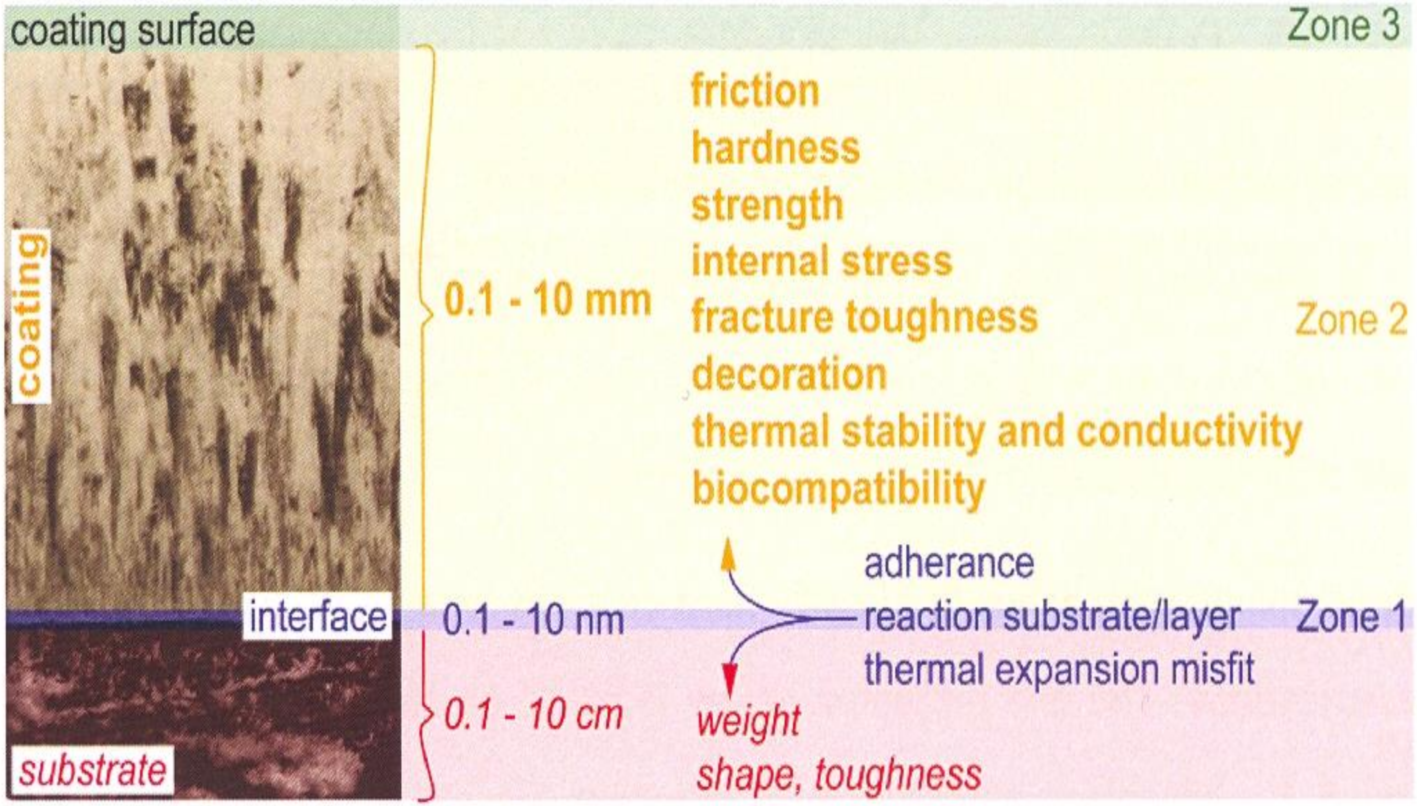


Figure 1 *Characteristics of a cross-section through the substrate, interface and coating on the example of a WC-Co substrate coated by a ZrN layer. The photograph was taken by transmission electron microscopy. Some desired coating properties are listed on the right side of the arrows.*

III. *Hard PVD ceramic coatings* – The development of superlattices

Further improvement to the properties of hard PVD coatings was achieved in the third generation of hard PVD coating development through the deposition of multilayers and superlattices. Multilayers become superlattices when the period of the different layers is less than 10 nm.

Multilayered coatings of materials with similar crystal structures tend to form columnar crystals built of alternating epitaxial lamellae which extend through the whole coating, provided that the thickness of the individual lamellae is sufficiently thin, typically 5–25 nm. Such coatings are referred to as superlattice coatings.

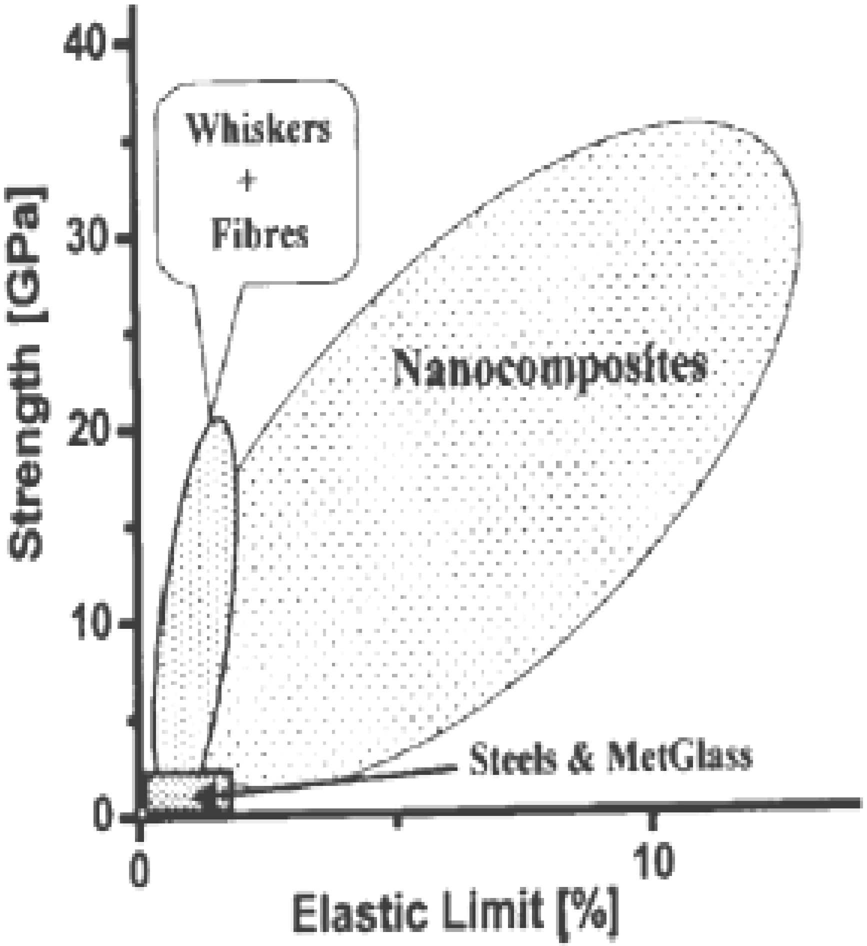
One of the first examples of superlattice coatings was obtained by combining TiN/VN and TiN/NbN. Several authors have shown that this type of multilayered coating structure can improve the hardness as well as the toughness, compared to single layers of the same materials. By selecting a suitable combination of materials for the multilayered structure it is possible to improve the resistance against wear, corrosion, oxidation, etc.

Supermodulus effect: the hardness of superlattices depend on the period and shows a maximum at superlattice period of about 5-10 nm.

IV. *Hard PVD ceramic coatings* – The recent development of nanocomposite coatings

PRINCIPLES

A nanocomposite coating consists of at least two phases: a nanocrystalline phase and an amorphous phase, or two nanocrystalline phases. The basic idea for the design of nanocomposites is based on the thermodynamically driven segregation (inmiscibility of the components) in binary (ternary, quaternary) systems. The phase separation leads to the spontaneous self-organization of a stable nanoscale structure. This generic concept has recently led to the development of nanocomposite PVD coatings. These PVD coatings have nm sized grains and exhibit enhanced yield strength, hardness and toughness properties as a result of the well-known Hall-Petch effect.



-combine hard crystalline grains (e.g. carbide) and amorphous DLC or CN_x with high elastic modulus to achieve correspondingly high hardness and elastic recovery;

-maintain nanocrystalline grain sizes at the 10~20 nm level to facilitate grain boundary sliding and restrict initial crack formation;

-separate the nanograins by an amorphous matrix of thickness above 2 nm to prevent interaction of atomic planes in the adjusted nanocrystalline grains, but less than 10 nm to restrict the path of a straight crack.

Veprek at al.: **J. Vac. Sci. Technol. A 21** (2003) 532

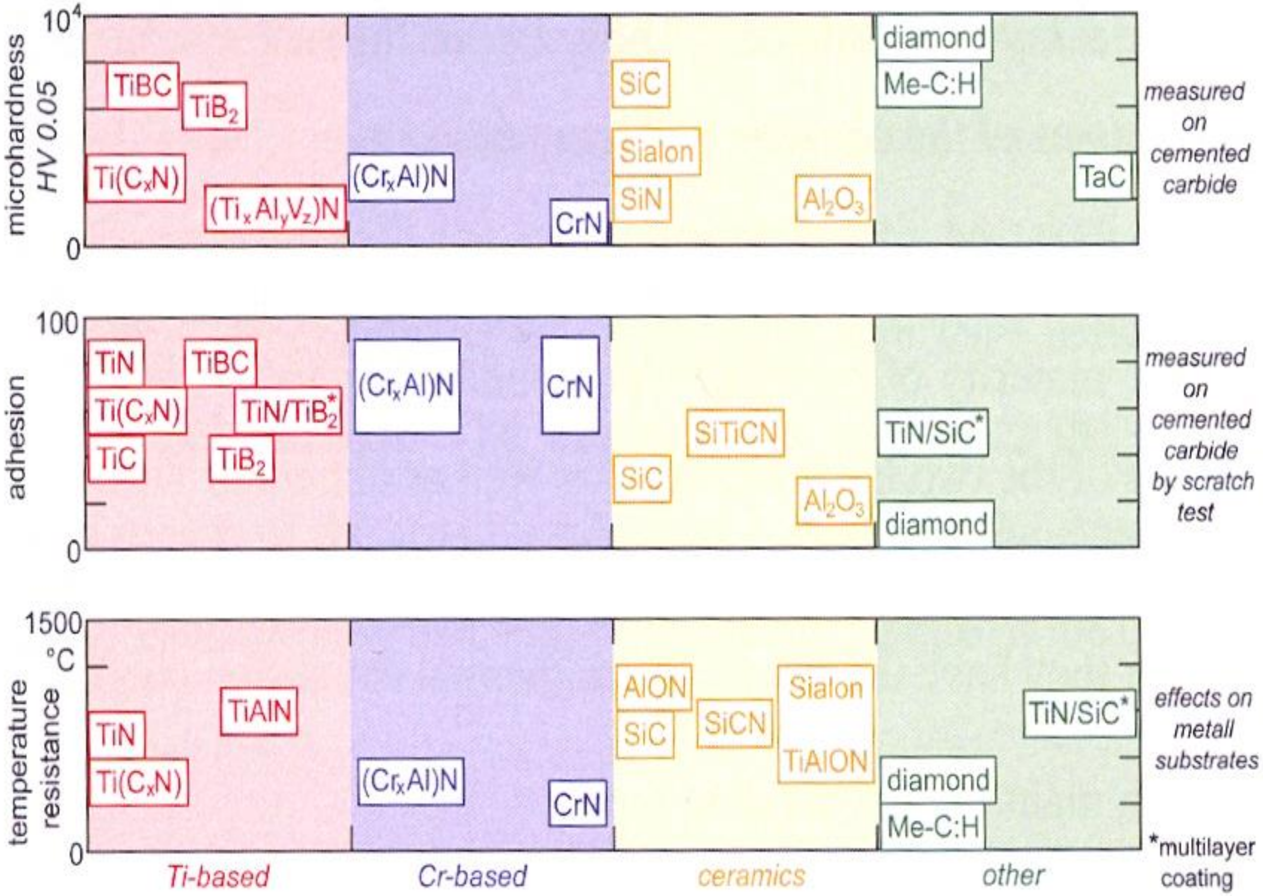


Figure 3 *Properties of various coating systems; some of which are only qualitative (redrawn after F. Löffler [Löf 1994]).*

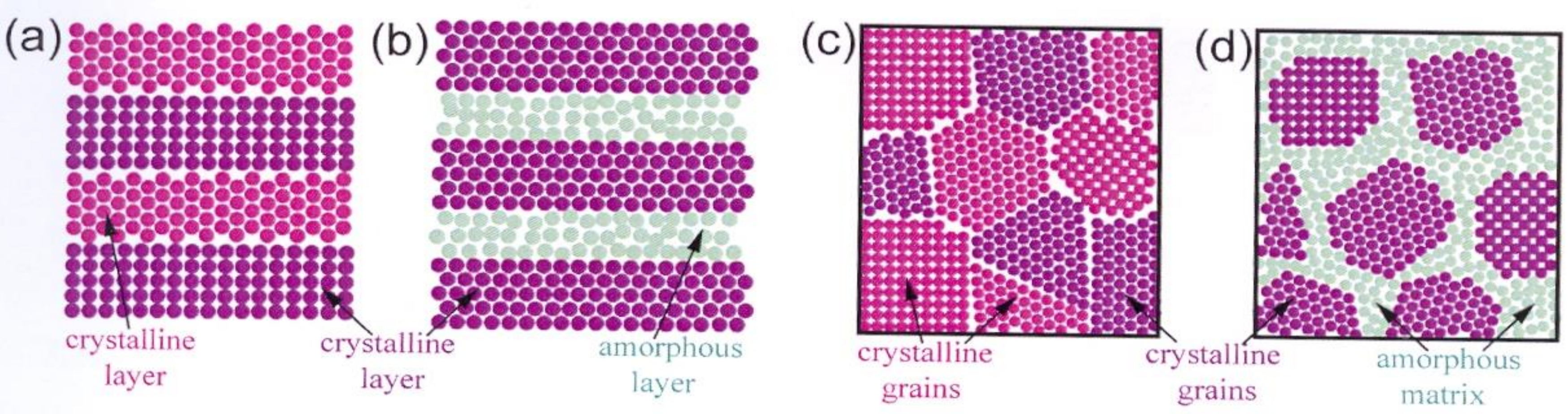


Figure 5 *Layouts of structures commonly used for hardness enhancement engineering in coatings:* **(a)** *Alternated crystalline layers;* **(b)** *Alternated crystalline and amorphous layers;* **(c)** *Nanogranular with adjacent crystalline grains;* **(d)** *Nanogranular with crystalline grains embedded in an amorphous matrix.*

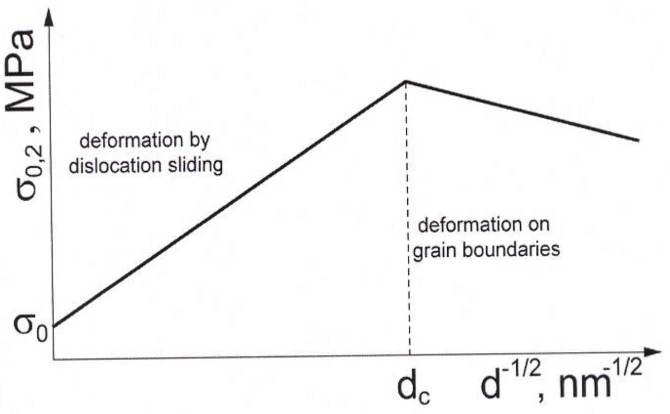
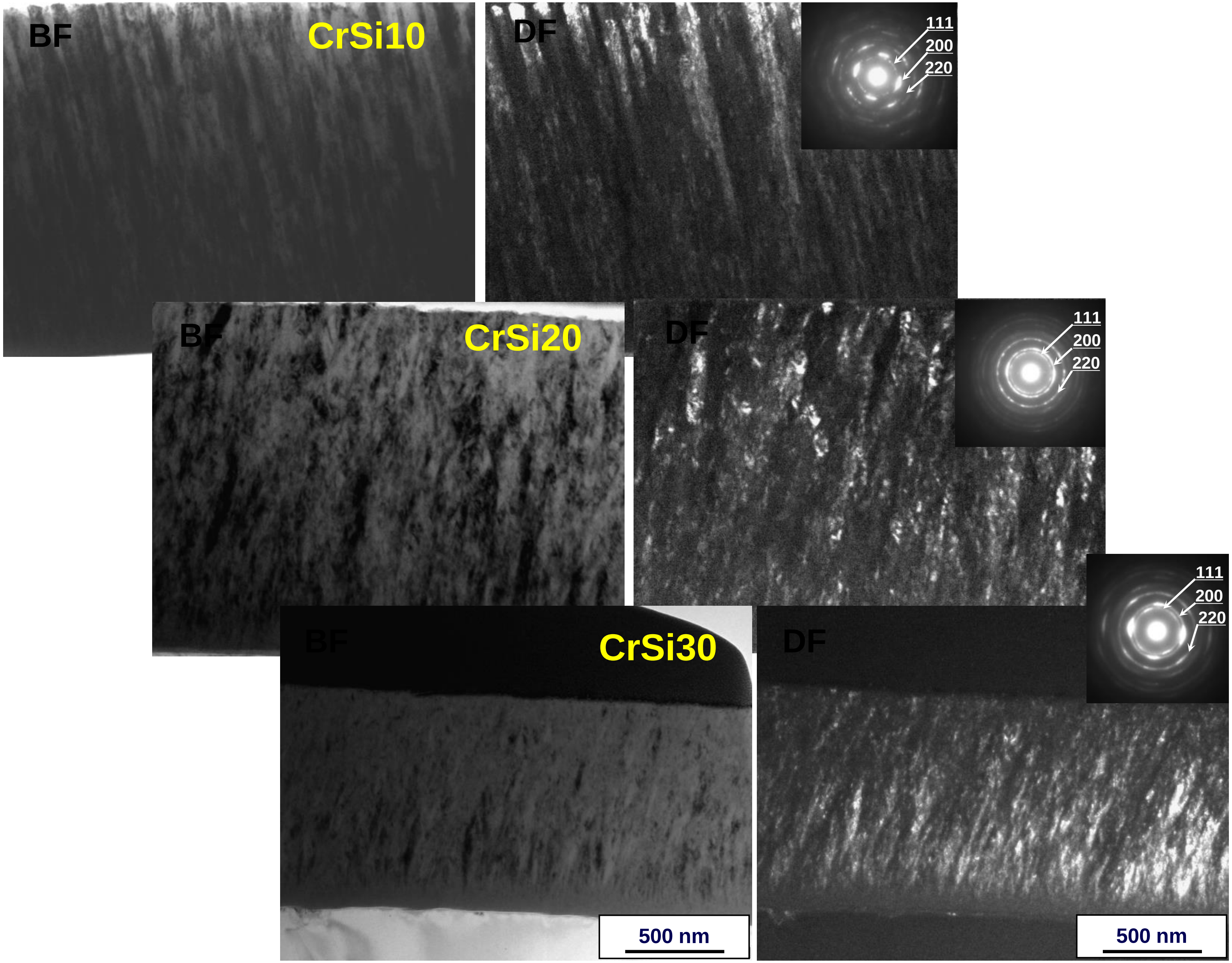
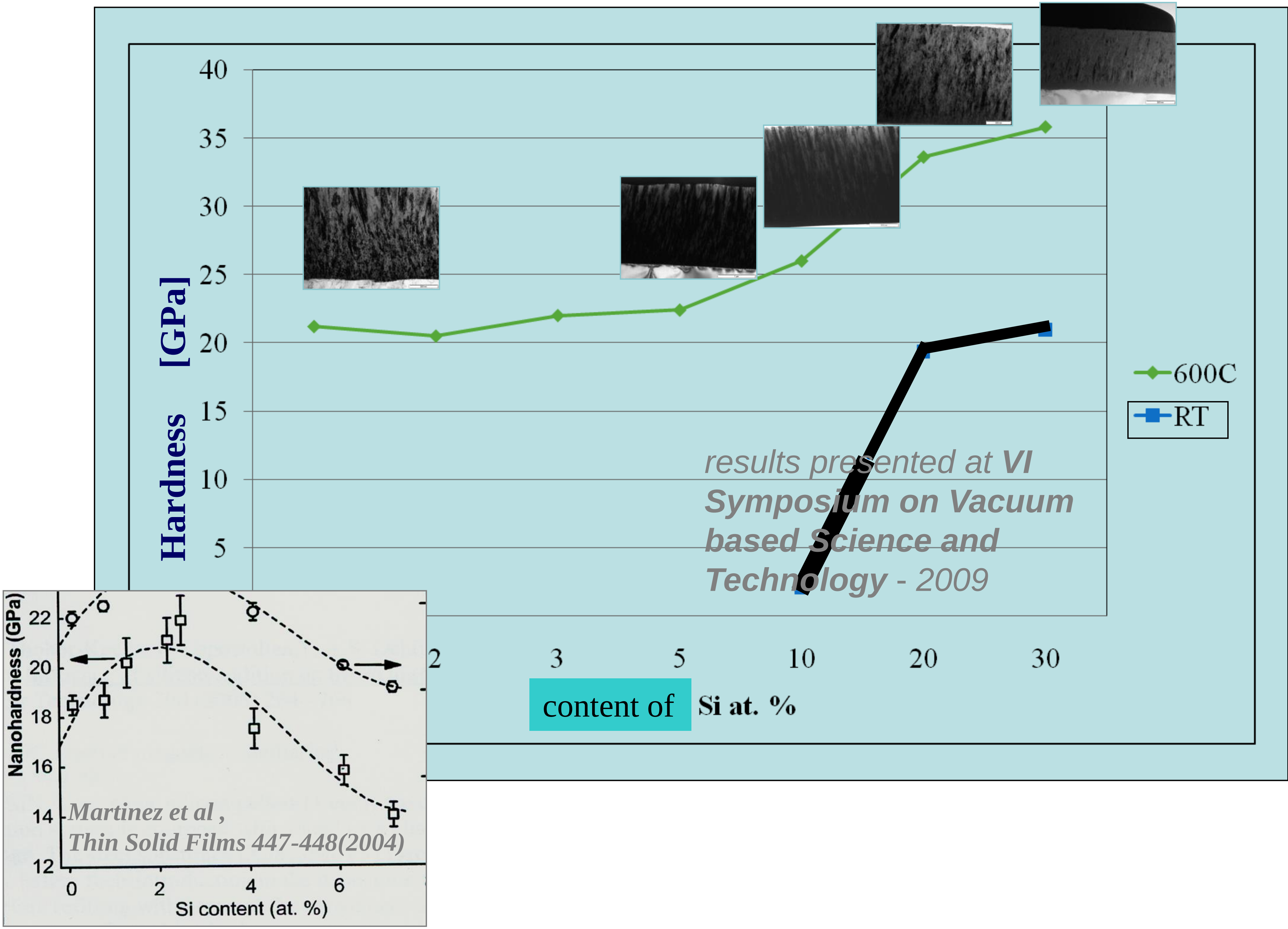


Figure 6 *Schematic representation of the Hall-Petch relation for nanocrystalline materials: above a certain critical value d_0 the deformation mechanism changes from dislocation sliding to grain boundary sliding and the hardness of the materials drops – inverse Hall-Petch effect, redrawn after Kurzydłowski et. al. [Kurz 2010].*

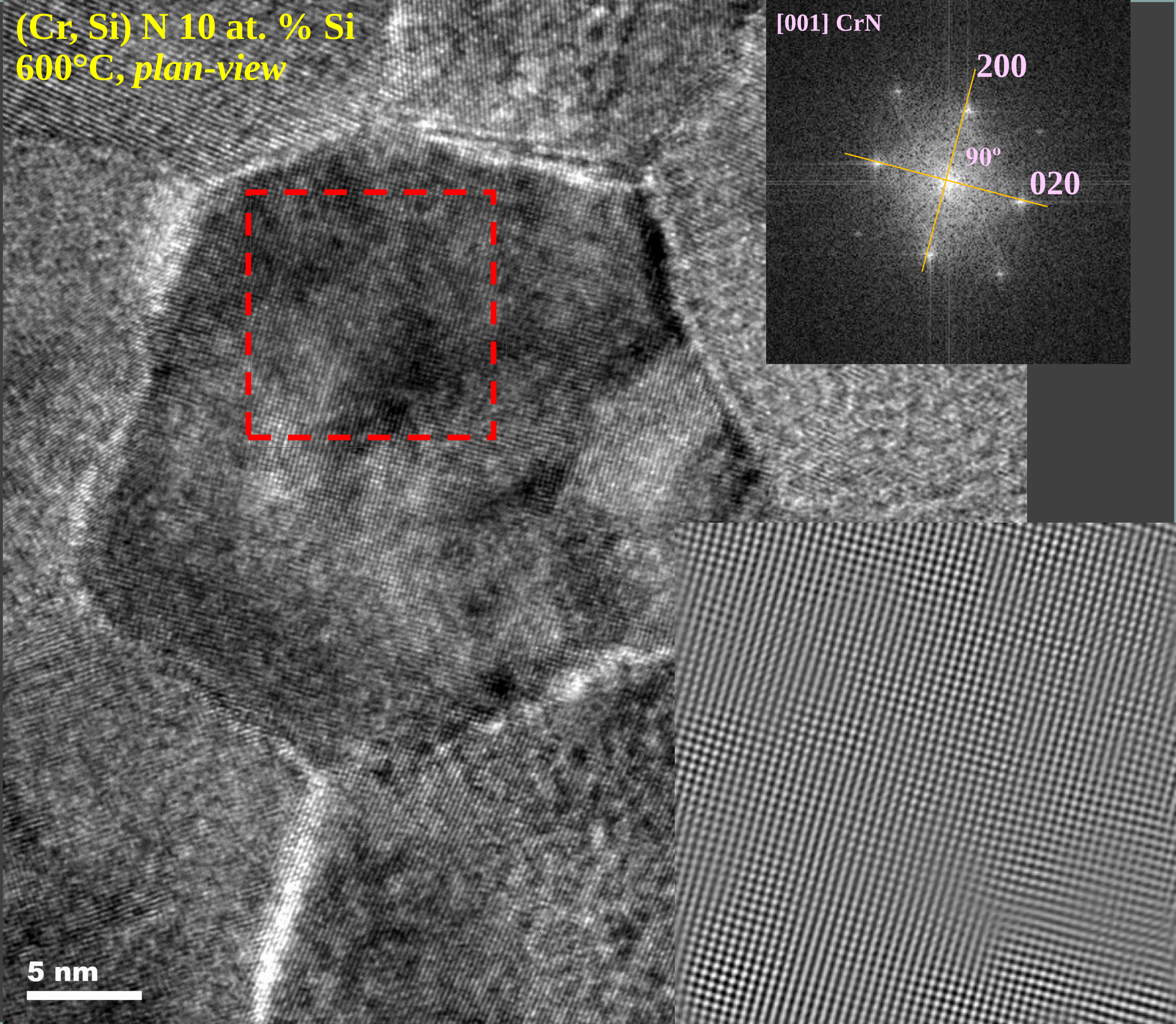
TEM characterization in *cross-section*



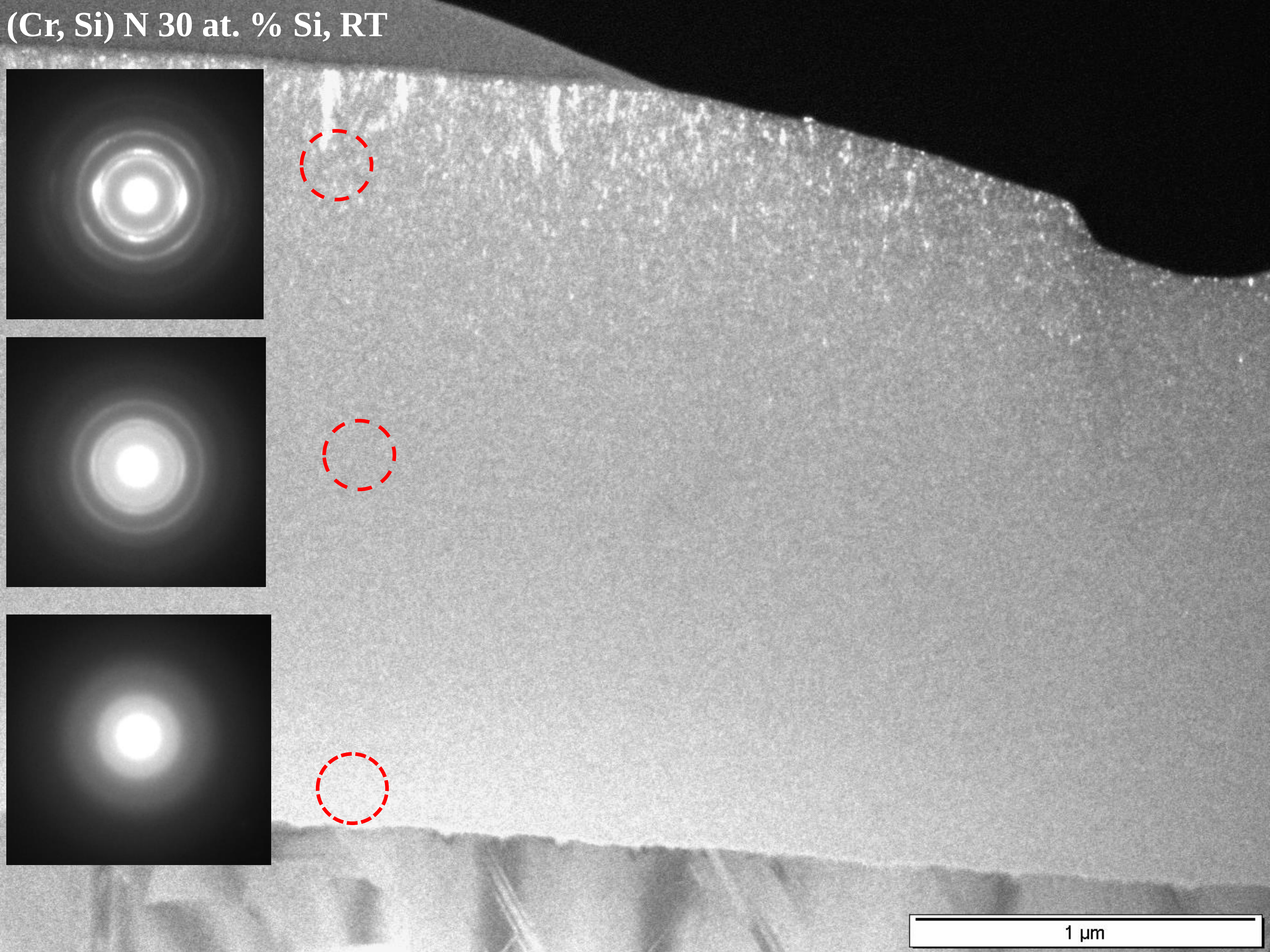


*results presented at **VI Symposium on Vacuum based Science and Technology** - 2009*

Martinez et al ,
Thin Solid Films 447-448(2004)

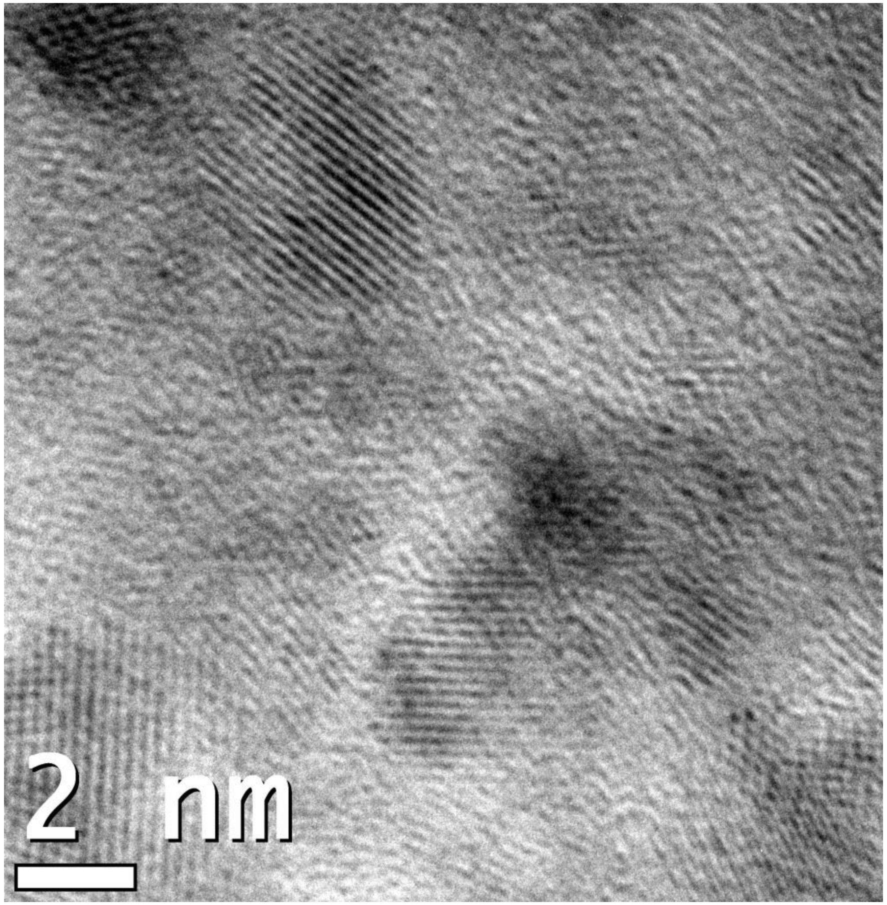

(Cr, Si) N 10 at. % Si
600°C, *plan-view*
[001] CrN
200
90º
020
5 nm

(Cr, Si) N 30 at. % Si, RT



(Cr, Si) N 30 at. % Si, RT *plan-view*

HREM image



GIF composite image

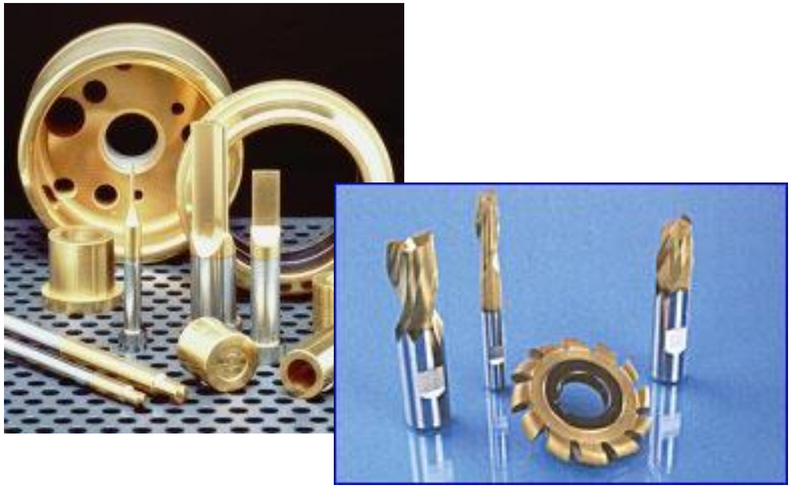
Cr_red Si_yellow

Janos Labar, KFKI, Budapest

Charakteristics of materials

TiN

Temperature resistence: ~500°C
Hardness ~ 24 GPa

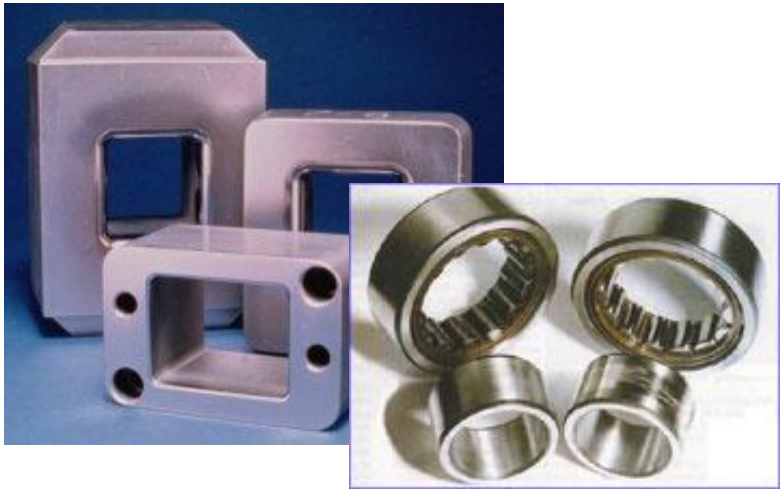


TiN/Si_3N_4

Close to superhard>40 GPa
(requires cooling)

CrN

Temperature resistence : ~700°C
Hardness ~ 16 GPa



CrN/Si_3N_4

Possible dry cutting

Superhard coating materials are defined by hardness values that exceed 40 GPa. For this purpose:

Hall-Petch relation:

$$H = H_o + K_y d^{-1/2}$$

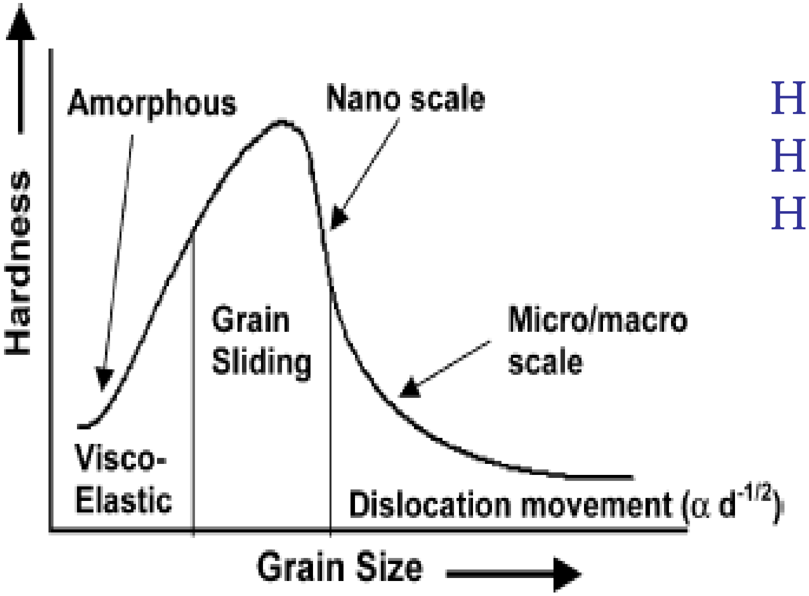


Fig. 1. Schematic depiction of hardness as a function of grain size.

The main mechanisms of low deformability can be summarized as follows:

Hinder dislocation generation
Hinder dislocation movement
Increase the blocking power of grain boundaries
Hinder GB sliding
Hinder crack generation
Hinder crack propagation

The strength of (super)hard coatings is due either to structural properties or the incorporated internal stresses during growth.

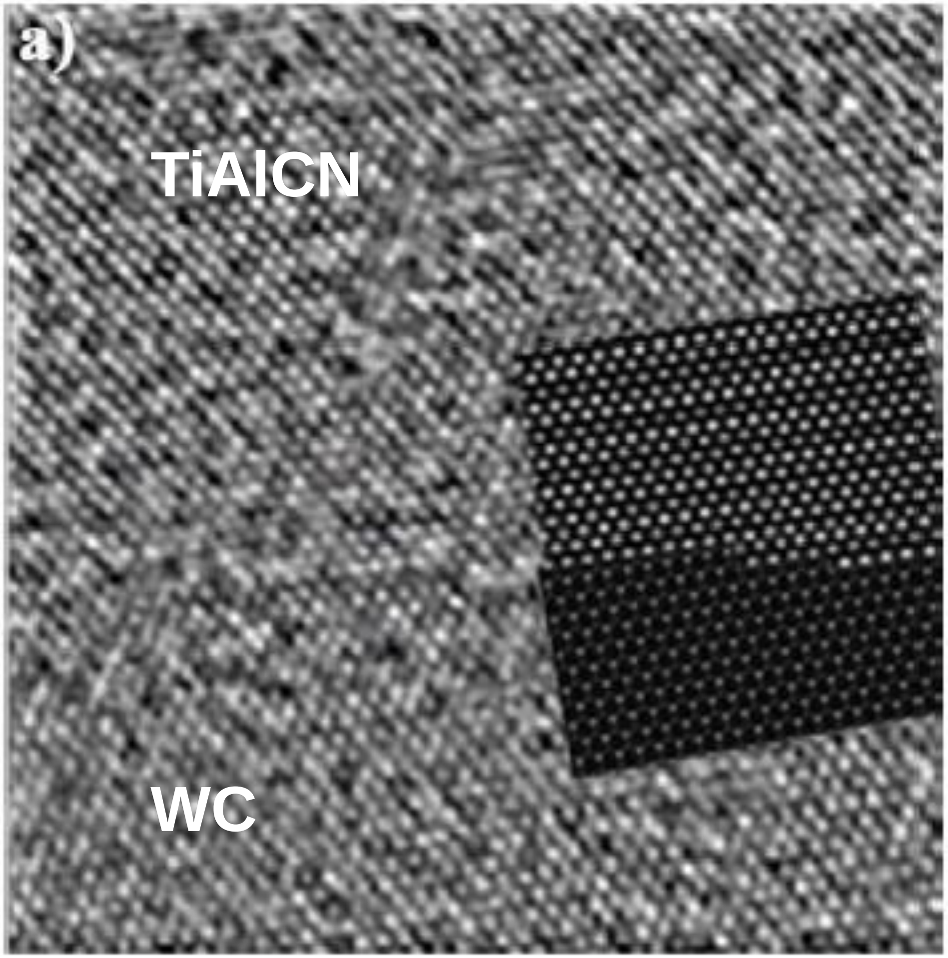
N.B. Dahotre, S. Nayak / Surface & Coatings Technology 194 (2005) 58–67

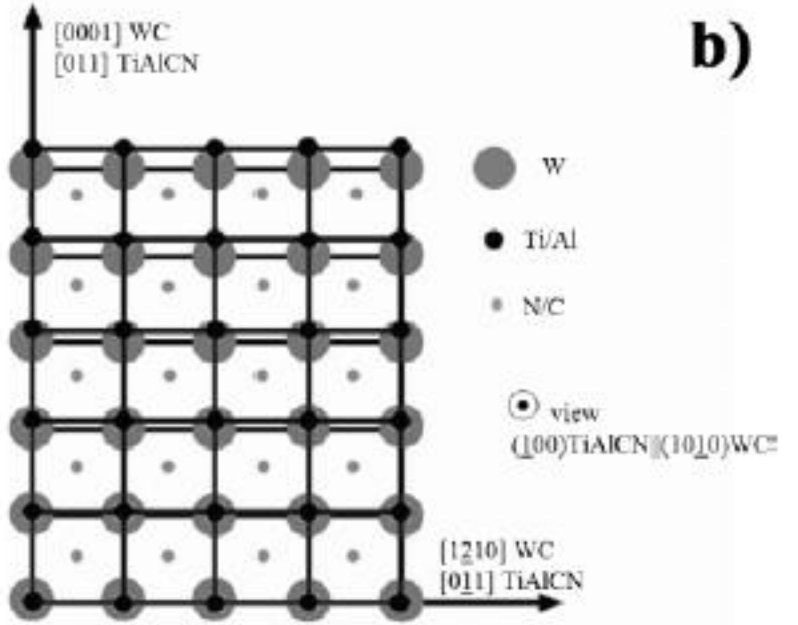
VI. *Hard PVD ceramic coatings –*
Low friction coatings

Attention recently has focussed on the development of hard, wear resistant, low friction coatings such as Graphit-iC™, MoST™ and Dymon-iC™, with the automotive industry again the driving force.

Coating materials: graphite, MoS_2, WS_2, oxides, minerals in nanocomposites with nitrides.

The coefficient of friction must be below 0.1, sometimes close to 0.01.





FFT filtered HRTEM image (a) with simulated image of the transition between WC substrate and TiAlNC coatings. (b) the atomic view of the interface from the direction of the normal of the interface.

A critical feature of the industrially applied coatings is the durability, which depends much on the properties of the substrate-coating interface.

A.Kovács, B.Veisz, P.B.Barna, G.Radnóczi, and M.Stüber
EMC abstract

V. Hard PVD ceramic coatings – Amorphous hard coatings, DLC and CNx

DLC (diamond like carbon) film growth- by energetic particles – subplantation, 10 eV

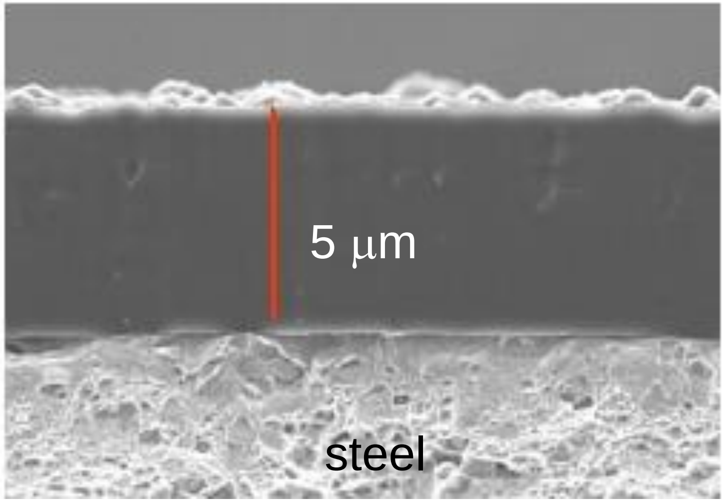
Compressive stress develops 1-10 GPa

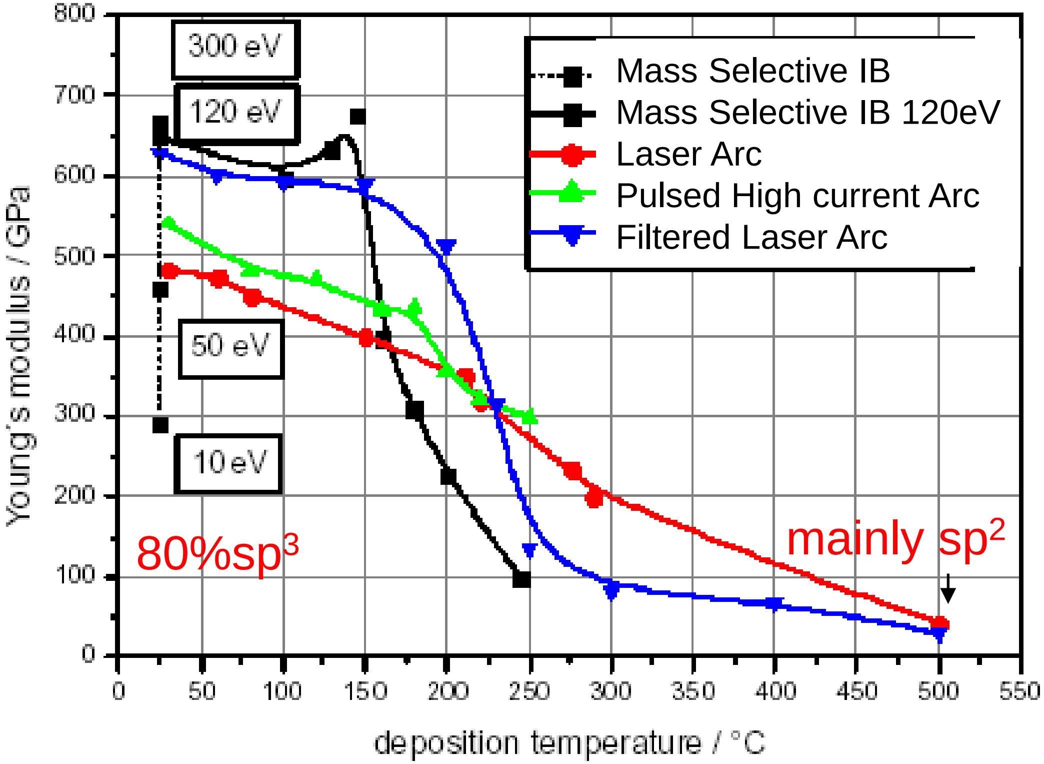
Relaxations during growth: above 100 ^oC
during annealing above 400 ^oC in oxygen or air
above 600 ^oC in vacuum

Corresponding to the subplantation process the general structure of ta-C films consists of three zones:

1) a transition zone as an intermixing of the surface substrate elements with carbon,
2) the real DLC layer with dominating sp^3 bonds and
3) a more graphitic thin surface layer.

As a well-proven rule of thumb, the hardness lies above one tenth of the Young's modulus: $H > E/10$.
The Young's modulus is directly determined by the stiffness and the density of the atomic bonds and correlates with the fraction of sp^3 bonds. Correspondingly, the Young's modulus varies for amorphous carbon films over an extreme range from < 100 GPa up to > 700 GPa (for perfect diamond polycrystals E=1143 GPa).





B. Schultrich, H.-J. Scheibe, V. Weihnacht
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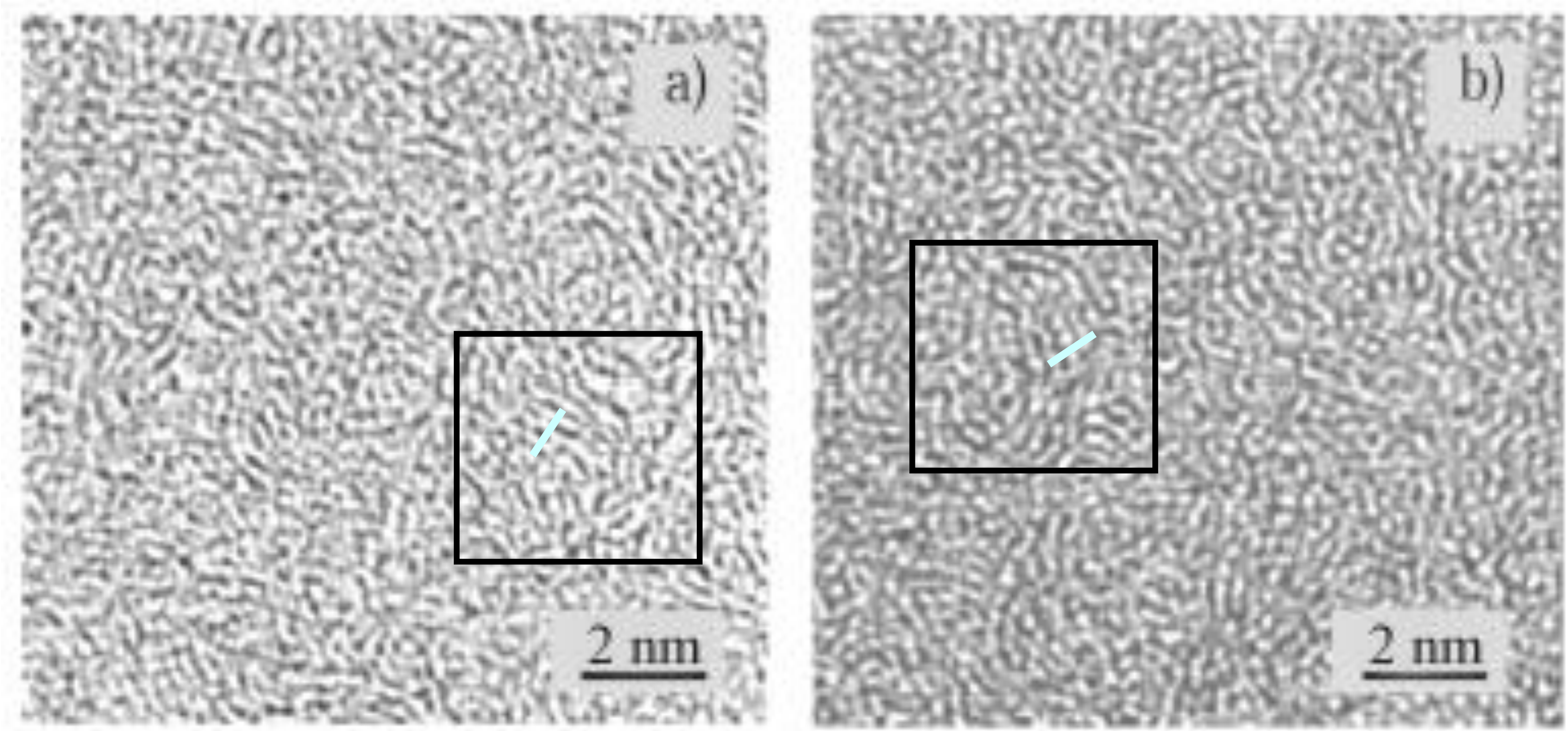
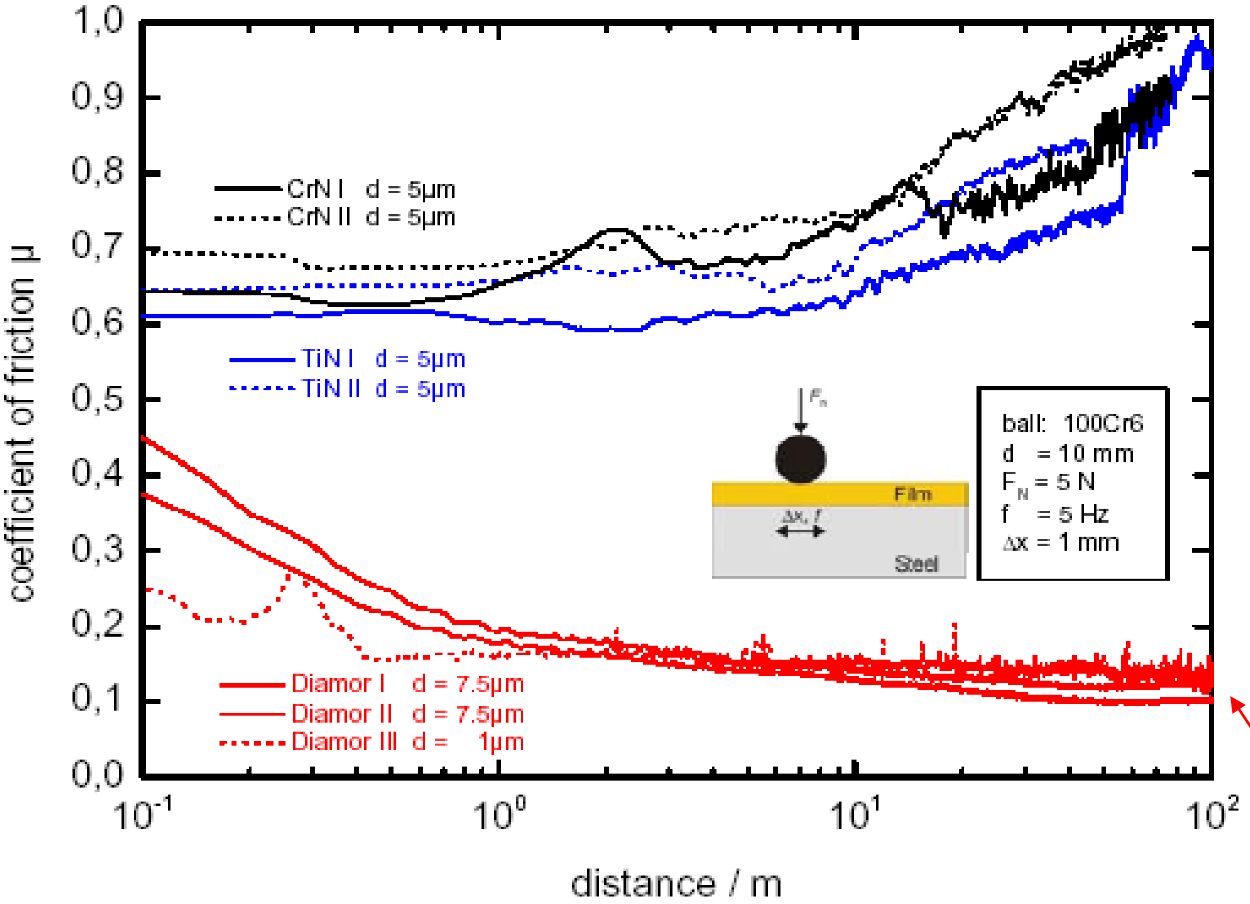


Plan-view high-resolution electron micrographs of structures for Si-C-N films grown at 350 ^{o}C, corresponding to region I (a) and region III (b).

T. Berlind, N. Hellgren, M.P. Johansson, L. Hultman: Surf. and Coatings Technology 141 (2001) 145-155



Friction behavior of Diamor® and nitride films on steel against 100Cr6 ball.

„the real DLC layer with dominating sp³ bonds and **a more graphitic thin surface layer”**

The friction behavior of Diamor® is studied by a fretting tribometer (ball on disk) in comparison to classic hard coating (TiN, CrN). No lubrication was used. This result demonstrates the improvement in the tribological properties in comparison to classic hard coatings, which can be obtained with DLC films under this testing condition.

B. Schultrich, H.-J. Scheibe, V. Weihnacht
Fraunhofer Institute for Material and Beam Technology IWS, Dresden, Germany

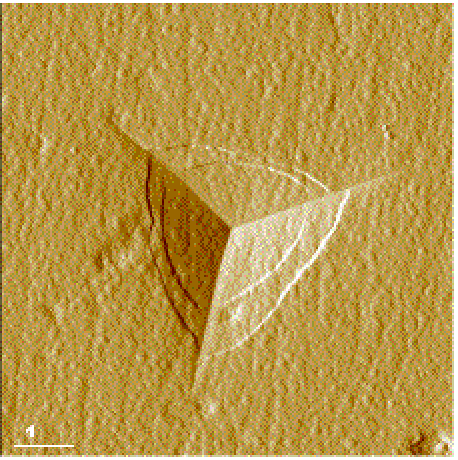
VII. Hard PVD „ceramic” coatings – Metal-metal nanocomposites

In many prospective applications other than cutting tools, where the substrate stiffness and strength may be comparatively low, ultrahard ceramic films (which tend also to exhibit high stiffness) are rarely the ideal solution. Hard, stiff ceramic films are fundamentally mismatched to these soft, low elastic modulus materials.

As has been demonstrated previously, by bearing designers and polymer tribologists, a bulk materials approach to wear which utilises both the hardness (H) and the elastic modulus (E) of the material gives more predictable results in ranking wear performance of engineering coatings. In this respect, a high H/E ratio is desirable, since this implies a longer ‘elastic strain to failure’ (ie. improved resilience) for the material. It is often metallic films which (if sufficiently hard) give superior results, due primarily to a combination of resilience and toughness more closely matched to the substrate material properties.In essence, such coatings tend inherently to be more ‘damage tolerant’.

Properties: brittle (TiN, diamond and other ceramic materials),
elastic (CNx, some nanocomposites, e.g. CNx-Ni)
plastic (tough, soft, like Sn-Al)

To fit the properties of the substrate and coating, for softer materials metallic coatings can be better.



“*On the significance of the H/E ratio in wear control : A nanocomposite approach to optimised tribological behaviour.*”
A.Leyland & A.Matthews *Wear* 246 (2000) 1.

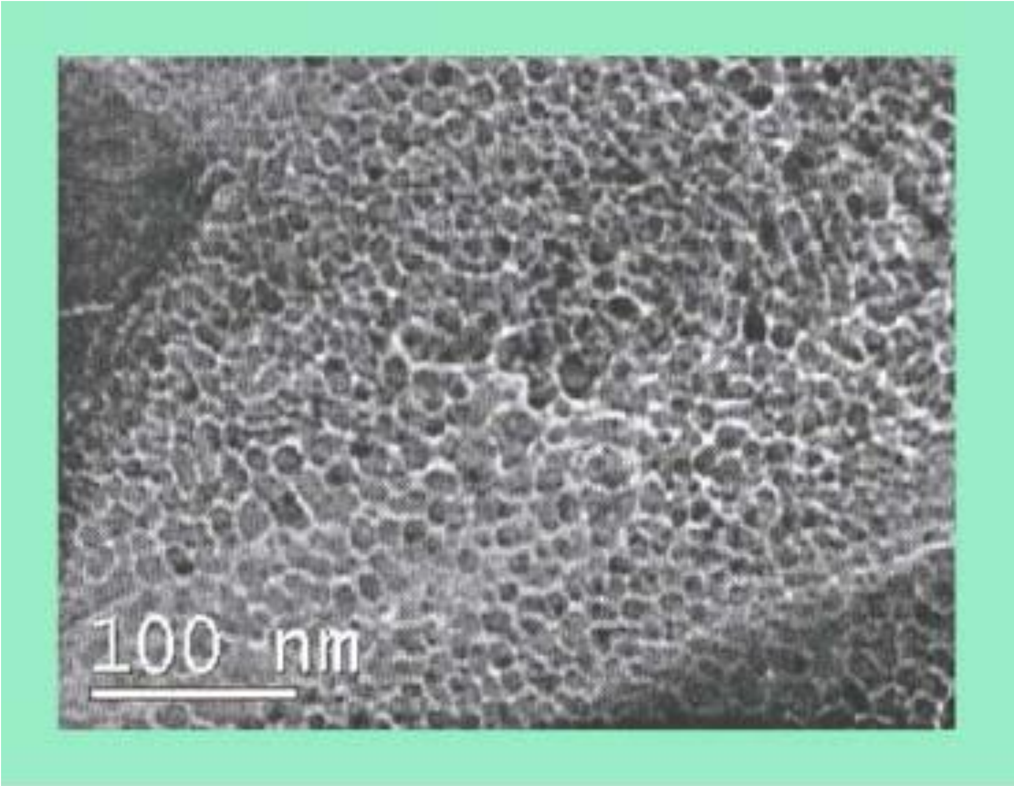
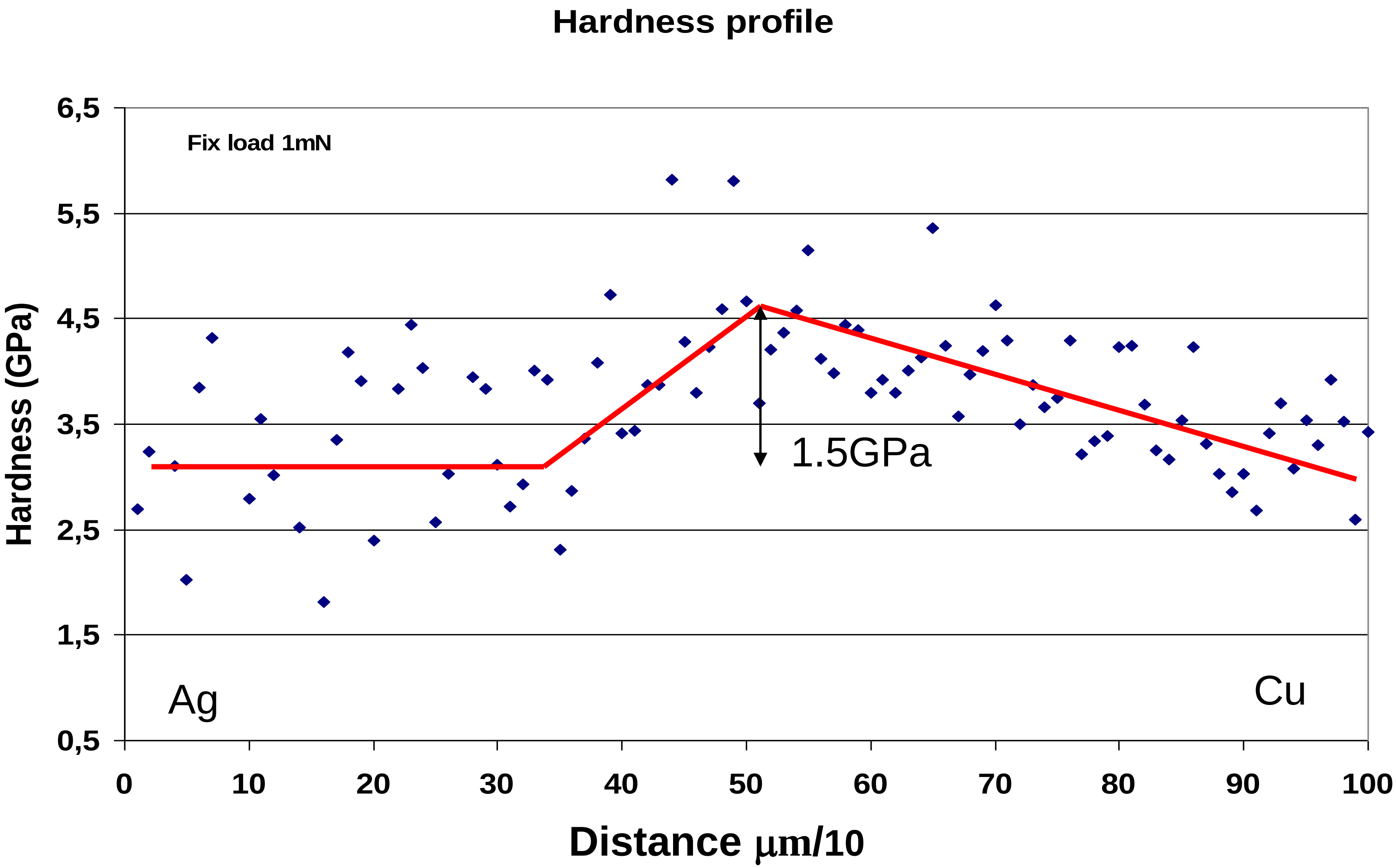
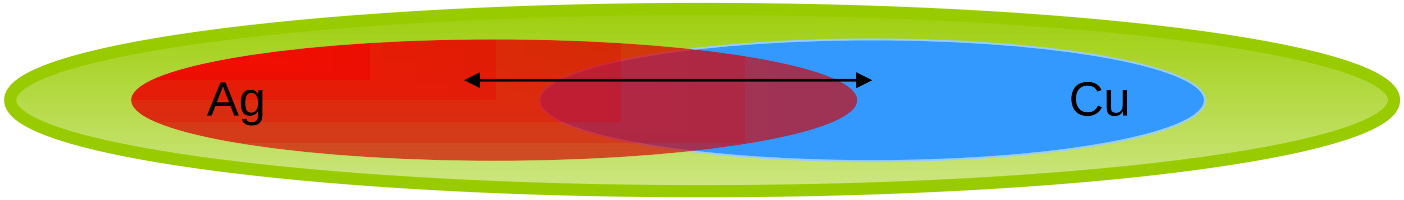


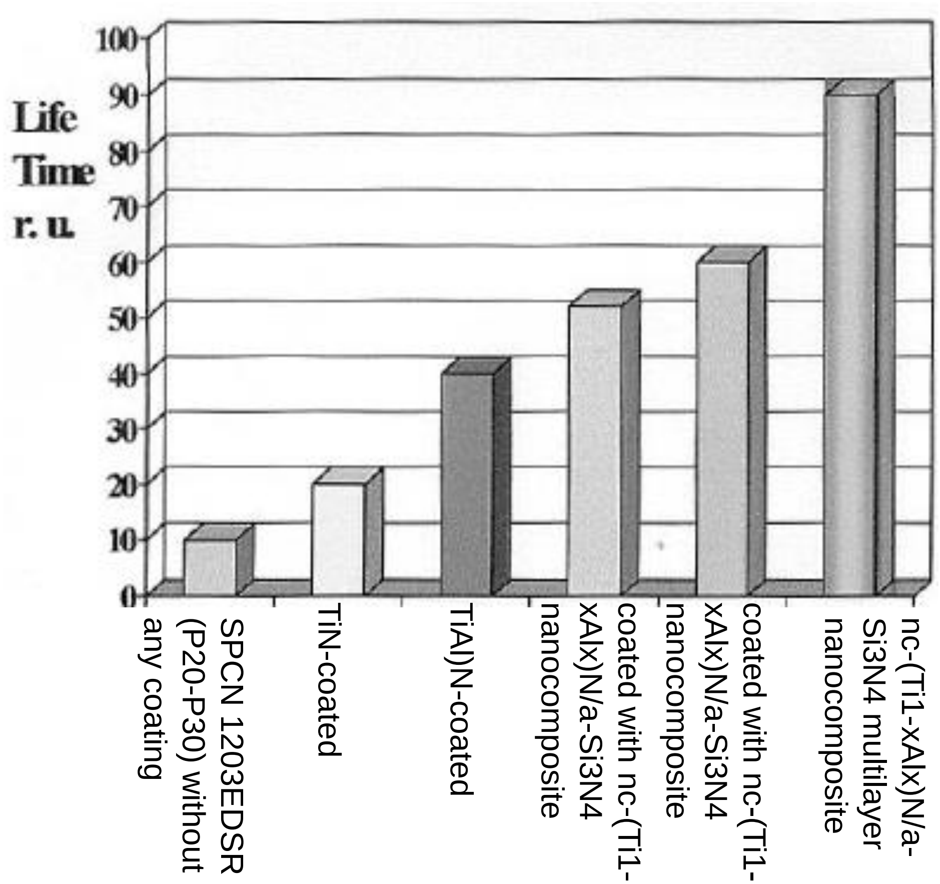
Figure 1 TEM bright-field plan-view of CrCu(N) coating nanostructure





Load controlled mode 1mN fixed load.
Loading and unloading rate 0,02mN/s.

F. Misjak, T. Ujvári, G. Radnóczi



Example of the cutting performance of various coatings. Symmetric milling of steel CK45, feed 0.23 mm/tooth, depth of cut 2 mm, cutting speed 179 m/min.

A variety of tools for dry and fast turning, milling, drilling are coated and successfully used by the customers. Under the conditions of the dry machining, which saves the environmentally risky coolants and saves costs, the temperature of the cutting edge and of the rake reaches 600–800 °C. This illustrates the need of thermally stable and oxidation resistant coatings.

S. Veprek and M. Jilek: *Pure Appl. Chem.*, Vol. 74, No. 3, pp. 475–481, 2002.

SUMMARY

The phases constituting a nanocomposite can be:

a nanocrystalline phase and an amorphous
two nanocrystalline
two amorphous phases.

The basic idea for the design of nanocomposites is based on the thermodynamically driven segregation in binary (ternary, quaternary) systems. The segregation leads to the spontaneous self-organization of a stable nanoscale structure. Kinetic limitation of any changes at the application conditions.

This generic concept has recently led to the development of superhard (>40GPa) and multifunction nanocomposite PVD coatings.