

Carbon based nanocomposite thin film coatings for wood processing tools – a review and possible solutions.

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Introduction

Coatings for wood processing tools have to meet requirements which are substantially different from those, defined for metal processing. Due to properties of wood, its heterogeneous structure containing very often hard inclusions, its low thermal conductivity, humidity and incorporation of highly corrosive substances, coatings protecting wood processing tools should be impact resistant, chemically inert and corrosion resistant. These features should be accompanied by commonly required high adhesion, limited internal stress, abrasive wear resistance and low friction.

Required properties and functionalities of coatings have to be considered together with tool material (Low Alloy Steel – LAS, High Speed Steel - HSS, cemented carbides, stellites), tool geometry and processing conditions (cutting speed, cutting feed and depth) as well as type of processed material (rough wood, laminated particle boards, MDF boards). Particular requirements refer to extremely sharp cutting edges with the angle below 20° and cutting edge radius smaller than $15\mu\text{m}$.

It is nearly impossible to meet all these requirements simultaneously. Thus, the coating type has to be selected for particular category of tools and wood processing conditions.

In the group of coating materials studied but also applied by wood industry or more precisely saying by wood processing tool manufacturers, there are two main subgroups:

- single- and multi-component nitrides and to smaller extend carbides of transition metals (Ti, Cr, W) combined with light elements (Al, Si),
- carbon based materials, including hard and hydrogen free or hydrogenated tetrahedral amorphous carbon (ta-C or ta-C:H), hydrogenated amorphous carbon (a-C:H) and a wide spectrum of carbon based nanocomposites containing nano-sized inclusions of: (i) metals (Ag, Cu, Ni, Co, Cr) with low reactivity to carbon or (ii) metal carbides (TiC, WC, MoC, NbC).

These materials are deposited in the form of single or multilayer coatings with the sub-layer period down to nanometers.

The aim of this work is to review the state of the art in the field of carbon based coatings and to focus on those of them which could be considered as candidates for applications in wood processing industry.

Amorphous carbon - classification

Carbon – the matrix material for all of these C-based coatings has been classified, dependent on sp^3 and/or sp^2 bonding fraction and hydrogen content as shown in Fig. 1. [1].

As described by Robertson [1,2], the great versatility of carbon materials arises from the strong dependence of their physical properties on the ratio of C-C sp^2 (graphite-like) to C-C sp^3 (diamond-like) bonds. In general, an amorphous carbon can contain any mixture of sp^3 , sp^2 bonds. The content of hydrogen can reach up to 60 at.%. In the left part of the triangle – Fig. 1, along the sp^2 - sp^3 line, material with higher sp^3 content is termed tetrahedral amorphous carbon (ta-C) and its hydrogenated analog: ta-C:H.

Going down to sp^2 corner we find graphite-like carbons. With increasing hydrogen content ta-C transforms into softer a-C:H – hydrogenated amorphous carbon.

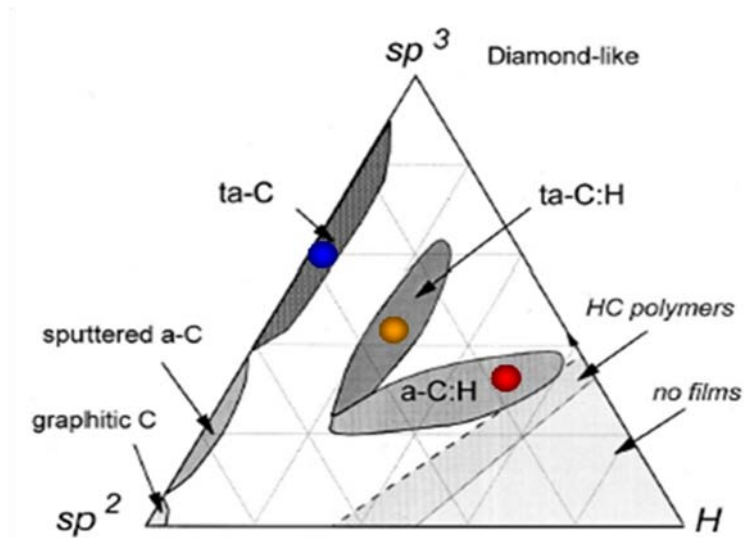


Fig. 1. Ternary phase diagram of amorphous carbons. The three corners correspond to diamond, graphite and hydrocarbons, respectively [1].

The most reliable identification technique for different carbon phases is Raman spectroscopy commonly used for this purpose. Widely recognized in depth analysis of experimental data and interpretation method of Raman spectra for amorphous carbon phases has been proposed by Ferrari and Robertson [3,4]. Also some basic properties of a-C:H like density, Young's modulus, optical band gap and refractive index are related to hydrogen content as well as sp^3/sp^2 ratio, as has been shown by C. Casiraghi et al. [5] who analyzed Raman spectra recorded for 514nm and 244nm laser wavelength.

It should be kept in mind that the information gained from the amorphous carbon films is usually "statistical" in nature since at the present, there is still a lack of direct atomic characterization method that can be used over a large scale. In addition, because of the complex structure of carbon films, inner stress, dangling bonds and dislocations, characterization of the carbon film structure may not be definite. In the most cases, to tackle the problem, the parallel use of multiple techniques (UV and VIS Raman, IR Spectroscopy, EELS, XPS, HRTEM, AFM) is recommended [6].

Tetrahedral amorphous carbon (ta-C) and a-C hydrogen free coatings

Thin film coatings based on hydrogen free tetrahedral amorphous carbon (ta-C) with sp^3 fraction up to 90% are usually deposited by DC or pulsed vacuum arc evaporation of graphite targets. Relations between deposition conditions (ion energy, substrate temperature, deposition rate) and ta-C coating structure/properties and stress state have been discussed by Chhowalla [7], Inkin et al. [8] and recently by Lau et al. [9]. Their high hardness and Young's modulus (around 70 and 700 GPa, respectively), low friction and chemical inertness make them good candidates for challenging wear-resistant applications [1,7]. Simultaneously, high compressive stress reaching up to 12 GPa substantially limits the the thickness of adherent coatings to about 100nm – Fig. 2.

The stress magnitude is directly related to sp^3 fraction which again depends on deposition conditions (carbon ion energy and substrate temperature. These relations have been discussed in numerous reports [1,7,8,10]. To overcome the problem of low adhesion of highly stressed

ta-C coatings to standard substrate materials (HSS, cemented carbide, Ti6Al4V), several solutions have been proposed.

They consist in multistep deposition processes including:

- substrate (Ti6Al4V) pretreatment by carbon ion beam (1 keV C⁺) [7],
- substrate (Low Alloy Steel AISI 4140) pretreatment by Ti ions (> 1 keV) followed by intermediate Ti layer deposition [11],
- substrate (AISI 4140) gas nitriding to 650 HV (6.5 GPa without compound layer) or to 850HV (with 5μm thick γ' compound layer) [11],
- deposition of multilayers with softer a-C component [12],
- deposition of thin, Ti or Al interlayer before ta-C deposition [13],

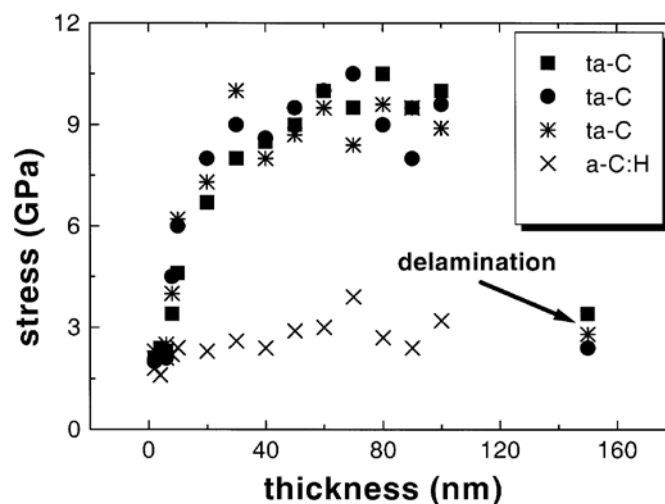


Fig. 2. Compressive stress vs. the film thickness for ta-C and a-C:H [7].

Hakovirta reported on significant improvement of cutting performance and tool life time for hardmetal (WC-Co) woodcutting tips coated by filtered cathodic arc deposition of ta-C/Cr multilayers [14]. These results have been attributed to compressive stress relief into softer Cr layer. Chromium has also played a role of corrosion preventing component [15].

An interesting aspect of coating stability and failure characteristics of CVD ta-C films on cemented carbides used for machining of wood-based composites has been discussed by Sheikh-Ahmad et al. [16]. Authors have found that honing of cutting edge significantly reduces early edge breakage, reducing residual stresses and micro cracking of the ta-C coating.

New approach to analysis of relation between mass density and mechanical properties of ta-C films deposited by FCVA (Filtered Cathodic Vacuum Arc) was proposed by Tan et al. [17]. A simple model was established between the density and elastic behavior of ta-C films. The model predicts the experimental data quite well from the plot of modulus and hardness vs. mass density for the films.

The load carrying capacity of coating-substrate system depends also on properties of the substrate material. The elastic-plastic contact between a rigid ball and hard coatings of varying thickness on various substrates has been simulated using the finite element method [18]. Yield strengths and modulus values representing typical values for high-speed steel, titanium and aluminum alloys differentiated between the substrates. The effects of such important parameters as the thickness of the coating and properties of the substrate material on the initiation and development of plastic deformation and the load bearing capacity of the coating/substrate systems have been investigated.

The results show that in most of the coating/substrate systems, plastic deformation is initiated in the substrate at the coating/substrate interface and plastic deformation does not initiate in the coating until a large plastic zone has been developed in the substrate. Substrate strength and coating thickness have a significant influence on the plastic deformation behaviour and the load bearing capacity of the composite [Sun95]. In that context duplex processes with substrate pretreatment (nitriding) prior to deposition of hard ta-C coating [11] should be extensively studied.

It should also be noted that tribological properties of ta-C coatings, i.e. friction and wear, are strongly dependent on humidity of the environment as has been extensively discussed by Voevodin [19] and Erdemir [20]. Since σ -bonds of surface carbon atoms are passivated by water molecules, friction coefficient for that type of coatings remains relatively low (0.2). Behaviours of hydrogen free ta-C coatings tested in terms of humid wood cutting applications have been recently reported by Tillmann et al. [21].

S. Zhang and his team, searching for the way to improve adhesion and increase toughness of hard carbon films tested “bias-graded” coatings deposited by magnetron sputtering of graphite. High adhesion strength at low bias and high hardness at high bias may combine to produce high adhesion and high hardness coatings to suit specific applications through a bias-graded deposition (gradually increase the bias power as deposition proceeds). The range of hardness from 18 to 28 GPa is adequate for most tribological applications. The graphitization adds more benefit aside from reducing friction: the graphite layer can considerably reduce the adhesive wear since it prevents the asperities of the two surfaces to be adhered to each other [22,23].

Sheeja et al. reported on deposition of low stress ta-C coatings by FCVA. The study reveals that the origin of the coating instability, and the high internal compressive stress, can be overcome by preparing it in conjunction with substrate pulse biasing.

A shorter pulse on-time of about 0.125% (duty cycle) reduces the stress by about 85% - Fig. 3, but at the same time it preserves the smoothness as well as the hardness of the coating to a certain extent [24].

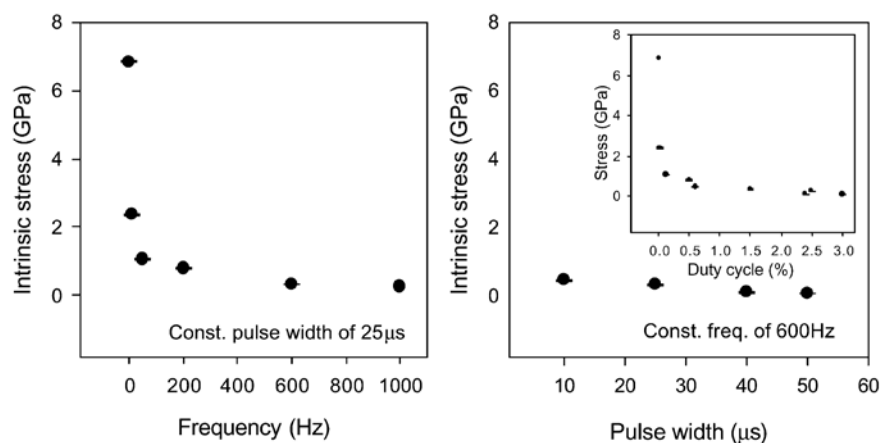


Fig. 3. Intrinsic stress in the coatings deposited at pulse biased substrates of different frequency and pulse width [24].

However, a longer pulse on time reduces the stress further a bit, but diminishes the smoothness as well as the hardness – Fig.4. The study suggests that a frequency of 50 Hz and a pulse width of 25 ms is enough to produce thick and relatively good quality films [24].

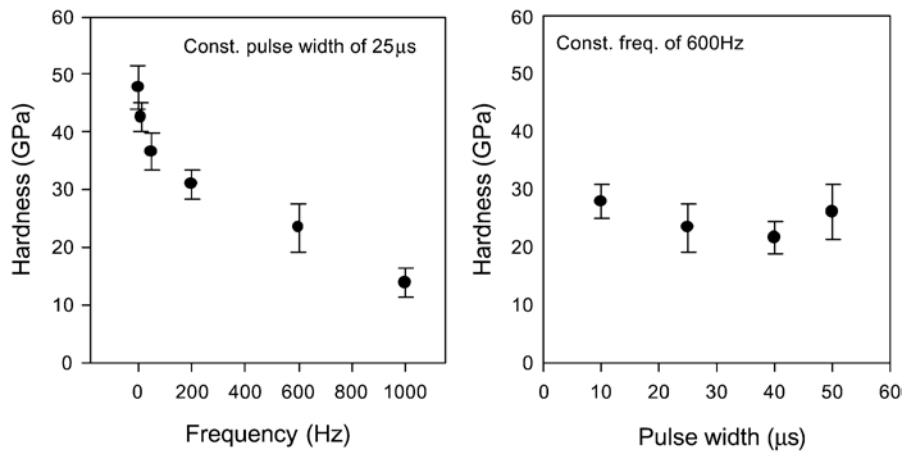


Fig. 4. Hardness of ta-C coatings deposited at pulse biased substrates of different frequency and pulse width [24].

Recently also other reports clearly suggest that it is possible to tune the sp^3 content in ta-C films just by varying pulse width at particular frequency and bias voltage to the substrate [25].

Metal doped Me/ta-C and Me/a-C hydrogen free coatings

Very good tribological properties of ta-C coatings but also high compressive stress resulting in their limited toughness and adhesion were a driving force for search of new solutions aiming at design of carbon based materials free of these disadvantages.

The concept of carbon based nanocomposite coatings have been introduced by Voevodin and coworkers [26-29] and in the next decade developed in numerous laboratories. Titanium, known for its high reactivity to carbon and thermodynamically stable carbides was the first doping element used in these composite materials.

While number of reports on deposition and properties of titanium carbide containing nanocomposites with hydrogenated amorphous carbon (a-C:H), which will be discussed later on is very high, TiC/ta-C composites attracted less attention. However, some recent reports point at enhanced toughness and adhesion of that type of coatings [30, 31].

Yang et al. reported on structure and tribological properties of low temperature deposited Ti-a-C coatings prepared by middle frequency magnetron sputtering of Ti and graphite targets [32].

Authors pointed at the structure of coatings deposited at the substrate temperature below 100°C and at bias voltage of -100V , where nanocrystallites of non-reacted metallic titanium can be found in the amorphous carbon matrix. The composite coating containing 4 at.% of Ti had shown hardness of 20 GPa accompanied by very low friction (<0.1 measured at relative humidity of 60% against WC-Co ball) and wear rate below $10^{-16} \text{ m}^3/\text{Nm}$.

Zhang et al. discussed the ways towards highly adherent and tough a-C coatings [33].

These authors also stressed that the incorporation of metals into hydrogen-free a-C matrix is an effective way in reduction of growth-induced stress through co-sputtering metal to act as a stress-relaxant. Among stress relaxing elements (Ti, Al, Si, etc.), Al was found to be one of the most effective elements in relieving stress [34,35]. However, the incorporation of Al, which doesn't form carbides, results in reduction of hardness due to reduced sp^3 hybridization: about 60% of the coating hardness is lost when it is doped with only 10 at.% of aluminum as shown in Fig. 5 [34].

To restore hardness, Zhang had co-sputtered Ti, Al and C to produce randomly orientated nanocrystalline TiC grains embedded in Al-containing a-C matrix and form a nanocomposite coating of nc-TiC/a-C(Al) [37].

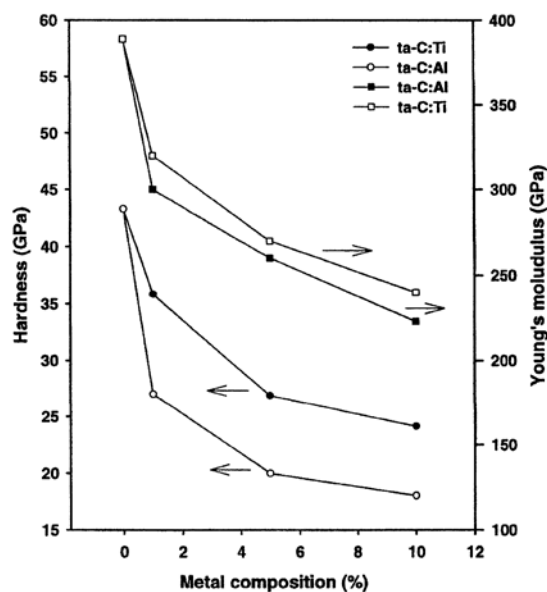


Fig. 5. Influence of metal composition in the target on the microhardness and Young's modulus of Ti/ta-C and Al/ta-C: films [34].

These coatings have shown low residual stress, high hardness and toughness.

In Tay's investigation [35], an off-plane double bend filtered cathodic vacuum arc (FCVA) technique was used to deposit metal doped a-C composite films by using the Si/C, Al/C, Ti/C, Fe/C, Ni/C and Co/C targets with different metal compositions.

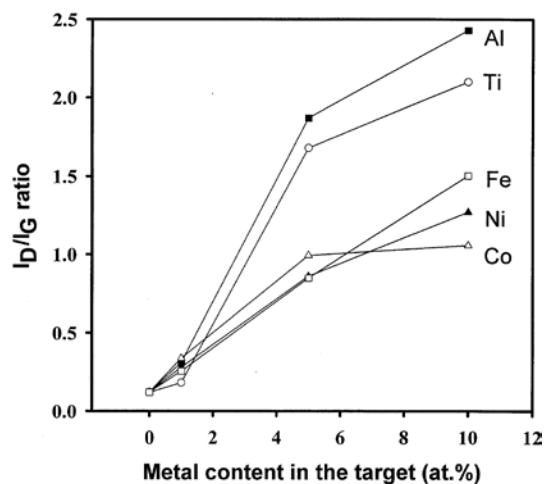


Fig. 6. Change in I_D/I_G ratio of a-C:Me films as a function of metal composition in the targets [35].

As has been shown in Fig. 6, the influence of metal composition in the target on the intensity ratio of G peak and D peak (I_D/I_G) of Al, Ti, Fe, Ni and Co containing a-C films. The incorporation of metal into films leads to the increase of I_D/I_G ratio. This variation suggests that incorporation of metal in the films results in the increase of sp^2 phase fraction and the size of sp^2 C clusters [35,36].

The incorporation of Al, Ti, Fe, Ni and Co leads to the decrease of the internal stress in the films, whereas the hardness and Young's modulus still remain at relatively high values –

Fig. 7. Due to the formation of carbide, the hardness of a-C:Ti film is higher than that of Al/a-C film. The decrease in internal stress of a-C:Me films provides a way to prepare thicker and high hardness films for mechanical applications such as hard coatings. Authors conclude however that FCVA technique costs were high, deposition rate low when compared with conventional cathodic vacuum arc deposition process.

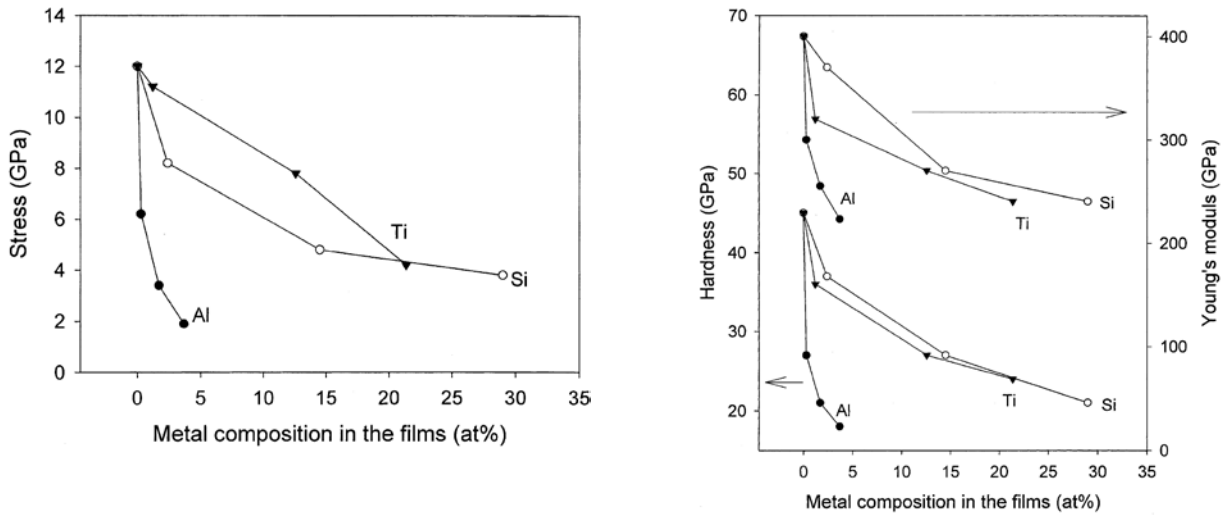


Fig. 7. Stress magnitude and hardness of Me-aC coatings vs. metal content in the film [35].

The mechanical properties and the atomic bond structure of the Si incorporated ta-C films were investigated over a wide range of Si concentrations by Churl Seung Lee et al. [39]. The most important result of this work is that a small amount of Si addition to ta-C films could significantly reduce the residual stress with a little degradation of the mechanical properties – Fig. 8.

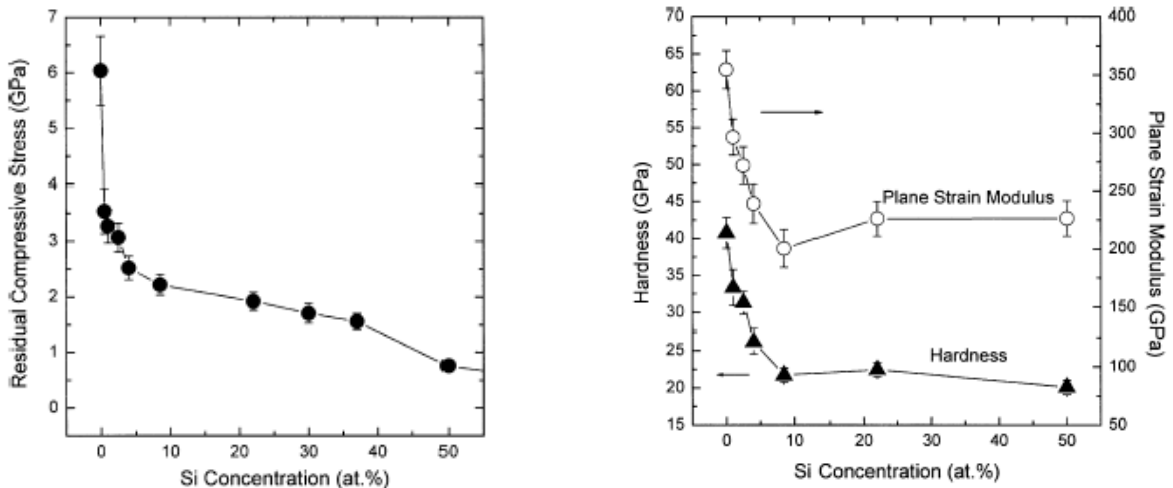


Fig. 8. Residual stress, hardness and plane strain modulus vs. Si content in the coating [39].

When the Si concentration was higher than 10 at.%, the residual stress and the mechanical properties were saturated to the values of SiC phase – Fig. 8. The observed behavior could be understood in terms of the changes in the atomic bond structure caused by the Si incorporation.

The first apparent effect of the Si incorporation was to substitute the sp^3 carbon atoms, generating weaker Si–C bonds. The large strain of the weaker Si–C bonds caused the relaxation of distorted C–C bonds near the Si. However, this change in atomic bond structure did not change the fraction of sp^3 bonds in the film.

Therefore, the hardness and the elastic modulus which are intimately related with the three-dimensional interlinks gradually decreased with Si concentration. Further increasing the Si concentration generated the SiC phases, resulting in the saturated mechanical properties comparable to those of SiC [39].

There are worth mentioning results published by X.T. Zeng et al. who deposited Cr/a-C coatings on HSS by multisource magnetron sputtering from graphite and chromium targets [40]. An exceptional load-bearing capacity, high scratch-test adhesion ($>95\text{N}$) and high wear resistance ($10^{-17}\text{m}^3/\text{Nm}$ against alumina) has been observed for these, mainly sp^2 bonded material with high electrical conductivity.

Substrate geometry effects on uniformity of Cr/a-C magnetron deposited coatings have been than studies by X. Ding et al. [41].

Metal doped Me/a-C:H hydrogenated amorphous carbon coatings

Amorphous hydrogenated carbon (a-C:H), is an amorphous network composed of carbon and hydrogen. This network consists of strongly cross-linked carbon atoms with mainly sp^2 (graphitic-like) and sp^3 (diamondlike) bonds. The properties of these coatings depend strongly on the hydrogen content and the sp^3/sp^2 ratio, which in turn, depend on the deposition process and its parameters. The deposition method to grow these films and their properties are described in the review articles by Robertson [1,2].

The hydrogenated a-C films are classified into four types [50]:

- a-C:H films with the highest H content (40–60 at.%). These films can have up to 70% sp^3 . However, most of the sp^3 bonds are H terminated (i.e. C–H instead of C–C bonds) and the material is soft and has low density
- a-C:H films with intermediate H content (20–40 at.%). Even if these films have lower overall sp^3 content, they have more C–C sp^3 bonds than the previous types of a-C films. Thus, they have better mechanical properties.
- Hydrogenated tetrahedral amorphous carbon films (ta-C:H). The C–C sp^3 content can be increased while keeping a fixed H content. Because of the higher sp^3 content (~70%) and 25–30 at.% H, ta-C:H films dispose a higher density (up to 2.4 g/cm^3), and Young's modulus (up to 300 GPa) when compared to a diamond-like a-C:H.
- a-C:H with low H content (less than 20 at.%), having a high sp^2 content and sp^2 clustering. These films are called graphite-like a-C:H and they are usually deposited by PECVD at high bias or magnetron sputtering.

The design concept of hard, tough, highly adherent and low friction coatings based on amorphous hydrogenated carbon and also on other materials like Si_3N_4 or SiC, able to form amorphous matrix, is based on the following assumptions [42]:

- a graded interface layer is applied between the substrate and crystalline/amorphous composite coating to enhance adhesion strength and relieve stresses (combination of functional gradient and nanocomposite design)[28];
- encapsulation of 3-10 nm sized hard crystalline grains in an amorphous matrix restricts dislocation activity, diverts and arrests macro-crack development, and maintains a high level of hardness similar to superhard coating designs [43,45,46];
- large volume fraction of grain boundaries provides ductility through grain boundary sliding and nano-cracking along grain/matrix interfaces [47-49].

The primary differences between superhard and tough coating designs are: selection of a matrix phase with a lower elastic modulus, relaxation of the requirement for strong binding between matrix and grains, and selection from a greater range of acceptable grain sizes of nanocrystalline phase in tough coatings.

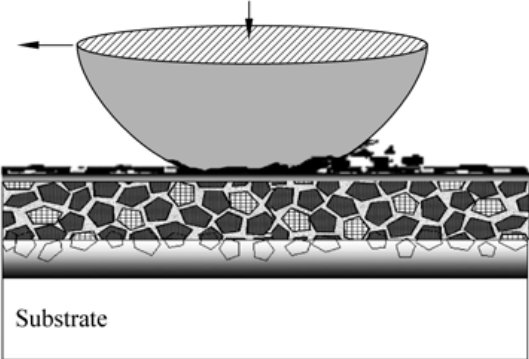


Fig. 9. Schematic of a tough nanocomposite coating, featuring a noncrystalline/amorphous design in the main coating layer for cohesive toughness and a functionally gradient interface layer for adhesive toughness [42].

Combination of the nanocrystalline/amorphous designs with a functionally graded interface, as shown in Fig. 9, provides high cohesive toughness and high interface (adhesive) toughness in a single coating. Several examples of tough wear resistant composite coatings have been reported.

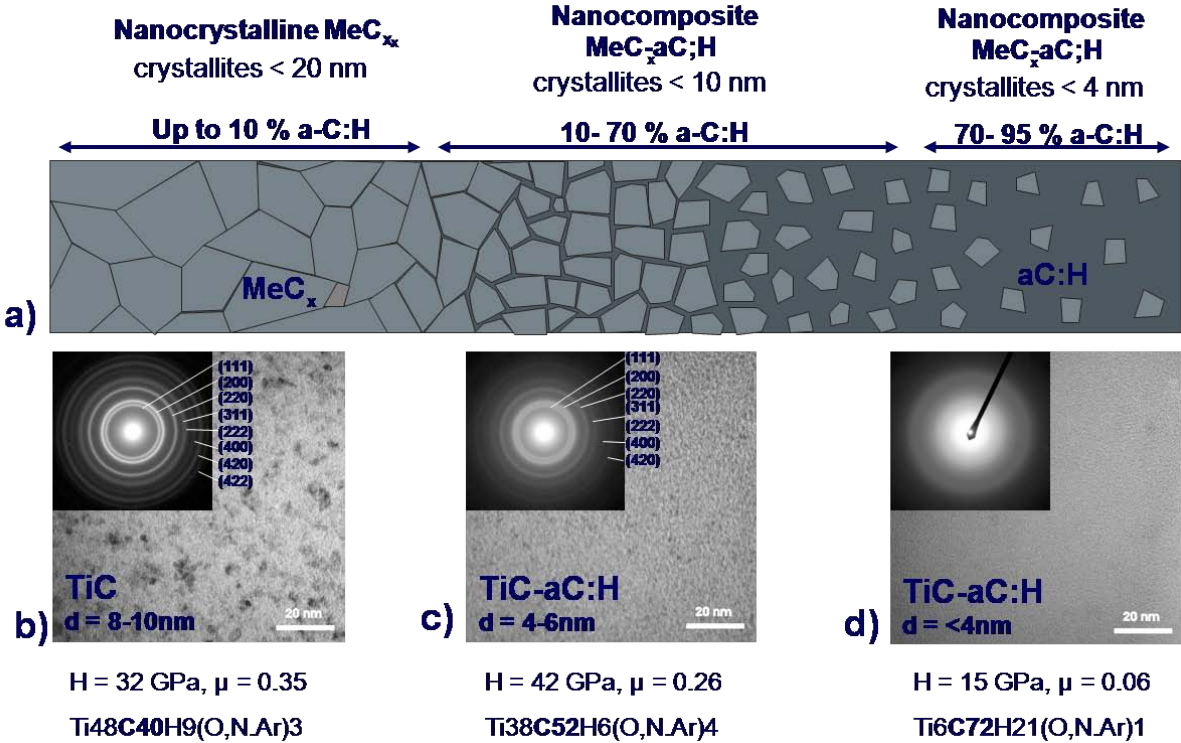


Fig. 10. Evolution of the microstructure and properties of TiC/a-C:H coating with increasing carbon content [51].

A typical structure and properties evolution with increasing fraction of amorphous carbon matrix for TiC/a-C:H nanocomposite coatings has been shown in Fig.10.

Enhanced toughness and still high hardness as well as Young's modulus is observed for the coatings' structure where the grain size drops below 10nm.

Coatings of that type, deposited usually in reactive processes with gaseous hydrocarbon (CH_4 , C_2H_2) as a carbon source contain 20-40 at.% of hydrogen, dependent on deposition conditions [51,52].

The hardness and elastic modulus of such coatings show the metal content dependent maximum as shown in Fig. 11.

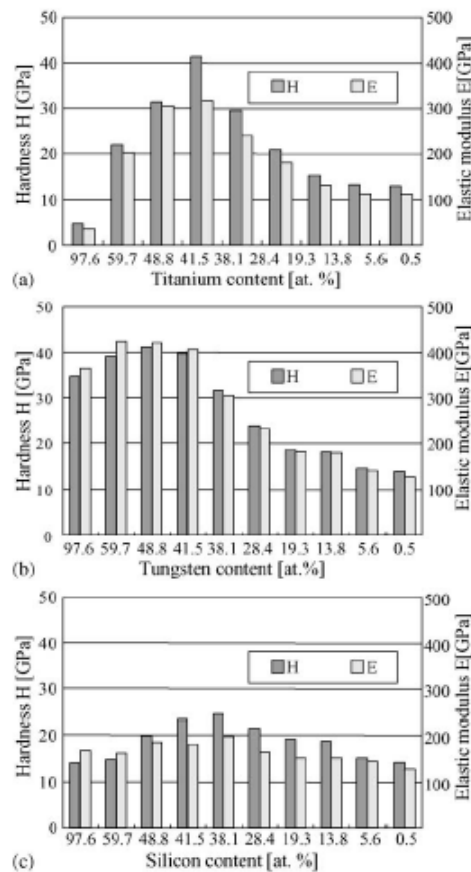


Fig. 11. Hardness and elastic modulus evolution for metal (Ti, W) and silicon doped hydrogenated amorphous carbon coatings [51].

An interesting interpretation of catalytic role of transition metals promoting sp^3 carbon bonding has been proposed by Sung et al. [53]. According to these authors transition metals with intermediate reactivities can attract carbon atoms in graphite without forming a carbide. The ability for a transition metal to react with carbon increases with its number of electron vacancies in d-orbitals. Elements (e.g. Cu, Ag, Zn) with no d-orbital vacancies are inert relative to carbon. Elements (e.g. Fe, Co, Ni) with few d-orbital vacancies are effective carbon solvents. Elements (e.g. Ti, V) with many d-vacancies are carbide formers.

The model proposed predicts that the most powerful elemental catalysts are Co, Fe, Mn, Ni and Cr. These transition metals are the most commonly used catalyst components for the commercial production of synthetic diamond under high pressure.

This idea has been developed by Y.Y. Chang et al. [55] who studied mechanical and tribological properties of Ti, Zr and Cr containing nanocomposite coatings reactively deposited by cathodic vacuum arc (CVA).

The coating structure consisted of metal nitride sublayer followed by gradient transition to nanocomposite layer, as shown in the Fig. 12.

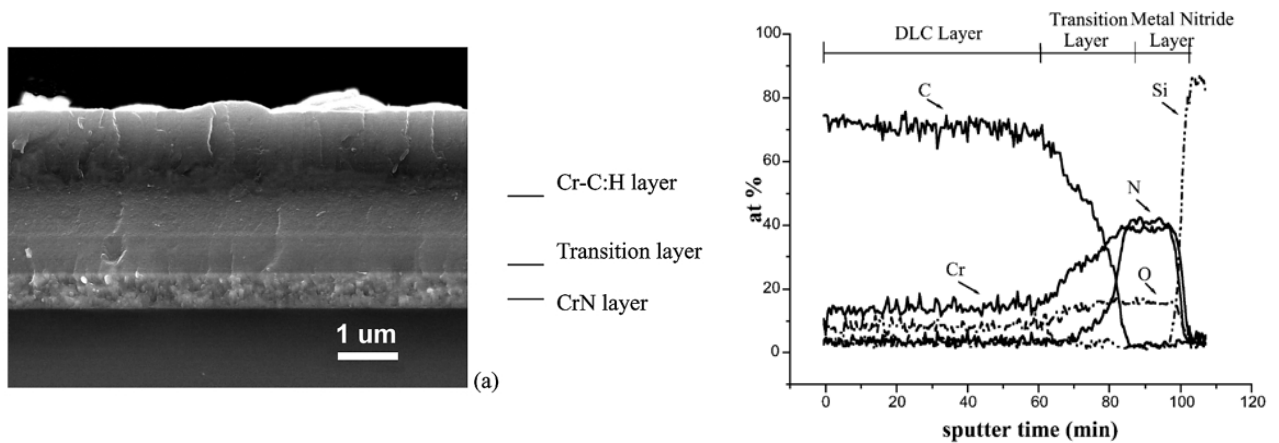


Fig. 12. Complex coating built of adhesive CrN layer, gradient transition layer and nanocomposite top layer. Coatings' cross-section and AES depth profiles of elements [55].

The best results have been found for chromium containing coatings. Reported microhardness, compressive stress and wear rate (WC counterpart, 10N) of Cr/a-C:H coating, containing 14 at.% of Cr and deposited on M2 tool steel, was 25GPa, 1.5GPa and $2 \times 10^{-17} \text{ m}^3/\text{Nm}$, respectively [55].

Magnetron deposited metal doped a-C:H coatings have also been tested for their impact repetitive impact resistance. Such a feature of coatings is so important in terms of shock loads possible during wood machining.

Even though reported research [56] was done with the aim to improve wear performance of gears, results obtained are of more general meaning. Among tungsten and chromium doped a-C:H coatings, superior repetitive impact resistance was found for Cr/a-C:H coating deposited on 52100 steel – Fig. 13.

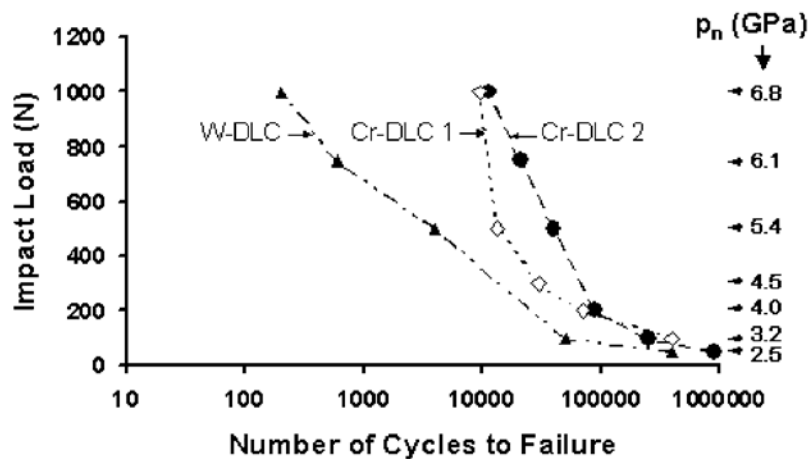


Fig. 13. Semi-log plots of impact failure curves. p_n is the nominal maximum Hertzian contact pressure normal to the sample surface [56].

Cr/a-C:H nanocomposite coatings attracted attention of other researchers who studied their deposition, mechanical and tribological properties [57] as well as thermal stability and oxidation resistance [58]. Recently also effect of nitrogen incorporation on structure and properties of Cr doped amorphous carbon coatings was reported [59].

Carbide forming metal (W, Nb and Mo) doped a-C:H composite coatings have also been studied in terms of composition-structure-properties relations [60-64]. Although, results presented contribute to the knowledge on properties of these materials, they are of less importance for this review.

Worth mentioning however is contribution by Djouadi et al. reporting on wood processing tests of tungsten doped a-C:H coatings deposited on low alloy steel (60SMD8) tools [65]. The coating performed better than standard TiN and (Ti,Zr)N materials. Much better cutting edge stability has been achieved for Cr_xN_y based coatings.

Conclusions

Even though results reported in the literature of the subject are highly scattered and no systematic research on application of carbon based coatings on wood processing tools has been done, there are several conclusions which can be drawn from presented analysis.

Coatings based on predominately vacuum arc deposited, **hydrogen free ta-C hard carbon** should be the main focus of undertaken research. Deposition conditions related to ion energy and substrate polarization (pulsed bias) need to be carefully adjusted.

Well established and experimentally proven methods of internal stress relaxation by metal doping together with deposition of transition (adhesive) gradient layers should allow for elaboration of coatings able to withstand harsh conditions of woodworking process. Recent results show that **chromium** is an optimal choice as a doping element. Addition of small amounts of **Al or Si as a strong stress relaxing agents** should also be considered.

Also mainly sp² bonded a-C carbon coating deposited in hydrogen free magnetron sputtering processes (graphite sputtering) are of interest due to their very high toughness accompanied by still high hardness.

In these both cases (ta-C and a-C) still much research is necessary to tune structure and properties of new coatings to specific requirements of particular woodworking processes.

Nanocomposite coatings of Me/a-C:H type, based on amorphous hydrogenated carbon could be an alternative solution everywhere high toughness and adhesion accompanied by medium hardness is required. Here again chromium is considered as an optimal doping element.

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