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HARDNESS OF HYBRID PVD-PECVD W-C:H COATINGS VS. SUBSTRATE TYPE

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Abstract. The effects of substrate on the measurement of hardness (and indentation modulus) - penetration depth profiles were investigated on hybrid PVD-PECVD W-C:H coatings made with the additions of C_2H_2 or CH_4 using High Power Impulse Magnetron Sputtering (HiPIMS) method. The substrates involved 100Cr6 bearing steel, Al2024 aluminum alloy and (111) Si wafer. Although no clear influence of the substrate type on hardness and indentation modulus of the coatings at different acetylene and hydrogen additions was observed, when both measured properties were combined in $H_{IT}E_{IT}$ ratio, significant shift of H_{IT}/E_{IT} ratio dependencies obtained on Al alloy vs. steel and Si wafer substrates occurred. Thus, the effect of substrate type on the measurementlevaluation was confirmed.

Keywords: Hardness, indentation modulus, substrate effect, W-C:H coating.

1. Introduction

Tribological properties of hard coatings, especially their wear resistance, coefficient of friction (COF) depend on large number of parameters including loading and environmental conditions but also material system used for the coating, its structure, surface roughness and such properties as hardness, elastic modulus, and others. It was reported that the wear properties of hard coatings more strongly correlate with H/E ratio than just with the hardness itself [1]. Moreover, it was also found out that the H/E and/or H^3/E^2 ratios are related to the level of plasticity and can be used to estimate changes in the toughness of the coatings [2–4]. This is of significant interest because toughness is among the main parameters, besides hardness, Young's modulus, COF, wear, scratch, oxidation and corrosion resistance of the coatings for engineering applications. The measurement of mechanical properties, involving hardness, elastic modulus and toughness in the coatings with the thickness in the range of few micrometers is a challenge even by nanoindentation because of the inevitable influence of the substrate on the measurement of the coating properties. To reduce this influence, the indentations depths used for the determination of coating hardness should be substantially smaller than the thickness of the coating. Physical explanation is that the stress field under the indenter, corresponding to the zone with the stresses above the yield stress (zone of plasticity), has to be fully confined in the coating. So called "10 % (of the coating thickness) rule" is often applied to determine such maximum depth and true hardness of the coating, respectively [5–10]. Another approach to eliminate substrate influence and to determine true coatings properties is to use hardness (and elastic modulus) – indentation depth profiles obtained from continuous multi-cycle (CMC) or continuous stiffness measurements (CSM) [11]. The coating properties correspond to the maximum or plateau on the corresponding depth profile at the depths smaller than 10 % of the coating thickness. However, the liability of 10 % rule is limited by the accuracy of the measurement at coating thicknesses below 1 µm related to tip surface area calibration function, by indenter tip radius [12], surface roughness, pile-up or sink-in behavior [13], residual stresses as well as by the ratio between the yield stresses and the elastic moduli of the coating and the substrate, respectively [9, 14]. The measurements of indentation modulus are much more sensitive to substrate properties than hardness because the elastic stress field under the indenter would be much larger than the zone of plasticity and therefore, 10 % rule may not be sufficient. Thus, the problem of proper measurement of hardness simultaneously with the elastic modulus in thin hard coatings persists and it is even emphasized by the applicability of the H/E ratio for toughness and wear resistance estimations. In our earlier works, the influence of indenter tip radius on the hardness – depth profiles has been analyzed using a combination of the experimental and finite element modelling approaches [12]. However, the influence of the Young's modulus of the substrate on the nanoindentation measurements was not investigated. Therefore, the aim of the present work is to investigate the influence of the substrate properties on the measurements of hardness, and indentation modulus in thin hard coatings used for engineering applications. The measurements were performed on HiPIMS (High Power Impulse Magnetron Sputtering) W-C and W-C:H coatings deposited using hybrid PVD-PECD (Physical Vapor Deposition – Plasma Enhanced Chemical Vapor Deposition) process with different acetylene and hydrogen additions on three different substrates.

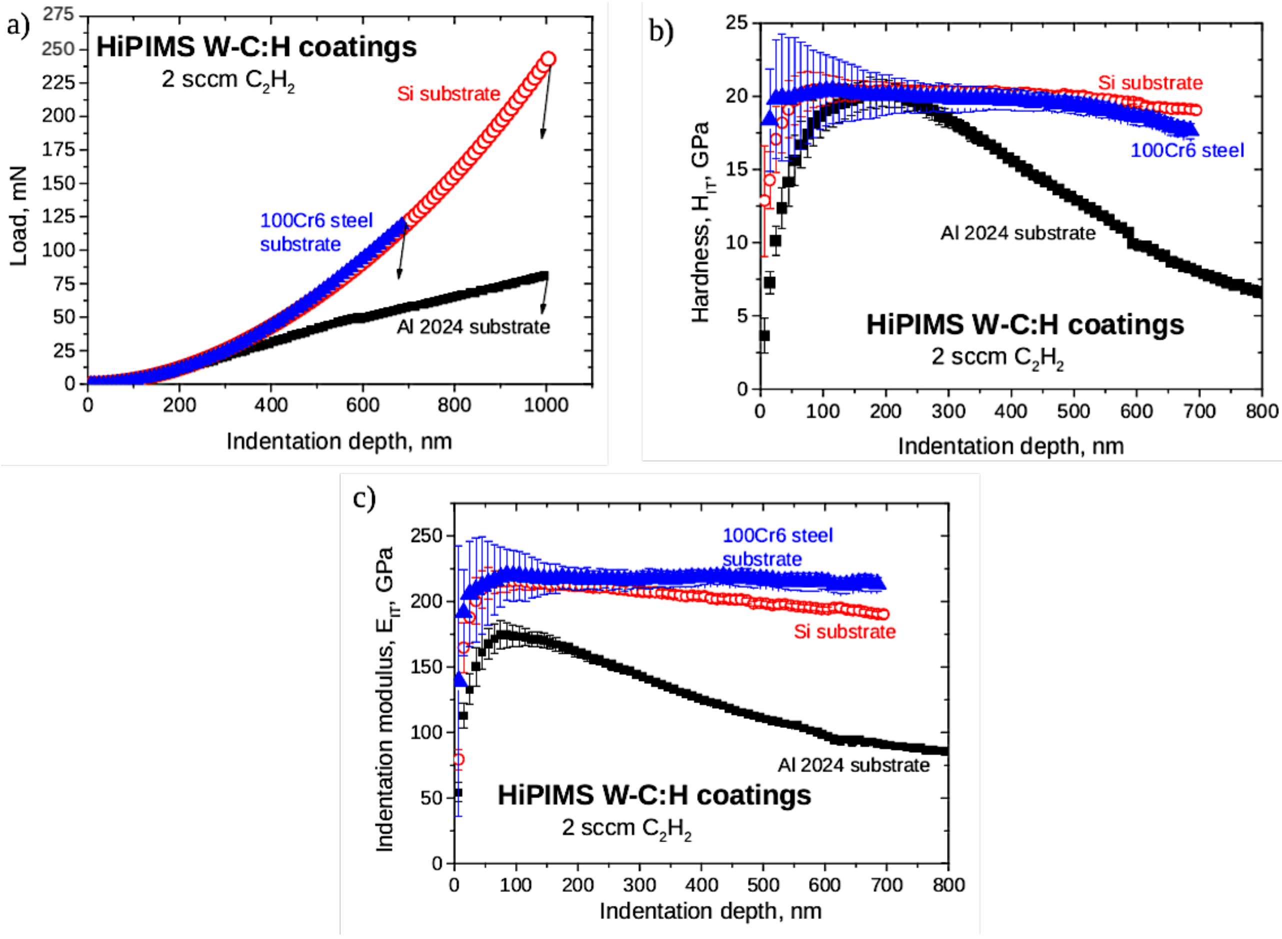

Figure 1. Load – indentation depth curves from the nanoindentation tests on the HiPIMS W-C:H coatings deposited with 2 sccm C_2H_2 on Si wafer, 100Cr6 bearing steel and Al 2024 alloy substrates – a) The depth profiles of hardness – b) and indentation modulus – c).

2. Experimental material and methods

The studied W-C:H coatings were simultaneously deposited on three different substrates: polished tempered bearing steel 100Cr6 discs (diameter – 25mm, thickness – 3mm), polished Al2024 aluminum alloy discs with similar size and on approximately 1cm^2 polished (111) Si wafer fragments with $\sim$ 200nm Cr bond layer. The deposition was carried out at a minimum working pressure of 0.5 Pa in a magnetron deposition system (Cryofox Discovery 500, Polyteknik, Denmark) using High Power Impulse Magnetron Sputtering (HipIMS) source at 350 W average power achieved at 2.62% duty cycle related to the frequency of 150Hz and impulse length of 175 μs. A set of 14 coatings with variable additions of C_2H_2 precursor (0, 2, 4, 6, 8 sccm) and (0, 5, 10, 20 sccm) into Ar atmosphere was prepared for the study. The thicknesses of the coatings were in the range from 0.7 µm up to almost 3 µm depending on the amount of precursor gas additions [15–18].

The nanoindentation tests were carried out on a nanoindenter (model G200, Agilent, USA) using a diamond Berkovich tip in CSM mode with the preset maximum penetration depth of 1000 nm, strain rate of 0.05 s^{-1}, frequency of 45 Hz and amplitude of 2 nm on a set of 16 indents. The hardness and indentation modulus depth profiles were obtained by averaging the results of at least 10 measurements. The Young's modulus and Poisson's ratio of the diamond tip used for calculations were $E_{tip} = 1141$ GPa and $\nu_{tip} = 0.07$, respectively. The indenter tip was calibrated on a fused silica reference sample. The Poisson's ratios of the coatings of v = 0.25 was used for the evaluation of the corresponding properties.

3. Results and discussion

3.1. Substrate effects on hardness and indentation modulus in HiPIMS W-C:H coatings

Fig. 1a - 1c illustrate the differences between load - indentation depth curves, hardness – indentation depth and indentation modulus – depth profiles in the studied W-C:H coating deposited with the addition of 2 sccm C_2H_2, respectively. The load – displacement curve in the coating on Al alloy differs significantly from those on Si and steel substrates, which were practically identical, at the displacements above 400 nm

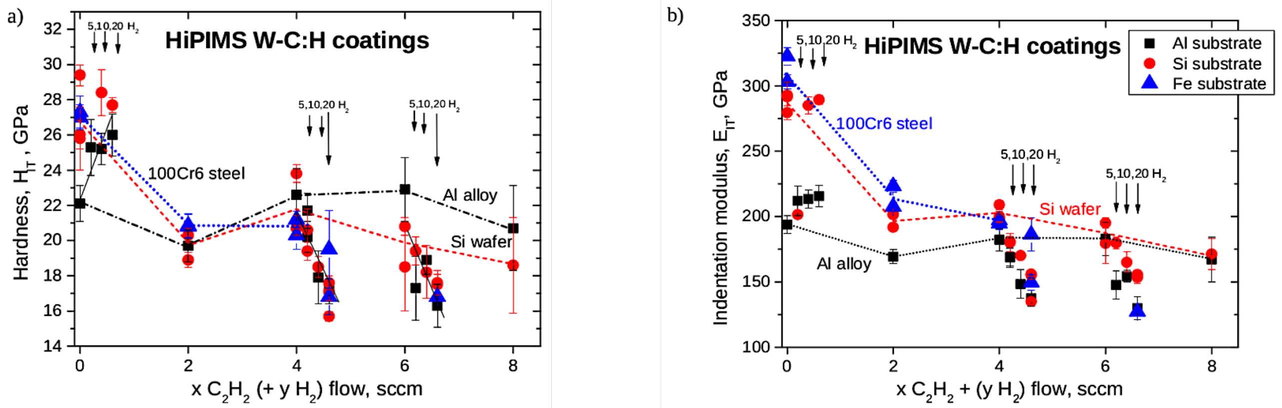

FIGURE 2. The comparison of the hardness, H_{IT-} a) and indentation modulus, E_{IT-} - b) in HiPIMS W-C:H coatings deposited at different acetylene (and hydrogen) additions on three types of substrates. The data-points corresponding to 5, 10 and 20 sccm H_2 additions were intentionally shifted by 0.2, 0.4 and 0.4 sccm respectively, for better visibility.

(Fig. 1a). However, this difference is not important for the determination of the hardness and indentation modulus, because they have to be determined from the indentation depths within the range of 100 - 300 nm due to the earlier mentioned 10 % rule. Fig. 1b shows the depth profile of hardness: on Si and steel substrates, very wide plateau at their maxima of around 20 GPa extending up to almost 500 nm depth can be seen. In contrary, the influence of substrate is much stronger in the case of measurement on Al substrate: the onset of hardness decrease occurred already at 250 nm. Such difference is a natural consequence of lower Young's modulus of Al alloy in comparison with steel and Si wafer. However, the maximum of the hardness profile obtained on Al alloy overlapped with those on the other two substrates and essentially no difference of the substrate on hardness can be seen. However, the situation was different in the case of indentation modulus profiles. A plateau at around 225 GPa extending up to 500 nm can be seen on steel substrates but the measurement on Si wafer resulted in a maximum plateau at around 220 GPa only up to $\sim$ 300 nm. The effect of Al alloy substrate was much more pronounced: the maximum was around 175 GPa and it extended only to 150 nm indentation depth. The values of H_{IT} and E_{IT} determined from the corresponding depth profiles according to the above mentioned way are summarized in Fig. 2a and 2b, respectively. They reveal number of effects and differences. They involve the effects of substrate type but also of acetylene and hydrogen additions during hybrid PVD-PECVD.

The PVD process without additional precursor gases resulted in (possibly over-stoichiometric [18]) WC coatings exhibiting much lower values of hardness (22 GPa) and modulus (< 220 GPa) in the coatings deposited on Al alloy substrates than on Si and steel substrates (26 – 29 GPa and 280 – 340 GPa, respectively). It is known from earlier works on DC magnetron sputtered and HiPIMS W-C:H coatings [17, 18] that the structure of the PVD coatings without additions of acetylene may vary from nano-columnar to nanocrystalline, which resulted in the variations of hardness from 34 GPa to 28 GPa, respectively. The additions of acetylene caused gradual increase of the content of hydrogenated free carbon phase and a transition from nanocomposite to amorphous structure accompanied by a decrease of hardness [16–18]. The substrate itself may also play significant role in the formation of the coating structure and its morphology [15]. Without detail structure observations, it is difficult to decide, which of the mentioned effects could be responsible for the changes of hardness and indentation modulus in the studied W-C coatings. As expected, the additions of acetylene resulted in gradual decrease of these properties. There were certain variations among the values obtained on various substrates, but they were within the scatter bars of the measurements and the differences decrease, especially in the case of elastic moduli (Fig. 2b). Apparently, the amorphization of the structure at high acetylene additions seems to result in the unification of the properties and has stronger effect than the possible influence of the substrate. Thus, the differences in coating properties deposited on different substrates seem to be statistically significant only in the cases without or with very small acetylene additions. However, they may interfere with the effects of coating structure and therefore, cannot be fully attributed to the substrate effect.

Figs. 2 also show the influence of hydrogen additions; it should be noted that the data-points corresponding to 5, 10 and 20 sccm H_2 additions were intentionally shifted by 0.2, 0.4 and 0.4 sccm from the position of the corresponding acetylene addition to show the tendency of the changes without overlap. It can be seen that the hydrogen additions have different effects on H_{IT} and E_{IT} in PVD W-C coatings and in hybrid PVD-PECVD W-C:H coatings made with acetylene additions. In the first case, hydrogen additions resulted in the increase of hardness and elastic modulus whereas they were decreased in the coatings made with 4 sccm and 6 sccm acetylene additions regardless of the substrate. Moreover, the corresponding values principally followed the dependencies described for the coatings without hydrogen additions and agree with the above conclusions concerning exclusivity of W-C coatings compared to W-C:H coatings.

The above results indicate only a small influence of substrate type on hardness and indentation modulus. However, they are measured simultaneously and it is reasonable to check the simultaneous effect of both properties on different substrates. Thus, the results from Fig. 2a and 2b were replotted as a function of H_{IT}/E_{IT} ratio on acetylene (and hydrogen) additions in Fig. 3. The obtained plots show that the acetylene and hydrogen additions usually result in gradual H_{IT}/E_{IT} increase and that the difference between substrates was strongly magnified. Although the differences between H_{IT}/E_{IT} in the coatings on 100Cr6 steel and Si substrates were negligible in the studied additions range, the corresponding values on Al alloy substrates followed the same tendency but they were by 0.02 – 0.025 higher. Since both hardness and indentation modulus decrease with the acetylene addition increase, the increase of H_{IT}/E_{IT} has to result from faster decrease of indentation moduli. Another consequence of the shift of the dependencies between steel, Si and Al alloy substrates was that all H_{IT}/E_{IT} values obtained on Al alloy were above the plasticity limit of 0.1 while the identical coatings deposited on Si and steel substrates at 0 and 2 sccm acetylene (and hydrogen) additions would be below that limit. Obviously, such systematic differences in H_{IT}/E_{IT} on the same coatings do not have real physical reason. They have to be related to the influence of the substrate type on the measurement method and/or data evaluation rather than on true hardness and indentation modulus changes. It is a clear indication that the substrate type definitely affects the nanoindentation measurements. The question is what is the main parameter controlling the influence of the substrate. Young's moduli of steel and Si substrates are rather similar (210 GPa vs. 193 GPa) while that of Al alloy is considerably lower ($\sim$ 73 GPa) and this difference is reflected in the difference obtained Fig. 3. However, the yield strength and hardness of substrate materials should play a role because they control plasticity of the substrate

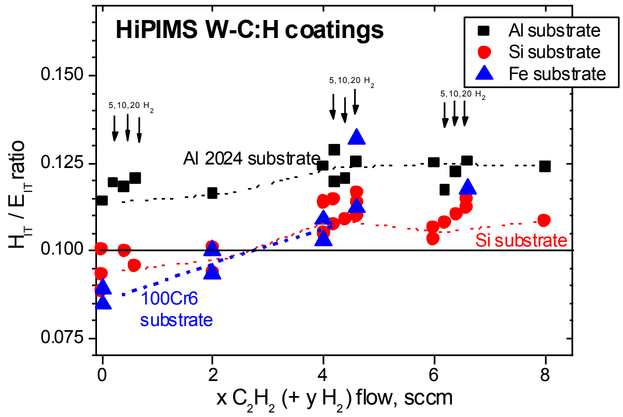

Figure 3. The dependence of H_{IT}/E_{IT} ratio in HiPIMS W-C:H coatings on the substrate type at different acetylene (and hydrogen) additions. Note that the data-points corresponding to 5, 10 and 20 sccm H_2 additions to the corresponding acetylene flows were intentionally shifted to emphasize the role of hydrogen additions.

4. Conclusions

The investigations of the influence of the substrate type on the measurements of hardness and indentation modulus in HiPIMS W-C and W-C:H coatings with different acetylene and hydrogen additions on Si wafer, 100Cr6 steel and Al 2024 aluminum alloy substrates revealed:

- Significant influence of substrate type on H_{IT} and E_{IT} in PVD W-C coatings deposited without the additions of acetylene. However, these differences may overlap with the influence of substrates on the coating structure.
- An enhanced scatter of the measured properties in hybrid PVD-PECVD W-C:H coatings with the additions of acetylene on the studied substrates. The differences between the substrates were within the scatter of measurement.
- When the effects of substrate type on hardness and indentation modulus were combined in H_{IT}/E_{IT} ratio, significant shift between the dependencies obtained on Al alloy vs. steel and Si wafer substrates was obtained. Thus, the effect of substrate type on the measurement/evaluation was confirmed.
- The effect of substrate properties on nanoindentation measurements cannot be related only to the difference in Young's moduli of the substrates and further investigations are required to find the way to eliminate this influence.

The above conclusions imply that the reliable evaluation of the wear resistance and fracture toughness of thin coatings based on H_{IT}/E_{IT} ratio requires the elimination of the influence of the substrate type on H_{IT}/E_{IT} ratio.

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