RECENT PROGRESS IN HARD NANOCOMPOSITE COATINGS

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The paper reports on new advanced hard nanocomposite coatings [1-4]. The paper is divided into two parts. The first part of the paper is devoted to the thermal stability of hard nanocomposite coatings and protection of the substrate against oxidation at temperatures above 1000°C. It is well known that the coating nanostructure is a metastable phase. It means that in the case when the temperature T under which the coating is operated achieves or exceeds the crystallization temperature, T_{cr}, the coating material starts to crystallize. This process results in destruction of the coating nanostructure due to formation of large grains and/or due to the change of the crystalline structure of coating. It is a reason why the nanocomposite coatings lose their unique properties and easily oxidize at temperatures $T \geq T_{cr}$. Unique properties of hard nanocomposite coatings including the hard nc-MeN/a-Si_3N_4 nanocomposite films with low (≤10 at.%) Si content, most often produced so far, are thermally stable up to a temperature $T \approx 1000$°C only. This temperature is, however, too low for many applications.

The thermal stability of nanocomposite coatings above 1000°C is demonstrated on thermal cycling of the magnetron sputtered Si-Zr-O nanocomposite coating [3]. It is shown that the nanocomposite coating is thermally stable as far as its structure does not change during heating and subsequent cooling. This fact is demonstrated by (1) the evolution of structure of the Si-Zr-O composite coating with low amount of Zr (<5 at.%) during thermal cycling from room temperature (RT) to a maximum annealing temperature T_a and subsequent cooling to RT given in *Fig.1* and (2) no change of its hardness H and effective Young's modulus E^* during thermal cycling.

From this figure it is seen that as-deposited coating is X-ray amorphous, nanocrystallization starts at $T_a \approx 900$°C, nc-t-ZrO_2/a-Si_3N_4 composite is formed and the tetragonal structure of ZrO_2 grains does not changed up to $T_a \approx 1500$°C which is called structure conversion temperature $T_{str\ conv}$; the coating structure strongly changes at $T_a \geq 1500$°C when interaction between coating and substrate takes place. Long-time thermal stability increases with increasing difference between $T_{str\ conv}$ and $T_{a\ max.}$. The Si-Zr-O coating is well resistant to thermal cycling up to 1400°C.

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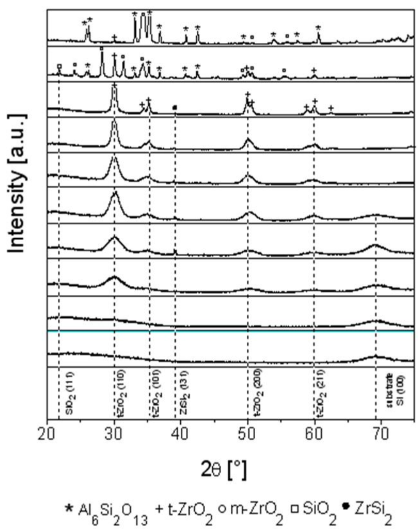


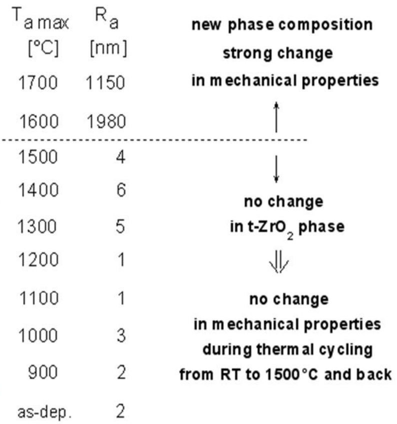
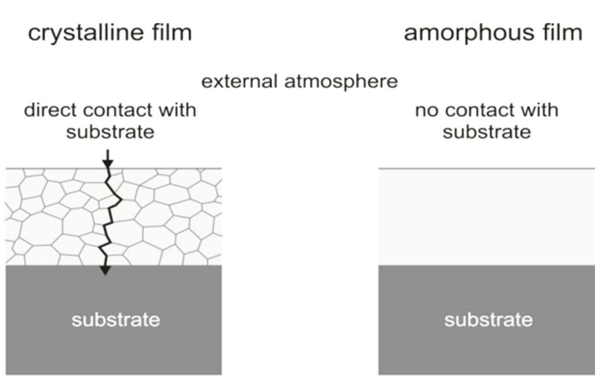


Fig.1 - Evolution of structure and surface roughness R_a of 7000 nm thick $Si_{31}Zr_5O_{64}$ composite coating during thermal cycling from RT to $T_{a\,max}$ to RT [3]

In summary it can be concluded that the coating material is thermally stable and exhibits no change in its properties as long as the coating structure does not change. More details are given in [3].

The protection of the substrate against oxidation is perfect only in the case when the coating perfectly separates the external atmosphere from the substrate surface. It can be easily achieved with amorphous coatings, see *Fig.2*. Amorphous materials contain no grains.



a) b)

Fig. 2 – Comparison of the protection of substrate against oxidation by protective coatings with a) crystalline and b) amorphous structure [1]

Therefore, there is no contact of the external atmosphere with the substrate and every reaction of the external atmosphere with the substrate is eliminated. Therefore, it is vitally important to develop amorphous coatings with thermal stability above 1000°C.

It is shown that (1) there are at least two groups of hard , X-ray amorphous coatings (XRAC) based on nitrides with thermal stability T > 1000°C: (a) a-(Si_3N_4/MeN_x) coatings with high (≥ 50 vol,%) content of Si_3N_4 phase and (b) a-(Si-B-C-N) coatings with strong covalent bonds; here Me=Zr, Ta, Ti, Mo, W, Al, etc. and x=N/Me is the stoichiometry of MeN_x metal nitride phase, (2) XRAC exhibit considerably higher resistance against oxidation compared to that of crystalline coatings, see *Fig.3*, and (3) both a-(Si_3N_4/MeN_x) and a-(Si-B-C-N) coatings exhibit excellent oxidation resistance in flowing air; up to ~1500°C and ~1700°C, respectively.

The second part of paper is devoted to the nanocomposites composed of small amount of nanograins (NG) dispersed in an amorphous matrix (AM). These nanocomposites, due to low values of the effective Young's modulus E^* satisfying condition $H/E^* \geq 0.1$, are very elastic (the elastic recovery $W_e \geq 70\%$); here H is the coating hardness, $E^* = E/(1 - \nu^2)$ is the Young s modulus and ν is the Poisson s ratio. The NG/AM nanocomposites with $H/E^* \geq 0.1$ and low E^* containing a well lubricate phase exhibit the lowest values of (i) friction ($\mu \leq 0.1$), (ii) wear ($k \leq 2x10^{-7}$ mm^3/Nm) and (iii) erosion.

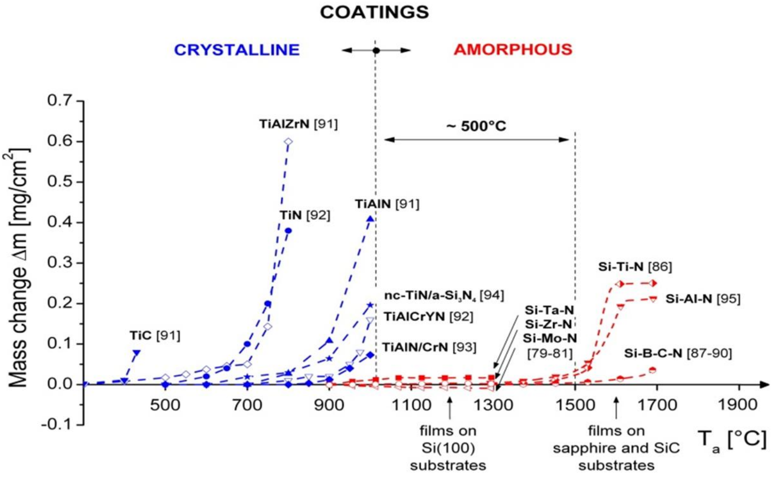


Fig. 3 – Oxidation resistance of selected hard (1) crystalline binary, ternary, quaternary nitride coatings and (2) amorphous (i) a-(Si_3N_4/MeN_x) composite coatings and (ii) a-(Si-B-C-N) quaternary coatings characterized by the mass increase Δm as a function of annealing temperature T_a [2]

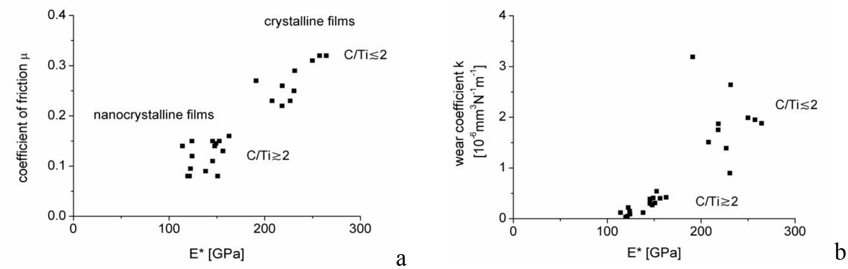


Fig. 4 – (a) Friction and (b) wear of sputtered TiC/a-C composite films as a function of the effective Young's modulus E^* [4]

These facts are demonstrated in *Fig.4* where the friction and wear of the TiC/a-C composite films as a function of the effective Young s modulus E^* are displayed.

The correlation between H, E^*, H^3/E^{*2} H/E^* and CoF, wear and erosion are discussed in detail. More details on hard nanocomposite coatings are given in references [5-7].

At the end, trends of next development of high-rate sputtering of oxide coatings [8] and hard nanocomposite coatings with enhanced toughness will be briefly outlined [9].

Acknowledgements

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