PHYSICAL CHEMISTRY

Effect of Characteristic Defects on the Strength of Metal Nanolayers Applied to a Polymer Surface

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Received September 7, 2007

DOI: 10.1134/S0012501608020024

The effect of defects in real solids is a key issue of solid-state physics. It is now beyond question that defects have a decisive effect on the actually determined strength of solids [1]. At the same time, it has been hitherto impossible to experimentally compare the strengths of a real solid and its defect-free analogue. Particularly intriguing is the question of the strength of nanosized solids. In this context, it is very important to develop new research methods capable of giving new information on the properties of nanomatter. Although the data on the properties of matter in the nano state are extremely significant, this problem is still far from having been solved.

We have recently proposed a new approach to characterizing the strain-strength properties of solids in nanosized layers [2]. We estimated the strain-strength properties of nanosized coatings applied to the surface of polymer films. Deformation of polymer films with applied coatings is accompanied by the formation of a special sort of relief whose parameters contain information on the mechanical properties of the material of the coating. The established [3–8] relationship between the directly measured parameters of this relief and the properties of the material of the coating underlies the proposed method for estimating the mechanical properties of nanosized solids [2].

Figure 1 presents typical results of such a study. It is well seen that the strengths of both metals are virtually independent of their thicknesses within the range 15-30 nm. The strengths of both metals in this thickness range varies within 180-220 MPa for gold and 250-300 MPa for platinum. These values quantitatively agree with the known values of strengths of bulk metals (176-250 MPa for gold and 240-350 MPa for platinum). At the same time, Fig. 1 shows that, beginning with a thickness of approximately 15 nm, the strengths of both metals strongly increase with a decrease in the applied coating thickness. The strengths of platinum and gold reach 1800 and 3700 MPa, respectively. As is seen, the metal strength in nanolayers is at least an order of magnitude higher than the strength of bulk metal.

The result obtained is the first quantitative estimation of the metal strength experiencing uniaxial stretching in so thin layers. First, this result shows that the properties (in this case, such a fundamental property as strength) of matter in nanolayers actually differ qualitatively from the properties of bulk material. Second, the approach used to estimating the strength properties of material at the nano level is efficient and universal. At the same time, the question of which strength (taking



Fig. 1. Dependence of the strengths of (1) gold and (2) platinum coatings on their thickness as determined by analyzing the pattern of their fragmentation while deforming a polyethylene terephthalate support at 20°C at a rate of 0.2 mm/min, and the strengths of bulk (3) gold and (4) platinum.

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Fig. 2. Scanning electron micrograph of a polyethylene terephthalate specimen with a 4-nm-thick platinum coating after stretching at 100° C at a rate of 0.1 mm/min by 100% and subsequent additional stretching by 50% at higher stress.

into account characteristic defects or not) is estimated by the proposed approach remains open.

In this work, we attempted to obtain objective data on the strength of solids of nanometer size and the effect of characteristic defects on them. Methodological issues were described earlier [2].

The results of previous structural studies [3-8] allow us to reasonably assume the nature of strength of a coating experiencing multiple fragmentation while stretching the support polymer. It turned out that, early in the deformation of the polymer support, the coating cracks to form a set of fragments of various sizes [9]. This process is caused by the presence of randomly located microdefects discussed above. Each such defect, being a stress raiser, gives rise to a crack, and all such defects cause the formation of the set of fragments with a wide size distribution. However, after the emergence of this set of fragments, a unique process of destruction of each of the fragments begins because, after the random destruction of the coating into fragments, the stretching of the support continues and each forming fragment remains loaded. The stress in each forming fragment is distributed highly nonuniformly. Obviously, the stress at the ends of a fragment is zero, increases with distance from the ends, and is maximal at exactly the center of the fragment. In further stretching of the support, the stress in each fragment increases and reaches the ultimate strength at exactly the center of the fragment. These properties lead to the surprisingly nice process of destruction of the coating by halving each segment, which is demonstrated in Fig. 2. The polymer specimen shown in Fig. 2 was stretched at a relatively low stress, after which the stress in this specimen was abruptly increased by decreasing the stretching temperature. It is clearly seen that each fragment is divided into two absolutely equal parts. This destruction of the coating by halving each segment continues until the weak polymer support transfers to each fragment the pressure sufficient for its destruction. After reaching this limit, further stretching does not cause splitting of fragments. Fragments, retaining their sizes, simply recede from one another on the support being stretched. For these reasons, the sizes of fragments become similar and, on the support surface, a set of coating fragments with rather narrow size distribution emerges.

Thus, the method used divides the fragmentation of a solid (coating) into two stages. At the first stage of stretching the polymer support, characteristic defects in the coating act, each giving rise to a crack. Since these defects in the coating are located randomly, a set of coating fragments of different sizes emerges on the surface of the polymer support. At the second stage of stretching, the mechanism of regularly halving each forming fragment is switched on. In essence, the method developed determines the strength of a nanosized solid in which all characteristic defects have acted, each producing a single crack.

Thus, the data in Figs. 1 and 2 allow us to estimate the strength of metal layers applied to a polymer surface without characteristic defects. First, this result shows that the properties (in this case, such a fundamental property as strength) of matter in nanolayers actually differ qualitatively from the properties of bulk material. Second, the approach used to estimating the strength properties of material at the nano level is efficient and universal.

Let us try to estimate the "ordinary" strength of a metal coating with a set of characteristic defects. For this purpose, using a precision dynamometer, we obtained curves of stretching polymer films with metal coatings of various thicknesses (Fig. 3). It is seen that, unlike the curves for pure polymer, these curves have a pronounced maximum, after reaching which the stress in the specimens sharply decreases. Obviously, the stress increases until the coating applied to the polymer surface is continuous and can bear mechanical load. Once the first crack intersects a cross section of this coating, the stress in the specimen begins to rapidly decrease. Actually, in this case, we record the stress that can be reached in the specimen before the first, most dangerous, defect in the coating acts. The data obtained

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Fig. 3. Curves of stretching a polystyrene film with a gold coating at 150° C a rate of 5 mm/min at coating thicknesses of (1) 0, (2) 2.5, (3) 5.0, (4) 26.0, and (5) 32.0 nm.

allow us to determine the coating strength related to the growth of the crack produced by the most dangerous defect, i.e., the strength that is usually determined in routine stretching tests. This strength can be elementarily found from the data in Fig. 3. Indeed, if the coating thickness, the widths of the deformed specimen, and the stress at which the first crack in the coating is initiated (maximum in the stretching curves) are known, then it is easy to calculate the ultimate strength of the applied coating.

Figure 4 presents the dependence of the strength of a gold coating on its thickness as determined using a dynamometer while stretching a polystyrene film with the gold coating at a constant rate of 5 mm/min at 150°C. Figure 4 shows that the metal strength is virtually independent of its thickness until approximately 20 nm. With a further decrease in the coating thickness, the metal strength abruptly increases. The increase in the strength with a decrease in the thickness of the coating on the polymer surface is observed for both types of the determined strength, both taking into account characteristic defects and not.

Using the data in Figs. 1 and 4, we can first compare under comparable conditions the strengths of solids in thin layers that either contain or do not contain characteristic defects. The results obtained suggest two important conclusions. First, as might be expected, the strength of a solid, regardless of its size, is significantly lower if it contains defects. Even thinnest nanosized solid films contain defects capable of destroying the films. Although this conclusion is rather obvious, this is



Fig. 4. Dependence of the strength of a gold coating on its thickness as determined from stretching curves in Fig. 3.

first proven in this work. Note that the difference of the strengths of both types turned out to be very significant, which emphasizes the importance of taking into account defects in solids in estimating their strength.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project nos. 05-03-32538 and 06-03-32452) and the Program for Support of Leading Scientific Schools of Russia (grant no. NSh-4897.2006).

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