

---

---

## EXPERIMENT

---

---

# A Method for Evaluating the Strain–Strength Properties of Metal Nanolayers on Polymers

A. L. Volynskii<sup>a</sup>, D. A. Panchuk<sup>a</sup>, S. V. Moiseeva<sup>b</sup>, L. M. Yarysheva<sup>a</sup>, and N. F. Bakeev<sup>a</sup>

<sup>a</sup> Chemistry Department, Moscow State University, Moscow, 119992 Russia

<sup>b</sup> Chemistry Department, Moscow Pedagogical University, Moscow, 119882 Russia

**Abstract**—A new method is proposed for evaluating the strain–strength properties of nanolayers of solid materials on polymers. The underlying idea of the method is analysis of parameters of the microrelief generated by strains in polymer films with a thin coating. We demonstrate that the yield strength and ductility of precious metals in uniaxial extension increase manifold if the thickness of the metal layer is less than 30 nm. A mechanism of the observed phenomena is suggested and discussed.

**DOI:** 10.1134/S1995078008010102

Transition from the micro- to nanoscale range of characteristic sizes considerably changes the physical, mechanical, physicochemical, and other properties of the material. New investigation methods capable of supplying reliable data on the properties of nanomaterials become significant in this context. Although data on the properties of nanomaterials are of paramount importance, this problem is far from being solved. Indeed, it is difficult to understand how conventional methods can test the properties of a solid body whose geometric sizes are several or tens of nanometers. Most data on the mechanical properties of substances in this state is supplied by indentation techniques [3–5]. These approaches, however, have several methodological weaknesses. In particular, they cannot really evaluate the important parameters of solids, such as Young's modulus, the breaking extension, or the breaking stress (tensile strength).

This work demonstrates a new approach to evaluating the strain–strength properties of nanomaterials, i.e., materials that contain structural elements whose geometric sizes, at least in one direction, do not exceed 100 nm.

Thin metal coatings on polymer substrates are certainly such objects.

## EXPERIMENTAL

A commercial film of amorphous, unoriented polyethylene terephthalate (PETP) 100  $\mu\text{m}$  thick was used in this work; samples were cut from this film in the form of bilateral spatulas with their working part equal to  $6 \times 20$  mm. Thin gold or platinum layers were applied to the surface of a sample using plasma-ion deposition on an Eiko IB-3 setup. To ascertain the thickness of the metal coating on the polymer, it was determined as a function of the time of deposition onto glass plates under standard conditions. This was done

as follows. Gold or platinum layers with various thicknesses were deposited, by varying the deposition time, onto glass plates; then, the coating on glass was scratched with a wooden spike. The break in the coating was studied with a Nanoscope-2 (Digital Instruments) atomic-force microscope (AFM) in the contact force mode. We should note that the same procedure, with a polymer substrate instead of the glass one, did not give the desired result. The polymer surface was too ductile; the wooden spike scratched it to a large depth, and it was impossible to ascertain the film thickness.

Representative results of this evaluation are as in Fig. 1. The light part in the micrograph on the left represents a gold layer; the dark part on the right is the glass surface. The break in the coating is clearly detected by AFM (Fig. 1a); the corresponding profilogram (Fig. 1b) gives an estimate of the coating thickness with a rather high accuracy. The coating thickness versus time data were subsequently used to deposit the desired gold or platinum thickness onto a PETP film.

Dynamometric measurements were carried out using an Instron-1122 dynamometer. The surface structure of strained polymer films with metal coatings was studied with a Hitachi S-520 scanning electron microscope (SEM). The average sizes of destruction fragments of the coatings were derived by digitizing electron micrographs using Femtoscan Online software [6]. The structure of the metal layer was studied on ultrafine (100-nm) sections cut by a diamond knife on a Reichert-Jung microtome using a LEO 912AB transmission electron microscope (TEM) equipped with an OMEGA filter.

## SCIENTIFIC RATIONALE AND PRINCIPLES OF THE METHOD

The rationale for developing the new method of evaluating the strain–strength properties of thin (nanometer-

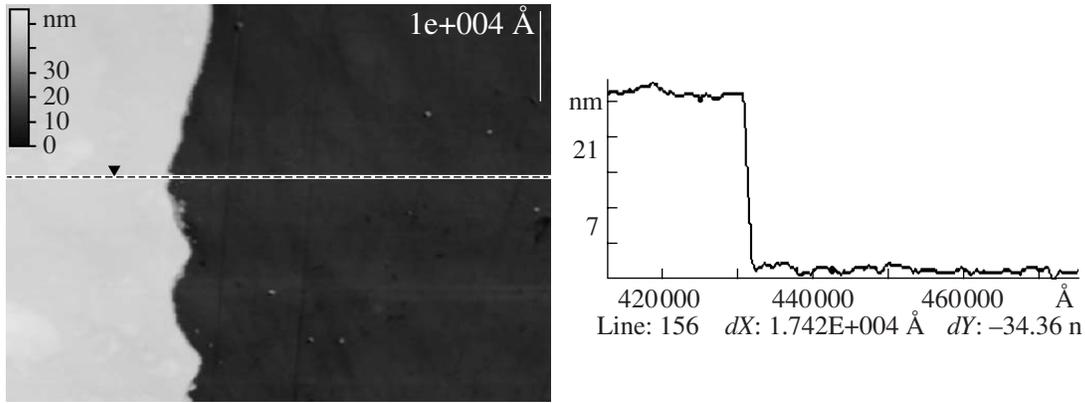


Fig. 1. AFM image and the corresponding profilogram for a glass surface coated with a thin gold layer.

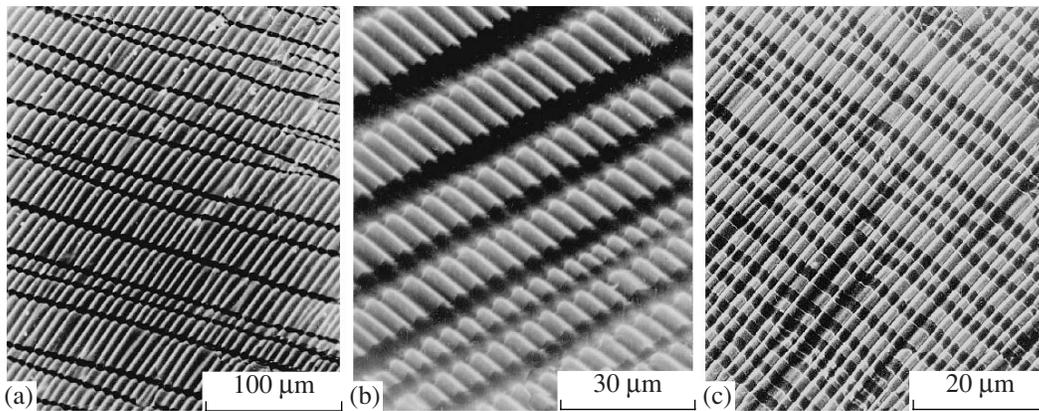


Fig. 2. SEM micrographs of films: (a) natural rubber with a thin (10-nm) gold coating after 50% extension at room temperature, (b) polyvinyl chloride with a thin (10-nm) platinum coating, and (c) PETP with a thin (15-nm) platinum coating after 100% extension at 90°C.

thick) metal layers was provided by recent studies of the structural-mechanical behavior of polymer films with a thin solid coating [7–10]. These studies revealed a correlation between the mechanical properties of metal layers and reliable structure data.

Let us consider the theoretical basis for the proposed method in more detail. In [7–10], the surface of polymer films with thin solid coatings after straining was studied by electron microscopy. Figure 2 displays electron micrographs of the surface relief of polymer films with thin metal coatings after their uniaxial stretching. The values of the strain are indicated in the figure legend. Light bands are fragments of the destructed coating; dark ones are cracks in it. It is well seen that the destruction of the coating on the polymer substrate generates an ensemble of fragments with rather uniform sizes. In the context of this article, we believe it necessary to briefly describe the mechanism of regular fragmentation of the coating during the stretching of the polymer substrate.

#### MECHANISM OF REGULAR FRAGMENTATION OF COATINGS

The regular fragmentation of a hard coating is due to the specifics of transfer of mechanical stresses from the ductile substrate to the hard coating through the interface. Here, we should note that the character of regular fragmentation of the coating depends, in particular, on the mechanism of substrate straining. It is well known that polymer films can be strained uniformly (affinely, i.e., as rubbers) or nonuniformly (as glassy or crystalline polymers). In the latter, an intact, unstrained polymer fragment and a strained, oriented polymer fragment (a so-called neck) continuously coexist during straining. In spite of the fact that the fragmentation of the solid coating in both cases occurs regularly, this regularity is achieved by the different mechanisms [11].

Regardless of whether a ductile substrate is strained uniformly or not, the average size ( $L$ ) of a destruction fragment in the direction of the extension axis is equal to [9, 12]

$$L = 2h\sigma^*/\sigma_0, \quad (1)$$

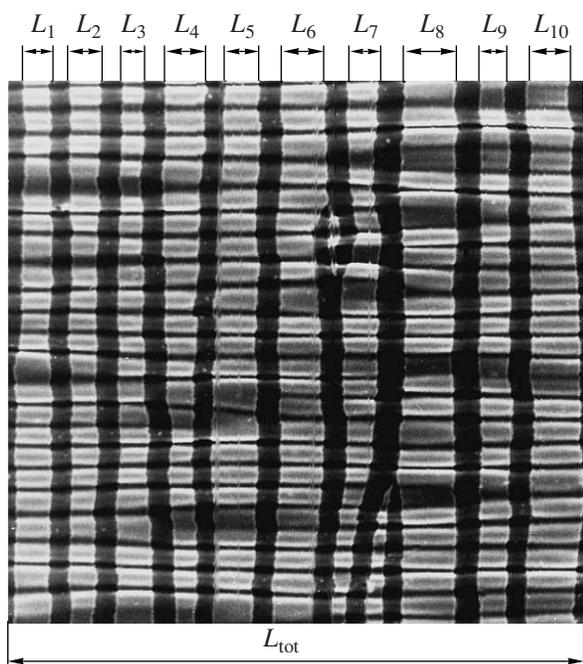


Fig. 3. Scheme used to calculate plastic strains in a solid coating after the extension of a polymer substrate.

where  $h$  is the coating thickness,  $\sigma^*$  is the yield strength of the coating, and  $\sigma$  is the stress in the substrate.

Thus, the strain in a polymer with a thin solid coating makes it possible to relate the tensile strength (an essential parameter of a solid) to the average size ( $L$ ) of destruction fragments generated by straining polymer films coated with a thin solid layer. The specified average fragment size is easily determined in direct microscopic experiments (Fig. 3). Evidently, relationship (1) provides the basis for a simple and straightforward method of evaluating the strain–strength properties of solids in layers of any thickness, including the nanometer range.

#### EVALUATION OF PLASTIC STRAIN IN COATINGS

The potential of the approach developed in [7–12] is not exhausted by the evaluation of the strength of solid nanomaterials. Deposition of coatings onto polymer films followed by their deformation offers a means for the direct determination of the plastic strain, another important mechanical parameter of coatings.

In [12, 13], a method was developed for the determination of plastic strains in metal coatings on polymer films using direct microscopic data.

Let us consider the electron micrograph in Fig. 3, which demonstrates a representative fragmentation pattern of a metal coating during the stretching of a polymer substrate. Evidently, the sum of the lengths of metal (or any other) fragments of the destroyed coating in the direction of the extension axis is as follows:

$L_{\text{coat}} = 1 + \epsilon_{\text{coat}}$ , where  $\epsilon_{\text{coat}}$  is the irreversible (plastic) strain in the coating. For the same sample (or some its fragment) in which  $L_{\text{coat}}$  was measured, its total length is evidently as follows:  $L_{\text{tot}} = 1 + \epsilon$  ( $\epsilon$  is the strain in the polymer substrate, which is set by the tensile machine). Then,

$$\frac{L_{\text{coat}}}{L_{\text{tot}}} = \frac{1 + \epsilon_{\text{coat}}}{1 + \epsilon} = \frac{\lambda_{\text{coat}}}{\lambda_{\text{pol}}}$$

Here,  $\lambda_{\text{coat}}$  and  $\lambda_{\text{pol}}$  are the degrees of extension of the coating and substrate, respectively. Therefore, the target value of plastic strain is

$$\lambda_{\text{coat}} = \frac{L_{\text{coat}}}{L_{\text{tot}}} \lambda_{\text{pol}}$$

If the irreversible (plastic) strain  $\epsilon_{\text{coat}}$  is expressed in percent, then

$$\epsilon_{\text{coat}} = \left( \frac{L_{\text{coat}}}{L_{\text{tot}}} \lambda_{\text{pol}} - 1 \right) \times 100. \quad (2)$$

From Eq. (2), the plastic strain of the coating can be found by directly digitizing micrographs, i.e., measuring  $L_{\text{coat}}$ , the sum of the lengths of coating fragments in the extension direction;  $L_{\text{tot}}$ , the total length of the sample for which  $L_{\text{coat}}$  was measured (Fig. 3); and  $\lambda_{\text{pol}}$ , the known strain of the polymer substrate set by the tensile machine.

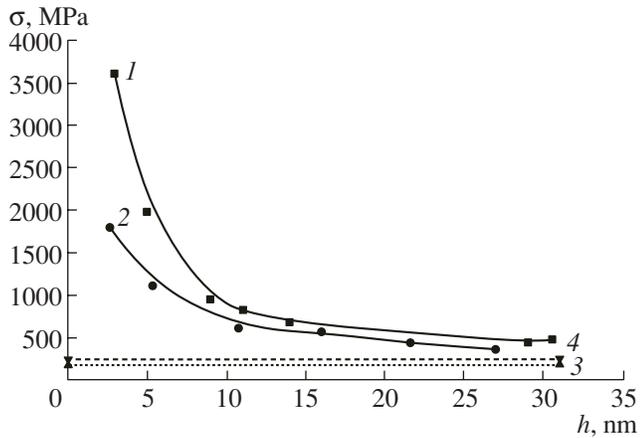
Blanks showed that the plastic strain of a carbon coating,  $\epsilon_{\text{coat}}$ , for the 60% extension of a PETP substrate at 90°C is zero [12, 13]. This result proves that, first, the carbon film is incapable of noticeable inelastic straining and, second, relationship (2) makes it really possible to estimate the plastic strain of a thin coating during inelastic stretching of a polymer substrate.

Equations (1) and (2) were supported experimentally [14]. The good agreement between theory and experiment validates the postulated mechanism of surface structuring during the straining of a coated polymer film.

#### YIELD STRENGTH AND DUCTILITY OF THIN (NANOMETER-THICK) SOLID LAYERS AS PROBED BY DIRECT MICROSCOPY

Let us consider the results of strength determination in thin (nanometer-thick) layers using relationship (1).

Figure 4 exhibits the yield strengths of platinum and gold found from relationship (1) as functions of the thickness of the metal layer on a PETP film. From Fig. 4, the strength of both metals is virtually independent of their thickness in the range from 30 to ~15 nm. The strength values in this range of thicknesses are 180 to 220 MPa for gold and 250 to 300 MPa for platinum, quantitatively matching the known values of the bulk strength for the metals studied (176–250 MPa for gold and 240–352 MPa for platinum [15]). At the same time, the strength considerably increases with decreasing



**Fig. 4.** Yield strength of (1) gold and (2) platinum coatings calculated from Eq. (1) vs. coating thickness in straining of a PETP substrate at 20°C with a loading velocity of 0.2 mm/min.

coating thickness starting at about 15 nm. The strength values for platinum reach 1500–1700 MPa; for gold, they exceed 3500 MPa (Fig. 4). One can see that the metal strength in nanolayers is at least one-tenth of an order of magnitude of the strength of the bulk material.

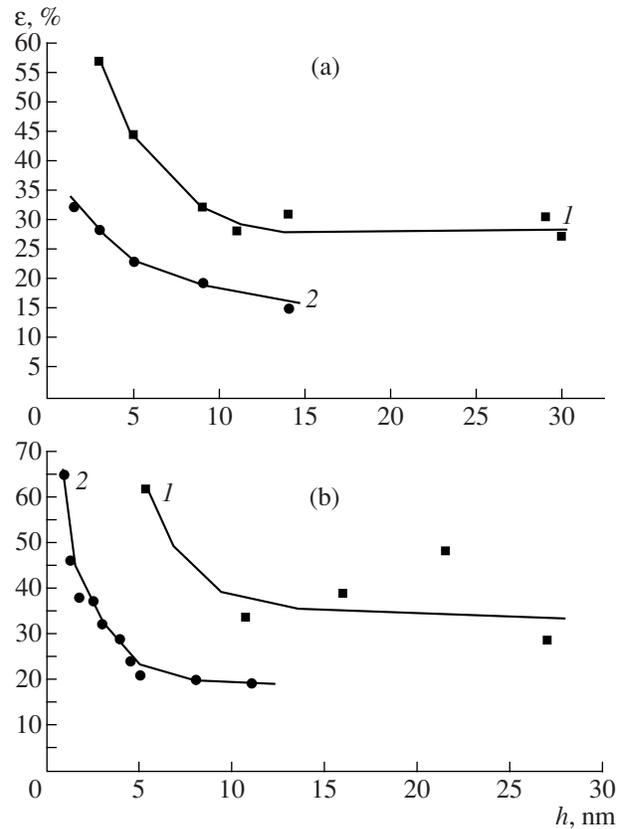
The efficient and universal method for evaluating the strength of thin (nanometer-thick) solid layers estimates their breaking strength in layers of virtually any strength. This result is the first quantitative estimate of the uniaxial tensile strength of metals in such thin layers.

The deposition of nanocoatings on polymers offers a means for estimating their plastic strength from direct microscopic measurements with the use of relationship (2).

Let us consider some examples to illustrate the utility of relationship (2) for estimating the plastic strain of a hard thin coating during the extension of a polymer substrate. Figure 5 displays the plastic strain calculated from relationship (2) for gold (panel a) and platinum (panel b) coatings strained at room temperature (with necking) and at 90°C (100%).

One can see that the plastic strain increases substantially in the range of nanometer coating thicknesses. We should note that this is a universal phenomenon: the plastic strain of a metal does not depend on its nature in any noticeable way; in both cases, the plastic strain increases considerably when the metal layer thickness is less than 15 nm.

The plastic strain is also affected by the stress and strain levels in the polymer substrate (Fig. 5). The PETP substrate at 90°C (above its glass-transition temperature) yields at rather low stresses (Fig. 5, curves 2). At room temperature, PETP is glassy, and it is strained at sufficiently high stresses in the forced elasticity mode. Above its glass-transition temperature, the polymer is strained uniformly; in the experiment whose results are illustrated by Fig. 5, the polymer extension



**Fig. 5.** Plastic strain of (a) gold and (b) platinum vs. coating thickness during in straining of a PETP substrate (1) at room temperature with necking and (2) at the substrate temperature equal to 90°C with 100% extension at a loading velocity of 10 mm/min.

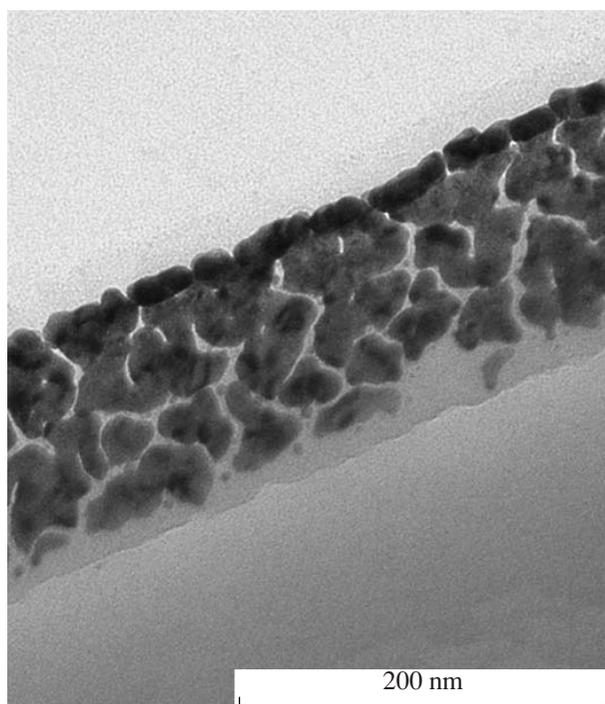
is 100%. Below its glass-transition temperature, PETP is strained nonuniformly, and its natural extension (in the neck) is about 320%. Both factors (the tensile stress of the polymer substrate and the value of its strain) enhance the rise in the plastic strain of the metal coating [12, 13].

Thus, a decrease in the metal coating thickness to the nanometer range leads to a considerable and simultaneous rise in its tensile strength and plastic strain in the extension of the polymer substrate.

The above results require separate discussion; several works [16, 17] showed that nanostructured materials, although demonstrating high strength and hardness, are frequently brittle and have low ductility. The combination of high strength and ductility in one material is extraordinary, as follows from our data.

#### SUGGESTED REASONS FOR THE COMBINATION OF HIGH STRENGTH AND DUCTILITY IN THIN (NANOMETER-THICK) METAL COATINGS

Let us discuss a possible mechanism of the phenomena discovered. Increased strengths of crystalline solids



**Fig. 6.** TEM micrograph of an ultrathin section of a 10-nm gold coating on PETP.

are, as a rule, associated with the reduction in grain size to nanoscale dimensions [18]. In this context, many researchers have concentrated their efforts to create a fine-grained structure in crystalline bodies, in particular, metals. One method for generating such nanostructures is intense plastic straining [19], which can be implemented by creating high shear strains under the condition that the volume of the strained materials remains unchanged. These conditions can be generated by torsional strains in cylinder-shaped billets, with hydrostatic pressure simultaneously applied for avoiding cracking and pore generation in the material [20, 21]. Such strains make it possible to generate uniform fine-grained structures with mean grain sizes of 100–200 nm. The above-described treatment, generating a fine-grained structure, strongly affects the strain–strength properties of the material. The yield strength and hardness rise with decreasing grain size due to the appearance of extra grain boundaries, which hinder the migration of dislocations; inasmuch as nanometer grain sizes are reached, the rise in strength is due to the low density of extant dislocations and the difficult generation of new ones. A possible reason for this phenomenon is that the plastic strain mechanism associated with the generation and migration of dislocations is not always operative in nanosized grains [22].

The grain sizes and shapes are very important parameters, but not unique ones, to ensure the appearance of new properties in nanostructured materials. The grain-boundary structure is also of importance. In par-

ticular, high internal stress levels were noticed in metals subjected to intense plastic straining as a result of high defect densities inside crystals and along their boundaries [23]. The creation of nanometer-thick coatings on polymer films is, in fact, a method for controlling the grain sizes intrinsic to metal structures. We repeat here that metal-grain fining to the specified (nanometer) sizes leads to a considerable rise in mechanical parameters, in particular, yield strength.

In this context, the results of recent studies that discovered the combination of a high yield strength and ductility in crystalline nanosystems are of particular importance [24–26]. In [27], nanostructured copper was obtained using a special temperature and force treatment, with the bimodal structure composed of micron-sized grains (their volume fraction was 25%) surrounded by nanometer-sized grains. This material retained its high ductility in combination with high yield strength. Similar results were obtained by implementation of a bimodal structure in zinc [28], copper [29], and an aluminum alloy [30].

Another approach to increasing the ductility of nanostructured materials was demonstrated in [31]. The underlying idea of this approach is as follows: disperse particles of secondary phases are generated in a nanostructured metallic host to change the propagation of the slipping band during straining, thus increasing ductility.

Still another approach is to generate an ultrafine-grained structure with certain types of grain boundaries. For example [32, 33], the generation of high-angle and nonequilibrium grain boundaries can provide for intergrain slipping in plastic strain even at room temperature. It was demonstrated [34] that the rise in the yield strength and, simultaneously, ductility of the nanostructured material is influenced by low-temperature annealing (for titanium, at  $\sim 300^\circ\text{C}$ ). The rise in the yield strength and ductility in this experiment is due to the increased rate sensitivity. An increased rate sensitivity is an indicator of viscous flow and a key factor in the superductility of nanostructured materials [35, 36]. However, this postulate also agrees with the development of grain-boundary slipping [37, 38].

The increased ductility of nanostructured materials is thought to arise from the change of the strain mechanism from dislocation creep to grain-boundary slipping. Grain-boundary slipping is a diffusion-controlled process, which is usually observed only at high temperatures. It is believed that nonequilibrium grain boundaries with far higher diffusion rates exist in nanostructured materials. Experiment shows that diffusion coefficients in nanostructured materials manufactured by intense plastic straining are considerably (two- to three-tenths of an order of magnitude) higher than ordinary values, because of the nonequilibrium state of grain boundaries [39, 40]. Possibly, grain-boundary slipping in nanostructured materials is easier in straining even at low temperatures, making these materials more ductile.

High ductility in nanostructured materials is ensured by their specific fine-grained structure. The results of the above-cited studies show that bulk nanostructured metals can, in principle, combine high yield strengths with ductility. This occurs in cases where a specific fine-grained structure of the metal is generated with certain types of grain boundaries. The solid-coating-on-polymer-substrate system under consideration can also have some structural features required for the aforementioned combination of properties.

Transmission electron microscopy was used to highlight the structural features of nanometer coatings on polymer films. Representative results of these studies are illustrated by Fig. 6. The TEM micrographs demonstrate the fine-grained structure in metals applied to a polymer substrate by plasma-ion deposition. Grain sizes in such nanolayers range from several nanometers to several tens of nanometers depending on the coating thickness. In the small thickness range, i.e., where the ductility of metals increases, the coating is, in fact, some nanocomposite in which very fine metal crystallites alternate with polymer interlayers. Likely, this morphology enhances the change in the metal deformation mechanism from dislocation creep to intergrain slipping, thus increasing the plastic strain.

#### ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project nos. 05-03-32538, 06-03-32452-a, and 06-03-08025-ofi) and the State Program for Support of Leading National Scientific Schools (grant NSh 4897.2006).

#### REFERENCES

- G. B. Sergeev, *Nanochemistry* (Moscow State University, Moscow, 2003; Elsevier, Amsterdam, 2006).
- I. P. Suzdalev, *Nanotechnology: Physicochemistry of Nanoclusters, Nanostructures, and Nanomaterials* (KomKniga, Moscow, 2006) [in Russian].
- Y. Xiang, X. Chen, T. Y. Tsui, J.-I. Jang, and J. J. Vlassak, *J. Mater. Res.* **21**, 386 (2006).
- X. Chen and J. J. Vlassak, *J. Mater. Res.* **16** (10), 2974 (2001).
- S. U. Jen and T. C. Wu, *Thin Solid Films* **492**, 166 (2005).
- A. S. Filonov and I. V. Yaminskii, "FemtoScan Online" *Scanning Probe Microscope Image Processing Software Manual: Version 2.0.5.1* (Center for Advanced Technologies, Moscow, 2005), p. 103 [in Russian].
- A. L. Volynskii, S. L. Bazhenov, and N. F. Bakeev, *Russ. Khim. Zh.* **42** (3), 57 (1998).
- A. L. Volynskii, S. L. Bazhenov, O. V. Lebedeva, and N. F. Bakeev, *J. Mater. Sci.* **35**, 547 (2000).
- A. L. Volynskii, S. L. Bazhenov, O. V. Lebedeva, A. N. Ozerin, and N. F. Bakeev, *J. Appl. Polym. Sci.* **72**, 1267 (1999).
- S. L. Bazhenov, A. L. Volynskii, V. M. Alexandrov, and N. F. Bakeev, *J. Polym. Sci. Part B: Polym. Phys.* **40**, 10 (2002).
- A. L. Volynskii, *Nauka v Rossii*, No. 3, 4 (2002).
- A. L. Volynskii, E. E. Voronina, O. V. Lebedeva, S. L. Bazhenov, A. N. Ozerin, and N. F. Bakeev, *Dokl. Akad. Nauk* **360** (2), 205 (1998) [*Dokl. Phys. Chem.* **360**, (1–3), 151 (1998)].
- A. L. Volynskii, E. E. Voronina, O. V. Lebedeva, S. L. Bazhenov, A. N. Ozerin, and N. F. Bakeev, *Vysokomol. Soedin., Ser. A* **41** (9), 1435 (1999) [*Polym. Sci.* **41** (9), 921 (1999)].
- S. L. Bazhenov, I. V. Chernov, A. L. Volynskii, and N. F. Bakeev, *Dokl. Akad. Nauk* **356** (1), 54 (1997) [*Dokl. Phys. Chem.* **356** (1–3), 283 (1997)].
- Handbook of Chemistry and Physics*, Ed. by C. D. Hodgman (CRC, Cleveland, OH, 1955), p. 1982.
- C. C. Koch, *Scr. Mater.* **49**, 657 (2003).
- D. G. Morris, *Mechanical Behaviour of Nanostructured Materials* (Trans. Tech., Uetikon-Zurich, 1998).
- M. Yu. Gutkin and I. A. Ovid'ko, *Defects and Plasticity Mechanisms in Nanostructured and Non-Crystalline Materials* (Yanus, Moscow, 2000), p. 182 [in Russian].
- N. P. Lyakishev and M. I. Alymov, *Russ. Nanotekhnol.* **1** (1–2), 71 (2006).
- O. A. Kaibyshev and F. Z. Utyashev, *Superplasticity, Structure Refinement, and Treatment of Difficultly Deformed Alloys* (Nauka, Moscow, 2002) [in Russian].
- A. P. Zhilyaev, S. Lee, G. V. Nurislamova, R. Z. Valiev, and T. G. Langdon, *Scr. Mater.*, **44**, 2753 (2001).
- R. Z. Valiev, *Russ. Nanotekhnol.* **1** (1–2), 208 (2006).
- I. V. Aleksandrov, A. R. Kil'mametov, and R. Z. Valiev, *Metally* **1**, 63 (2004).
- R. Z. Valiev, I. V. Alexandrov, Y. T. Zhu, and T. C. Lowe, *J. Mater. Res.* **17**, 5 (2002).
- R. Z. Valiev, *Nature (London)* **419**, 887 (2002).
- Y. M. Wang and E. Ma, *Acta Mater.* **52**, 1699 (2004).
- Y. Wang, M. Chen, F. Zhou, and E. Ma, *Nature (London)* **419**, 912 (2002).
- X. Zhang, H. Wang, R. O. Scattergood, J. Narayan, C. C. Koch, A. V. Sergueeva, and A. K. Mukherjee, *Acta Mater.* **50**, 4823 (2002).
- H. Mughrabi, M. Kautz, and R. Z. Valiev, *Z. Metallkd.* **94**, 1079 (2003).
- Y. S. Park, K. H. Chung, N. J. Kim, and E. J. Lavernia, *Mater. Sci. Eng., A* **374**, 211 (2004).
- D. G. Morris, *Mechanical Behaviour of Nanostructured Materials* (Trans. Tech., Uetikon-Zurich, 1998).
- R. Z. Valiev, I. V. Alexandrov, Y. T. Zhu, and T. C. Lowe, *J. Mater. Res.* **17**, 5 (2002).

33. R. Z. Valiev and I. V. Aleksandrov, *Nanostructured Materials Obtained under Severe Plastic Deformation* (Logos, Moscow, 2000) [in Russian].
34. R. Z. Valiev, A. V. Sergueeva, and A. K. Mukherjee, *Scr. Mater.* **49**, 669 (2003).
35. O. A. Kaibyshev, *Plasticity and Superplasticity of Metals* (Metallurgiya, Moscow, 1975) [in Russian].
36. T. O. Nie, J. Wadsworth, and O. D. Sherby, *Superplasticity in Metals and Ceramics* (Cambridge University Press, Cambridge, 1997).
37. H. van Swygenhoven, P. M. Derlet, and A. G. Froseth, *Nat. Mater.* **3**, 399 (2004).
38. Z. Budrovic, H. van Swygenhoven, P. M. Derlet, P. van Petegem, and B. Schmitt, *Science* (Washington) **304**, 273 (2004).
39. Yu. R. Kolobov, G. P. Grabovetskaya, M. B. Ivanov, A. P. Zhilyaev, and R. Z. Valiev, *Scr. Mater.* **44**, 873 (2001).
40. Yu. R. Kolobov, R. Z. Valiev, G. P. Grabovetskaya, A. P. Zhilyaev, E. F. Dudarev, K. V. Ivanov, M. B. Ivanov, O. A. Kashin, and E. V. Naidenkin, *Grain-Boundary Diffusion and Properties of Nanostructured Materials* (Nauka, Novosibirsk, 2001) [in Russian].