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Effect of heat treatment and tension on the surface morphology of thin Pt foils

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We investigated the formation of nanostructures on the surface of rolled thin platinum foils at the heating and "tension–compression" cycles in ultrahigh vacuum. The surface was characterized by LEED, AES, AFM, optical microscopy and micro Raman spectroscopy (MRS). Quantitative characterization of the surface relief was made by fractal analysis. About 95 % of the Pt foil surface was made by close packed Pt (111) face with unidirectional rippled multi-scale relief. Under the applied tension, changes in the LEED and AFM patterns were observed and it was found that, preceding the formation of the main crack, the surface becomes difractionally disordered with relief fractality turning to an isotropic one. Moreover, at the foil surface, near the clips of the sample holder (about 5 % of the surface area), the surface groups of micro crystals with sizes about 10 μm were observed which were identified by MRS as microdiamonds and diamond-like carbon.

Keywords: surface relief of Pt foil, fractals, dynamic re-crystallization, microdiamonds.

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1. Introduction

It has been found that by varying the regimes of cold rolling, re-crystallization and loading of thin Pt foils, one can obtain flat, practically single-crystalline substrates Pt (111) promising for preparation of nanosensors – gas analyzers [1, 2] On the contrary, applications in catalysis require thin Pt foils with more developed surface with multiscale nanorelief [3]. Furthermore, thin Pt foils with fractal unidirectional rippled surface relief may serve as a base for manufacturing of reflective diffraction gratings resistant to high temperatures that can operate in a broad range from the infrared to vacuum ultraviolet [4]. Combination of such methods as LEED and AFM permits one to obtain a better judgment on the morphology of surface layers. The aim of the present work is to investigate the effects of dynamic re-crystallization and mechanical tension on the atomic structure and surface relief of Pt, as well as the formation of diamond microcrystals and diamond-like carbon on the surface.

2. Experimental

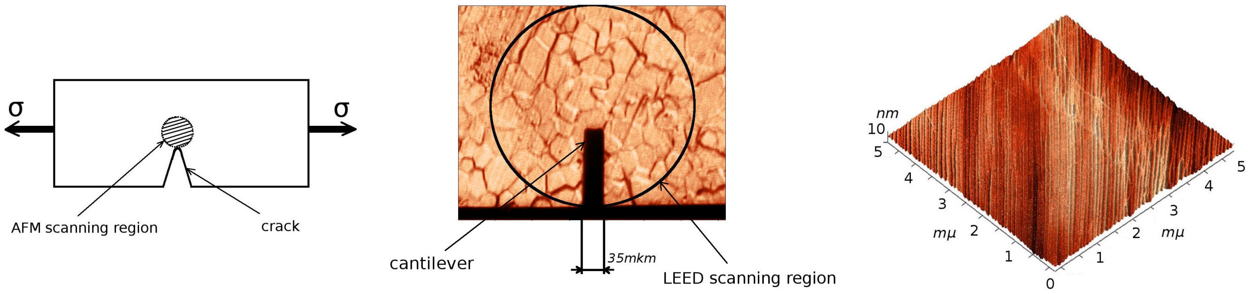
The samples were $30 \times 3 \times 0.02$ mm strips cut from 99.99 % pure cold-rolled Pt foil. The samples were polished with GOI paste #2* [5]. Before re-crystallization, the surface was cleaned with isopropanol and acetone. After that, the samples were subjected to cycles of dynamic re- crystallization annealing in UHV and in oxygen atmosphere under O_2 pressure of 10^{-4} Pa at temperatures of 1000 – 1800 K. Sample heating was carried out by a current transmission trough the sample. The temperature in the vicinity of the sample holders was 500 – 1300 K. The surface was characterized by LEED, AES, AFM, optical microscopy (OM) and micro Raman spectroscopy (MRS).

3. Results and discussion

3.1. Effect of dynamic re-crystallization and tension

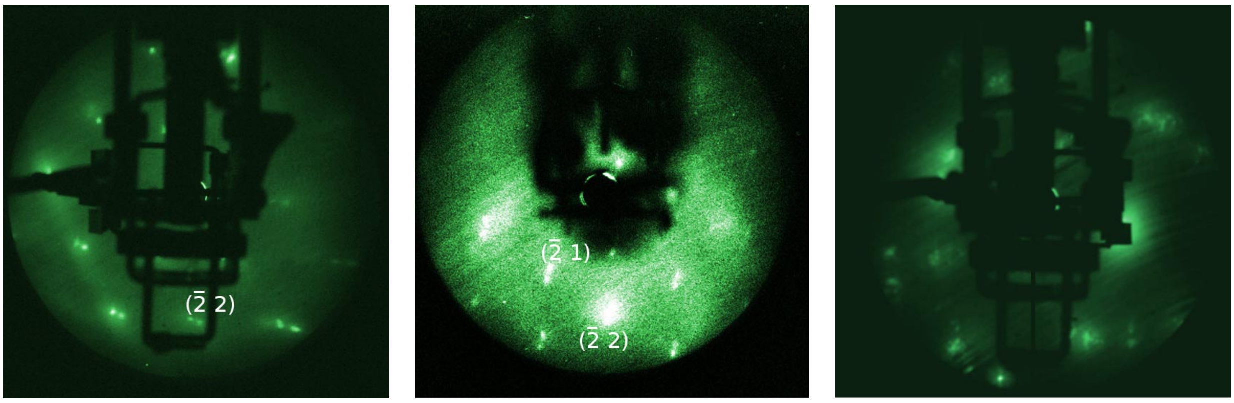
Figure 1 shows a scheme of the sample stretching (a), optical pattern of the region covered by the primary electron beam at diffraction (b) and typical AFM image of the surface after dynamic re-crystallization (c). Such AFM images were obtained from about 95 % of the surface. Fig. 2 displays LEED patterns after dynamic re-crystallization in UHV (a) and under the tension (b,c). Analysis of the optical (Fig. 1b) and LEED pattern (Fig. 2a) showed that after the dynamic re-crystallization the surface of the Pt foil is represented by the close-packed Pt (111)

*Composition of the GOI paste: Cr_2O_3 – 65 to 74 parts, stearine – 10 parts, split fat – 10 parts, kerosene – 2 parts, oleinic acid – 2 parts, silicagel – 1 part, sodium bicarbonate – 0.2 parts



a b c

FIG. 1. Scheme of the sample stretching (a), optical picture of the surface (b), AFM topography of Pt surface after dynamic re-crystallization (c)



a b c

FIG. 2. LEED patterns of Pt sample: after dynamic re-crystallization (a), under tension of 50 MPa (b), under tension of 70 MPa (c)

face with misorientation of crystallites less than 1 °. Broadening of reflections (see Fig. 2a,b) we attribute to the segregated graphite originated from the migration of the dissolved carbon from the bulk to the surface.

Estimation of the fractal dimension of the surface by box counting, Gwiddion, Fraclab methods gave:

$$D_{Gw} \sim D_{\|} + D_{\perp} = 2.4,$$

where D_{Gw} is the total fractal dimension, calculated by Gwiddion, $D_{\|}$ is the fractal dimension along the ripples, $D_{\perp}$ is the fractal dimension across the ripples, calculated by Fraclab.

LEED patterns from the surface of Pt sample at the tension of 50 and 70 MPa are presented on Fig. 2(b,c). One can see that reflections become blurred and the surface relief becomes isotropic (see AFM image in Fig. 3a). Estimation of the fractal dimension for the sites 1×1, 3×3 and 30×30 μm gave a value of $D_{Gw} = 2.2$ – 2.4. At the state preceding the sample's fracture (i.e. formation of main crack, see Fig. 1a), the LEED pattern disappears, but the surface relief remains isotropic. Blurring of reflections and disappearance of the diffraction pattern give evidence for a turn of blocks and possible amorphization of Pt lattice. These phenomena may be considered as signs of the forthcoming rupture of the sample.

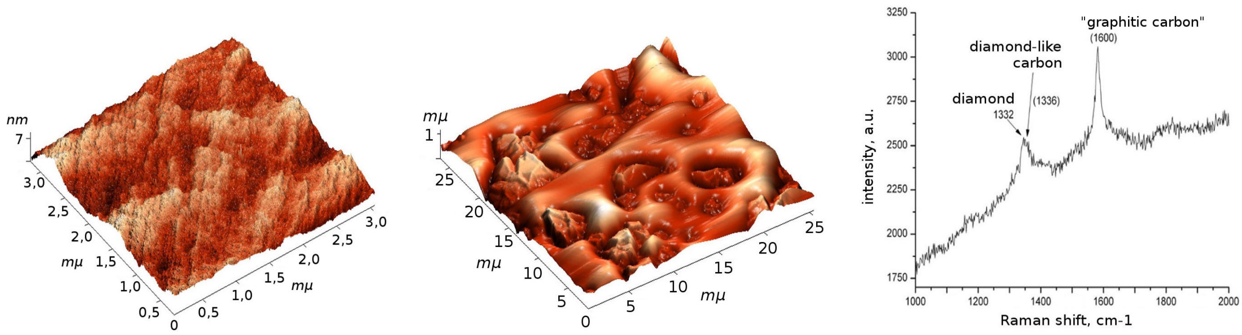
3.2. Formation of micro diamonds

It should be noted that in the present experiment, polishing of the samples with GOI paste, unlike polishing with diamond paste, excluded contamination of the Pt surface by micro- diamonds from the paste.

However, we suppose that most carbon is left on the surface after the polishing with GOI paste. Even cleaning of the sample's surface with acetone and isopropanol followed by alternating cycles (8 to 10) of annealing in UHV and O_2 does not completely remove carbon: some traces of carbon still remain according to AES and LEED [1]. Since the solubility of C in Pt increases with increasing temperature [6], there should be diffusion of C from colder to the hotter zone where C combines with O_2 and is eliminated from the system. However, in the colder zone, carbon can precipitate from the solid solution in Pt with formation of graphite, "graphitic carbon" [7] and the synthesis of microdiamonds occurs in the presence of hydrogen (traces of hydrogen were detected by mass spectrometry). The optimal substrate temperature in the CVD processes is about 973 K [8], which correlates with the temperature in the vicinity of the sample holder where the crystals were observed (500 – 1300 K).

Scratching with the polishing agent promotes the probability of micro diamond formation [9]. We noted that after cold rolling of Pt foils without polishing some crystals (less than 1 μm in size) were observed, but not identified.

The microcrystals obtained in the present work were identified by MRS technique. MRS spectra confirmed the formation of diamond and diamond-like microcrystals [10, 11] (see Fig. 3c).



a b c

FIG. 3. AFM topography of the samples surface preceding the fracture (a), diamond and diamond-like micro crystals (b), MRS spectrum of diamond, diamond-like micro crystals and "graphitic carbon" (c)

4. Conclusions

The forthcoming fracture of the samples is characterized by a turn of blocks on the close packed Pt (111) face and by a transition of surface fractality from an anisptropic to an isotropic form. Scratching of the sample surface by the polishing agent and dynamic re-crystallization in UHV apparently promote the formation of diamond and diamond-like carbon micro-crystals.

Acknowledgements

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