Elastoplastic Characteristics of Whiskers of Heavy Metal Azides (β – PbN_6 and AgN_3) Affected by Light

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Abstract – In this article elastoplastic characteristics of whiskers (W) of silver and lead azides are examined. Strength properties of Ws were analyzed with the help of specially designed deformation machines. The following methods of analysis were used: microhardness method, etching pit method, and microinterferometry.

It gave an opportunity to examine a number of elastoplastic characteristics and to prove that the mechanical strength of the silver and lead azides is structurally sensitive.

Strength properties of the whiskers of lead azide β-PbN_6 and silver azide AgN_3 were analyzed on specially designed deformation machines of two types: one of them allows to deform Ws by bending; another – by uniaxial tension.

Anisotropy of strength properties of Ws of heavy metals azides (HMA) was examined by the microhardness method.

The lamp PRK-4 was used as a source of light, the area of self-absorption was cut out with the wavelength of 365 nm.

The vertical deformation machine is a loading device executed on the basis of the microscope MBR-1. Tensile stresses are created due to the smooth rise of the mobile part of the microscope while turning the microscrew carried out by the engine via a multistage reducer. The deformation process can be stopped at any time, i.e., if necessary Ws can stay under the fixed load for a long period of time. Registration of a tension during the process of deformation is carried out by the movable-electrode tube 6MH1S, transforming the force or bias into electric signal, which goes to the recording single-coordinate potentiometer Endim 620.01 and at the same time – to the digital voltmeter F 330. The Ws holders served as electrodes for electrometric measurements and for analysis of strong electric fields influence on the Ws plasticity. This type of deformation machine allows to perform analysises of photoplasticity and photoconductivity, because Ws are in optic axis focus of the monochromator spectrophotometer SF-4. Ws absolute elongation, as well as dislocation slipbands, were observed in the optical microscope. The loading speed at an uniaxial tension on the given type of the machine was changing within the limits of $3\cdot10^{-4}\div3\cdot10^{-6}$ N/sec registrating simultaneously the spectral dependence of the Ws photoconductivity.

The ultraviolet irradiation of Ws of HMA affects the plastic characteristics at the chosen loading speeds. Originally at irradiation time of 1ч5 min and intensity of $7{,}3\cdot10^{18}$ quantum/(m^2·sec) a tendency to durability increase and plasticity reduction is observed; then, not reaching the tension of the plastic flow, Ws are being destroyed fragilely. For example, irradiating Ws of β-PbN_6 for 30 min. at temperature 293 K the ultimate strength decreases approximately by 30 % and makes up $8{,}5\cdot10^7$ N/m^2 (Fig. 1, curve 3).

Light effect (photoplastic effect) and electrical field influence (electroplastic effect) on semiconductors elastoplastic characteristics were first discovered and examined by Yu.A. Osipyan and his co-authors [2–4]. This phenomenon was explained by the active interaction of the moving dislocations with an electronic subsystem of a crystal. Unlike the regularities observed in works [2–4], which appear at the moment of direct light effect on the electronic subsystem of the crystal, the change of HMA plasticity keeps after being irradiated by ultraviolet light from the self-absorption band and depends on exposure time [5].

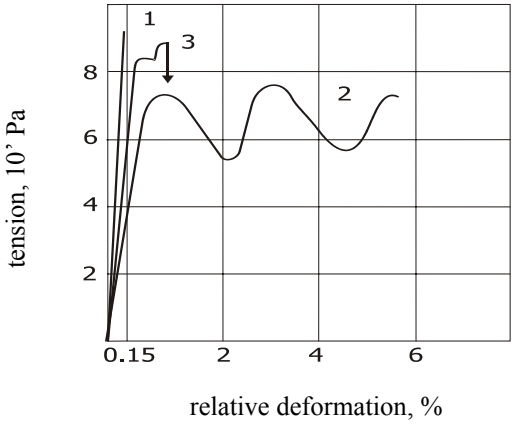

Fig. 1. Deformation curves in coordinates – tension and Ws relative deformation: curves *1, 3* – Ws of β-PbN_6; *2* – Ws of AgN_3

The measurement of the plastic characteristics in Ws of AgN_3 and β-PbN_6 affected by the light was carried out by the microhardness method using the instrument for microhardness measurement PMT-3.

Depending on radiation time not only a positive hardening plastic effect is observed, but also a

negative softening plastic one. Long periods of irradiation result in photochemical decomposition, accompanied by metal molecular and nitrogen extraction (Fig. 2.). Experimentally etching pit method and laser microinterferometer proved that the photoplastic effect in a hardening mode is accompanied by appearance of single slipbands for Ws of AgN_3, as well as for Ws of β-PbN_6 (Fig. 4 and Fig. 3). In a softening mode, i.e. long ultraviolet irradiation, a system of multiple twinning slipbands is observed which can be visually seen in the polarized light described similarly in work [6] (Fig. 3, *b*). According to the character of loading and geometry of tension distribution in Ws of β-PbN_6 five planes of dislocation slip can be found: [100], [001], [011], [010], [110], dislocation multiplication being discovered by the decoration method, perhaps due to Frank-Reed's source [5].

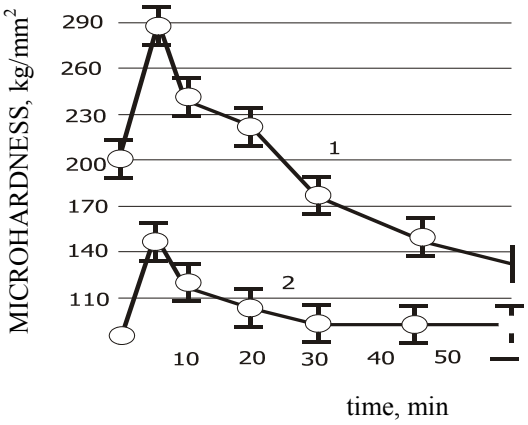

Fig. 2. Microhardness dependence of Ws of β-PbN_6 and AgN_3 from radiation time: 1 – Ws of β-PbN_6; 2 – Ws of AgN_3. Length of a light wave 365 nm; light intensity – 10^{18} quantum/(m^2·sec)

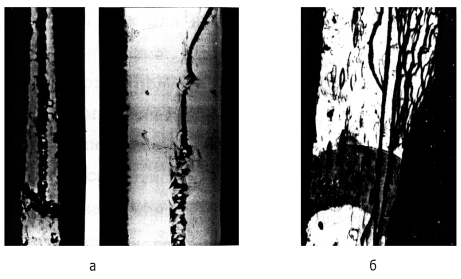

Fig. 3. Dislocation slipbands in Ws of β-PbN_6: *a* – single slipbands x 200; *b* – slipbands system observed in the polarized light x 250

The analysis of the reasons of W of HMA hardening and softening being affected by the light from the self-absorption band we shall make on the basis of the interaction between point defects and available dislocations by the diffusion mechanism [5] and processes proceeding at photochemical decomposition. As a reason of the diffusion flow of point defects to the dislocation can serve not only the supersaturation of point defects in crystal volume, but also the presence of the force acting on the dislocation in a direction, normal to its plane of slipping.

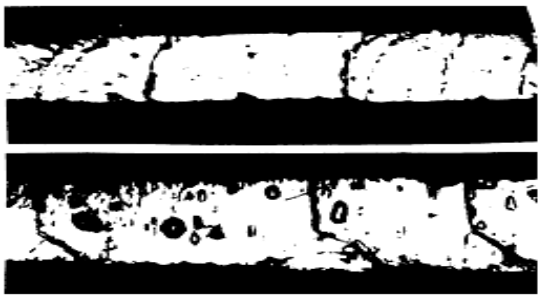

Fig. 4. Dislocation slipbands on the surface [100] in Ws of silver azide

Let dislocation be in the tension field, creating force $\overline{F}$, applied to the unit of length dislocation. Then while dislocation slips, the work determined in the unit time by the value of $\overline{F}\overline{V}_n$, where $\overline{V}_n$ – the speed component of dislocation is normal to its plane slipping. This work referred to one vacancy, having settled on the dislocation, in case of pure margin rectilinear dislocation is expressed in the following way [8]

$$\partial R = \frac{a^3}{b^2}[\overline{b};\overline{r}]\overline{F} = \frac{a^3}{b^2}[\overline{b};\overline{r}]\overline{F} = \quad a^3 p'_{xx}, \quad (1)$$

where the OX axis is directed along Burgers vector dislocation $\overline{b}$; *a* – lattice parameter; $b_\perp$ - component of Burgers' vector, perpendicular to the line of dislocation in the given point; $\overline{r}$ – single vector, tangent to the dislocation; p'_{xx} – appropriate component of the strain tensor-deviator.

Believing, that in process of the dislocation slipping the equilibrium concentration of point defects on the dislocation axis remains constant, thus, without discussing kinetics of the point defects settlement [5] on the dislocation, we can write down a boundary condition for the change of chemical potential ∂μ on the dislocation tube surface based on the equation (2) of the following form:

$$\partial\mu_b\big|_{r=r_0} = a^3 P'_{xx}, \qquad (2)$$

The presence of the small supersaturation far from dislocation is taken into account by the following condition on infinity:

$$\partial\mu_b\big|_{r=\infty} = \frac{\partial\mu(c)}{\partial c}\delta c = kT\frac{\delta c}{c_0}, \qquad (3)$$

where δc – some supersaturation of vacancies; c_0 – equilibrium concentration of vacancies in the absence

of external loadings; k – Boltzmann's constant; T – temperature.

A.L. Roytburd and B.A. Vershok [9] proved, that the considered diffusion sum is reduced to the Laplace equation, i.e. the chemical potential of vacancy μ_b can be viewed as a harmonic function satisfying conditions (3) and (4). Density of diffusion flux in this case is defined by the formula

$$j = -\frac{c_0 \cdot D_b}{a^3 kT} grad\mu_b, \qquad (4)$$

where *Db* – diffusion factor of vacancies.

Let's consider a separate rectilinear dislocation, parallel to the OZ axis. Dislocation slip occurs along the OY axis at a speed of $V_g=a^3I/b$. Substituting chemical potential μ_b, which satisfies to conditions (3) and (4), we shall calculate according to the equation (6) a full vacancy flux *I*, falling to the length unit of dislocation:

$$V_y = -\frac{2\pi c_0 D_b}{b\ln(l/r_0)}\left\{\frac{a^3 p'_{xx}}{kT} - \frac{\delta c}{c_0}\right\}, \qquad (5)$$

were *l* – dislocation length or crystal size.

At the moment of initiation of the stationary diffusion flux it is possible to suppose, that the vacancies concentration in the crystal is equilibrium ($\delta c=0$). Then

$$V_y = -\frac{2\pi c_0 D_b}{b\ln(l/r_0)}\left(\frac{a^3 p'_{xx}}{kT}\right). \qquad (6)$$

Slip of the dislocation in the considered case can be finished only after its exit on the external surface of the sample. The similar dislocation exit on the surface means the disappearance of the superfluous nuclear half-plane in the crystal – its complete "dissolution". The possibility of such nuclear half-plane dissolution can be provided only by the presence in the crystal of a infinite-dimensional sink of interstitial atoms (source for vacancies), which is able to absorb all the half-plane dissolved substance. Not supposing the mechanism of complete absorption of superfluous substance contained in this half-plane, its accumulation in the crystal volume should be taken into account. Then the point defects concentration during the deformation process would have changed with time in accordance to equation (5), and the slip of dislocation could not have happened in a stationary way. The similar situation, apparently, is observed in Ws of AgN_3 in Figure 2 (curve 2) and in Ws of β-PbN_6 (curve 1).

Macroscopic deformation, i.e. observed and plastic one, can be created only while moving of the significant quantity of dislocations. For the simplification of the consideration we believe, that at Ws uniaxial tension there is a large number of identical parallel marginal dislocations, which at their slip into the stress field will cause average plastic deformation with speed

$$\varepsilon_{xx}^{пл} = -\rho_0 b V_y = \frac{2\pi c_0 \rho_0 D_b}{b\ln(l/r_0)}\left(\frac{a^3 p'_{xx}}{kT}\right), \qquad (7)$$

where ρ_0 – dislocations density (number of dislocations, going through the area unit on the Oxy plane).

If there are two or several parallel dislocation slipbands in the crystal, whose planes of slipping are perpendicular, then the crystal's diffusion dislocation flux has the speed proportional to any other equal conditions of vacancy concentration [8]:

$$\varepsilon_{xx}^{пл} = -\varepsilon_{yy}^{пл} \approx \rho_0 c_0 D\frac{a^3 P}{kT} \approx \frac{c_0 D a^3 P}{L^2 kT}, \qquad (8)$$

where c_0 – dislocations density; L – average distance between dislocations in the plane, perpendicular to their axes ($c_0 = L^{-2}$); *P* – uniaxial tension effort.

We use the received expression for the explanation of the ultraviolet light effect and electric field on Ws of HMA plasticity.

The most non-conflicting scheme of molecular nitrogen formation at thermal, photochemical and electric field decomposition of HMA includes a stage of hole localization (radical N_3^0) on cation vacancy with V_k-centre formation. At this stage there is a reduction of equilibrium concentration of cation vacancies responsible for plasticity according to the diffusion-dislocation mechanism. Further on, when the concentration of cation vacancies decreases not less than in 3 times, as it is shown in our work [12], there is a repeated capture of the hole on the V_k-centre and molecular nitrogen extraction accompanied either by restoration of the initial quantity of cation vacancies and increase of the anion ones (mechanism offered by V.G. Kriger with his co-authors [11]), or significant growth of their concentration due to the formation of Frenkel's pairs at energy dissipation 10 eV, extracted at chemical reaction [12]. Thus, the registration of chemical interaction between vacancies and active radicals N_3^0 fully explains the character of the plastic characteristics change of the Ws HMA affected by light irradiation from self-absorption area, that in its turn is an indirect evidence considered in [11, 12] stages of the decomposition mechanism.

Summing up the results of the analysis of the mechanical properties of β-PbN_6 and silver azides it is necessary to note, that a number of their elastoplastic characteristics, which can not be found in the scientific literature, were examined, also it was shown that the mechanical properties of azides of such metals are structurally sensitive not only to the simultaneous light effect and electric field influence, as it was proved for the photosensitive semiconductors, but also to posttransformations taking place in the crystal lattices.

The above given experimental results of photo- and electroplasticity and their discussion can also extend the possible explanation mechanisms of the semiconductors phenomenon such as A_2B_6, where it

was originally found. The suggested diffusion-dislocation model agrees with the existing conception about the elementary stages mechanism of the silver azides and β-PbN_6 decomposition, which is being developed in the Kemerovo State University.

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