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Investigation of primary nanocracks of atomically smooth metals

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A new analytical model for calculating the characteristics of primary cracks that appear in atomically smooth metals is proposed. A technique has been developed for calculating the length of nanocracks in atomically smooth metals based on the study of the physical properties of crystals. For the first time, the parameters of primary cracks were calculated using the example of atomically smooth metals. The results obtained on the basis of the developed method are compared with the results of applying known models of nanocrack formation. It is shown that our results are consistent with previously known results.

Keywords: surface, surface energy, surface layer, nanostructure, melting point, atomic volume, atomically smooth crystal.

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A metal crystal consists of a surface layer with thickness R_1, which is hereinafter referred to as phase $\gamma 1$, and the bulk material (phase $\gamma 2$). Since surface energy γ_1 of the $\gamma 1$ phase layer is three time lower than surface energy γ_2 of the bulk phase, the origin of fracture of metals is at the surface layer. In crystals with same-type atoms, the fraction of space occupied by them in a single cube is 68 and 74% for BCC and FCC transition metals, respectively. The remaining part of crystals (32 and 26% for metals with BCC and FCC lattices, respectively) is void space. This space after relaxation or reconstruction is hereinafter referred to as the maximum field of primary cracks. It is of importance for our study that crack length L is equal to thickness R_1 of the surface metal layer. This crack length is representative of a feature that is related both to the geometry of crystal lattices and physical properties of crystals.

What are the sizes of primary nanocracks of atomically smooth metals? This question is a complicated one and has not been answered yet, since nanocracks and their growth specify the conditions of fracture of solids [1–7]. A number of models of nanocrack formation were presented in [1,8–10]: the Griffith model (Griffith examined the variation of energy of a body with a crack under load and derived an energy fracture criterion [1]); the Zener–Stroh–Petch, Cottrell, Bullough–Gilman, Orowan–Stroh, Coble, Nabarro–Herring models; etc. However, the authors of these models did not provide the results of calculation of the nanocrack length.

In our view, stresses associated with the formation of a surface nanostructured metal layer due to surface relaxation or reconstruction processes, which lead to the formation of pores and normal and lateral dislocations, are the ultimate cause of emergence of nanocracks even in atomically smooth crystals. We have proposed a model for calculating thickness R_1 of the near-surface metal layer [11] and its anisotropy [12]. An experimental value of R_1 may be determined in high vacuum using X-ray techniques or other methods ($R_1 = 3.2\,\text{nm}$ for germanium, while gold has $R_1 = 1.2\,\text{nm}$) [13,14].

The aim of the present study is to develop a calculation procedure, calculate the length of nanocracks in certain metals with cubic crystal lattices, and compare the results with the Griffith theory.

Size effects in a layer with thickness R_1 are specified by the entire ensemble of atoms in the system (collective processes). Such „quasi-classical“ size effects are observed only in nanoparticles and nanostructures [11,12,15]. They may be observed in experiments with high-purity single crystals under grazing incidence of X-ray radiation when the incidence angle is equal to (or smaller than) the critical angle of total internal reflection.

It was found in [11] that

$$L = R_1 = 0.17 \cdot 10^{-9} \upsilon\,[\text{m}]. \tag{1}$$

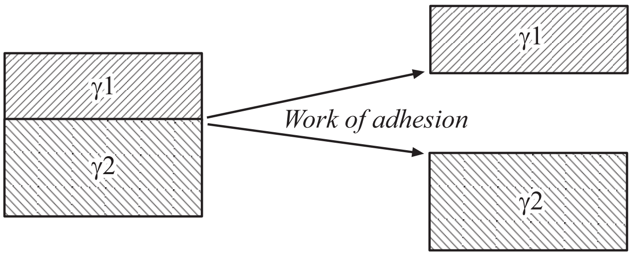
Equation (1) demonstrates that a layer with thickness R_1 is defined by molar (atomic) metal volume $\upsilon = M/\rho$ (M is molar mass and ρ is density). It was demonstrated in [15] that surface energy of bulk metal γ_2 is equal (accurately to within 3%) to

$$\gamma_2 = 0.78 \cdot 10^{-3} T_m\,[\text{J/m}^2]. \tag{2}$$

The work on separation of phases $\gamma 1$ and $\gamma 2$ (see the figure), which is called work of adhesion W_a, is determined using the Dupre relation [16]:

$$W_a = \gamma_1 + \gamma_2 - \gamma_{12} \approx \gamma_1 + \gamma_2 = 1.3\gamma_2 \approx 10^{-3} T_m\,[\text{J/m}^2], \tag{3}$$

where γ_{12} is the surface energy at the interphase boundary, which is negligible in virtue of a second-order phase transition. As was demonstrated in [15], $\gamma_1 \approx 0.3\gamma_2$.



Work of adhesion W_a on separation of metal phases $\gamma 1$ and $\gamma 2$.

Internal stresses σ_{is} between phases $\gamma 1$ and $\gamma 2$ may be calculated using the following formula [16]:

$$\sigma_{is} = (W_a E/R_1)^{1/2}\,[\mathrm{Pa}]. \tag{4}$$

The adhesion force for a metal is

$$F_1 = \gamma_1 R_1. \tag{5}$$

The data from [17] are needed to estimate the anisotropy for metals:

$$Im3m,\ Z = 2,\ l_{100} = R_1,\ l_{110} = R_1 2^{1/2},\ l_{111} = R_1/(3^{1/2}),$$

$$Fm3m,\ Z{=}4, l_{100}{=}R_1, l_{110}{=}R_1/(2^{1/2}), l_{111}{=}2R_1/(3^{1/2}). \tag{6}$$

The initial data for calculations by formulae (1)–(6) for certain BCC ($Im3m$) and FCC ($Fm3m$) transition metals are listed in the table: surface layer thickness (crack length) $R_1 = L$ (the number of metal monolayers $n = R_1/a$, where a is the lattice constant, is indicated in brackets), work W_a and force F_1 of adhesion, internal stresses σ_{is}, and Griffith crack length L_G.

Adhesion force F_1 (intermolecular force) assumes a value of $(0.2-0.6) \cdot 10^{-9}$ N in transition metals. For comparison, the force of attraction between an electron and a proton in a hydrogen atom is $F = 0.2 \cdot 10^{-9}$ N, and the sound pressure force in a human ear at the threshold of hearing is $F = 2 \cdot 10^{-9}$ N. Internal stresses σ_{is} are maximized in refractory metals (tungsten). Tabulated data indicate that layer thickness R_1 and crack length L in d-transition metals do not exceed 2 nm, while the thickness for f-elements is close to 4 nm (i.e., is two times greater). The values of $R_1 = L$ in the Li → Cs series (not listed in the table) vary from 2.2 to 12.1 nm. Number n of monolayers does not exceed 3–5 for d-metals and is approximately equal to 11 (Eu) for f-metals. The numbers of monolayers for lithium and cesium are $n = 6$ and $n = 20$, respectively.

An energy criterion [1] allowing one to determine the conditions of fracture of a solid body due to nanocrack growth has already been formulated. According to this criterion, fracture occurs if the variation of elastic energy is equal to (or greater than) the adhesion energy. The energy variation is in this case written as

$$\Delta W = \big((\sigma_{is})^2 \pi (L_G)^2/2E\big) + 2(\gamma_1 + \gamma_2)L_G, \tag{7}$$

where ΔW is the energy variation in a plane stress state of the considered solid body, σ_{is} is the applied stress, L_G is the crack size, E is the Young's modulus, and γ_1 and γ_2 are the specific surface energies of a layer with thickness R_1 and internal layers of the considered solid body.

New surfaces with their specific surface energies represented by quantities γ_1 and γ_2 in formula (7) emerge in the course of development of a nanocrack.

The value of critical stress under which a crack is capable of unstable growth may be derived from the following conditions:

$$\partial W/\partial L = 0, \qquad (\sigma_{is})^2 \pi L_G/E = 2(\gamma_1 + \gamma_2). \tag{8}$$

Crack lengths L_G calculated in accordance with formula (8) are listed in the table and differ from crack length L by 9% on the average. This verifies the validity of our model with the length of primary cracks characterized by expression $L = 0.17 \cdot 10^{-9} M/\rho$. This model is applicable not just to metals; it holds true for any solids, polymers and minerals included.

Thus, most studies on nanocrack formation (dating back to the works of Griffith, which were published in the 1920-s) lack quantitative estimates of the nanocrack length. It was demonstrated in our study that a primary nanocrack develops due-to noncompensation with atoms located on the surface and in the bulk. A surface layer with thickness R_1 forms in this case. Atomic relaxation or surface reconstruction proceed in this layer, and internal stresses, which induce dislocations, emerge in it. These dislocations are the cause of formation of pores and nanocracks the sizes of which depend on the mass and density of crystal elements.

The proposed model is universal in nature. Note that a simple method for determining the thickness of a surface layer for arbitrary compounds has not been proposed yet. We match this thickness R_1 to length L of a nanocrack that emerges due to stresses induced by surface relaxation and governs the fracture of any structural material.

As was demonstrated in [18,19], nanocracks of this size (see the table) form within several nanoseconds. This method relies on fractoluminescence, which is the emission of a light signal (luminescence) with a time resolution of 1–2 ns occurring when atomic bonds break on the surface of nanocracks in the process of fracture of solids. The fractoluminescence spectrum of oligoclase in the process of surface fracture was recorded in [19]. The length of signals was approximately 50 ns, and the time interval between them varied from 0.1 to 1.0 μs. The spectrum features four maxima associated with the crossing of barriers preventing the motion of dislocations along sliding planes. Dislocations form primary cracks with a size of 10–20 nm in this case. Oligoclase is a mixture of 10–30% of anorthite $CaAl_2Si_2O_8$ and 70–90% of albite $NaAlSi_3O_8$. The result of our calculations performed in accordance with formula (5) was $L = R_1 = 16.8-17.2$ nm, which agrees fairly well with experimental data [19].

Initial data and results of calculations

Metal	$R_1 = L$, nm (n)	F_1, 10^{-9} N	W_a, J/m^2	σ_{is}, MPa	L_G, nm
Cr	1.23 (4)	0.61	2.130	21977	1.02
Mo	1.60 (5)	0.68	2.896	24413	1.33
W	1.62 (5)	0.86	3.695	30611	1.35
Mn	1.30 (2)	0.35	1.517	15199	1.08
Fe	1.21 (4)	0.42	1.812	17776	1.01
Ni	1.12 (3)	0.40	1.726	17550	0.93
Cu	1.21 (3)	0.32	1.357	12000	1.01
Ag	1.75 (4)	0.29	1.235	7665	1.41
Au	1.73 (4)	0.31	1.337	7810	1.44
Ce	3.52 (7)	0.29	1.072	3198	3.04
Eu	4.93 (11)	0.26	1.099	2015	4.25
Yb	4.22 (8)	0.26	1.097	2272	4.26
Th	3.35 (7)	0.47	2.028	6914	2.78

Nanocracks still remain understudied (especially in metals and metallic structures). A model for calculating the length of primary cracks induced in metals by a surface layer with thickness R_1 was proposed. This new method was used to calculate the length of primary nanocracks, and the obtained data agree well with the results reported earlier. The calculated Griffith length L_G of a crack differs from crack length L by 9% on the average, thus providing support for our theory. This model is applicable not just to metals; it holds true for any solids, polymers and minerals included.

Conflict of interest

The authors declare that they have no conflict of interest.

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