Modeling plasticity of materials with nanostructure

N R Kudinova

Department of Physics of Materials, Charles University, Prague, Czech Republic

Abstract. A new approach to modeling of the plasticity of materials with the particle size in the range from 3 to 20 nm (nanostructure) has been proposed. It is based on classical thermodynamic approach employing the surface tension of nanoparticles. Its main advantage is the minimum number of physical parameters in use. In the context of the proposed model, we calculated the dependence of the melting temperature on the nanoparticle size which is consistent with experimental data. The volume density of the surface energy of nanoparticles was also determined. This energy is assumed to be a significant part of the internal energy during deformation Yield point was interpreted as the result of changes of grains surface energy during the deformation. The obtained yield point dependence on the grain size was related to the Hall–Petch law, and this resulted in confirmation of the hypothesis on the crucial role of surface tension forces in the initial stage of plastic deformation of nanomaterials.

1 Introduction

Nanocrystalline materials exhibit potential for applications in a wide range of areas, particularly because of their high strength when compared with their coarse-grained counterparts. Classically, the Hall–Petch [*Petch*, 1953] relation predicts that the yield strength increases with decreasing grain size:

$$\tau = \tau_0 + Kd^{-\frac{1}{2}}, \quad (1)$$

where τ_0 is the friction stress in the absence of boundaries, K is a constant and d is the grain size. This relation was experimentally found to be consistent with experimental data for materials with grain sizes ranging from 1 millimeter down to 1 micrometer. Consequently, it was believed that if the average grain size decreased even further to the nanometer length scale the yield strength would continue to increase. However, experiments on many nanocrystalline materials demonstrated that if the grains reached a small enough size, typically around 10 nm, the yield strength would either remain constant or decrease with decreasing grains size [*Conrad et al.*, 2000]. This phenomenon has been termed the reverse or inverse Hall–Petch relation. A number of different mechanisms have been proposed to explain this phenomenon. As suggested by Carlton [*Carlton et al*, 2007] et al., they fall into four categories: (1) dislocation-based [*Gutkin et al,* 2003] (2) diffusion-based [*Kocks* ,1970], (3) grain-boundary shearing-based [*Kim*, 1998; *Ovid'ko et al*, 2011], (4) two-phase-based. [*Carlton et al*, 2007].

Figure 1 displays schematically the well-known break-down of the Hall-Petch behavior, i.e. the rise of the stress with decreasing grain size in polycrystalline metals, when the grain size drops into the nanometre range resulting in a peak plastic resistance at a grain size of about 10 nm.

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.
Published under licence by IOP Publishing Ltd

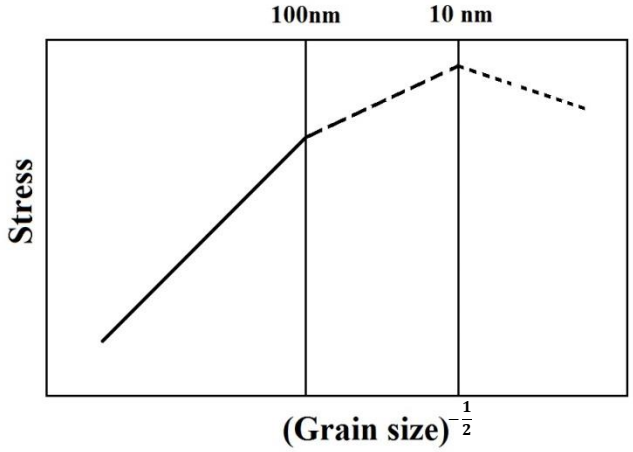


Figure 1. Stress of a material as a function of the grain size [*Kumar et al*, 2003].

2 Thermodynamical approach

In this chapter we will introduce the different approach for explaining the inverse Hall-Petch relation. It is based on the surface (or interfacial) tension - a fundamental thermodynamic parameter - related to the work spent on reversible isothermal formation of the interface [*Frank*, 1955]. Surface tension is considered as a measure of the excess free energy in the surface layer compared to the free energy in the volumes of coexisting phases [*Dadashev*, 2008].

The surfaces tension appears in many equations of physics. It determines such parameters and phenomena as the capillary pressure, wetting (contact) angle, saturated vapor pressure, adsorption, capacitance of the double electrical layer, work spent on the formation of critical nuclei, length of capillary waves, etc. Due to recent advances in the physics and chemistry of nanomaterials, interest in the phenomenon of surface tension has noticeably quickened [*Andrievskii et al*, 2005]. A central point here is the deducing of the size dependence of the surface tension. The Gibbs–Tolman–Koenig–Buff differential equation, which determines this dependence for the spherical surface, is well known [*Gibbs*, 1948; *Buff*, 1955; *Koenig*, 1950; *Tolman*, 1949; *Ono et al*, 1960].

3 Modeling of the surface tension

Gibbs–Tolman–Koenig–Buff [*Gibbs*, 1948; *Buff*, 1955; *Koenig*, 1950; *Tolman*, 1949; *Ono et al*, 1960] equation for a spherical particle is the following:

$$\frac{\partial \ln \sigma}{\partial \ln r} = \frac{\frac{2\delta}{r}\left(1+\frac{\delta}{r}+\frac{1\delta^2}{3r^2}\right)}{1+\frac{2\delta}{r}\left(1+\frac{\delta}{r}+\frac{1\delta^2}{3r^2}\right)}, \tag{2}$$

where σ, r and δ are the surface tension, the radius of the particle and the Tolmen constant, respectively. The latter being equal to the surface layer thickness of the particle.

It has been believed until recently that Eq. (2) cannot be solved analytically, i.e., expressed through elementary fractions. Such a belief seems to rely upon Tolman's original work [R. C. Tolman, 1949], where this equation was solved asymptotically and the Gibbs–Tolman–Koenig–Buff equation (in its initial form) was integrated numerically. In order to solve the Eq. (2) approximately, the theory assumes that $r \gg \delta$ [*Ono et al*, 1960], so that parenthesized expressions

in the numerator and denominator on the right of (2) can be omitted. In this case, the straightforward integration yields the Tolman [1949] formula:

$$\sigma = \frac{\sigma^{(\infty)}}{1+\frac{2\delta}{r}}, \tag{3}$$

where $\sigma^{(\infty)}$ is the surface tension for a plane surface. When using the same condition ($r \gg \delta$), one obtains another analytical expression for the surface tension [*Yurov et al*, 2011]:

$$\sigma(r) = \sigma_{\infty} exp\left(-\frac{2\delta}{r}\right). \tag{4}$$

However, it is possible to obtain the general solution of (2), provided that δ does not depend on r. It can be expressed in an analytical form, with $s = \frac{r}{\delta}$ being introduced as the dimensionless variable. After separation of the variables in the equation (2) one obtains:

$$\ln\frac{\sigma}{\sigma^{(\infty)}} = -2\int_{r/\delta}^{\infty}\left(\frac{3s^2+3s+1}{3s^3+6s^2+6s+2}\right)\frac{ds}{s}. \tag{5}$$

The integral in (5) is calculated by expanding the integrand into elementary fractions. The final result is written in the form

$$\sigma = \frac{\sigma(\infty)r}{\delta}\, e^{\left(-\sum_{k=1}^{3}\frac{s_k^2\ln(\frac{r}{\delta}-s_k)}{3s_k^2+4s_k+2}\right)}, \tag{6}$$

where $s_k = \{-0.558; -0.721 + i0.822; -0.721 - i0.822\}$ - are the roots of the cubic equation $3s^3 + 6s^2 + 6s + 2 = 0$

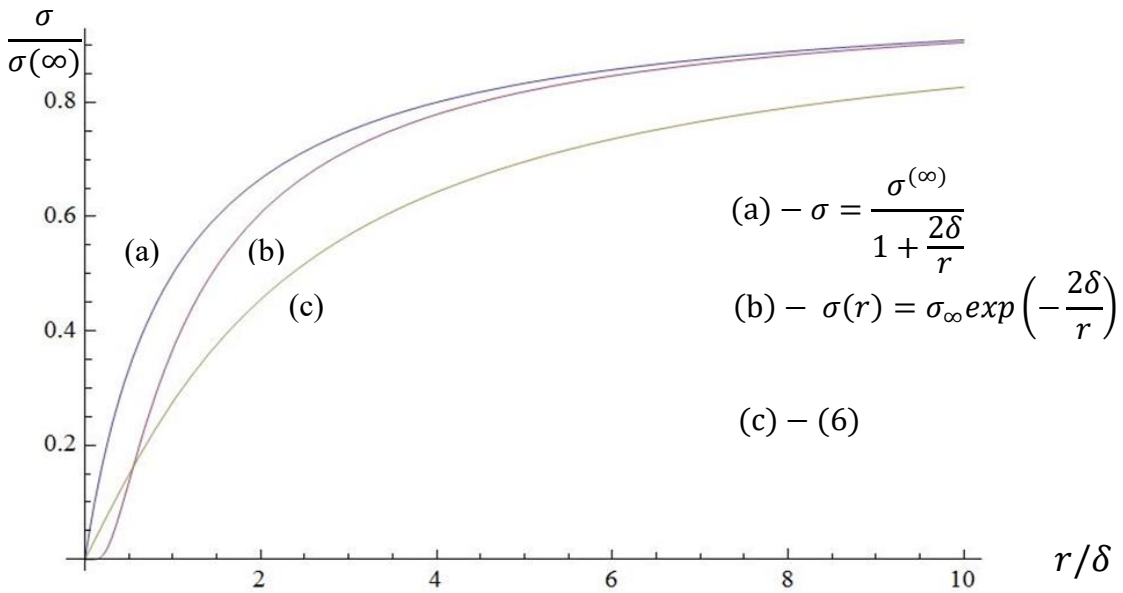


Figure 2. Scaled functions of surface tension for the exact solution (6) and the approximations (a), (b).

4 Dependence between melting temperatures and surface tension

The melting temperature of a bulk material is not dependent on its size. However, as the dimensions of a material decrease towards the atomic scale, the melting temperature scales with the material dimensions. The decrease in melting temperature can be of the order of tens to hundreds of degrees for metals with nanometer dimensions, e.g aggregated and powdered nanomaterials, metallic nanopowders of pure metals etc. This phenomenon is called melting-point depression and may be very strong in nanomaterials, which melt at temperatures hundreds of degrees lower than bulk materials [*Buffat et al*, 1976]. In Figure 3 the melting temperature dependence on particle size for Au is shown.

The variation of melting temperature is directly connected with the energy of surface tension since the probability of dislodging of individual atoms and molecules from a crystallite increases as a result of thermal motion. The effect of the surface tension of crystallites on the melting temperature has not been studied yet.

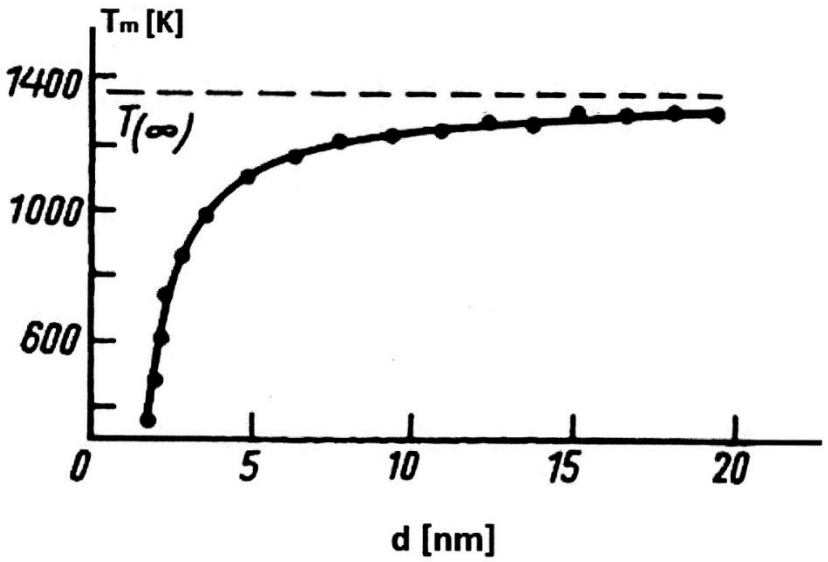


Figure 3. Melting curve for gold as a function of nanoparticle diameter, dots are the experimental data [*Buffat*, 1976].

Let us use the well-known linear dependence of physical properties on the size of the particles [*Yurov*, 2011]:

$$A(r) = A_0(1 - \frac{d}{r}) \tag{7}$$

where A_0 – is a physical property bulk sample, $A(r)$– physical property of small particle, d – the radius corresponding to the particle size at which the size effects begin to play a role.

The critical radius d may be expressed by the following formula:

$$d = \frac{2\sigma\vartheta}{RT}, \tag{8}$$

where ϑ is the – molar volume, and R is a gas constant.

From (8) one can see that the surface tension is linearly dependent on temperature:

$$\sigma = \alpha T \tag{9}$$

where $\alpha = \frac{dR}{2\vartheta} = 10^{-3} Jm^{-2}K^{-1}$ for all metals [*Yurov*, 2011].

Moreover, there is an experimental confirmation of the linear dependence of melting temperature on the surface tension [*Rehviashvili et al*, 2006].

Using the exact solution of GTKF (6), which was obtained above, and the relation (9) and assuming temperature being the physical property in eq. (7) we can derive the exact dependence of the melting temperature on the particle size:

$$T_m = \frac{T_0 r}{\delta} e^{\left(-\sum_{k=1}^{3} \frac{s_k^2 \ln\left(\frac{r}{\delta} - s_k\right)}{3s_k^2 + 4s_k + 2}\right)}, \quad (10)$$

where $s_k = \{-0.558; -0.721 + i0.822; -0.721 - i0.822\}$ - are the roots of the cubic equation $3s^3 + 6s^2 + 6s + 2 = 0$

Figure 4 shows such dependence for gold (experimental points) and calculated functions.

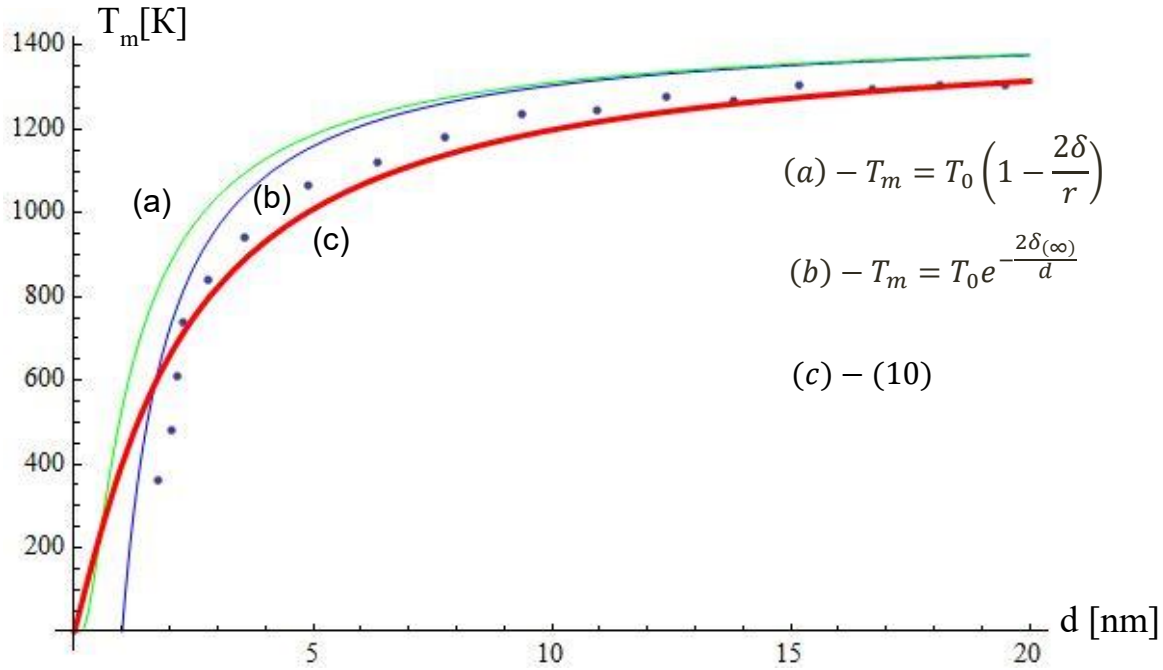


Figure 4. Dependence of the melting temperature for gold on the particle diameter d=2r. for the exact solution (10) and the approximations (a), (b).

Comparison of the plots shows that our exact solution describes well the experimental data in the range of the particle sizes from 3 to 20 nm. At the same time, the approximate functions suffer from very large (up to 100%) uncertainty. Thus the exact solution (10) provides an adequate description for variation of the melting temperature with particle size. This justifies its use in further calculations of surface energy and its density.

5 Surface tension and yield point

Nondislocation models of plasticity usually consider the relation between surface energy and the yield point. This assumption is based on the apparent similarity of the influence of the surface tension on the particle size with the Hall-Petch relation. Modeling of surface tension dependence on the particle size based on thermodynamic GTKB approach allows us to make some predictions of the influence of surface tension forces in crystallites on the yield point of the material. This is particularly true in materials whose structure elements were refined to nanometric scale.

The volume density of the surface energy of a spherical particle may be expressed by the form:

$$\rho_v = \sigma.\frac{S}{V} = \frac{\sigma}{\frac{4}{3}\pi r^3}, \tag{11}$$

where S and V is the surface and volume of the spherical particle, respectively.
Using the exact solution (6) of the Gibbs–Tolman–Koenig–Buff equation we can obtain the dependence of the volume density of surface energy on the particle size:

$$\rho_v = \sigma S = \frac{3}{r}\sigma = 3\frac{\sigma(\infty)}{\delta} e^{\left(-\Sigma_{k=1}^{3}\frac{s_k^2 \ln(\frac{r}{\delta}-s_k)}{3s_k^2+4s_k+2}\right)} \tag{12}$$

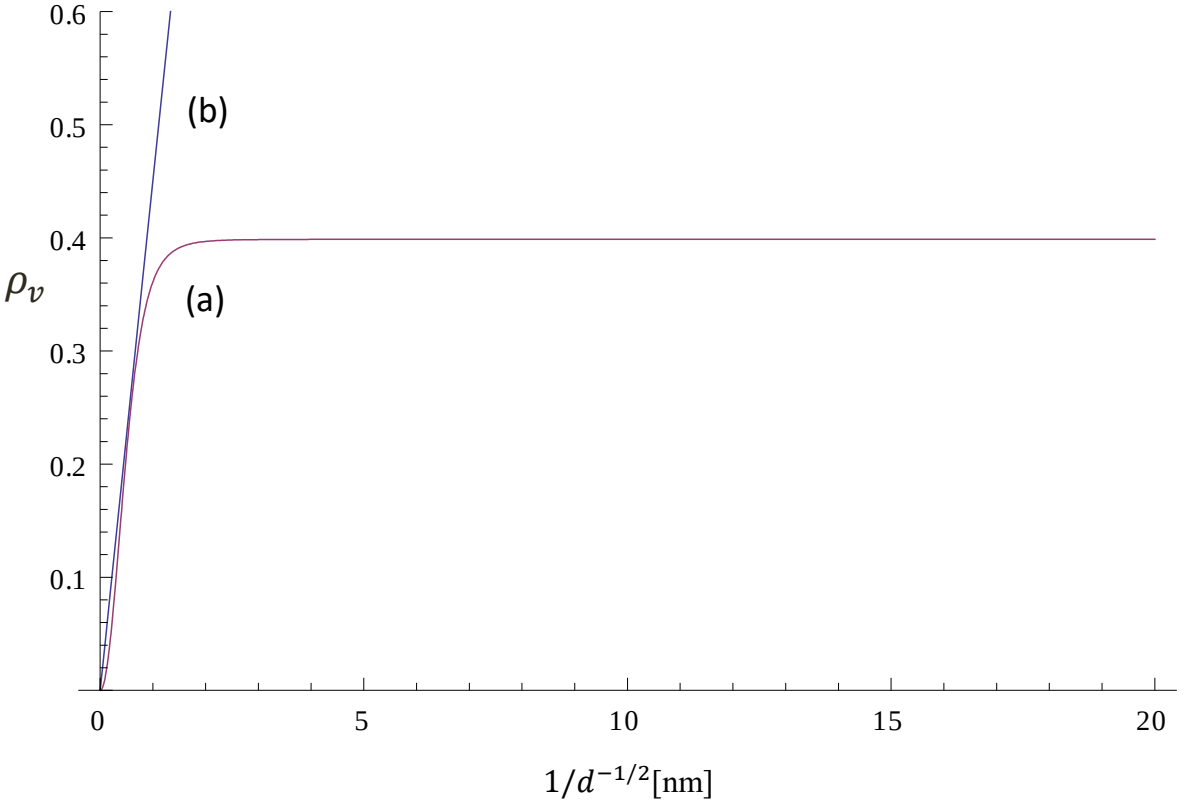


Figure 5. Scaled dependence of density of surface energy per the unit of volume for gold. a) eq. (12); b) approximation by the H-P law.

The following two regions can be distinguished in Figure 5. For grain sizes larger than 1 nm, the obtained dependence can be approximated using the H-P law, while at the sizes below 1 nm we obtain a finite value for the volume density of the surface energy. This is consistent with the well-known breakdown of the H-P relation for grains smaller than 10 nm, cf. Figure 1. Detail analysis of eq. (12) indicates that there is a limit of grain sizes ($r \approx 2\delta$) for which the volume density of surface energy reaches its limit value. This fact gives a reason to interpret plasticity as the variation of the surface energy. It means that the allowed value of the surface energy (shown in Figure 5 for gold) was exceeded in the material if it begins to flow. However, further considerations of relations

between stress and the release of elastic and plastic energy at the beginning of plastic deformation as well of the relation between surface energy of free particles and grains in a solid matter are needed to improve nondislocation models of plasticity, in particular to predict yield stress values from specific surface energies without involving dislocation interactions.

6 Conclusion

The energy of surface tension can play an important role in plastic deformation of micro and nano materials. This mechanism opens the possibility for constructing new models of plastic deformation without using dislocation theory.

Exact solution of the equation Gibbs–Tolman–Koenig–Buff allows more adequate description of the dependence of the melting temperature on the particle size in the range from 3 to 20 nm, that supports the hypothesis of the crucial role of surface tension forces in plastic yielding of micro and nano disperse materials.

Acknowledgments

This work was financially supported by the Grant Agency of Charles University under the grant number 1110816.

References

[1] Andrievskii R. A.and A. V. Ragulya, Nanostructured Materials ,*Akademiya*, Moscow, 2005. [in Russian]
[2] Buffat P.H., J.P. Borel, Size effect on the melting temperature of gold particles, *Phys. Rev*. A, 13, 2287, 1976.
[3] Buff F.P., Spherical interface II. Molecular theory, *Journal Chem. Phys.*,3, , 419, 1955.
[4] Carlton, C; Ferreira, P. J. What is Behind the Inverse Hall–Petch Behavior in Nanocrystalline Materials, *Mater. Res. Soc. Symp. Proc*.,976, 2007.
[5] Conrad, H; Narayan, J ,On the grain size softening in nanocrystalline materials, *Scripta Mater.* 42 (11), 1025, 2000.
[6] Dadashev R. Kh., Thermodynamics of Surface Phenomena, *Fizmatlit*, Moscow, 2007; *Cambridge International Science*, Cambridge, 2008.
[7] Frank P, Spherical Interface. II. Molecular Theory, *J. Chem. Phys*. 23, 419, 1955.
[8] Gibbs J.W., Collected Works, Vol.1, *New Haven*, 1948.
[9] Gutkin M.Yu. and I.A. Ovid'ko, Physical Mechanics of Deformed Nanostructures. Volume 1: Nanocrystalline Materials, *Yanus*, St.Petersburg, 2003.
[10] Hall E.O, Deformation and ageing of mild steel, *Proc. Phys. Soc. London, ser. B*, 64, (1), 747, 1951.
[11] Kim H.S. A composite model for mechanical properties of nanocrystalline materails, *Scripta Materialia.*, 39 (8), 1057. 1998.
[12] Kocks U.F., The relation between polycrystal deformation and single crystal deformation, *Metal. Trans.*, (5), 1121, 1970.
[13] Koenig F.O., On the Thermodynamic Relation between Surface Tension and Curvature, *The Journal of Chemical Physics* 18, 449, 1950.
[14] Kumar K.S., H.Van Swygenhoven, S. Suresh Mechanical behavior of nanosrystalline metals and alloys, *Acta Materialia.* 51 5743, 2003.
[15] Ono S., S. Kondo. Molecular Theory of Surface Tension. Berlin: *Springer-Verlag* 1960.
[16] Ovid'ko I., M. Gutkin, N. Skiba, Strengthening and softening mechanisms in nanocrystalline materials under superplastic deformation, *Acta Materialia.*, 51, (14), 4059, 2011.
[17] Petch N.J., The cleavage strength of polycrystals. *J. Iron and Steel Inst*., 174,1953.
[18] Rehviashvili S. Sh., E.V. Kishtikova: Model of a nanoparticle in the theory of inhomogeneous medium, *Technical Physics*, 56, 143, 2011.
[19] Tolman R. C., The effect of droplet size on surface tension, *J. Chem. Phys*. 17, 333, 1949.
[20] Yurov V.M., V.S. Portnov, N.H. Ibraev, S.A. Gurchenko, The surface tension of solid bodies, small particles and thin membrans, *Phys.-math*. №11, 2011.
[21] Yurov V.M. Superfecial tension of pure metals: *Eurasian Physical Technical journal* 8 (1), 10, 2011.