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Chemical Bonds in the Processes of Plasticity, Fluidity and Mechanical Destruction of Materials

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ABSTRACT. The strength change of materials is still a disputable and unsolved problem. Theoretically calculated material strength on break down is bigger than the one measured during the test for real bodies. There is no explanation for experimental facts connected with the decrease of the strength at thermal impact on the tested material. It is connected with the absence of the identified microorganism of the strength change. In the present paper we suggest new mechanism of the elementary act of the processes of plasticity, fluidity, mechanical destruction. The mechanism is based on anew suppositionof the motion of the atom in solid bodies due to decrease of chemical bond energy with neighboring atoms that can be done by thermal or non-thermal ways. In the present paper it is shown that for elementary act of changing material strength it is necessary to decrease chemical bond energy as a result of occurrence of antibonding electrons around the atom. Specific conditions of the start of the processes of plasticity, fluidity, mechanical destruction and their transition from one process into another at mechanical loading are considered. © *2016 Bull. Georg. Natl. Acad. Sci.*

Key words: plasticity, fluidity, chemical bonds, quantum state

Study of suchmaterial properties as plasticity, fluidity and mechanical destruction, defining their strength, is of great interest from practical and scientific points of view. A number of scientific and practical works are devoted to this problem and significant results on the improvement of material strength are achieved. It is shown that the task of strength is complicated and depends on many factors and many disputable and unsolved problems [1-3]. The latter, in our opinion, foremost concerns the absence of the clearly identified micromechanism of the strength break down at mechanical impact. Unfortunately, as till now we have no clear definition of the processes and phenomena taking place at the change of material strength we assume strength break down under mechanical impact such a state of material, when its constructive functions are broken and it becomes unfit for exploitation.

This state can correspond to the state of material when interconnected processes of plasticity, fluidity and mechanical destruction are realized with different intensities [1-3]. Micromechanisms of the processes explaining all the experimental data from the existing single point of view, despite several attempts,

are not established yet [4]. The rupture of theoretically calculated materials strength appeared to be much higher than determined experimentally for different real bodies [5]. Such divergence can be explained by the existence of special sections in the bodies, tension (crack) concentrators, where local overtension takes place upon application of the loading to the body [6].

An energetic method proposed by Griffith for ideal brittle materials and its modification for ductile metals by Irwin [7] and Orowan [8] allows establishing phenomenological relations between internal and external forces without detail analysis of the rupture mechanism of interatomic bonds at the end of the crack [1-3]. The modern approach to the study of the strength problems, considers the atomic-molecular structure of solids, which allows to apply the molecular-kinetic theory (MKT) [9] and create kinetic (statistical) theory of strength (KTS) [5,10]. According to the KTS, the essence of the destruction process is the disconnection of atoms in the stressed materials under the thermal fluctuations. Thus, contrary to other approaches of the strength problem, the KTS does not require the presence of the initial defect – crack, but provides its occurrence as a result of thermal fluctuations in the ideally perfect material. In spite of the significant progress in the understanding of the strength nature, KTS does not explain why theoretical value of the strength is significantly higher than the experimental data even for defectless bodies (e.g. whisker crystals [11]), as well many experimental data connected with the stress decrease under athermal effects on the test material, reduction of microhardness (MH) under the influence of light [12,13], electrical field [14], magnetic field [15], under doping [16,17], the effect of light on the polymer strength [18]). In the present paper we propose non-thermal mechanism of the elementary act of the start of the processes of plasticity, fluidity and mechanical destruction.

According to KTS, after disconnection of atoms inloaded materials, point-defects, interstitial atoms and vacancies, providing creation of more compli-
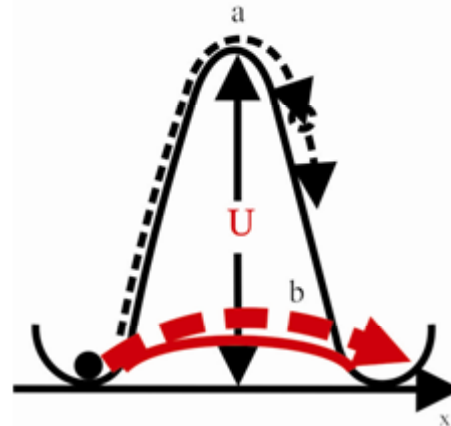

Fig. 1. Schematic illustration of the transition of an atom from one location to another: a-according to the MKT, U-the height of the potential barrier. b-according to the MPT.

cated defects (accumulation of point-defects, dislocation, cracks, etc.) must be irreversibly formed. There are two mechanisms of creation of point-defects: Frenkel mechanism, based on MKT [10] and another method based on the molecular-potential theory (MPT) [19-21]. According to the Frenkel mechanism, for the transition of an atom from one location to another one, it is necessary the occurence of the fluctuations of the kinetic energy nearby the atom, it is enough for neighboring atoms to break chemical bonds. This energy is described in MKT by the height of the potential barrier (Fig.1a). The probability of the transition W_A is expressed by the formula:

$$W_A = B\exp(-U/kT) \qquad (1),$$

where U is the height of the potential barrier (chemical bond energy of the given atom with the neighboring atoms), T – temperature, K – Boltzmann constant, B – a coefficient weakly dependent on the temperature (Fig.1a). According to the second mechanism, it is necessary to reduce the height of the potential barrier (Fig.1b), i.e. such change of the state of chemical bonds,which reduce their energy. Such change of the chemical bonds state can be reached by both thermal and non-thermal influences (light, electrical and magnetic fields, pressure, injection). It has been experimentally stated [22] that diatomic molecules are divided into two groups according to the change of bond energy when an electron leaves chemical bond, the chemical bond energy of one
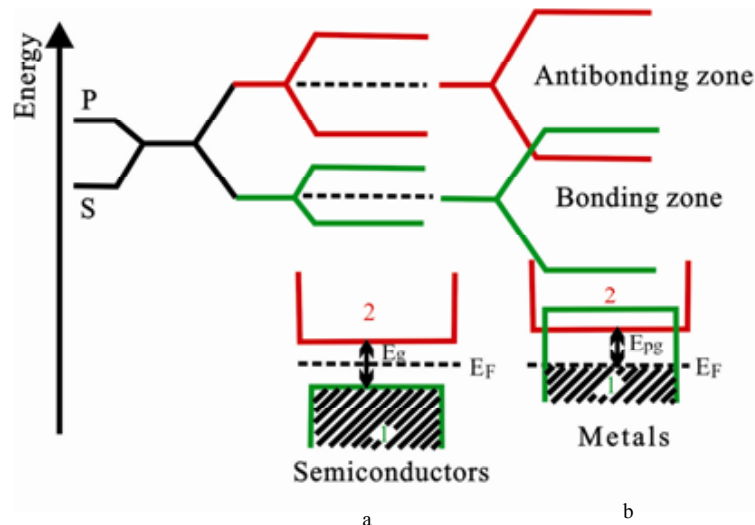
Fig. 2. During the approach of the atoms the formation (on the example of the 4-th group of the system) of hybridized orbitals and their further splitting on binding and antibonding orbitals, of which bonding and antibonding zones with further approach of the atoms are formed. Bonding and antibonding energy bands: a) semiconductor or dielectric, b) metal, where EF is the Fermi level, Eg is the band gap in semiconductors and Epg is the pseudo-gap in metals.

group decreases and in the other one increases. Thus, the electrons participating in the creation of the chemical bonds can be presented in two states. Being in one state they strengthen the bond, and in another – weaken it. In quantum mechanics, one of them is known as bonding state (bonding orbital), and another – the antibonding state (antibonding orbital). Electrons located in that orbital, i.e. energy levels are named as bonding and antibonding electrons. The ratio of the numbers of above-men tioned electrons are determines the energy of the chemical bond with the neighboring atoms [22]. The more electrons on the bonding energy levels in comparison with those on antibonding levels, the greater the energy of the chemical bondis. If these quantities are equal, then the chemical bond energy is equal to zero (i.e. there are no chemical bonds, the substance passes into the gaseous state), as gained system energy conditioned by bonding electrons (energy minimum) is lost by antibonding electrons (energy maximum).

In the solids (consisting of great number of atoms), bonding and antibonding states are transformed into corresponding zones of the certain energy [23]. In dielectrics and semiconductors, these bands are isolated by energy gap the so-called, "forbidden zone"; in metals they are overlapped (Fig.2).

As a result of the transition of electrons from the bonding band into the antibonding, an electron appears there and vacancy, the so-called"hole"is created in the bonding band. Both quasi-particles reduce the energy of chemical bonds between atoms, nearby which they appear during the chaotic movement, therefore, they are called as antibonding quasi-particles (AQP) [20,21].

Obviously, as the greater is the concentration of AQP, the weaker is the chemical bond in the material, and it becomes easier for atoms to change location. At the same time, it should be noted that the concentration of AQP can be increased by both thermal and non-thermal ways (pressure, light, injection, electrical and magnetic fields). In the case of a solid body, if AQP is created in a non-thermal way, the solid should undergo to softening and widening without heating (in parallel with the decrease of an energy of a chemical bond its length, i.e. a distance between atoms increases [22]) that was proved experimentally [12-17,24]. In both cases, there is the proof concerning the existence of AQPand its influence on the increase of the probability of atoms W_A translocation in the substance. Based on the new MPT conceptions regarding the probability of atoms W_A translocation in the substance, the following expression is obtained:

$$W_A = A(n_{AQP}/N_a)^\beta W_{ph,} \qquad (2)$$

where A - almost constant value, n_{AQP} - concentration of AQP, N_a -- concentration of atoms (molecules) of the substance, β - is a number of AQP nearby the given atom, needed to diminish the height of the potential barrier, W_{ph} - probability of the presence of phonons of maximum energy at the melting point nearby the given atom [20,21]. As seen from the formula, W_A does not depend on the difference in temperature from the equation (1), which demonstrates the exponential dependence on the temperature. Thus, it is clear, that Frenkel mechanism is true at high temperatures in comparison with another mechanism (equation 2), which works at low temperatures too, in the case of non-thermal influences of the test material [12-17,24,25]. In the works concerning KTS, [5,10,18,26,27] an assumption is made that "namely the fluctuations (of kinetic energy) allow to overcome the potential barrier for elementary acts of destruction" [18]. In the present work, the decrease of the potential barrier for elementary acts is explained by the appearance of AQP generated in different ways (pressure, light, injection, temperature, electrical and magnetic fields). It should also be stated that even at the thermal impact the weakening of chemical bond takes place as a result of the influence of AQP, generating by a temperature. This is proved by the following experiment: Fig.3 [20,21,28] shows temperature dependences of microhardness (MH) of Si measured in darkness (1) and under the illumination of

Fig. 3. Temperature dependences of Si microhardness measured in darkness (1) and under influence of the light of different intensity I_1 (2) and I_2 (3). $I_1 < I_2$

white light with different intensities (2,3), where a sample was heated with maximal intensity less than by one degree. Besides MH the concentrations of free carriers, i.e. AQP were measured. As it is shown in Fig. 3 at initial stages (low temperatures) temperature does not effect on the value of MH, at the same time it was found that the concentration of AQP generated by the light n_l is much more than that of AQP generated by the temperature n_T, $n_l > n_T$. Beginning from the same values the temperature begins to influence, then $n_l \approx n_T$, and at $n_l = n_T$ confluence of curves 0 MH measured in darkness (1) and under illumination takes place. It should be noted that the temperature values are different for different intensities of light. At higher temperatures when $n_l < n_T$ an illumination does not influence. The results prove definitively that the decrease of the material hardness is defined by the AQP concentration, generating by the temperature at thermal impact too.

At the loading of the test material depending on the ratio of crystallographic directions of materials (in the case of non-crystalline materials of certain directions) and pressure directions the bonding and antibonding bands will shift to the energy scale differently: closer to some directions [29-31]. In those areas of materials where the approach is closer due to more intensive transitions of electrons from the bonding bands into the antibondings, the concentration AQP and the probability of the change of the atoms location are greater at the given temperature, which will provide the formation of the initial defect necessary for the beginning of plasticity, fluidity and mechanical destruction processes. It should be underlined that in materials' probability of the formation of the initial defect is much higher on the surface than in the volume; as even on the atomically clean surfaces of the samples always are incomplete atomic layers and island regions of needless layers of atoms, which, naturally, in the surface area of the sample it causes the bending of energy bands in the direction of the surface coordinates (Fig.4). At the extreme points of the bands due to minimum energy, free electrons and holes accumulate, i.e., AQP. There-
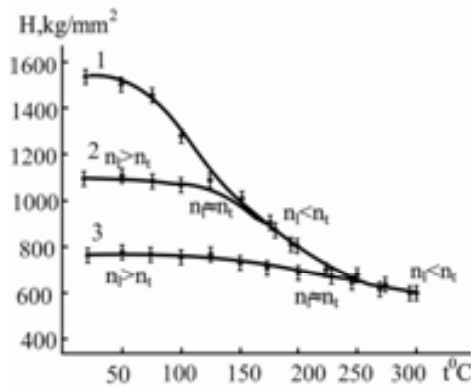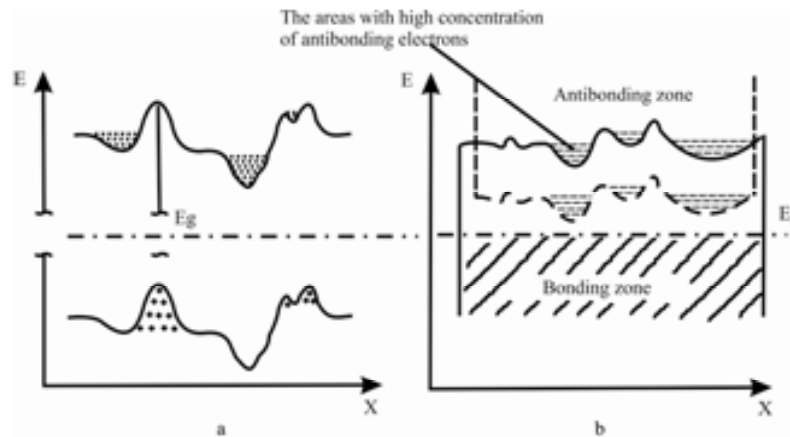
Fig. 4. Schematic view of bending of energy bands along the atomically clean surface of the material: a) semiconductor (dielectric) and occupation of their extremes by AQP (electrons and holes). It is evident that minimums for electrons and holes are space-divided that impedes their recombination; b) in the case of metals due to the band crossing and presence of free electrons only, which can be in both bonding and antibonding states, more antibonding electrons will be in the minimums of antibonding zones than in the unbent region. In both cases, the probability of motion of atoms is correspondingly greater in the areas with high concentration of antibonding electrons.

fore, the concentration AQP will be higher in those regions, than the average of the surface and in the volume, correspondingly the probability of the formation of an initial defect will be higher. Due to that, plasticity, i.e., sliding of one part of the material relatively to another will take place in certain directions with the greater concentration of AQP. With the increase of pressure the regions with the higher concentration of AQP will be grown and overlap; that will lead to increase the quantity of plasticity directions. At further increase of pressure, the concentration of AQP will grow and in some regions of the material it will reach a critical value locally, at which melting of the solid and the fluidity process begins irrespective of its temperature [20,21,32]. From the all above-mentioned it becomes understandable why the actual strength is always less than its theoretical value. The fact of melting of solid body as a result of non-thermal impact is proved experimentally [20,33]. This is supported by the formation of solidified molten region of crystalline solids around the implemented indenter in the experiments to measure nano- and microhardness (the so-called trixotropic effect [34-36]). Enormous pressure develops in the process of the indentation under the sharp end of the indenter, which closes bonding and antibonding bands in such short distance that a critical concentration necessary to melt, appears at a low indentation load and at the room temperature. It is known that at high pressures solids transit from the solid state into the molten without increasing the temperature [37]. Formation of the molten regions in the directions crossing the sample causes its separation into parts. In the case of the so-called brittle destruction surfaces of the borders of the segmented parts have no melting traces because the bending of energy bands in the regions of the joining of those segmented parts has a deep and thin minimums (only a few interatomic distances). The minimums are not covered with neighboring ones even at the accumulated critical concentration of AQP necessary for melting, therefore plasticity process does not begin and there occurs local melting of the segmented parts, as a result of which they are separated. Materials of a mosaic structure, e.g. most of the metals, have such borders between the parts [38]. Thus, it is shown in the paper that material strength is defined by the state of chemical bonds between atoms composing it; the mentioned state can be changed by various external impacts and in the case of the mechanical loading it is changed under the pressure. We believe that the present conception expresses physical nature of the strength well and it is prospective for further development of the science about strength.

არაორგანული ქიმია

ქიმიური ბმები მასალების პლასტიურობის, დენადობის და მექანიკური რღვევის პროცესებში

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**აკადემიის წევრი, საქართველოს მეცნიერებათა ეროვნული აკადემია, თბილისი

მასალების მექანიკური დატვირთვისას სიმტკიცის შემცირების საკითხში არსებობს ბევრი საკამათო და გადაუჭრელი პრობლემა. კერძოდ, მასალების თეორიულად გამოთვლილი სიმტკიცე ბევრად აღემატება ექსპერიმენტულად დამშერილს. არ არის ახსნილი ექსპერიმენტული ფაქტები სიმტკიცის შემცირებისა ათერმული ზემოქმედების შედეგად. ეს გამოწვეულია იმით, რომ არ არსებობს ცალსახად დადგენილი სიმტკიცის ცვლილების მიკრომექანიზმი. ნაშრომში შემოთავაზებულია მასალების პლასტიურობის, დენადობის და მექანიკური რღვევის ელემენტარული აქტის ახალი მიკრომექანიზმი. ეს მექანიზმი ეფუძნება მყარ სხეულებში ატომის გადაადგილების შესახებ ახალ წარმოდგენებს, რომელიც ხორციელდება მოცემული ატომის ქიმიური ბმის ენერგიის შემცირებით მის მეზობელ ატომებთან და შეიძლება განხორციელდეს როგორც თერმული, ისე ათერმული გზით. ნაჩვენებია, რომ სიმტკიცის შემცირების ელემენტარულიაქტის განსახორციელებლად აუცილებელია ატომის ქიმიური ბმის ენერგიის შემცირება მოცემულ ატომთან ანტიდამაკავშირებელი კვაზიწყვილა კების წარმოქმნით. განხილულია მასალების მექანიკური დატვირთვის დროს პლასტიურობის, დენადობის და მასალების რღვევის დაწყების და მათი ერთმანეთში გადასვლის კონკრეტული პირობები.

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