Rehbinder Effect. Engineer View.

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DOI: 10.48348/g2561-3319-9991-t

Abstract.

The Rehbinder effect is defined as the material strength decreasing during tension in the Surface Active Mediums, Surfactants (SA). In theoretical descriptions of the effect its physical mechanism is considered as SA molecules penetration into the micro cracks, which existed on the specimen surface. In some experiments it was not confirmed. Another physical mechanism of the effect specified for metals supposed in present paper. It not contradicts to the observed experimental data.

It based on the plastic flow physical model which has developed by author earlier. The flow model there is presented as unstable surface atoms penetration into the metal structure. The effect phenomenon is the decreasing of the elastic limit – increasing of the quantum transition probability – rapture of the surface atom electronic bonds. The continued acting of the SA medium cause the process reproduction till to the complete specimen fracture. The technique of the SA influence factor experimental definition supposed in the paper. Numerical estimation of it was fulfilled. The effect existence recognized as direct confirmation of the irreversible mass transfer in transverse direction.

Key words: Tension, Elastic Limit, Surfactant, Mass Transfer, Fracture

B. Nudelman, Rehbinder Effect. Engineer View.

I. Traditional definition.

In a conventional sense, this effect is a phenomenon of reduction of the material's yield stress and strength under the influence of surfactive (SA) mediums. Only polycrystalline metals properties at tension are hereby examined. From the traditional point of view, this effect is caused by absorption-diffusion processes on the specimens' surfaces. In theoretical descriptions of the effect and experimental works, insertion of SA molecules into the micro cracks on the surface is considered [1]. Multiple dislocations on the near-surface layer were also observed, resulting from the inward insertion of SA atoms into the specimen under the long-term exposure to surfactive environmental mediums [2]. Many works, notably experimental ones, present possible variations of the effect being manifested under different conditions [2, 3, 4]. There is no reason to dispute the existence of diffusion-absorption process. However, physical nature of the phenomenon is not entirely revealed.

II. Model of the plastic strain start.

The model is based on the analysis of the plastic strain of metal single crystal [5]. In compliance with [5], this process presented as a sequence of physical changes on the surface. The irreversible tensile strain is a result of a penetration of the unstable surface atoms into the regular crystal lattice. According to [5], all inherent effects of the tensile test are considered as direct consequence of the mentioned plastic strain model. The only exception is the Rehbinder Effect, which is discussed in this work.

A. Elastic limit.

The tensile elastic limit in the model is introduced as a strain level at which the probability of penetration of surface atoms drastically increases. Herewith each penetration act induces a relaxation of the tensile stresses in restricted volume and new dislocations appearance. Supposedly, the speed of the relaxation spread in the

volume is defined by the material properties of a specimen under given external conditions (temperature).

This model of a plastic strain start may be undoubtedly applied to poly crystals, including the multi-component ones. Due to multiple structural defects in poly crystals, decrease of the proportional limit is anticipated.

B. Equilibrium conditions of single atom of surface.

It is known that atoms in a crystal lattice are continuously oscillating relatively to their equilibrium position. Let's consider the equilibrium of a single atom of surface. With reference to the external conditions, the most probable value of an oscillation amplitude is taken as a general characteristic parameter. For simplification only the transverse component (A) is considered. Fig. 1

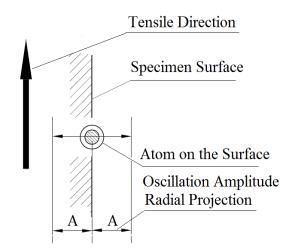


FIG.1 Surface Atom Equilibrium

Such simplifying of the model provide the introduced parameter with some conventional meaning. According to the adopted model, the penetration of surface atoms is characterized by the following features:

1) The displacement of the surface atom inwards, results the decrease of the distance to the first hemisphere of the adjacent atoms and is accompanied by a decrease in the resistance to displacement after the transition to the unstable state.

- 2) An increase in linear tensile strain leads to an increase of penetration probability; when the strain reaches the elastic limit there is a significant increase in the probability and frequency of events.
- 3) Undoubtedly, there is a possible correlation between the oscillation energy and the elastic limit. In this case, the probable oscillation energy value may be considered as critical. Without certain values of oscillation and more abstract surface energy, it is possible to determine the correlation between the energy value and the introduced value of the transverse component of the oscillation amplitude (A). This dependence is always increasing. Based on the macro properties of the sample and the model of simple oscillations, it corresponds to a quadratic relationship. Energy transverse component:

$$W_{tr} = \int_0^A k \cdot x dx = \frac{k}{2} A^2 \quad , \tag{1}$$

where x – is a transverse displacement from the atom's equilibrium position: k – is a coefficient of proportionality.

Therefore, it is logically reasonable to introduce a critical amplitude value A_{cr} , as a displacement from the equilibrium position, which, in summation with the elastic strain displacement, leads to atom's instability, a quantum transition and the beginning of the penetration process. Based on physical similarity conditions, the value of the critical elastic strain, according to the Poisson's ratio is:

$$\varepsilon_{trcr} = \mu \cdot \varepsilon_{cr} \quad , \tag{2}$$

where $\, arepsilon_{trcr} \,$ - $\,$ transverse component of the relative deformation,

 ε_{cr} - a value of the critical relative longitudinal deformation. It is worth to measure the value of ε_{trcr} directly in the experiments. In nano scale of single surface atom: $\delta_d = d \cdot \varepsilon_{trcr}$ (3)

where δ_d – is a transverse displacement of an atom due to elastic strain, change of the distance to the first hemisphere of the adjacent atoms,

d - a lattice parameter, a conventional distance to the first hemisphere.

Based on the isotropic properties of the poly crystal, the transverse stress equals:

$$\sigma_{trcr} = E \cdot \varepsilon_{trcr} \tag{4}$$

In single crystal, the value of modulus of elasticity (E) depends on orientation. In this case E is assigned a certain average-likely value.

A total force, according to the area of influence of a single atom is:

$$P = \sigma_{trcr} \cdot d^2 \tag{5}$$

Respectively, a total critical displacement of an atom equals:

$$\Delta_{cr} = \delta_d + A_{cr} \tag{6}$$

Therefore, somewhat conventional, but rather simple physical scheme of the process is formed: a mutual correspondence between the oscillation amplitude and the proportional limit. Actually this relation exists with rather high probability [6, 7].

III. Effect of the SA mediums on the tension process.

The model of plastic strain described above allows to imagine the physical mechanism of the SA medium influence, particularly their effect on the tensile elastic limit of the metal specimens. Equilibrium conditions of single atom on a surface are changed in presence of the SA medium. Whereas the basic properties of metals are defined by their internal electrical interactions, therefore the SA medium influence appraised by the changes in electrical properties on the surface.

A. Characteristics of SA agents.

Salts of carboxylic acids, being usually a derivative of alkali metals and ammonium, are typical as SA agents for metal specimens. Other SA agents were not considered yet. Structurally SA present a compound of a metal atom linked to an acid residue with a linear hydrocarbon chain. Majority of them are soluble liquids. Molecules possess a significant dipole moment [8].

B. Mechanism of the SA medium influence on a metal specimen

B1. Model of the mechanism.

The metal specimen is placed in the SA medium, either solution or saturated liquid. In this state the SA molecules get prevail orientation with dipole toward specimen surface. Consequently, a depicted charge is induced on the surface, counterbalancing the dipole with an opposite orientation. Attraction force occurs between the dipole and the induced electric charge. Therefore unstable surface atoms get displacement inward due to the repulsion of a positively-charged dipole. (Fig 2).

Under new conditions, the value of this displacement is to be considered while determining a critical displacement balance as per (6):

$$\Delta_{cr} = \delta_d + A_{cr} + B_{sa} \quad , \tag{7}$$

where B_{sa} – is a displacement due to dipole's influence.

Dipole's interaction with a single atom depends on its random orientation. The probability of a favorable (Fig. 2) orientation is subject to a random variables distribution function.

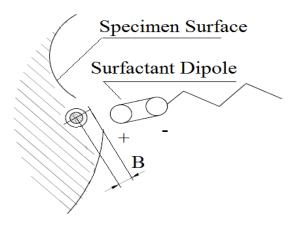


FIG.2 Surfactant schematic influence on the surface atom

Along the whole surface of the contact, there is always a certain number of interactions in a depicted pattern (FIG 2) between single atoms and dipoles or whole groups of them. The value of $B_{\rm sa}$, just like the value of A_{cr} , is always conventional, since such factors as a dipole's influence on the electronic interactions of the surface atom are not considered.

B2. Discussion of the mechanism of a SA medium on the plastic flow start.

Mechanism of an irreversible strain, according to [5], is defined as a penetration of the crystal lattice by unstable surface atoms. The influence of SA environmental medium on this process results only in the decrease of an elastic limit. The mechanism, thus, is the same.

From the traditional point of view, the process is characterized by the insertion of a SA agent in the specimen's surface. The presented comparison of these two concepts is based on several features.

First: absorption of a SA agent by the surface is common for both processes. There can be no interaction without absorption.

Second: According to the evaluation of energy consumption, the balance is not in favor of the insertion of SA molecules. For a surface atom to be inserted, a simple rearrangement of interatomic bonds is required. However, for insertion of a SA molecule to occur, it is also necessary to completely break all interatomic bonds and reorganize atoms in the lattice in a new order. This can occurred only under the condition: certain surface relief - a fold that may evolve into an initial crack [2, 4]. Examples of SA environmental medium's influence, leading to plasticizing, the increase of plastic deformation, do not confirm such a mechanism. Besides, a continuity in the process of crack propagation requires constant reproduction of the conditions for penetration of SA molecules inside the specimen.

Third: temporal characteristics of the process. There is sufficient data to estimate the time required for reaching the elastic limit under loading. For instance, for mild steel [6, 10]:

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in quasi-static mode under standard loading speed: - \dot{\varepsilon}=10^{-4}~\frac{1}{s}, elastic limit - \varepsilon_e=10^{-3}, time required for reaching the elastic limit - t_e=10s.
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In SA environmental medium, ε_e and t_e are decreased. The probability of insertion of SA atoms into the surface is also decreased. For a significant influence to take place, a multitude of insertions should occur, sufficient enough for the plastic zones developing.

Fourth: a possibility of diffusion of SA atoms into the metal structure. Conditions required to realize this possibility are as follows: negative electrical potential of ionization and high external pressure. However, in the actual strain experiments such conditions do not exist. Therefore, the probability of diffusion in a short period of time is considered negligible.

According to [1, 2, 3] the reason why SA agents influence the strain process lies in breaking or weakening interatomic bonds on the surface. This is where both variants coincide. According to [5], the insertion of surface atoms is only possible with the breaking of electronic bonds.

C. Numerical evaluation of the dipole's effect on a surface atom.

C1. Determining of the values of δ_d and A_{cr} .

In the formulas (6) and (7) only the first addendum, δ_d , is presented as a linear displacement. Its value is determined according to a rather certain experimental data, obtained through the principle of physical similarity. The conventional value of the second term A_{cr} is adopted by definition. Only the transverse component of atom's oscillation was apprised. For complete physical model, it makes sense to include the effect of two other components, tangential and axial (in case the round specimen crossection), on the electronic interactions on the surface. Despite the fact that temperature-dependent properties of metals are fully described in numerous theoretical works, experimental data should prevail in this case. Transition from temperature – T to the linear value of A_{cr} enables to exploit the additivity feature. According to (6),

$$\Delta_{cr} = \delta_d + A_{cr} \tag{6}$$

With the relative values: $\varepsilon_{trcr} = \frac{\Delta_{cr}}{d} = \frac{\delta_d}{d} + \frac{A_{cr}}{d}$, $\varepsilon_{trcr} = \varepsilon_d + \varepsilon_A$

From two consequent experiments for two certain temperature values and two measured values of elastic limit:

$$T_1; T_2; \ \varepsilon_{d1}; \varepsilon_{d2}$$
, difference $\varepsilon_{A1} - \varepsilon_{A2} = \varepsilon_{d2} - \varepsilon_{d1}$. (9)

After processing of the experimental data (9) it is possible to extrapolate the values ε_{A0} , A_0 for any base point (reference point) – T_0 on the temperature scale. Thus, the dependency $\varepsilon_A(T)$, A(T) becomes defined.

C2. Determining the value of $B_{\rm SA}$.

Values of the surfactive environmental medium influence (B_{SA} , ε_B) can be determined in the same manner as A(T). The relative value ε_B from experiments under the same temperature:

- in the atmosphere according to (8): $\varepsilon_{trcr} = \varepsilon_{d1} + \varepsilon_A$
- in the surfactive medium: $\varepsilon_{trcr} = \varepsilon_{d2} + \varepsilon_A + \varepsilon_B$

$$\varepsilon_B = \varepsilon_{d1} - \varepsilon_{d2} \quad , \tag{10}$$

(8)

where ε_{d1} , ε_{d2} - measured values.

C3. Dispersion of the numerical estimation.

Definition of values ε_d , ε_A and ε_B transformation of experimental data as in (9) and (10) does not worsen their initial dispersion.

Dispersion of the temperature-dependency of the elastic limit, does not exceeds the acceptable values if the experiment is conducted correctly, [6, 9]. Regarding the SA factor, experimental data is expected to be significantly inconsistent. It's due to the variability of the factors of influence. First - material and structure of a specimen. In case of poly crystal, it relates to numerous and randomly dispersed defects on the surface, as well as random orientation of the crystallites. It corresponds with the single crystals heterogeneity, postulated by J.J. Gilman.

The second factor - material and conditions of SA medium, its structural formula, concentration. A dipole moment should be particularly noted as the only characteristic determined physically.

The third and finalizing factor - the variability of the process, ambiguous interaction of the SA medium with the surface. Any combination of chance factors is enough to cause the process of deformation in the area.

D. Application of the criterion of the SA medium influence.

Two occasions of SA medium influence are known in practice. The first one when SA medium is used to decrease the resistance of metals during processing or improve their tribological properties. In this case, it is reasonable to use the smallest values of the factor by (7). The second occasion is when the influence of surfactive environmental medium is undesirable due to reduction of strength. In this case, the biggest values of the influence factor should be taken into account.

E. Influence of the SA medium on the specimen's strength.

In the course of most experiments of specimens in the SA medium, reduction of strength is recognized as the main influence feature. The strength here refers to resistance to disruption – the tension stress upon fracture or maximum engineering stress by the loading diagram $\sigma_u = \sigma_{eng\ max}$. Such an approach to the strength appraisal is not well grounded physically. It doesn't refer to changes inside the specimen during loading. Maximal stress in this case is considered as a temporary resistance to fracture.

E1. Deformation of poly crystals.

Traditionally, the complete diagram of plastic deformation is depicted by three consequent hardening phases. The mild steel typical diagram is presented on Fig.3.

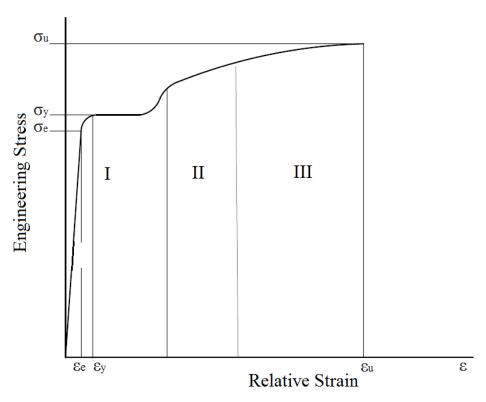


FIG.3 Mild steel typical Stress – Strain diagram.

In the analysis of single crystals [5] the concept of physical changes was developed only for the first phase. From the respective of physics, substantial description of the loading process on phases II and III does not exist at present. It has to be the subject of a further analysis. It is proposed for now to accept as the hypothesis that: 1) irreversible mass transfer on the II and III phases is realized by analogy to the phase I – in the transverse direction; 2) difference in values of σ_u and σ_e for quasi-static loading mode is positive and limited: $\sigma_e < \sigma_u$. There is sufficient evidence to confirm this condition [6, 7, 9]. This suggests the correlation of the elastic limit σ_e with the temporary resistance σ_u , including the SA medium influence. According to the model described in [5], when the elastic limit is exceeded, two parallel processes occur in the specimen: uniform strain with a constant speed and a pulsating

transverse deformation, with the restricted volumes relaxation. This determines unequal distribution of stresses and strains along the specimen's section. The second process always lags behind the first. As the consequence the maximum stresses are on the internal layers of the section. A more significant consequence of the second process lag, is the dependence of the maximal strain on section dimensions – scale effect. The bigger dimension (diameter or thickness), the bigger the stresses difference between the surface and the center of specimen's section. Due to the adopted hypothesis, the stresses difference remains throughout the II and the III phases of deformation (FIG.3).

E2. Deformation in the SA medium.

Elastic limit in the SA medium - σ_{esa} ; - ε_{esa} is decreasing. Meanwhile, resistance during phases II and III is also decreasing. This implies that the influence of SA medium remains unchanged throughout the whole process.

E2.1 Embrittlement.

Embrittlement effect, which occurs under the SA medium, is considered to be a typical feature of the process [2]. The author does not consider it rightful to dispute the existing common knowledge on the embrittlement mechanism. According to Griffith, it is a process of crack formation and critical crack propagation. Which later leads to catastrophic disruption with little manifestation of deformation. With that, the possibility of another mechanism of the effect, which also leads to disruption – quasi-embrittlement, may be a subject of interest. It should be examined in a certain example. The process of loading the specimen in the SA medium with data, as stated below: tensometr length (0.1m), d_{s} diameter (0.01m), quasi-static relative loading speed: $\dot{\varepsilon}$ (10⁻⁴ $^{1}/_{S}$), absolute $v = \dot{\varepsilon} \cdot l_{s}$ (10⁻⁵ m/s). As was shown in the paragraph III.C.3, random distribution of SA factor may lead to a localization of a primarily initiated process of irreversible deformation. For instance on the length section of $l_u = 0.001l$ (10⁻⁴ m). The SA medium influence, decrease of the elastic limit to - $0.25 \cdot \sigma_e$; - $0.25 \cdot \varepsilon_e$, from the dispersion interval, for instance $0.8\sigma_e > \sigma_{es} > 0.2\sigma_e$. For mild steel $\sigma_e = 200Mpa$, $\varepsilon_e = 0.001$;

 $\varepsilon_{es} = 0.25\varepsilon_e \ (2.5\cdot 10^{-4})$. Time for reaching the elastic limit, ε_{es} : $t_{es} = \frac{\varepsilon_{es}}{\dot{\varepsilon}}$, (2.5 s). Supposedly, the speed of the relaxation is insufficient to compensate the deformation in the middle of a section. In this case, time for reaching the ultimate strain (tensile strain in the plastic area without increase of the general load):

$$t_u = \varepsilon_u \cdot \frac{l_u}{v}, (1.3 \text{ s})$$

where $\varepsilon_u=10\dots13$ % - limit of deformation according to the diagram of standard loading for mild steel, a point of σ_u ; ε_u , at which violation of continuity begins—beginning of the fracture. Meanwhile, general stresses and strains along the length of specimen remain mostly unchanged. General deformation would be:

$$\varepsilon_{gen} = \begin{bmatrix} 0.0999 \cdot 10^{-4} (2.5) + 10^{-4} \cdot 10^{-4} \cdot 1.3 \end{bmatrix} /_{0.1} , \quad (2.49 \cdot 10^{-4}), \quad \text{a lesser}$$
 value than the standard yield point. That is to say, fracture in case of such a deformation can be easily regarded as brittle.

E2.2 Plasticizing.

Similar to embrittlement, plasticizing was observed during tensile tests in the SA medium [2, 3, 4]. Random distribution of the influence factor, as mentioned in paragraph **III.C.3**, assumes that plastic deformation areas are likely to form along the whole surface or on its most part with little time difference. Respectively, the deformation level prior to disruption will be close to maximum. This will probably require a relative homogeneity of surface properties.

E3. Destruction of Liberty ships. (A class of cargo ship built in the United States during WW II)

Unexpected destruction of several Liberty ships during the World War II was studied by various specialists right up to the present time [10, 11]. Just like many other famous catastrophic events, these were not properly explained.

E3.1 Pieces of Evidence.

As with any other investigation, primarily the pieces of evidence are being studied.

- 1. Nature of the damage: vertical crack, emerging on the top and splitting the side plating and the deck in two. Localized cracks in the side plating have been detected on many vessels of the same type.
- 2. The destruction process was sudden and uninterrupted.
- 3. Time till destruction: from several days after launching.
- 4. Destruction of vessels started both during navigation and while being docked at the port.
- 5. One of the causes of destruction mentioned in previous studies, which is an insufficient plasticity of a side plating, is taken into account.

E3.2. Several steps of preliminary analysis.

E3.2.1. Load in a static condition.

Naturally, it is assumed that destruction may be possible only under loading conditions, stresses in the side plating. The least possible load acts in a static state (while being docked at the port). In that situation there are possible tensile stresses due to bending caused by a difference of loading forces: distributed along the vessel weight and Archimedes force, acting on its underwater part. Meaning that the highest tensile stresses act on the top parts of the side platings. It should be noted that it is still several times less than the same stresses in dynamic regime.

E3.2.2. Possible causes.

Among all possible causes of destruction mentioned above we shall consider only three.

The first one is scale factor [12]. Interesting discourse is presented in this work regarding the destruction scenarios of large scale objects and vessels, including Liberty ships. On the other hand, no physical ground exists to support the influence of scale factor as an actual phenomenon. Only consequences are examined, but not the causes. According to [12], the large sizes of the vessels entailed trivial rise in workloads. The plating thickness shown with physical ground as indirect size

influence. As a result, under particular conditions, tension stresses become unequally distributed, leading to reduction in load capacity.

The second one is the quality of steel. In the past, numerous studies have confirmed the compliance of the properties of steel in its original condition with the standard requirements. Notably, the standard value of relative elongation $\delta \geq 22\%$, approved for the vessels as a plasticity characteristic, was also maintained. Separately, embrittlement under low temperatures was also noticed. This is typical for many types of mild steel. However, temperature drop usually increase the strength characteristics, as it is shown in [9]. Therefore, temperature-dependent embrittlement cannot be the only cause of destruction.

The third one is tensile stress concentration [11]. Concentrators (sharp edges of the sections, weld seams) always create local zones of increased stresses. However, conclusions of the previous studies don't sign out mistakes of construction or assembling technology (welding). Furthermore, there is a known adaptability of constructions that compensate the elevated stresses in a local area. That's why the requirement for increased plasticity of steel exists.

E3.2.3. Conclusions.

None of the mentioned factors can be seen as the sole cause of crack formations in the side plating. Especially not the cause of their growth to Griffith's critical size. An important condition for such cracks to be formed is a drastic decrease of strength properties of the side platings.

E3.2.4. Version.

Obviously, among all these possible causes the only one that was not considered - is the Rehbinder effect. And it's despite the fact, that from the moment of its discovery in 1927 enough time has passed till the dramatic events of the 1940th, and another 70 years till the present time. The author suggests that the reason for this lies in the lack of understanding of the physical nature of the effect.

It should be noted that this version does not contradict with any of the pieces of evidence, presented in paragraph **III.E.3.2.2** or conclusions in paragraph **III.E.3.2.3**. For the influence of the SA medium to occur, the following conditions should be met: 1) presence of SA agents and 2) their contact with the side plating of the vessel (a possibility for absorption).

Regarding the presence of SA agents two variants should be mentioned. The first one is a separation of a covering layer on the vessel's side and contact of the surface of the side plating with the seawater. Most active substances of the seawater are Potassium Chloride (KCl) and Sodium Chloride (NaCl). According to [8], dipole moments of KCl - 10.5D; NaCl - 9.5D. An alternative scenario of destruction is a significant damage to the surface plating. In this case, the impact of SA agents cannot be lasting and recurring enough, because of the oxidation process on the surface.

The second variant is when SA elements are among the components of the cover layer composition. In that way, constant contact of the SA medium with the metal's surface exists. However, dipole moments for organic substances are usually much lower than the above-mentioned ones. In addition, there is no data on the correlation of the SA medium influence with the value of dipole moment. In any case, the suggested version cannot be accepted without experimental confirmation.

IV. Conclusion.

The Influence of SA agents on a strain effect, as presented in paragraph **III.B**, doesn't contradict any of the observed features of a phenomenon.

An approximate conventional criterion of numerical estimation of the SA medium's influence, formulated in paragraph **III.C** is fully based on determining the components in the course of experiments. That's why it is relevant and has no restrictions to be used in engineering practice.

According to analysis [5], of the irreversible shaping, all the inherent effects of the strain process are presented as direct consequence of the physical mechanism. Particularly, from the transverse direction of mass transfer process. Rehbinder's effect, SA medium influence on the tensile strain process leading to disruption, may be considered as the direct evidence of this mechanism.

This paper helps to understand one more physical property of metals. So it makes one more step to the strength problem formulation.

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