On the Nature of Positive Hydrogen and Nitrogen Effects on Fatigue of Austenitic Steels

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The hydrogen and nitrogen effects on fatigue life of austenitic steels are discussed using the *ab initio* calculations of electron structure, analysis of atomic distribution and dislocation substructure. As shown, both elements increase the concentration of free electrons in the f.c.c. iron softening thereby the crystal lattice, decreasing specific energy of dislocations and increasing their mobility. As a result, the dominant occurrence of short-range atomic order in the metal solid solutions causes localization of plastic deformation and consequent formation of dislocation slip bands. A combination of these factors realizes in the localized reversible planar slip of dislocations, which prevents their intersection with nucleation of submicrocracks and decreases the crack growth rate during fatigue tests, *i.e.*, prolongs the fatigue life.

Key words: austenitic steel, fatigue life, hydrogen, nitrogen, interatomic interactions, dislocations.

Вплив водню та азоту на втомність аустенітних криць аналізується базуючись на *ab initio* розрахунках електронної структури, близькому атомовому порядку і дислокаційній структурі. Одержано, що обидва елементи підвищують концентрацію вільних електронів в ГЦК-залізі, пом'якшуючи кристалічну ґратницю, зменшуючи питому енергію дислокацій та збільшуючи їх рухомість. За наявности близького атомового порядку твердому розчині це приводить до локалізації пластичної деформації і формуванню дислокаційних смуг ковзання. Комбінація цих чинників реалізується у локалізованому зворотньому планарному ковзанню дислокацій, що протидіє їх взаємному перетину із зародженням субмік-

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ротріщин, зменшуючи тим самим швидкість росту втомної тріщини в процесі циклічного механічного навантаження.

Ключові слова: аустенітна криця, втома, водень, азот, міжатомові взає-модії, дислокації.

1. INTRODUCTION

While studying hydrogen effect on fatigue of the gaseous hydrogen charged AISI type 304 and 316L austenitic steels using the compression-tension tests, Murakami *et al.* [1] found out the unexpected phenomenon of hydrogen-increased fatigue life. For example, see Fig. 1, the hydrogen-caused accelerated growth of the fatigue crack in steel 304 containing 23.9 wt.ppm of hydrogen was replaced by its slowing down with further increase of hydrogen concentration. The authors interpreted this result in terms of hydrogen-caused softening-hardening supposing the pinning of dislocations by hydrogen atoms located at dislocation core and the increase in their mobility when dislocations are released from hydrogen.

According to this model, hydrogen atoms diffuse into the zone of high hydrostatic tensile stresses ahead of the crack tip and, before their trapping by dislocations, enhance dislocation mobility causing slip localization. Outside the plastic zone, hydrogen produces the increased yield stress pinning the dislocations and, thereby, blocking the enlargement of plastic zone and retarding the growth of fatigue crack.

Discussing this interpretation, it is worth noting that all available data on the hydrogen-induced hardening in iron and austenitic steels were obtained using the only electrochemical hydrogen charging; see, *e.g.*, [2−5]. However, as shown by Mogilny *et al.* [6, 7], electrochemical charging is accompanied by plastic deformation, which causes hardening, whereas the hydrogen-induced softening occurs in the case of gaseous hydrogenation [7, 8].

A quite different interpretation was proposed by Kirchheim [9] based on his concept of formation and motion of kinks under the effect of mobile solute atoms. According to Kirchheim, two factors control the strain rate: time τ_g for double kink generation and time τ_m needed to move the kinks to the ends of a dislocation segment. Solute atoms segregated at dislocations reduce the energy for kinks formation and, therefore, decrease τ_g. On the condition of $\tau_m < \tau_g$ still being valid, it leads to the increased strain rate, *i.e.*, to softening. With increasing contents of solutes, they enhance the dragging force on the moving kinks, which increases τ_m and results in $\tau_m > \tau_g$. In the case of austenitic steels supersaturated by hydrogen atoms, their drag on the kinks dom-

inates over hydrogen-caused enhancement of kink formation leading to the decreased strain rate, *i.e.,* to the hardening.

However, the Peierls relief is rather shallow in the f.c.c. crystal lattice of austenitic steels. Moreover, hydrogen causes a further decrease of the Peierls relief, see [10, 11] for hydrogen in iron, so that formation of kinks on the dislocations becomes insubstantial. For example, just for this reason, the Snoek−Köster relaxation interpreted by Seeger [12] as formation and motion of paired kinks does not occur in the f.c.c. metallic solid solutions including austenitic steels. The exceptional case, see [13], is the hydrogen S−K relaxation in nickel having the high stacking fault energy, SFE, of $\cong 120-130 \ \mathrm{mJ/m^2}$ [14] and, consequently, narrow dislocations where kinks are easily formed.

Moreover, because of the shallow Peierls relief, mobility of dislocations under applied stress in the f.c.c. metals are controlled by their intersections, not by kink formation and motion, see, *e.g.,* Seeger's theory for the yield stress in the f.c.c. crystals [15, 16] and its experimental confirmation for austenitic steels by Obst and Nyilas [17], Nyilas *et al.* [18], Gavriljuk *et al.* [19] and for Cu, CuNiMn and AlMgMn alloys by Obst [20].

A more appropriate analysis of hydrogen effect on the fatigue life of austenitic steels can be performed taking into account a specific character of plastic deformation during the fatigue tests. Margolin *et al.* [21] were possibly the first to analyse the fatigue crack initiation in the compression-tension tests depending on the dislocation slip character. The reversed cycling during fatigue tests produces formation of folds accompanying the wavy slip in Cu and Al, whereas these folds disappear in the case of Cu−7.5Al alloy characterized by the planar slip mode. As a result, the reversible gliding of dislocations on the same slip planes is accompanied by the annihilation of dislocations having the opposite signs.

The planar slip of dislocations and formation of parallel slip bands is a feature of the cold worked hydrogen-charged austenitic steels. Just the same dislocation substructure is formed in the nitrogen austenitic steels during plastic deformation, see, *e.g.,* [22]. This similarity in the produced dislocation substructure makes reasonable the comparison of hydrogen and nitrogen effects on the fatigue crack rate in austenitic steels searching for a reason of the prolonged fatigue life in both cases.

2. FATIGUE CRACK LIFE AND FATIGUE STRESS IN NITROGEN AUSTENITIC STEELS

Like hydrogen effect detected by Murakami *et al.* [1], the fatigue crack propagation rate da/dN with the crack length a and cycle number N measured at 295 K in the AISI 304 type steel Cr18Ni10 steel was earlier found to decrease by Tobler and Reed [23] with increasing nitrogen

content from 0.039 to 0.240 wt.%. The residual carbon content in the several studied heats statistically varied between 0.028 and 0.094 wt.% and did not dominantly change the effect of nitrogen.

The opposite nitrogen effect, namely the nitrogen-increased crack propagation rate was observed by Tobler and Reed in the tests performed at 76 K and 4 K, where the $\gamma \to \alpha$ and $\gamma \to \varepsilon$ transformations occurred. In contrast to these data, Vogt *et al.* [24] observed a decreased crack propagation rate with increasing nitrogen content from 0.033 wt.% in austenitic steel 316L to 0.235 wt.% in the more stable steel 316LN, see comparison of the data mentioned by Tobler and Reed and Vogt in Fig. 2.

The nitrogen-increased low temperature fatigue life was also demonstrated by Nyilas *et al.* [18] by comparing the crack propagation rate in the high nitrogen austenitic steel CSUS-JN1 (Cr25Ni15Mn4N0.35) and in the low nitrogen steel 316LN (Cr17Ni13Mo3N0.15), see Fig. 3.

These studies were continued by Taillard and Foct [25] and Degallaix *et al.* [26] combined with a thorough analysis of dislocation substructure in steel AISI 316 alloyed with 0.08 or 0.25% of nitrogen. Presented in Fig. 4 are their fatigue stress data at two levels of strain
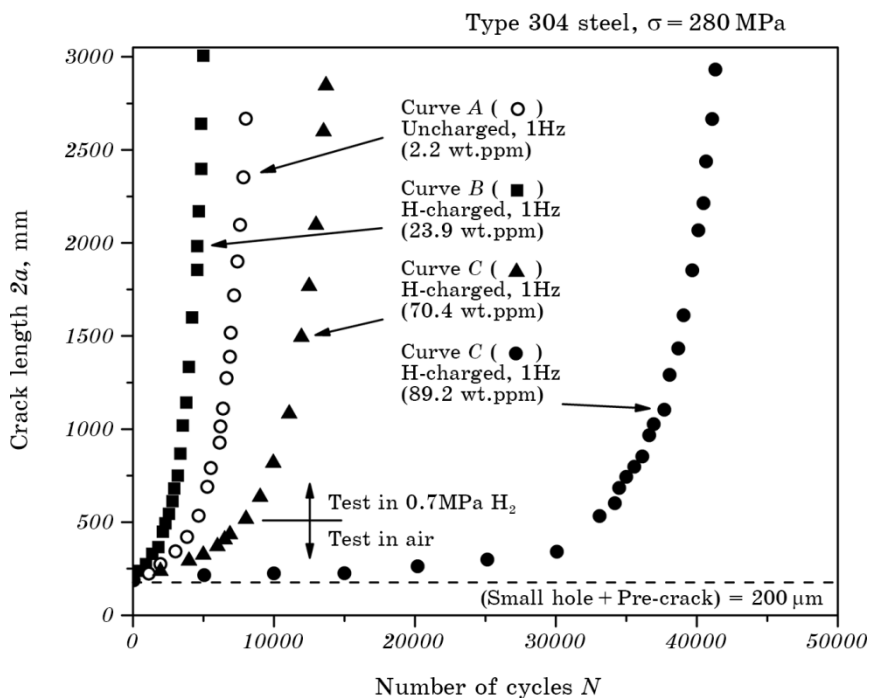

Fig. 1. Effect of hydrogen content on fatigue crack growth as redrawn from Murakami *et al.* [1].
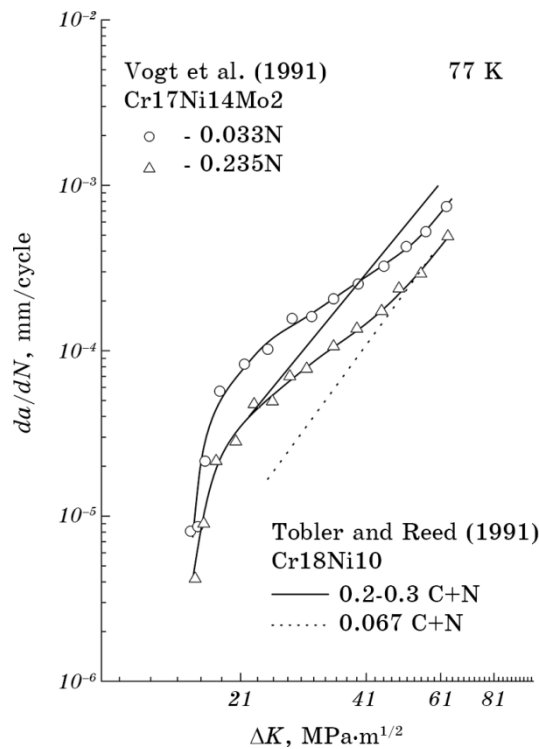
Fig. 2. Nitrogen effect on the fatigue crack growth rate at 77 K in steel Cr18Ni10 after Tobler and Reed [23] and steel Cr17Ni14Mo2 after Vogt [24].

amplitudes and characteristics of ensembles.

At the strain amplitude of 2%, softening of the nitrogen steel starts already above 10 cycles of the tests, whereas hardening continues up to the end of fatigue life if the steel is insignificantly alloyed with nitrogen. The observed softening is promoted by the dense planar dislocation arrays which can just be expected for reversible cyclic slip.

The presented data allow to see that hydrogen effect against hydrogen embrittlement found by Murakami *et al.* [1] is identical to that in the nitrogen austenitic steels. One can suppose that, in the both cases, it is caused by the reversibility of dislocation slip during fatigue tests provided that slip planarity occurs.

3. CONDITIONS FOR REVERSIBILITY OF PLASTIC DEFORMATION DURING FATIGUE TESTS

To shed light on the nature of crystal lattice softening, the hydrogen and nitrogen effects on atomic interactions was studied using *ab initio*
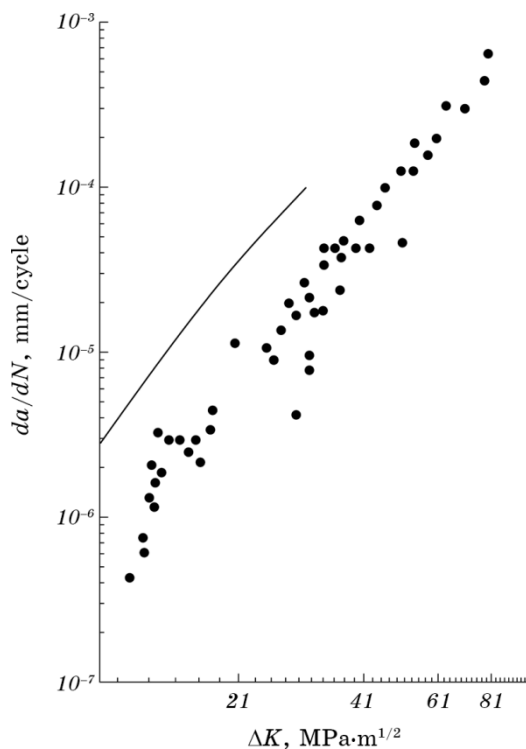
Fig. 3. Fatigue crack growth rate *versus* stress intensity factor at 12 K in steels Cr25Ni15N0.35 (filled circles) and AISI 316LN (solid line). After Nyilas *et al.* [17].

calculations of the electron structure in the iron.

Calculated were the atomic clusters containing 32 iron and 1 hydrogen or nitrogen atoms. As hydrogen induces ferromagnetism in the f.c.c. iron, the calculations for the $Fe_{32}H$ system were performed taking into account the spin polarization, see [27] for details. Important for the interpretation of nitrogen- and hydrogen-caused softening is a similar effect of hydrogen and nitrogen on the electron structure of austenitic steels, see Fig. 5.

As follows from these calculations, see the bound states at the bottom of the d band, the binding between interstitial and iron atoms is provided by the overlapping of Fe-3d and H-1s electrons for the Fe−H bonds and Fe-3d and N-2p electrons for the Fe−N bonds. The most significant is that, in contrast to the effect of carbon [28], the density of electron states at the Fermi level increases by hydrogen and nitrogen, see insets in the upper corners of Fig. 5.

This result suggests an increase in the concentration of free electrons, which was earlier observed in the experimental measurements
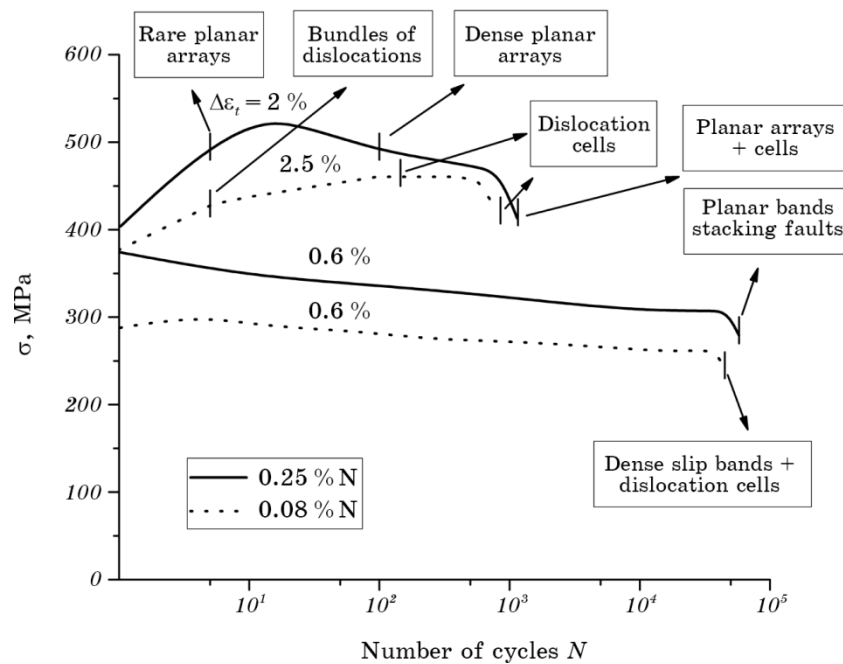
Fig. 4. Fatigue stress versus number of cycles for two austenitic steels with nitrogen contents 0.08 (dashed lines) and 0.25 mass% (solid lines) tested at ambient temperature with the strain amplitudes 0.6 and 2 (2.5)%. Dislocation substructures formed at different stages of fatigue tests are characterized in rectangles. Modified from Taillard *et al*. [25] and Degallaix *et al*. [26].

for hydrogen [29] and nitrogen [30] in the austenitic steels. The consequent weakening of interatomic bonds decreases the specific energy of dislocations, *i.e.,* their line tension, which enhances mobility of dislocations. These hydrogen and nitrogen effects on the atomic interactions are confirmed by the increased Snoek−Köster relaxation strength in the iron-based interstitial solid solutions; see, *e.g.,* [31], and by the enhanced strain dependence of internal friction; see, *e.g.,* [32].

The local increase of metallic character of interatomic bonds within the hydrogen or nitrogen atmospheres around the dislocations compensates the generally harmful effect of interstitial atoms and accelerates dislocation movement. Just for this reason, as shown in Fig. 1, a small amount of hydrogen, 23.9 wt.ppm, blocks dislocations and assists embrittlement, whereas the further increase of hydrogen concentration becomes sufficient for improving plasticity.

Thus, the softening of the crystal lattice caused by the increased concentration of free electrons is a common feature of hydrogen- and nitrogen-doped iron alloys. At the same time, the planar slip of dislocations in the hydrogen-charged and nitrogen-alloyed austenitic steels

has a quite different origin. The hydrogen-caused formation of slip bands is often attributed to a decrease in the stacking fault energy referring to the measurements performed by Pontini and Hermida [33] in their x-ray diffraction studies of the 304 type austenitic steel and by Ferreira *et al.* [34] based on the *in-situ* TEM observations of a 310S steel. The former authors obtained a decrease in the SFE of ~ 40% at the hydrogen content of 18 ppm, while the latter reported the hydrogen effect of $\cong$ 20% at its pressure of 40 Torr. The expected result amounts to easing the movement of split dislocations in their slip planes and retarding the cross slip. However, it remains unclear why the separate parallel slip planes should be accumulated into the slip bands.

A more realistic mechanism for localization of plastic deformation was proposed by Gerold and Karnthaler [35], according to which the short-range atomic order is responsible for the localized slip of dislocations regardless the stacking fault energy decreases or increases.

Relating to the hydrogen effect in austenitic steels, the inherently existing short-range atomic order, namely the short-range decomposition of the f.c.c. iron-based solid solutions, results in localization of
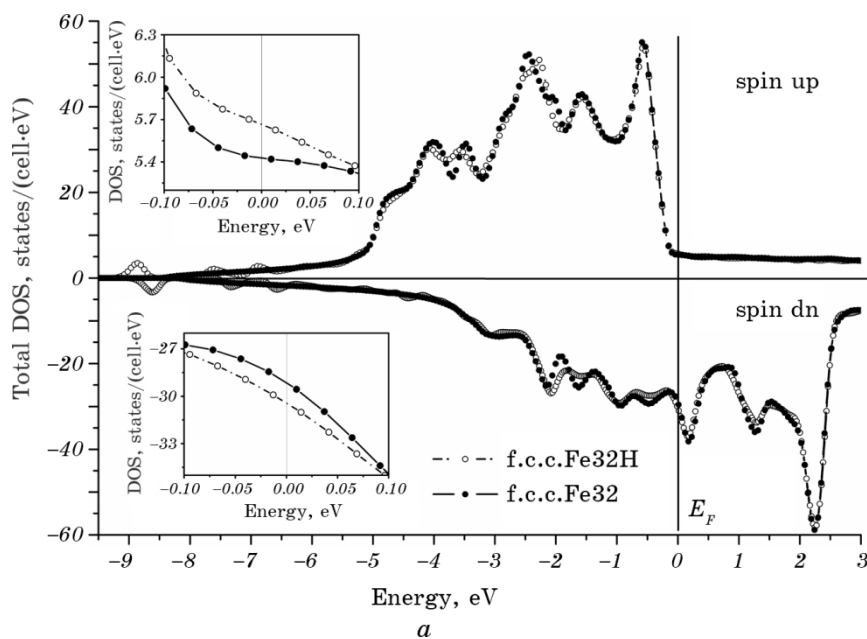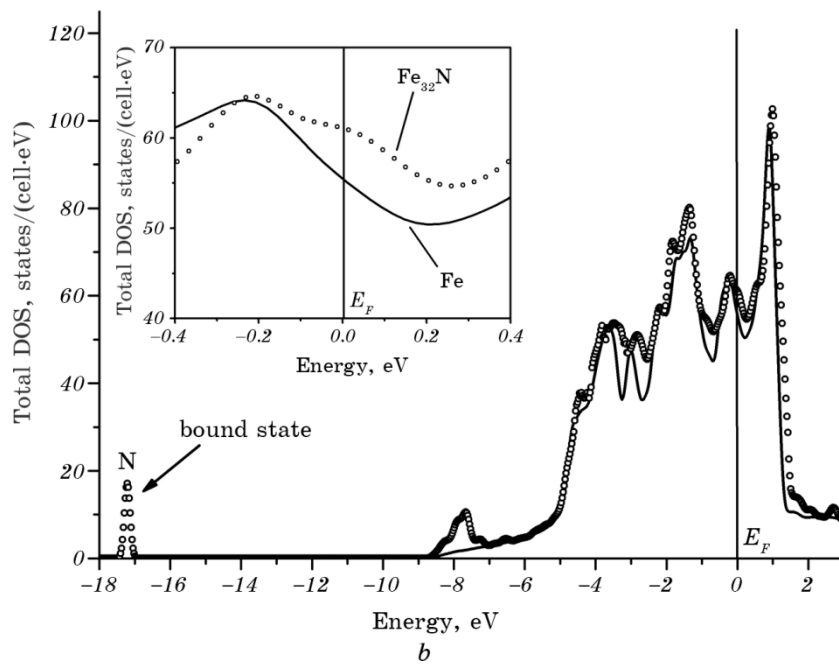

Fig. 5. Effect of hydrogen (*a*) and nitrogen (*b*) on the density of electron states at the Fermi level in the f.c.c. iron. The spin polarization, spin up and spin down, was taken into account during the calculations of electron structure of the Fe−H system. The situation at the Fermi level is shown in the insets on the both Figures.

Continuation of Fig. 5.

plastic deformation which is merely enhanced by hydrogen due to its different solubility in the submicrovolumes of different chemical compositions and, consequently, the increased mobility of dislocations in those of locally higher hydrogen concentration, see about details Gavriljuk *et al.* [36].

Slip planarity in the nitrogen austenitic steels is caused by the nitrogen-induced short range atomic ordering which is characterized by the prevailing nearest neighbourhood of the atoms of different kinds; see, *e.g.*, [37] about a correlation between the short-range atomic order and the electron structure. Despite the difference in the kinds of short-range atomic order, the slip bands in the both nitrogen and hydrogen cases are formed because the atomic order is destroyed by the first emitted dislocations so that movement of the next dislocations within the same areas requires a smaller expended energy.

It is also worth noting that Cu–Al solid solutions, where Margolin *et al.* [21] noted slip planarity, are also characterized by the short-range atomic order with formation of highly ordered atomic configurations including even separate SRO domains; see, *e.g.*, Epperson *et al.* [38].

Therefore, the high concentration of free electrons in combination with the short-range atomic order cause the slip planarity and enhanced dislocation mobility, which finally results in the prolonged re-

versible cyclic deformation.

4. SUMMARY

A decrease in the fatigue crack growth rate by hydrogen and nitrogen in austenitic steels is caused by reversibility of plastic deformation combined with localization of dislocation slip. Among possible mechanisms of the localized slip enhanced by hydrogen and induced by nitrogen, the short-range atomic order seems to be the most realistic. The reversible slip of dislocations is facilitated by softening of the f.c.c. crystal lattice caused in turn by the increase in the concentration of free electrons due to alloying of the iron-based solid solutions with nitrogen or charged with hydrogen.

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