# INFLUENCE OF HYDROGEN ON MECHANICAL PROPERTIES OF [012]–CRYSTALS OF AUSTENITIC STEEL Fe–18Cr–14Ni–2Mo

E.I. Kuprekova, K.V. Klimova, I.V. Kireeva, Yu.I. Chumlyakov*, I.P. Chernov

Tomsk Polytechnic University
*Siberian Physico-technical Institute, Tomsk
E-mail: eikuprekova@tpu.ru

*The influence of hydrogen alloying on critical shear stress, strain hardening coefficient and crystal plasticity depending on temperature of testing in the range of 77...400 K and hydrogen atom concentration has been investigated on monocrystals of austenitic stainless steel Fe-18Cr-14Ni-2Mo with low staking fault energy. Hydrogenation up to 14 at. % is shown to result in 1,5...2 increase of strength properties expressed by temperature dependence of critical shearing strains and to encourage development of local deformation by sliding.*

Austenitic stainless steel represent an important group of construction materials used in operation in corrosive environment, under the action of radiation, high temperatures and cyclic loads in hydrogen medium [1, 2]. Analysis of the literature data obtained for steel polycrystals [3–8] shows that the presence of hydrogen in austenite lattice conventionally has an adverse effect on mechanical properties of these materials: increase in strength is accompanied by a sharp decrease in plasticity and brittle character of destruction at grain boundary. Experimental study of the mechanisms of polycrystal deformation of austenitic stainless steels with low energy of stacking fault $\gamma_0$=0,02...0,03 J/m² indicate that depending on test temperature and concentration of Cr, Ni, Mn substitutional atoms and introduction of N, H these materials are deformed by gliding, twinning, undergo $\gamma \rightarrow \varepsilon \rightarrow \alpha'$ martensitic transformations [4–7, 9], simultaneous development of which results in production of high-strength steel with great plasticity during deformation. In this connection development of physical mechanisms of strength increase at plastic deformation and martensitic transformation (MT), mechanism of hydrogen influence on strength and plastic properties is an actual problem. In the given paper the study of influencing by hydrogen ligation on regularities of solid-soluble and deformative steel hardening of Fe-18Cr-14Ni-2Mo steel monocrystals in the absence of grain boundaries has been carried out.

Choosing the material for investigation we based on the fact that Fe-18Cr-14Ni-2Mo steel has the temperature of MT beginning under the load ($M_c^\gamma$) lower 4,2 K and the temperature of MT beginning at plastic deformation ($M_\varepsilon^\gamma$) lower than 300 K [7]. Consequently, martensite of cooling and strain in the steel involved is not observed and $\gamma \rightarrow \varepsilon \rightarrow \alpha'$-MT can take place only after plastic deformation by gliding or twinning, or can be induced by introduction of hydrogen into austenite lattice [5, 6]. For the research the crystals of [012] orientation which are characterised by high plasticity $\varepsilon \approx 50$ % at 300 K [9] and have close values of the Schmidt's factor for gliding $m_{gl}$ and twinning $m_{tw}$: $m_{tw}/m_{gl} \approx 1$, have been chosen. Therefore, necessary conditions of changing deformation mechanism from gliding to twinning and $\gamma \rightarrow \varepsilon \rightarrow \alpha'$-MT realization in [012] orientation should be achieved only after significant deformation by gliding as

it is the case with low-strength metals and substitutional alloys [10]. Owing to high strength and orientation for single gliding, [012]-crystals make possible to investigate precession of crystal axis and study the phase composition of steel depending on the size of plastic deformation.

## Methods of the experiment

The steel monocrystals Fe-18Cr-14Ni-2Mo (wt. %) with low $\gamma_0$=0,025 J/m² [9] was grown by the Bridgeman method on <011> inoculum in the argon atmosphere. After growing the crystals were homogenised in the argon medium at $T$=1423 K during 48 h. To test tension the samples were cut at electrospark discharge machine in the form of double blades 1,5×2,2×12 mm³. The samples were hardened in water after ageing in helium medium during 1 h at $T$=1373 K. Defects on the sample surfaces were removed by mechanical polishing, then the samples were electrolytically polished in the 50 g solution of $Cr_2O_3$+200 g of $H_3PO_4$ at 300 K during 1...2 min. Hydrogenation was performed by electrolytic method in 1 M solution of $H_2SO_4$ at the electrolyte temperature 300 K and current density $j$=10 mA/sm². Before the test hydrogenated samples were kept in liquid nitrogen. The orientation of sample strain axis and its transformation at plastic deformation in every 5...10 % of deformation was detected at diffractormeter DRON-3M. For determination of crystal phase composition after deformation the section plane was installed in the reflected position in such a way that at $2\Theta-\Theta$ scanning at $Fe_{K_\alpha}$ radiation the reflexes $\{222\}_\gamma$, $\{004\}_\varepsilon$ and $\{220\}_\alpha$ were simultaneously registered [5, 6, 9]. Mechanical strain tests were carried out at «Polany» device with tensometric system of load change and curve recording on electron self-registering potentiometer KSP-4. The test temperature varied in the range 77...400 K. The deformation rate was $\dot{\varepsilon}$=5·10⁻⁴ c⁻¹.

Concentration of hydrogen atom was determined by the X-ray method by the lattice parameters before and after hydrogenation using the Bragg equation for cubic materials [11]:

$$\lambda = 2d \sin\Theta = \frac{2a}{\sqrt{h^2+k^2+l^2}} \sin\Theta$$

and linear relation [6] between the lattice deformation $\Delta V/V$ due to hydrogen atoms and atom relationship H/Me($C_H$), obtained in assumption that hydrogen occupies octahedral interstices in face-centred cubic FCC materials and produce spherical lattice distortions:

$$\frac{\Delta V}{V} = \frac{a_H^3 - a_0^3}{a_0^3} = C_H \frac{\Delta v}{\Omega},$$

where $\lambda$ is the wavelength of radiation; $h$, $k$, $l$ are the Miller indices; $d$ is the interplanar spacing; $a_0$ and $a_H$ are the lattice parameters of the hydroden-charger and hydroden-free austenite, respectively; $\Delta v$ is the the volume change of the lattice per one hydrogen atom, $\Omega$ is the magnitude of atomic volume of a metal atom.

At hydrogenation during 2, 5 and 24 h hydrogen concentration in the samples amounted 2,8, 7,0 and 11,5 at. % respectively.

### Experimental results and discussion

In fig. 1 the temperature dependence $\tau_{\text{кр}}(T)$ for [012]-crystals, deformed by straining is presented without hydrogen $C_H$=0 at. % (curve 1) and with hydrogen 2,8 and 11,5 at. % (curves 2, 3). It is seen that alloying by hydrogen atoms at 2,8 and 11,5 at. % results in the growth of critical shearing strains $\tau_{\text{кр}}^{\text{H}_2}$ 1,5...3 times as large as the initial state $C_H$=0 at. %, and, consequently, hydrogen saturation of [012]-crystals leads to noticeable effect of solid-solution hardening.
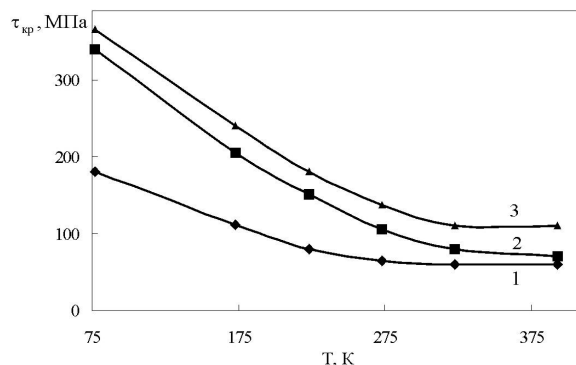


**Fig. 1.** *Temperature and concentration dependence $\tau_{\text{кр}}$ at hydrogen concentration $C_H$: 1) 0; 2) 2,8; 3) 11,5 at. %. Orientation of strain axis [012]*

The value of solid-solution hardening effect increased with test temperature decrease to 77 K. Thus, in the initial state $C_H$=0 at. % [012]-crystals are characterised by weak dependence $\tau_{\text{кр}}(T)$ in the range 77...400 K. From fig. 1 (curve 1) it is seen that the dependence at $C_H$=0 at. % consists of two parts. The first high-temperature part at $T>T_{\text{кр}}\approx290$ K is characterised by practically complete absence of dependence on temperature so that the reduced to the shift module $G(T)$ [12] the values $\tau_{\text{кр}}(T)/G(T)\approx$const. It is an athermic component of flow tension $\tau_{\text{кр}}^G$. The index G indicates that at $T>T_{\text{кр}}\approx290$ K critical shearing strains $\tau_{\text{кр}}$ depend just on temperature only through temperature dependence of elastic constant.

The second part $\tau_{\text{кр}}(T)$ at strain in [012]-orientation without hydrogen is observed at $T<T_{\text{кр}}\approx290$ K and characterised by increase in $\tau_{\text{кр}}$ with temperature decrease.

The dependence $\tau_{\text{кр}}(T)$ in the given part exceeds the temperature dependence of shift module $G(T)$ [12]. This part of the flow tension is thermally activated $\tau_{\text{кр}}^S$ and is usually defined from the graph $\tau_{\text{кр}}(T)$, using the relation $\tau_{\text{кр}}^S=\tau_{\text{кр}}(T)-\tau_{\text{кр}}^G$ [10]. According to the theory of thermally-activated motion by dislocation [10, 11] the increase in with temperature decrease means that there are some local obstacles in steel (substitutional atoms Mo, the sizes of which differ considerably from that of Fe «base» atoms; «forest» dislocation, concentration inhomogeneities), interaction of gliding dislocations with which it depends on temperature. The data obtained at the strain of [012]-crystals without hydrogen conform to the investigation data for low-resistant FCC-metals and substitutional alloys [10, 11].

Alloying of [012]-crystals with hydrogen to 2,8 and 11,5 at. % results in strong temperature dependence $\tau_{\text{кр}}^{\text{H}_2}(T)$ (fig. 1, curves 2, 3): increase in both thermally-activated $\tau_{\text{кр}}^{\text{H}_2}(T)$, and athermic component of flow tension is observed and at 77 K $\tau_{\text{кр}}^{\text{H}_2}(T)$ they increase 2,5...3 times in comparison with the state $C_H$=0 at. %. Previously qualitatively similar results were obtained for poly-and monocrystals of austenitic stainless steel alloyed with nitrogen [13], and were explained from the viewpoint of thermally-activated interaction of dislocations with nitrogen atoms. In [3, 8] it is shown that influence of hydrogen on dislocation mobility, magnitude $\gamma_0$, localization degree of plastic deformation and destruction of austenitic stainless steel appears to be similar to that of nitrogen. Therefore, strong temperature dependence $\tau_{\text{кр}}^{\text{H}_2}(T)$, revealed by us experimentally in [012]-crystals in hydrogen alloying $C_H$=2,8 and 11,5 at. %, like in the case with nitrogen, at 77 K can be explained by depression of thermally-activated overcoming of immovable hydrogen atoms. At $T\geq300$ K both dislocations and hydrogen atoms turn out to be mobile. Therefore, the features of forming temperature dependence of $\tau_{\text{кр}}^{\text{H}_2}(T)$ [012]-crystals at $T\geq300$ K are determined by facilitation of dislocation motion due to thermally-activated overcoming of hydrogen atoms as well as owing to screening effects of elastic stress fields in forming the Cottrell`s atmospheres from mobile hydrogen atoms at edge dislocations.

It was stated experimentally that hydrogen alloying is not always accompanied by increase in strength properties. Thus, at 77 K in [012]-crystals with hydrogen $C_H$=7,0 at. % hardening is observed: growth of $\tau_{\text{кр}}^{\text{H}_2}(T)$ with respect to crystals without hydrogen $C_H$=0 at. % (fig. 2). At the same time at 300 K in crystal tension with $C_H$=7,0 at. % softening (fig. 2, curves 1, 2): decrease $\tau_{\text{кр}}^{\text{H}_2}(T)$ of in comparison with the samples of $C_H$=0 at. % was stated.

From figure 2 (curve 1) it is seen that at 300 K in [012]-crystals oriented for single gliding, at $C_H$=0 at. % three stages of plastic yielding are observed: stage of easy gliding (stage I), linear stage II with high coefficient of strain hardening ($\Theta_{\text{II}}/G\approx2,3\cdot10^{-3}$, where $\Theta=d\sigma/d\varepsilon$, $G$=80 GPa is the shift module for steels of the given class at 300 K) and stage III is of dynamic recovery. Hence, at 300 K vicissitude of flow curves proves to be typical as it is in FCC-metals and substitutional alloys [11]. The basic mechanism of plastic deformation in the initial [012]-crystals ($C_H$=0 at. %) at 300 K is gliding that determines the vicissitude of flow curves and the coeffici-

ent $\Theta_{II}/G$. This conclusion is based on the research of metallographic gliding pictures, experiments on repolishing and subsequent etching as well as on study of precession of crystal axis, from which it follows that in the initial state [012]-crystals at 300 K are stable and plastic deformation does not lead to $\gamma\to\varepsilon\to\alpha'$-MT. In the repolishing and etching experiments twinning was not also observed. Precession of crystal axis occurs in the pole (fig. 2, a), which is a direction of gliding in the initial gliding system for FCC materials [9, 10].
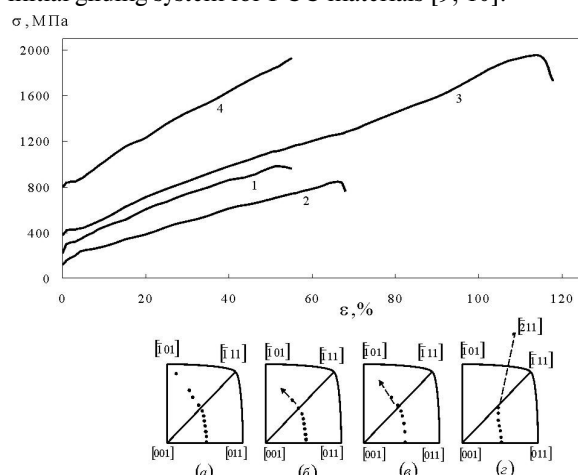


**Fig. 2.** *Curves of flow 1–4 and precession of crystal axis а-в at tension of [012]-crystals: 1, 2, a, в – 300 K; 3, 4, б, г – 77 K; 1, 3, a, б – $C_H$=0 at. %; 2, 4, в, г -7 at.*

Hydrogenation up to 7 at. % does not change sufficiently vicissitude of flow curves of [012]-crystals at 300 K: all three stages are observed at $\sigma(\varepsilon)$-dependence. From fig. 2, curve 2, it is evident that all curve of flow shifts down relatively to the curve at $C_H$=0 at. %. Decrease in strain hardening coefficient $\Theta_{II}/G\approx1,4\cdot10^{-3}$ in comparison with the state without hydrogen is observed, which is not conventional for FCC-materials: usually the coefficient $\Theta_{II}/G$ slightly changes at additional alloying [10]. We stated experimentally that saturation with hydrogen changes essentially (1,6 times) $\Theta_{II}/G$, in this case crystal plasticity increases by 15 %, but failure strain decreases from 970 MPa in the initial crystals to 850 MPa in those with hydrogen $C_H$=7 at. %.

Thus, the strong softening effect is observed in [012]-crystals at hydrogenation to 7 at. % and subsequent tension deformation at 300 K. The researches are conventionally carried out for polycrystal austenitic stainless steels [3, 5, 8] but data on softening of such materials at hydrogenation are absent in literature. Twinning in [012]-crystals at $C_H$=7 at. % and 300 K fails to be revealed by metallographic examination and experiments with repolishing and etching. Research of phase composition shows that crystals do not exhibit $\gamma\to\varepsilon\to\alpha'$-MT, precession of crystal axis takes place in the pole, corresponding to gliding in the initial system (fig. 2, в). Study of dislocation structure reveals that hydrogen contributes to development of localised gliding deformation: thick pileup which has been absent in the crystals without hydrogen is observed [9]. Hence, value decrease of $\Theta_{II}/G$ at hydrogenation in comparison with crystals without hydrogen is connected with the fact that in [012]-crystals oriented to single gliding hydrogen does not change the number of operating gliding systems, but results in shift localization in pileups. According to the theory [13] increase of shift localization leads to decrease of strain hardening coefficient.

At 77 K at tension in [012] orientations at $C_H$=0 at. % on the flow curve stage I at $\varepsilon<6$ % and two linear stages II (6 %$<\varepsilon<75$ %) and III ($\varepsilon>75$ %) of strain hardening are observed. At stage I plastic deformation is performed by gliding in the initial system $[\bar{1}01](111)$ by the Luderse band with the coefficient $\Theta_I\approx0$ to $\varepsilon<6$ %. At $\varepsilon>6$ % growth of $\Theta_{II}/G$ value in copmparison with stage I is observed up to the values of the order $2\cdot10^{-3}$ (fig. 2). Comparison of $\Theta_{II}/G(T)$ values at 77 and 300 K shows that coefficient $\Theta_{II}/G(T)$ does not depend on test temperature (fig. 2, curves 2, 3): the curves at the II stage are parallel to each other. Operation of one gliding system is observed metallographically; precession of crystal axis occurs in the pole and, consequently, values of $\Theta_{II}/G$ in [012]-crystals without hydrogen at 77 K are connected with gliding [9]. Stage III of strain hardening starts at $\varepsilon>75$ % and continues up to destruction (fig. 2, curve 3). At the given stage the growth of $\Theta_{III}/G$ value to $3,5\cdot10^{-3}$ is observed. Study of crystal axis precession indicates (fig. 2, b) that at stage III crystal axis continues to move in the direction of the pole corresponding to gliding [9]. In this case skipping of axis through a symmetral is observed, however investigating the phase composition of [012]-crystals at $\varepsilon>78$ % it is possible to note additional peaks corresponding to $\gamma\to\varepsilon$ martensite transformations (fig. 3, a). Consequently, increase in strain hardening coefficient in [012]-crystals without hydrogen $C_H$=0 at. % at 77 K is explained by induced $\gamma\to\varepsilon$ martensite transformations in the course of plastic deformation [6, 9].

At 77 K deformation of [012]-crystals alloyed with hydrogen to 7 at. %, from the very beginning of plastic flow is realised by the Luderse band with $\Theta_I/G\approx0$ (stage I). The length of this stage is not great 3...4 %. Then linear stage II with high coefficient $\Theta_{II}/G\approx3,0\cdot10^{-3}$, the values of which appears to be close to $\Theta_{III}/G$ on the crystal flow curve with $C_H$=0 at. % (fig. 2, curves 3, 4) is observed. Such values of strain hardening coefficient are not typical for gliding and could be connected with the induced $\gamma\to\varepsilon$-MT in the course of plastic deformation [6, 9]. Investigation of crystal axis precession shows (fig. 2, г) that up to $\varepsilon=30$ % the crystal axis at $C_H$=7 at. %. moves in the direction $[\bar{1}01]$, after that, near symmetral $[001]-[\bar{1}11]$ deviation of axis in the direction $[\bar{2}11]$ is observed. This direction is both the twinning direction and shift direction for $\gamma\to\varepsilon$-MT in the initial system $[\bar{2}11](111)$. Data of the phase analysis shows (fig. 3, б) that in [012]-crystals at $C_H$=7 at. % $\gamma\to\varepsilon$-MT take place at deformation $\varepsilon\geq30$ %, though in the repolishing and etching experiments martensite is revealed even at $\varepsilon=10$ %.

Thus, it has been experimentally stated that hydrogen alloying of steel monocrystals Fe-18Cr-14Ni-2Mo with low energy of stacking fault $\gamma_0$=0,025 J/m² to 7 at. % shifts the beginning of martensite transformations to less degrees of plastic deformation in comparison with the initial state before hydrogenation. Appearance of $\gamma\to\varepsilon$ MT in [012]-crystals with hydrogen $C_H$=7 at. %, at less deformation degrees in comparison with the initial crystals

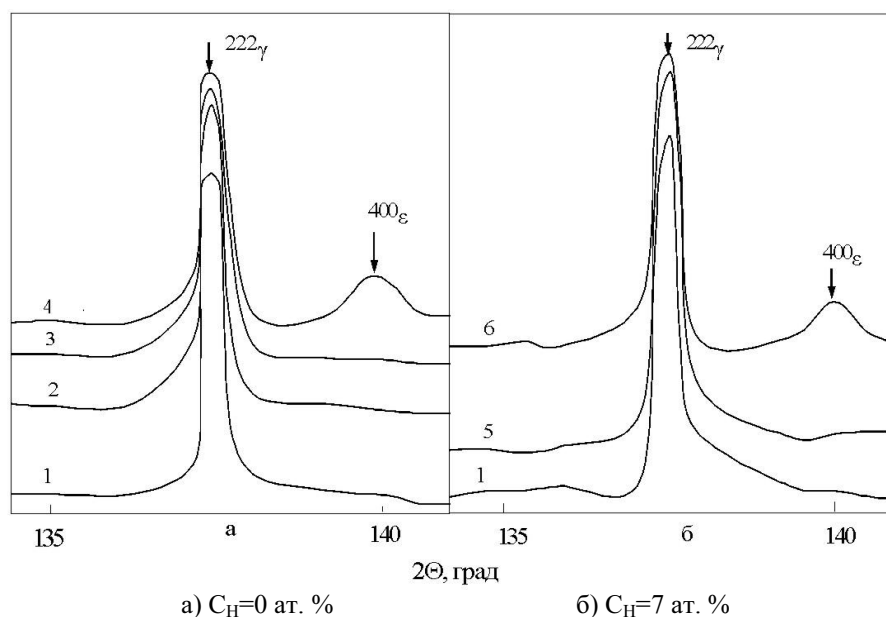a) $C_H$=0 ат. %          б) $C_H$=7 ат. %

**Fig. 3.** *Phase composition of [012]-crystals depending on the degree of plastic deformation ε at 77 K: 1) 0; 2) 15; 3) 45; 4) 78; 5) 10; 6) 31,5 %*

with $C_H$=0 at. % can be explained by combination of two factors. Firstly, as indicated in the study of austenitic steel polycrystals [8] hydrogen decreases the value $\gamma_0$ and regulates martensite transformations. Secondly, owing to solid-solution hardening with hydrogen atoms and high temperature dependence of critical shearing strains $\tau_{кр}^{H2}$ in Fe-18Cr-14Ni-2Mo steel at 77 K a high level of deforming strains is achieved; it is 20...40 times higher than in FCC pure metals and substitutional alloys. Therefore, in hydrogenated [012]-crystals $C_H$=7 at. %, conditions of forming subtraction stacking fault, plasticine plate of ε-martensite and twinning development, can be achieved due to solid-solution hydrogen hardening, but not in the course of plastic deformation as it is in the case with the samples not alloyed with hydrogen 0 at. % [9].

Thus, it has been experimentally stated that hydrogen alloying results in, firstly, strong effects of solid-solution hardening: increase in strength properties by a factor of 1,5...2 in comparison with the initial state before hydrogenation. Secondly, effects of solid-solution hardening appear to depend on test temperature and time of hydrogen saturation. Thirdly, hydrogen alloying of [012]-crystals leads to development of localised deformation by gliding. And at last, hydrogen saturation to 7 at. % of Fe-18Cr-14Ni-2Mo monocrystals with low energy of stacking fault 0,025 J/m², displaces the beginning of $\gamma \rightarrow \varepsilon$ martensitic transformations to less degrees of plastic deformation in comparison with the state before hydrogenation.

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