Estimation of the technical state of exploited heat resistant steels using the fracture mechanic characteristics and fractography features of degradation

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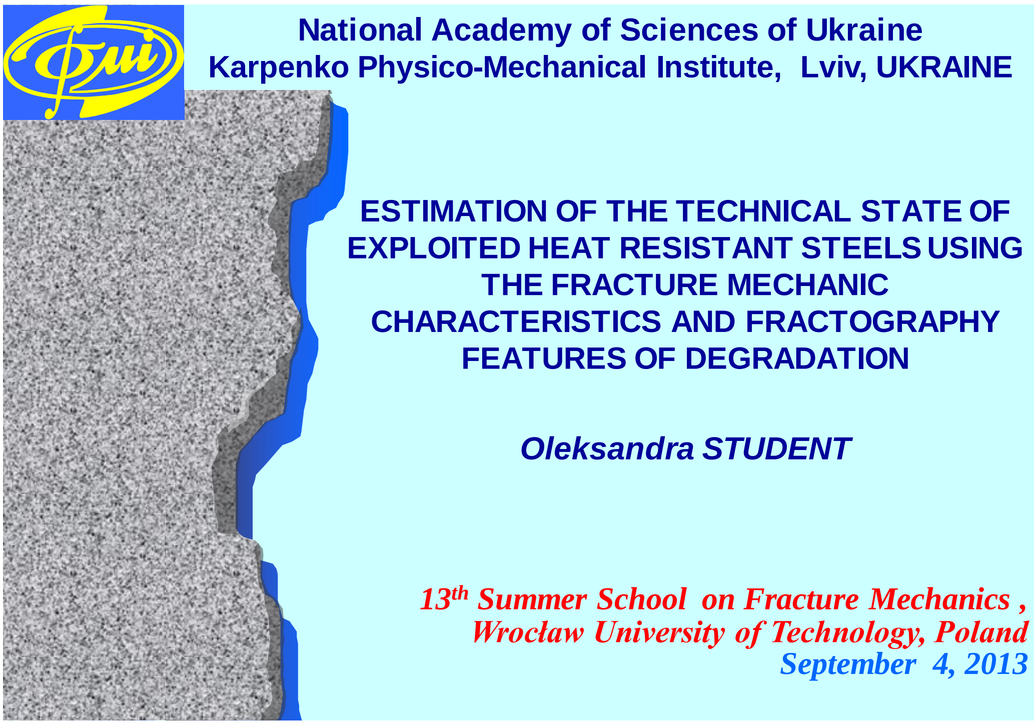

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Introduction

The design lifetime of the equipment of most thermal power plant in Ukraine is almost exhausted . The same problem is topical for EC too. As a result the damages of structural elements occur more frequently. This problem is important for power system, oil refining and chemistry industries.

One of the reasons for their failure are the degradation of metal. Many factors promote the degradation of steels. In particularly, these are hydrogenated environment and shutdowns of process. It is important to estimate their effects on the state of degraded metal to guarantee the structures serviceability.

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Degradation of heat-resistant steels appears as a change in their structure, reduction of mechanical properties and change of failure mechanism. A lot of the mechanical characteristics are used to estimate the degree of steels degradation. But it is necessary to ground the choose of the most sensitive among them.

Finally, fractographic details caused by degradation of steels identified in the specimens tested under certain laboratory test, can be used for examination of real damages and determination of their causes.

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THE GOALS OF LECTURE is:

- to compare the sensitivity to degradation of different mechanical characteristics of heat resistant steels and weld joints;
- to determine the mechanical characteristics of steels the most sensitive to degradation;
- to demonstrate the hydrogen and degradation effects on the creep characteristics of the heat resistant 2.25Cr-1Mo steel of oil hydrocracking reactor vessel;
- to substantiate the critical state of degraded steels;
- to propose the method of determining the technical state of long-term exploited heat resistant steels with account of the shut-downs effect on the high temperature hydrogen degradation;
- to allocate fractographic features caused by degradation of steels and weld joints;

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Tested materials

The following heat resistant steels were investigated :

- the 12Kh1MF and 15Kh1M1F steels used in thermal power plant for steam pipeline;
- the 15Kh2MF steel used as a vessel steel in nuclear power and oil refining industry;
- the 2.25Cr-1Mo steel for the oil hydrocracking reactor pressure vessel;

Table 1. Chemical composition of testing steels, mass %

Steel	C	Cr	Mo	V	Co	Ni	Si	Mn	S	P
15Kh1M1F	0,16	1,39	0,97	0,29	0,017	0,20	0,30	0,91	0,017	0,021
12Kh1MF	0,10	1,10	0,26	0,17	-	-	0,26	0,54	0,019	0,015
15Kh2MFA	0,15	2,8	0,70	0,3	-	0,40	0,25	0,45	0,015	0,012
2,25Cr-1Mo	0,14	2,2	1,00	0,01	-	0,1	0,2	0,6	0,003	0,006

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Operation conditions of the main steam pipeline:

Steel	Diameter of pipe, mm	Wall thickness, mm
15Kh1M1F	325	60
12Kh1MF	325	32

Steel	Temperature, °C	Steam pressure, MPa
15Kh1M1F	545	24
12Kh1MF	540	14

Steel	C	Cr	Mo	V	Co	Ni	Si	Mn	S	P
15Kh1M1F	0,16	1,39	0,97	0,29	0,017	0,20	0,30	0,91	0,017	0,021
12Kh1MF	0,10	1,10	0,26	0,17	-	-	0,26	0,54	0,019	0,015

12Kh1MF				15Kh1M1F			
σ_{UTS}, МПа	σ_{YS}, МПа	ψ, %	δ, %	σ_{UTS}, МПа	σ_{YS}, МПа	ψ, %	δ, %
445	285	74	30	530	340	63	20

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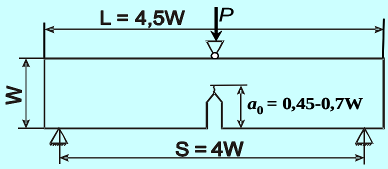
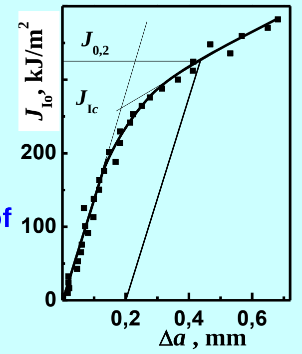
Estimation the fracture toughness of the J-integral method

Scheme of loading: three-point bending





The method of partial multiple unloading of specimens was used. Increment of crack was estimated by compliance and COD methods. Fracture toughness was determined from the J_R-curves

The formulas for the calculation of the J-integral

$$J_k = \frac{K_k^2(1-\nu^2)}{E} + J_{pl(k)}; \qquad J_{pl(k)} = \left[J_{pl(k-1)} + \frac{2}{b_{k-1}}\left(\frac{A_{pl(k)} - A_{pl(k-1)}}{B}\right)\right]\left[1 - \frac{a_k - a_{k-1}}{b_{k-1}}\right]$$

$$\partial e \quad K_k = \left[\frac{P_k S}{BW^{3/2}}\right] f(a_k/W); \qquad A_{pl(k)} = A_{pl(k-1)} + \left[F_k - F_{k-1}\right]\left[V_{pl(k)} - V_{pl(k-1)}\right]/2$$

$$f(a_k/W) = \frac{3(a_k/W)^{1/2}[1.99 - (a_k/W)(1 - a_k/W)(2.15 - 3.93(a_k/W) + 2.7(a_k/W)^2)]}{2(1 + 2a_k/W)(1 - a_k/W)^{3/2}}$$

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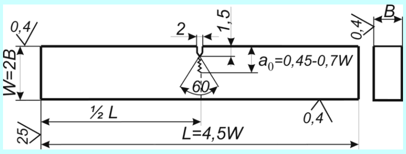
Fatigue crack growth test

scheme of loading - cantilever bending,
frequency of cycling – 10 Hz,
stress ratio - 0,05

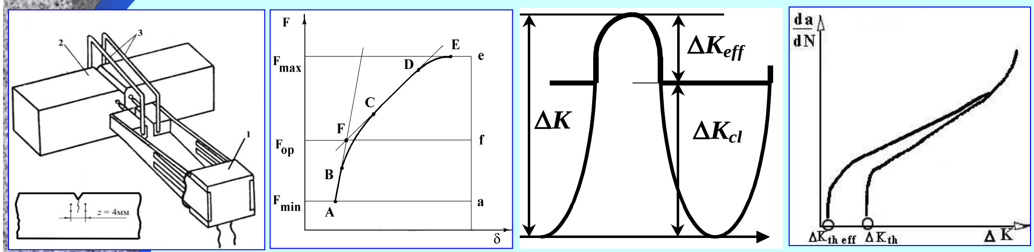


$$K = \frac{4.12M}{B\sqrt{W^3}}\sqrt{\alpha^3 - \alpha^3};\qquad \alpha = 1 - \frac{a_i}{W}$$

$$\Delta K = \Delta K_{cl} + \Delta K_{eff}$$

$$\Delta K_{th} = \Delta K_{th\,cl} + \Delta K_{th\,eff}$$

Compliance method for estimation of the crack closure effect



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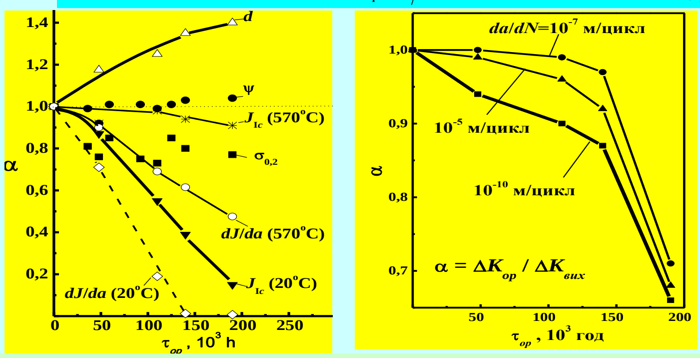
Sensitivity to degradation different mechanical characteristics of the heat resistant 12Kh1MF steel

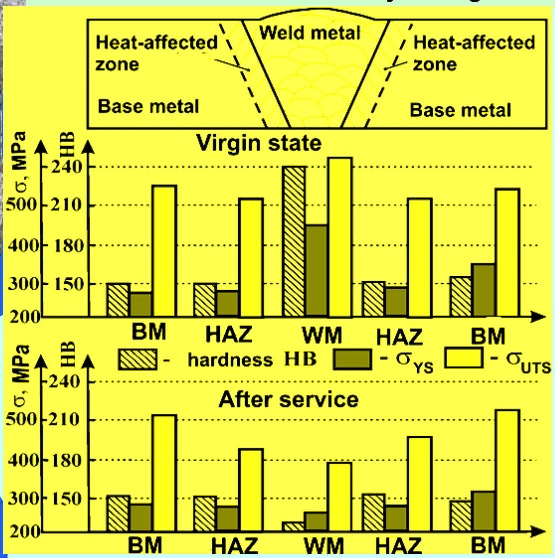
$$\alpha = P(J_{Ic}, dJ/da, \sigma_{YS}, \Delta K)_{operated} \big/ P(J_{Ic}, dJ/da, \sigma_{YS}, \Delta K)_{virgin}$$



Degradation effect of the 12Kh1MF steel caused by long term operation time τ_{op} on the steam pipeline of heat power plant was estimated by using ratio α which characterises the change of the structural (diameter of the ferrite grain), integral (reduction of area ψ and yield stress σ_{ys}) and local (J_{Ic} and *dJ/da* at room temperature and 570 °C, stress intensity factor range ΔK_{eff} at different fatigue crack growth rates *da/dN* = 10^{-5}, 10^{-7} *and* 10^{-10} *m/cycle*) parameters for exploited metal relative to corresponding ones for steel in virgin state. If ratio α is unity, there is no degradation effect. The smaller the ratio of characteristics from units the stronger negative effects of degradation is observed.

10 Specific feature of the high temperature hydrogen degradation of welded joints

Mechanical properties of the metal from different zones of the weld joint of the 15Kh1M1F steel caused by its degradation in service during $2{\cdot}10^5$ h



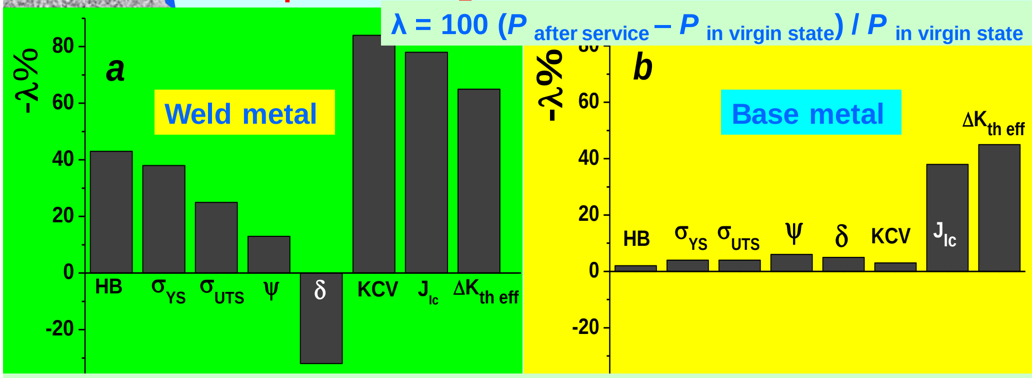
The weld joint was prepared by the multipass electric arc welding of a pipe from heat-resistant 15Kh1M1F steel.

In the initial state all characteristics of the weld metal is better than base metal. But after the operation they became the worst.

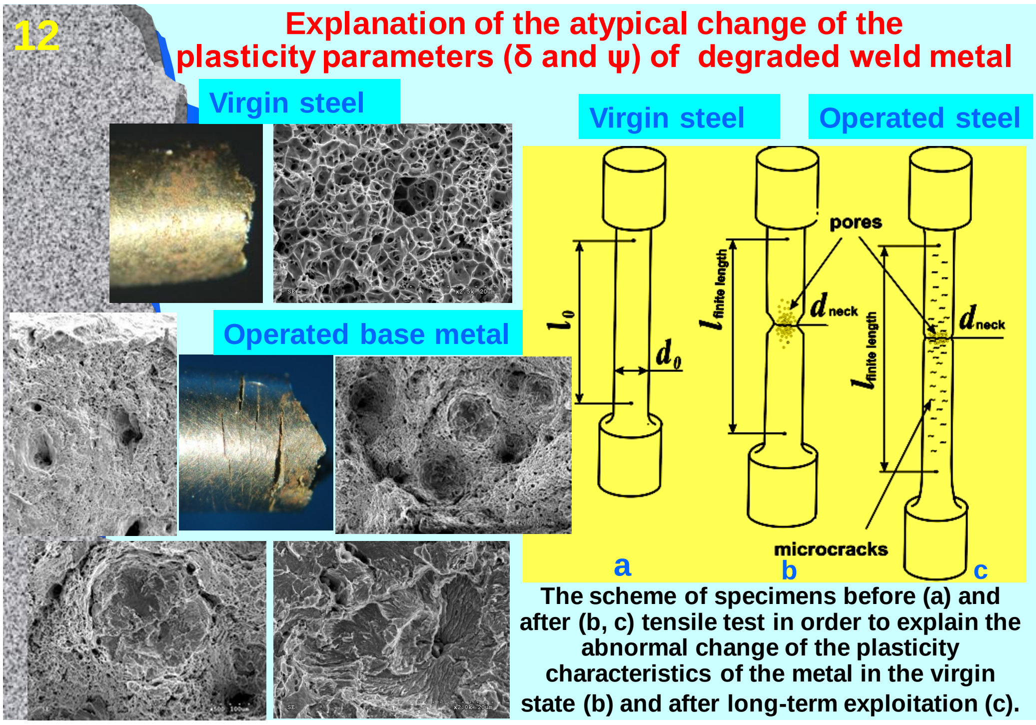
It means that degradation of the weld metal occurs more intensive in comparison with the metal from other zones of the weld joint. This phenomenon should be considered when evaluating operability exploited welds.

11 Sensitivity of different mechanical properties to high temperature degradation of weld and base materials

$\lambda = 100\,(P_{\text{after service}} - P_{\text{in virgin state}}) / P_{\text{in virgin state}}$



Comparison of the sensitivity of mechanical properties to high-temperature hydrogen degradation of WM (*a*) and BM (15Kh1M1F steel, *b*) after ~$2{\cdot}10^5$ h operation on the steam pipeline. For comparison the ratio λ was used. This ratio characterises the relative change of corresponding characteristics for metal after and before operation. Sensitivity to degradation all parameters is much higher for weld metal compared with base metal. Moreover the sensitivity to degradation of the fracture mechanics parameters is much higher than all other for both weld and base metals. Their strength and fracture toughness are simultaneously reduced. This is an unusual tendency of their changes. An untypical change in the mechanical characteristics of operated metal is caused by degradation. And finally an untypical opposite change in the characteristics of plasticity δ and ψ for exploited weld metal was revealed. Usually they are changed in a similar way.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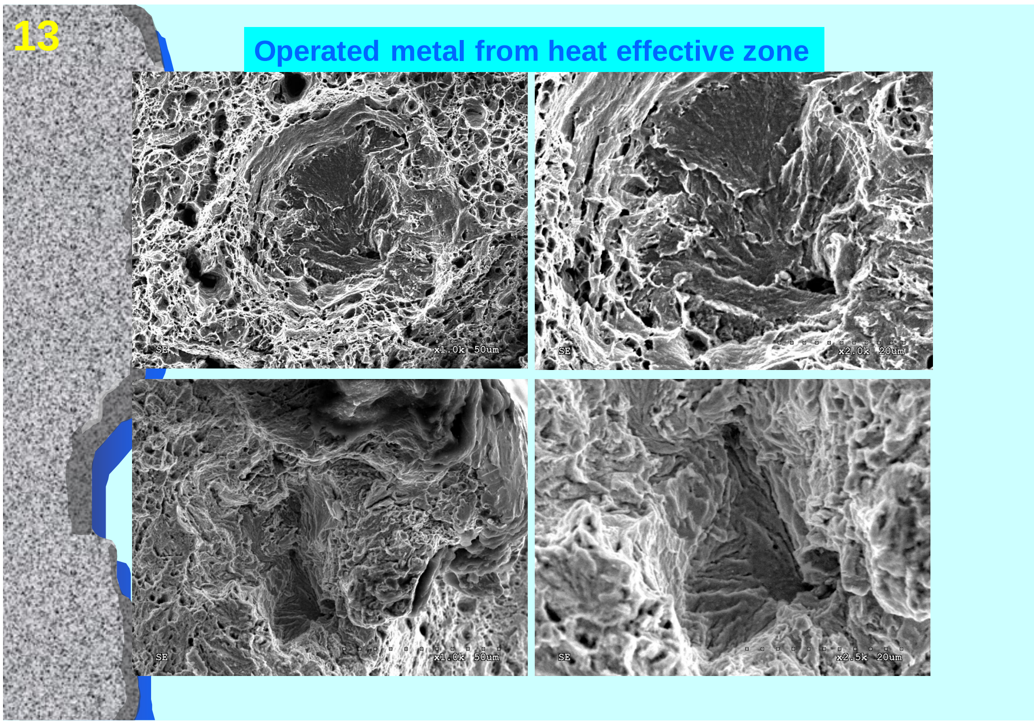
Explanation of the atypical change of the plasticity parameters (δ and ψ) of degraded weld metal
Virgin steel
Virgin steel
Operated steel
Operated base metal
pores
l_0
d_0
$l_{finite\ length}$
d_{neck}
$l_{finite\ length}$
d_{neck}
microcracks
a
b
c
The scheme of specimens before (a) and after (b, c) tensile test in order to explain the abnormal change of the plasticity characteristics of the metal in the virgin state (b) and after long-term exploitation (c).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Operated metal from heat effective zone

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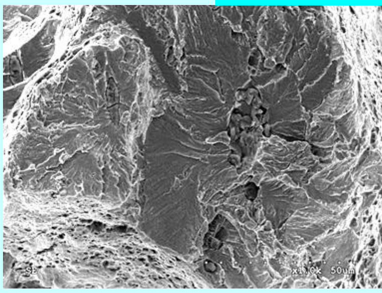
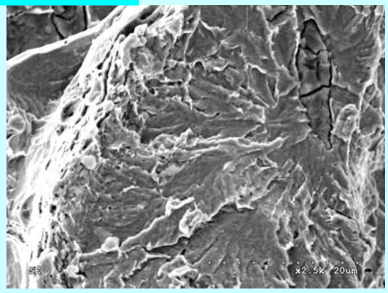
Operated weld metal





These round areas with transgranular cleavage mechanism on the background a ductile dimple structure of fracture surface were not founded in non-operational metal. Therefore, they were considered as fractography evidences of the degradation of metal from different zons of weld joint.

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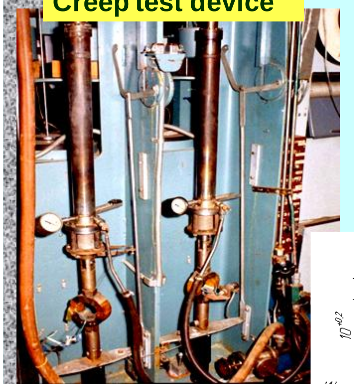
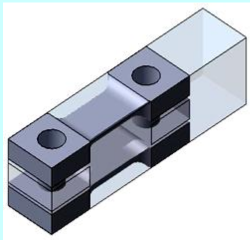
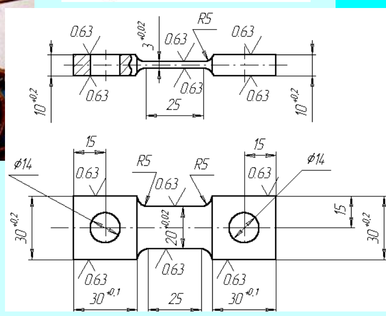
Features of creep test in hydrogen

CREEP TEST was carried out on the 2.25Cr-1Mo and 15Kh2MF steels at temperature 450 °C in air and hydrogen under the pressure 0,3 MPa.

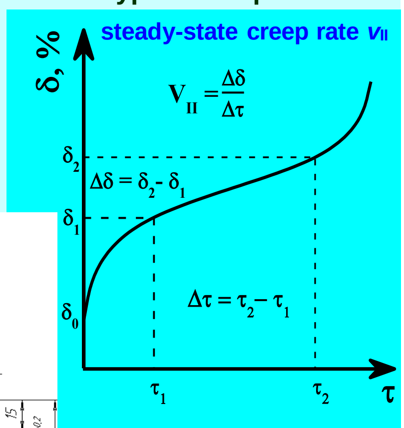
Creep test device







Typical creep curve



Specimen-witness

Specimen configuration for creep test

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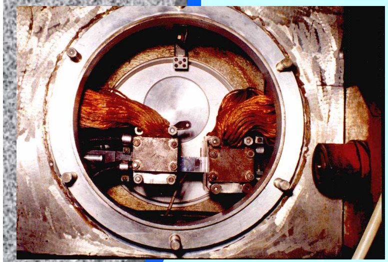
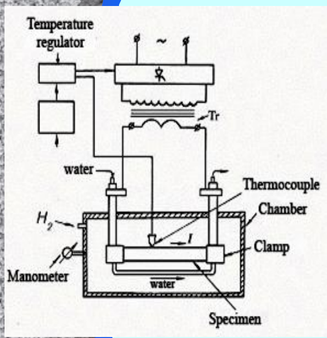
METHOD OF IN-LABORATORY DEGRADATION

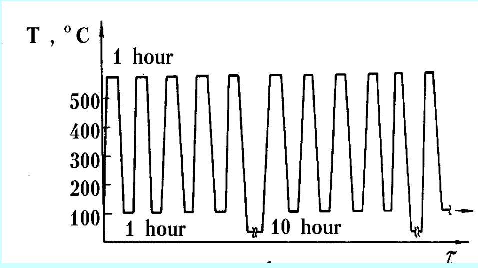
Chamber for thermocycling





The method is based on the thermocycling of specimens in the hydrogen environment. The choice of temperature range is based on the information about the operating temperature of oil hydrocracking reactor or steam pipeline on the power plant.

Thermocycling conditions: in hydrogen under the pressure 0,3 MPa from room temperature up to 450 °C (for 15Kh2MFA) and 570 °C (for 15Kh1M1F and 12Kh1MF steels), holding time at room and high temperature - 1 h, heating and cooling rates – 2 °C/s



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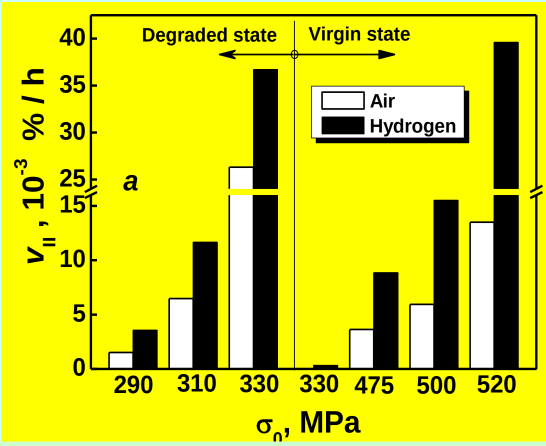
Hydrogen effect on the creep characteristics of the 2.25Cr-1Mo steel of the oil hydrocracking reactor

Steady-state creep rate of steel in air and hydrogen

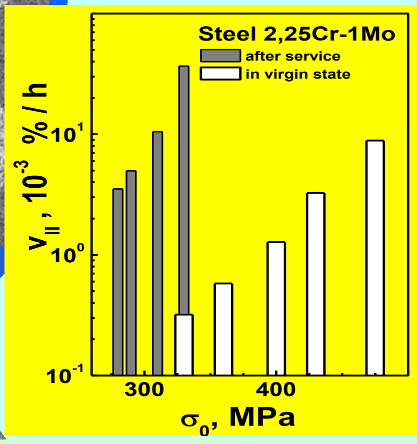


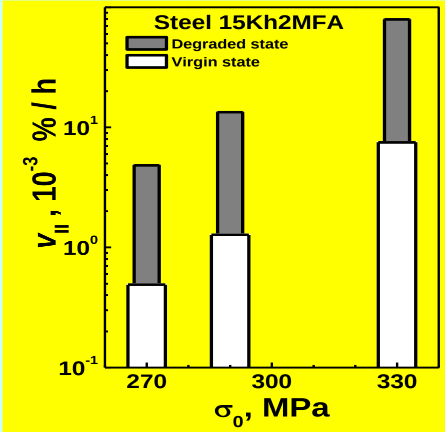
The steady-state creep rate v_{II} at different initial stress levels σ_0 during creep test at a temperature of 450 °C for the 2.25Cr-Mo steel in virgin state (on the right) and after ~$6\cdot10^4$ h holding inside oil hydrocracking reactor as a "specimen-witness" (on the left) obtained in air (white) and hydrogen (black bars).

18 Degradation effect on the steady-state creep rate in hydrogen of 2.25Cr-1Mo and 15Kh2MFA steels

Service degradation
Specimens were held in the reactor for ~6·10⁴ h

In-laboratory degradation
Specimens thermal cycled in hydrogen up to 160 thermal cycles



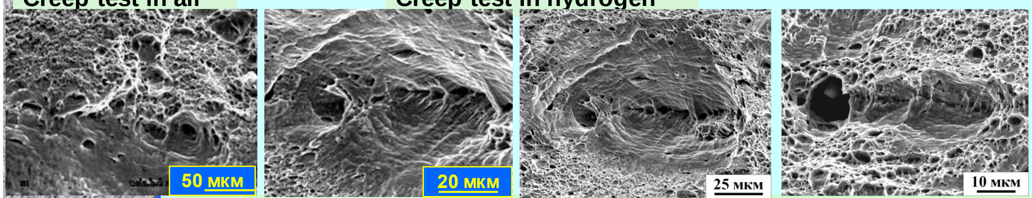


The steady-state creep rate v_{II} at different initial stress levels σ_0 during creep test in hydrogen at a temperature of 450 °C for the 2.25Cr-Mo (*a*) 15Kh2MFA (*b*) steels in virgin state (white column) and after ~6·10⁴ h holding inside a reactor as a "specimen-witness" (*a*, black) and after 160 thermocycles in hydrogen before creep test (*b*, black bars).

19 Hydrogen and degradation effects on the mechanism of creep fracture of the 2.25Cr-1Mo steel

Steel in virgin state — **Exploited steel**

Creep test in air — Creep test in hydrogen



The main feature of the hydrogen effect on the mechanism of steel fracture at creep test is the appearance of large and planar dimples formed by coalescence of smaller pores. Their traces are visible at the bottom of them. Big dimples appear not as a result of ductile fracture of jumpers between neighboring voids and their coalescence, but rather as growth of disk-like cracks under the influence of hydrogen accumulated in the fine pores. Stages of growth of these cracks can be observed on the surface of the planar dimples as oval-shaped markings. During creep testing in air such dimples were not observed. Moreover they are rarely observed on the creep fracture surface of virgin metal, but in operated metal they were dominated on background ductile type small dimples. Therefore, these planar dimples are considered as the fractographic features of hydrogen and degradation effects.

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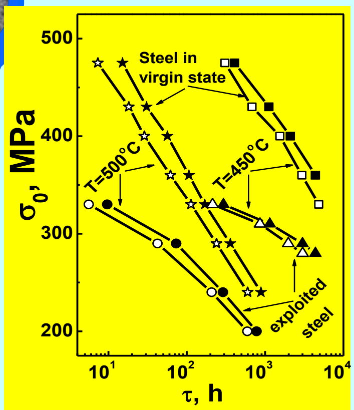
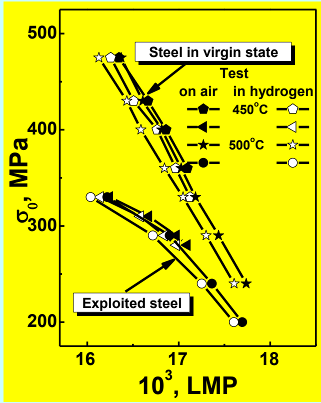
Estimation of the technical state of the 2.25Cr-1Mo steel using Larson-Miller parameter

Traditional long-term strength curves and curves built using Larson-Miller parameter





White points correspond to test in hydrogen, black - in air

$LMP = T(20+\lg\tau_f)$

T, K – test temperature; τ_f, h – failure time of specimens

Using Larson-Miller parameter the data were clearly placed in two separate bands for steel in virgin state and after service during 6·10⁴ h inside reactor.

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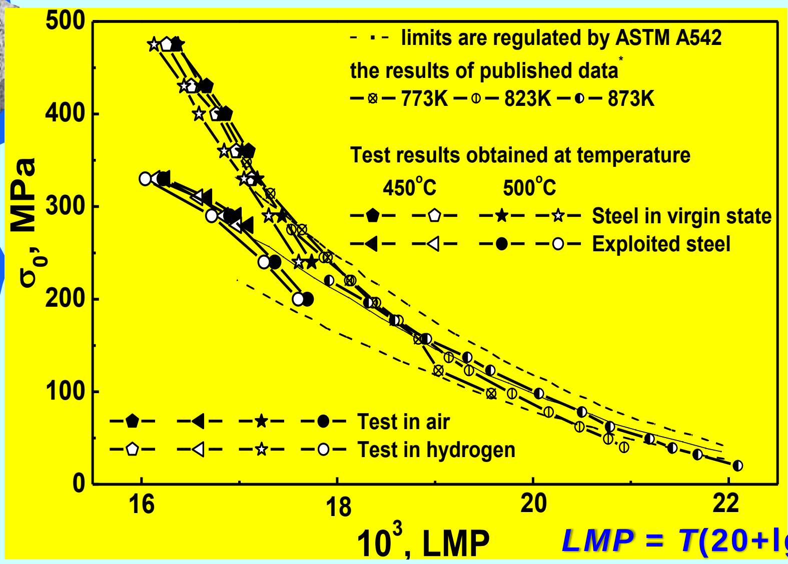
Estimation of the technical state of the 2.25Cr-1Mo steel using Larson-Miller parameter



$LMP = T(20+\lg\tau_r)$

[*A.K. Ray, K. Diwakar, B.N. Prasad, Y.N. Tiwari, R.N. Ghosha, J.D. Whittenberger. // Materials Science and Engineering. – 2007. – A 454–455. – P. 124–131.]

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Therefore the question arises: how to substantiate this critical state of steel?

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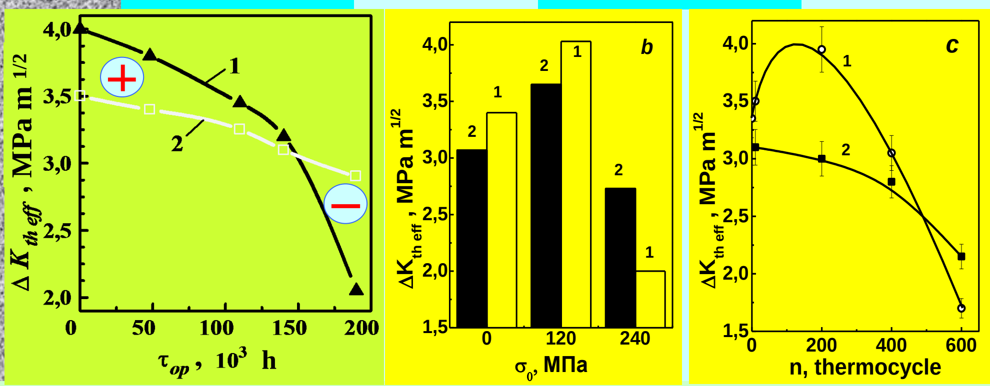
Degradation effect on the effective fatigue threshold of steels

12Kh1MF steel 15Kh2MFA steel



Effect of the service life time τ_{op} of the 12KhlMF steel on the steam pipeline (*a*), stress level σ_0 during 3 months of the isothermal (450 °C) aging (*b*) and a number of thermocycles (20…450 °C) *n* (*c*) in hydrogen of the 15Kh2MFA steel on the $\Delta K_{th\ eff}$ level for the hydrogenated (1) and outgassed (2) metal.
All fatigue tests were carried out in air at T = 20 °C, R = 0.05, and f = 10 Hz.
The ambiguous effect of hydrogen absorbed by metal during degradation was observed. Up to certain degree of steels degradation the $\Delta K_{th\ eff}$ level of hydrogenated metal is higher than for degassed one. After that the opposite tendency was observed.

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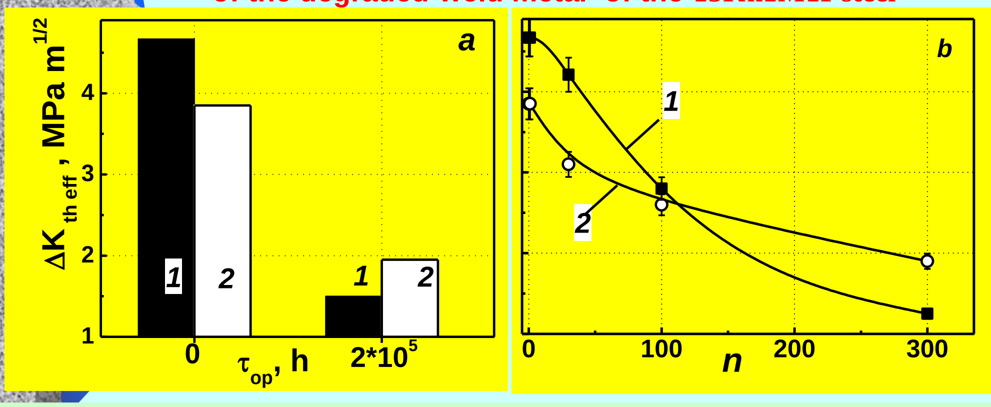
Hydrogen effect on the effective fatigue threshold of the degraded weld metal of the 15Kh1M1F steel



Change of the effective fatigue threshold $\Delta K_{th\ eff}$ of hydrogenated (*1*) and degassed (*2*) weld metal versus operating time τ_{op} (*a*) and a number of thermocycles *n* in hydrogen (*b*).

The ambiguous effect of hydrogen on the effective fatigue threshold was obtained for the weld metal degraded in service and laboratory conditions. Taking into account the dangers of reducing the crack growth resistance under the influence of hydrogen absorbed by metal during degradation it was suggested the state of metal at the point of intersection of curves for hydrogenated and degassed metal corresponds to a critical one.

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Method for estimation of the technical state of degraded steel taking into account shutdowns

To substantiate a method the following should be done:

- to show the correspondence of the structure changes of steel after degradation in service and in-laboratory conditions
- to estimate the critical state of degraded steel
- to propose the way for estimation of the steel technical state taking into account the number of shut-downs during long-term service.

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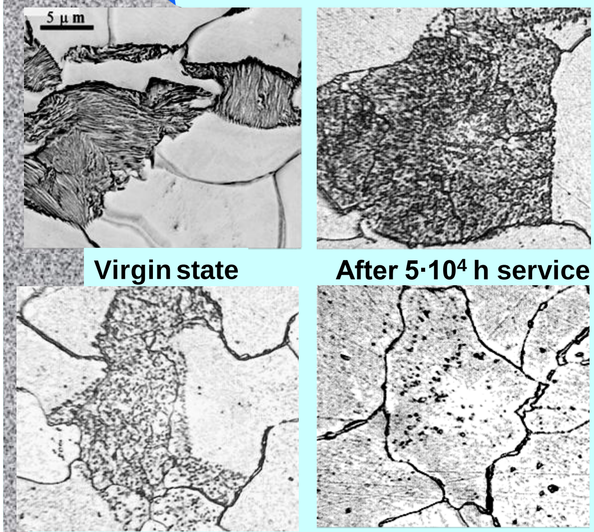
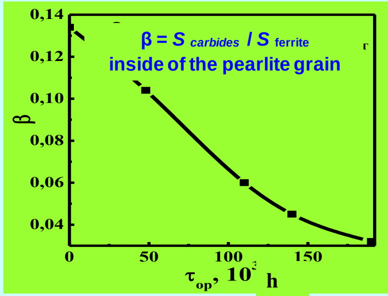
The structure changes of the 12Kh1MF steel after degradation in-service condition



Virgin state After $5\cdot10^4$ h service

After $11\cdot10^4$ h service After $19\cdot10^4$ h service

Change of 12Kh1MF steel structure after different service time at the steam pipeline



The main structural change take place inside perlite grains. There are spheroidizing and dissolution of cementite inside perlite grains and relocation carbides on the grain boundaries. The perlite grain boundaries dissipate and practically ferrite structure with big carbides along grains boundaries was obtained after more than 20 years of service. The ratio of the areas that correspond to ferrite and carbides in pearlite grains decreases with increasing of the steel operation time.

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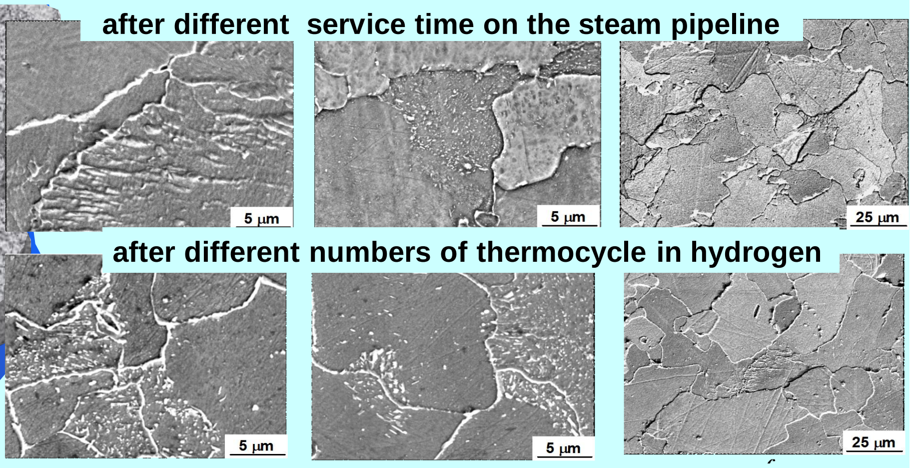
Comparison of the 12Kh1MF steel structure after degradation in service and laboratory conditions

after different service time on the steam pipeline

after different numbers of thermocycle in hydrogen



The microstructure of 12Kh1MF steel in virgin state (*a*), after $14\cdot10^4$ (*b*) and $19\cdot10^4$ (*c*) hours of service and after 50 (*d*), 150 (*e*) and 300 (*f*) thermocycles in hydrogen.

Structure changes in service and in-laboratory conditions is practically the same. But in-laboratory conditions the degradation of specimens was realized during few weeks whereas in-service one during more than 20 years. It enables us to state that shutdowns during operation are responsible for the structural changes of steel too.

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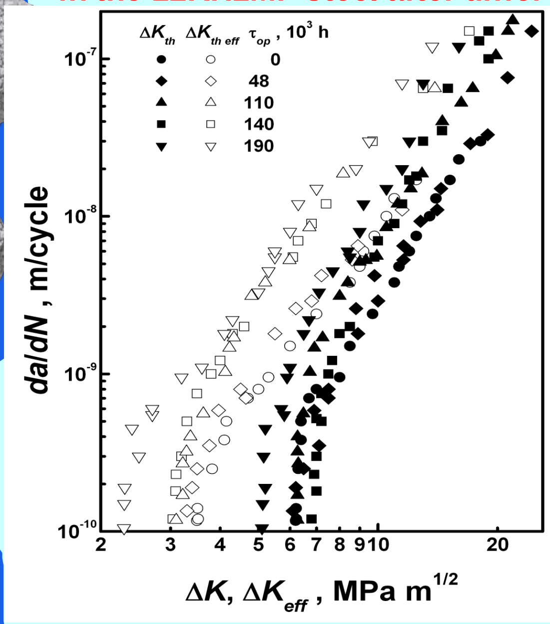
Fatigue crack growth rate in the 12KH1MF steel after different time of service



The nominal *da/dN* – ΔK (dark marks) and effective *da/dN* – ΔK_{eff} (light marks) diagrams of the fatigue crack growth for the 12Kh1MF steel after operation on the steam pipeline during different operation time τ_{op}.

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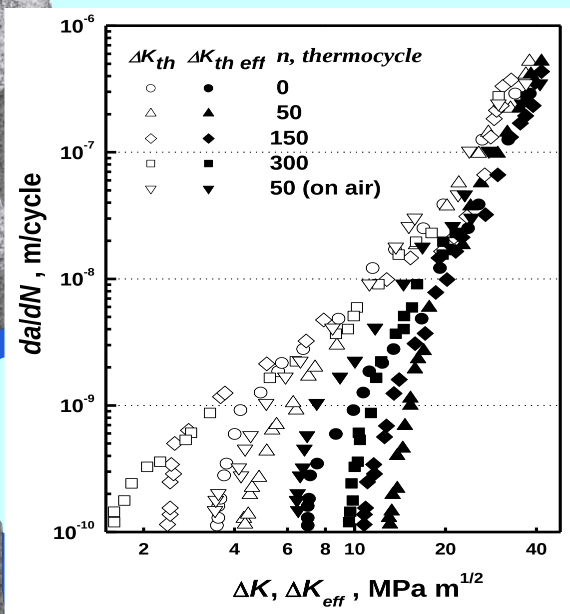
Fatigue crack growth rate in the 12KH1MF steel after thermocycling in hydrogen



The nominal *da/dN* – ΔK (dark marks) and effective *da/dN* – $\Delta Keff$ (light marks) diagrams of the fatigue crack growth for the 12Kh1MF steel after different number of thermocycles *n* in hydrogen and in air.

In both cases of degradation (in-service and laboratory conditions) the main effects of degradation are in the vicinity of threshold fatigue levels. Therefore the analysis of these levels is the most informative.

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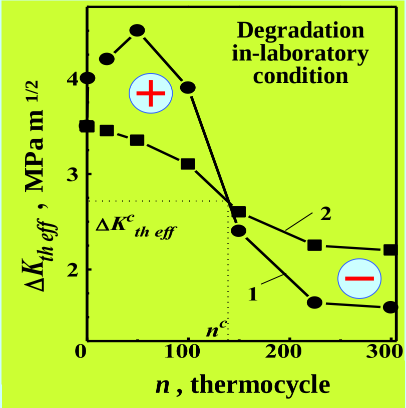
Estimation of the critical state of degraded 12Kh1MF steel



The effects of number thermocycles during degradation in model laboratory condition on the effective fatigue thresholds of the 12Kh1MF steel was estimated. Dependences $\Delta K_{th\ eff} - \tau_{op}$ were plotted for the 12Kh1MF steel tested after degradation (*1*) and after following vacuum degassing (*2*). If the number of thermocycles is less than n_c, internal hydrogen increases the $\Delta K_{th\ eff}$ levels of hydrogenated metal compared to the degassed one. After exceeding n_c the $\Delta K_{th\ eff}$ of hydrogenated metal becomes less than for degassed one. It means that after exceeding n_c steel steel becomes susceptible to hydrogen embrittlement. The critical state of degraded steel was determined in the crossing point of both dependences.

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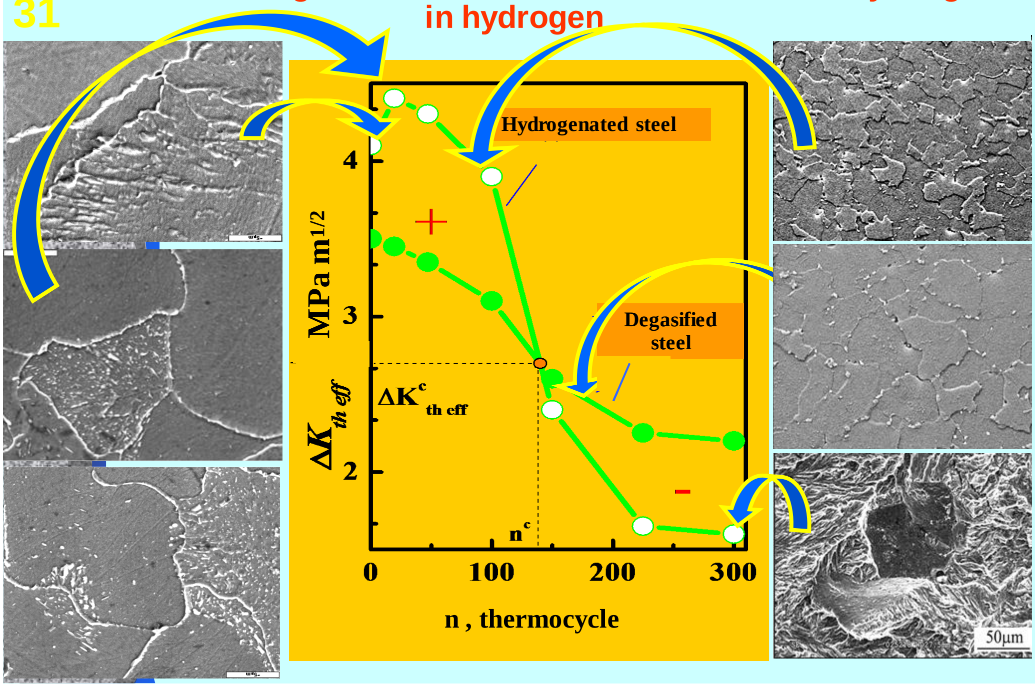
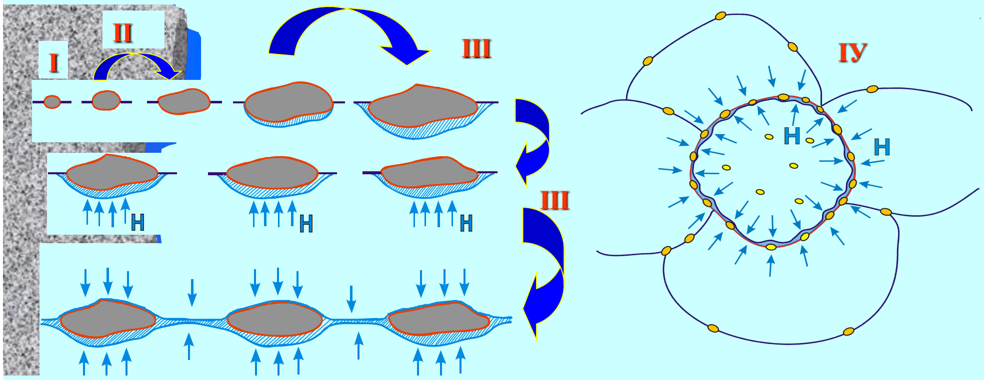
Structure change of the 12Kh1MF steel after thermocycling in hydrogen



32 The scheme of the step-by-step structure changes during degradation of heat resistant steels in hydrogen



During the first stage carbides relocate on the grain boundaries. During the second - carbides grow. During the third – the pores are nucleated, grew, coalescence and formed a chain of pores along the grain boundaries. The hydrogen accumulates inside them and facilitates their coalescence. And during the forth stage – the big defects comparable with the grain size and separated from the neighboring grains are appeared. It means that random way scattered big damages are appeared inside the metal. The metal still preserves the integrity, but the network of randomly placed large defects were already existed and weaken the working section of the structural elements. This is very dangerous if the hydrogenation of degraded metal is possible.

33 Approach for estimation of the technical state of exploited steel with account of shut-downs number during long-time service

The technical state of exploited metal was proposed to estimate in dependence of effective service time τ_{eff} (instead of nominal time τ_{op}). Its value was calculated by the empirical formula which took into account the τ_{op} values and the numbers of forced and planned shutdowns during service of steel on the steam pipeline:

$$\tau_{eff} = \tau_{op}\,[1+k] \quad ; \quad k = m\cdot(N_{for} / N_{\Sigma})^{n}$$

Coefficients m and n account possible effect of different cooling rates during planned and forced shutdowns and an influence of excess hydrogen inside the metal on acceleration of degradation process due to shutdowns respectively. Then equation for estimation of shutdowns effect on the steel degradation was written as $k = 5\cdot(N_{for} / N_{\Sigma})^{2}$.

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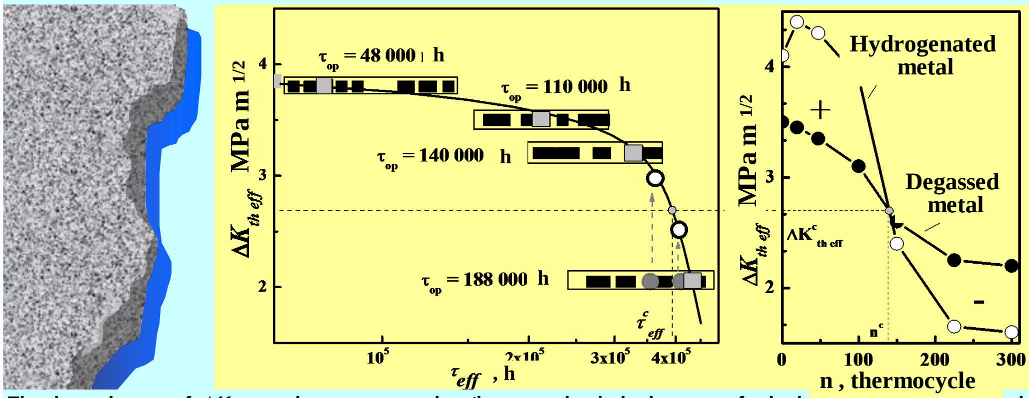
Realisation of approach to estimation of technical state of exploited 12Kh1MF steel with account of number shut-downs



The dependences of $\Delta K_{th\,eff}$ value versus number thermocycles in hydrogen *n* for hydrogenated and degassed steel allows to substantiate the critical state of degraded steel. The base diagram $\Delta K_{th\,eff} - \tau_{eff}$ for estimation of the technical state of the 12Kh1MF steel after service at different τ_{op}, N_{for}, N_{Σ} is shown on the left. Gray data points are obtained as a result of experimental estimation of effective fatigue threshold levels and calculation of corresponding τ_{eff} levels with the use of proposed expression. Black data points are obtained without realisation of fatigue test but only by calculation of τ_{eff} levels for steels from another power units for four selected operation times but at corresponding number of shut-downs for each of them. They are within the ranges of four selected operation times. For metal from two blocks with practically identical time operation, but with different numbers of shutdowns experimentally determined the effective fatigue thresholds. It was found that both round gray points are moved from the region black points on the base curve if accounting the corresponding values of effective threshold fatigue. It means that all calculated black points for another power units can be projected onto the base diagram without carrying out fatigue test. If thus obtained new data points will be situated on the left from the point corresponding to critical technical state of steel than the metal has not yet reached a critical level of degradation. In the opposite case the metal becomes sensitive to the hydrogen embrittlement and danger of incidents increases.

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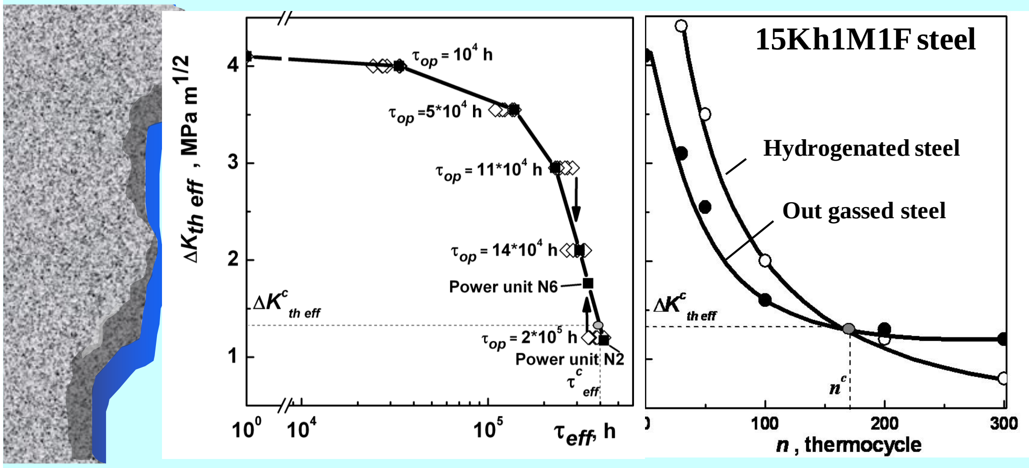
Estimation of technical state of exploited 15Kh1M1F steel with taking account of number shut-downs



After fatigue test of metal from both power units the $\Delta K_{th\ eff}$ values were obtained. Corresponding values of the effective time were calculated. According to the obtained points (black rhombus) a base curve was built. It was found the degree of degradation of metal from unit number 2 after greater number of shut-downs exceeded of the critical level, whereas for metal from unit number 6 with less number of shut-downs did not achieve this level. Therefore the pipes from unit number 2 must be changed whereas the pipe from unit number 6 can continue to operate.

Fractographic features of fatigue crack growth caused by operation of the 15Kh1M1F steel at different numbers of shutdowns

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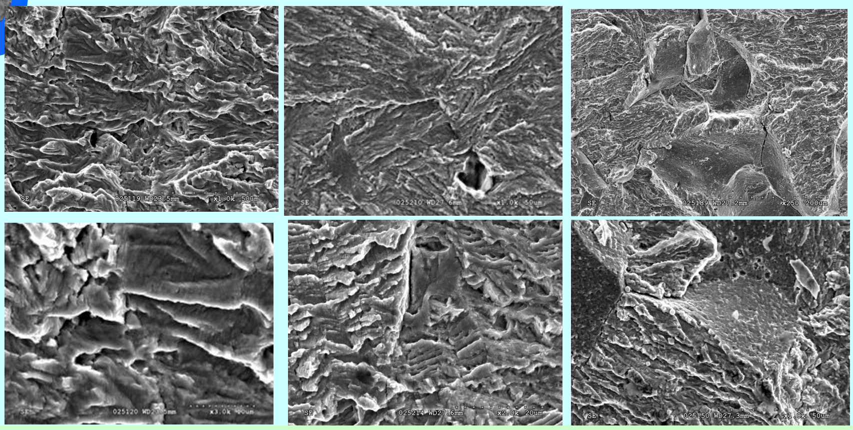
In virgin state

After operation during $2 \cdot 10^5$ h
at a smaller and greater
of shutdowns numbers



Areas of intergranular fracture on the background of classical relief of transgranular fatigue were identified in the steel after more shutdowns process. These regions were considered as the traces of damages formed during the operation and opened during fatigue testing.

Effect of numbers of shutdowns during operation of the 15Kh1M1F steel on its fracture toughness and fractographic features of fracture

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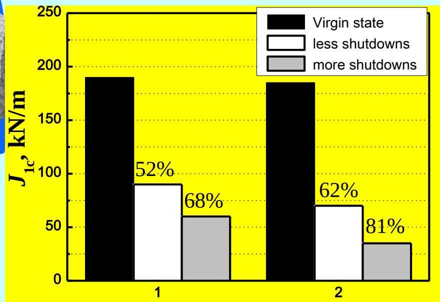
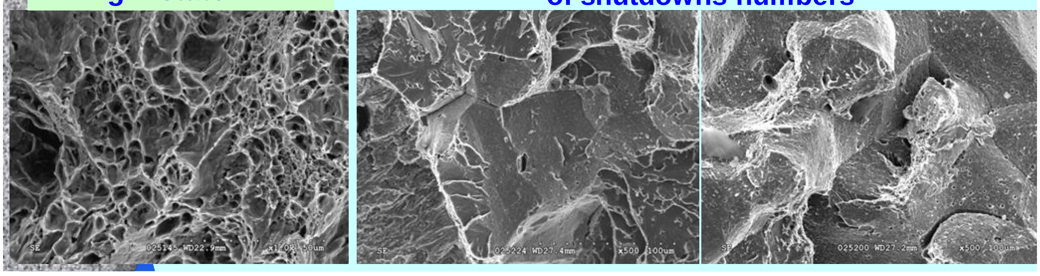


Fracture toughness J_{Ic} of the 15Kh1M1F steel in virgin state (black columns) and after ~$2 \cdot 10^5$ h operation at less (white columns) and more (grey columns) numbers of shutdowns, obtained on the tangential specimens cut out near external (1) and internal (2) surface of pipes.

After operation during $2 \cdot 10^5$ h
at a smaller and greater
of shutdowns numbers

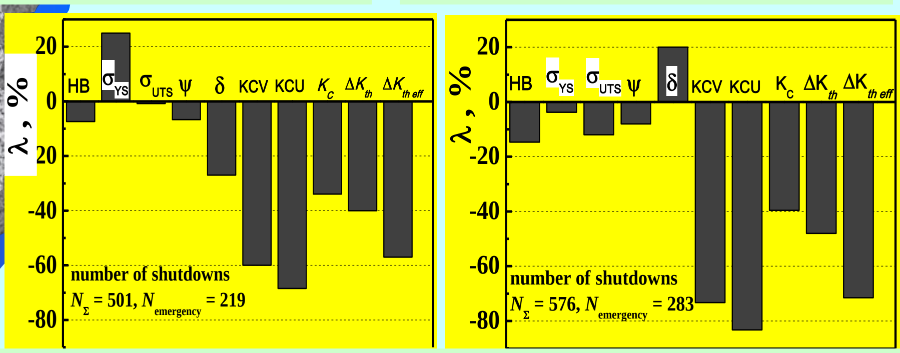
In virgin state



38 Comparison of the mechanical characteristics of exploited steel 15Kh1MF for their sensitivity to degradation

Effect of the process shutdowns at the different mechanical characteristics

Steel subjected less of shutdowns | **Steel subjected more of shutdowns**



Comparison of the sensitivity of mechanical properties to high-temperature hydrogen degradation of the 15Kh1M1F steel after ~$2\cdot10^5$ h operation at less (a) and more (b) numbers shutdowns of the process on the steam pipeline. Ratio λ characterizes a relative change of corresponding characteristics for steel after and before exploitation.

$$\lambda = 100\,(P_{\text{after service}} - P_{\text{in virgin state}}) / P_{\text{in virgin state}}$$

39 CONCLUSIONS

1. It is shown that independently of the conditions of degradation (in-service or in-laboratory) the effective fatigue threshold level of heat-resistant steels is one of the most sensitive parameters of fracture mechanics to high-temperature hydrogen degradation. This parameter uniquely decreases with increasing degree of degradation heat resistant steels.
2. Degradation of the heat resistant steels by thermocycling of specimens in hydrogen in a few weeks leads to the practically same change in the structure, as well as its operation in the steam pipeline of heat power plant during 20 years.
3. An ambiguous effect of internal hydrogen (accumulated by metal during thermocycling of specimens in hydrogen) at his effective fatigue threshold level was revealed. This phenomenon was used to substantiate a critical state of the degraded steels.

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4. **The approach for evaluation the technical state of exploited steels taking into account the effect of process shut-downs was proposed. Basic diagrams for 12Kh1MF and 15Kh1M1F steels enable to determine the technical state of degraded steels taking into account the intensifying effect of shut-downs on their degradation. It's enough to use the data of monitoring of the operating parameters during all time of operation steel on the steam pipelines.**
5. **By fractography analysis the defects caused by degradation of steels were revealed. They are randomly distributed in the bulk of metal and weaken the grain boundaries. During uniaxial loading test on the air of preliminary hydrogenated smooth specimen, these defects open and form round areas of transgranular fracture on the background of a ductile dimple relief. During creep test of degraded steels they form disk-like cracks on the background of ordinary ductile dimples. During fracture toughness and fatigue tests of degraded steels they are detected in the form of intergranular fracture.**