# Hydrogen Effect on the Mechanical Properties and Fracture Mechanism of the Degraded Welded Joints from Steam Pipeline

Oleksandra Student[1,a], Andriy Markov[1,b]

[1]Karpenko Physico-Mechanical Institute of the NASU, 5, Naukova St., 79601 Lviv, Ukraine

[a]student@ipm.lviv.ua, [b]markov@ipm.lviv.ua

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**Abstract.** It is shown that hardness, impact toughness, mechanical properties in tension, and the local parameters of fracture mechanics (static and cyclic crack growth resistance) are sensitive to the operating degradation of weld metal of steam pipelines of thermal power plants made of 15KhlMlF steel. The simultaneous decrease in the resistance to brittle and plastic fracture (hardness, strength, and impact toughness) represents a phenomenon of the operating degradation of weld metal. We have established a specific correlation between the characteristics of plasticity and other mechanical parameters of operated metal: the increase in δ of operated weld metal is in good agreement with the decrease in its strength, whereas the reduction of ψ correlates with the lowering of the resistance to brittle fracture. Electrolytic hydrogenation decreases the characteristics of strength and plasticity of operated weld metal much stronger than in the initial state and allow us to reveal the change of the weld metal and the base metal state after its service using integral mechanical properties. The anisotropy of the change of the weld metal mechanical properties after degradation under service conditions was revealed. A simulation of welding joint degradation, using in-laboratory method of thermal cycling in hydrogen environment, enables to substantiate the critical state of the weld metal by appearance of inversion effect of absorbed hydrogen on $\Delta K_{th\ eff}$ parameter. The ductile fracture of nonoperated metal is replaced by brittle intergranular failure in the operated metal. According to these results the method for estimating the state of the degraded weld metal, taking into account hydrogenation, is may be created.

## Introduction

Assessment of serviceability of heat-power engineering and petroleum equipment is a very actual task for Ukraine. The non predicted failures of equipment such as steam pipelines of thermal power plant (TPP) lead to great economic loss and serious ecological consequences. One of the main reasons of the workability loss of an such equipment is the degradation of heat-resistant steel during long-term operation. The aggressive conditions (high temperature environment and high stress level) intensify the structural changes in the metal [1], promote creep [2-5], and decrease the residual plasticity [6], static [7], fatigue [8-12] and corrosion-fatigue crack growth resistance of the exploited metal. Peculiar role of hydrogen in high-temperature degradation processes should be noted too.

The service damages of the heat-resistant steel equipment are caused more frequently by welding joints (WJ) [5]. Under combined long-term influence of hydrogenating environment and mechanical loading WJ are very sensitive to brittle fracture. The macro- and micro heterogeneity of chemical composition, structure and mechanical properties promote this fracture. Structural microdefects in WJ are energy-profitable traps for hydrogen getting into the metal during welding and from service environment. High-gradient residual stress fields in WJ provide hydrogen distribution inside WJ and make them very sensitive to hydrogen effect. Therefore it is supposed that the degradation inside the weld metal (WM) in hydrogen environment will be more intensive compared to the base metal (BM). Hence the investigation of degradation effect on the mechanical properties of WJ metal in high-temperature hydrogen environment is the important task of modern materials science.

**The aim of this paper** is to establish the WJ metal state and its serviceability in large-scale welded constructions based on investigations of the mechanical properties of heat-resistant steel steam pipelines WJ after high-temperature hydrogen degradation in modeling and service conditions.

**Testing technique**

The mechanical properties of the metal form different WJ zones made of low-alloying heat-resistant 15Kh1M1F steel in a virgin state and after high-temperature hydrogen degradation in model and service conditions were investigated.

The WJ from the vertical part of a steam main pipeline of TPP, made of 15Kh1M1F steel and after operation for ~ $2{\cdot}10^5$ h. was used. For comparison, a model WJ, which was used as the metal in the initial state was investigated. The external diameter and wall thickness of welded pipes were 325 mm and 65 mm, respectively. The model WJ was manufactured by the multipass electric arc welding with TML-3U electrodes according to the technology of carrying out repair welds accepted at the TPP. Prior to welding, the pipes were heated to a temperature of 300 °C. For one pass, we put a bead of thickness 4–6 mm. After welding the part of the pipeline with the WJ was slowly cooled (for 6 h) under heat-insulating mats, again heated to 600°C at a rate not higher than 200°C/hour, and, having reduced the heating rate to 100 °C/hour, brought up the temperature to 735 ± 15°C with subsequent holding for 3 h. The chemical composition of WM corresponds to 09KhlMF steel.

The service degradation in the laboratory was simulated using express-technique [10] of specimens thermocycling in hydrogen environment (hydrogen pressure 0.3 MPa) from operating temperature for a steam pipeline 570 $^{o}$C till room temperature. In this case the heating and cooling rate was about 2 $^{o}$C/s and soaking time under each temperature – 0.5 h.

To analyze the state of the metal the characteristics of Brinell hardness (HB), impact toughness (KCV), tensile strength and plasticity in air and under electrolytic hydrogenating conditions were used. The impact toughness was evaluated on the axial (*L-R*) and unaxial (*R-C*) specimens. Tensile mechanical properties were termined using smooth cylindrical specimens with a diameter of 3 mm. One part of these specimens was oriented along to the pipe axis (the investigated zone was located in the middle of specimen), other parts of specimens were oriented tangentially and radially in the diametric cross-section of the pipe (the whole specimen was placed in the investigated zone of WJ). Specimens were tested with loading rate $3{\cdot}10^{-3}$ $s^{-1}$ employing testing equipment UME-10T. For electrolytic hydrogenating this equipment was supplied with electrochemical cell. Specimens were preliminarily electrolytically hydrogenated for 15 min in a solution of sulphuric acid (pH 0) with an admixture of 2 g/l. of thiourea at the current density was 50 mA/cm$^2$.

The crack resistance parameters were established after fatigue testing of beam notched specimens (12×18×160 mm) in air under cantilever bending loading. Kinetic fatigue diagrams were built in the nominal and effective (taking into account crack closure) coordinates. The nominal $\Delta K_{th} = K_{th\,max} - K_{th\,min}$ and effective $\Delta K_{th\,eff} = K_{th\,max} - K_{th\,cl}$ fatigue thresholds were defined. The value $K_{th\,cl}$ corresponds to the part of the loading cycle at which the metal near the crack tip is cyclically nondeformed. This value was obtained by a compliance method.

The critical value of the *J*-integral $J_{Ic}$ was evaluated under three point bending testing [13] using the method of repeated partially unloading of the specimens.

## Results of Investigations and Discussion

*Mechanical properties*. It is shown that despite of the low sensitivity of integral mechanical properties of BM of the steam pipeline to degradation, these properties for WM considerably decrease after its service (Fig. 1). In the virgin state the WM mechanical properties (hardness and impact toughness) are higher than the corresponding properties of the BM. This is in agreement with the operative standard specifications and norms currently in force. But after ~$2{\cdot}10^5$ hour operating time the BM properties are practically invariable while hardness and impact toughness of WM become lower as prescribed critical level for the metal of steam pipelines.

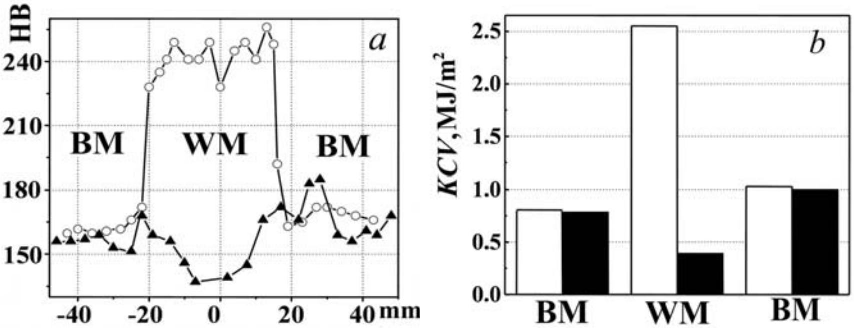



Fig. 1. Hardness *HB* distribution (*a*) and impact toughness *KCV* (*b*) for nonoperated (light) and exploited (dark symbols and bars) of 15Kh1M1F steel WJ.

Unlike the insignificant change of the strength and plasticity of the exploited BM, these tensile parameters of WM after service on the steam pipeline significantly decreased ($\sigma_B$ by 26 %, $\sigma_{02}$ by 37 %), but the plasticity parameters are changed atypically ($\psi$ decreases by 13 %, $\delta$ increases by 25 %). More intensive, compared to BM, degradation of WM can be caused by the aggressive influence of the working environment as a metal hydrogenating source. The hydrogen promotes the diffusion processes and consequently the changes of microstructure. The evaluated integral hydrogen concentration in the exploited metal of WJ is higher to compare to the virgin state (in BM hydrogen concentration increase by 30 %, in WM – 3 times).

In general the influence mechanisms of hydrogenation on mechanical properties of nonoperated metal are investigated in detail. Concerning the exploited BM and particularly WM these peculiarities are undiscovered. In our experiments to exclude possible effect of preliminary absorbed hydrogen on the mechanical properties of WJ, the specimens before tests were degassed in vacuum for 2 h. at temperature 540 $^{o}$C (operating temperature for steam pipelines). The obtained results show (Fig. 2) that electrolytic hydrogenation during tensile testing allow us to reveal the change of BM state after its service using the integral mechanical properties. Without hydrogenation it is impossible because the strength and plasticity of BM are low sensitive to the change of the metal state owing to the exploitation.

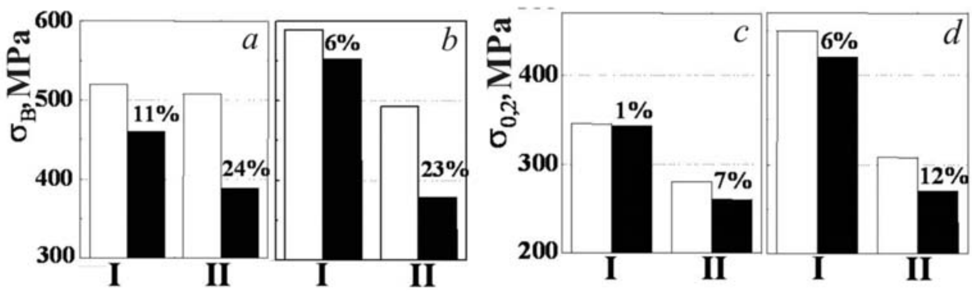



Fig. 2. Characteristics of strength (*a, b*) and plasticity (*c, d*) of WM from nonoperated (I) and operated for ~ $2{\cdot}10^5$ h (II) WJ of 15Kh1M1F steel, obtained in air (light bars) and under electrolytic hydrogenation (dark bars). Numbers indicate the relative change of the suitable characteristics.

After hydrogenation the ultimate strength ($\sigma_B$) and yield strength ($\sigma_{02}$) of the non-operated BM decreased by 11 % and less than 1 %, but for exploited BM – by 24 % and 7 % respectively (Fig. 2 *a*, *c*). Thus in spite of the low sensitivity of tensile strength in air to BM degradation, electrolytic hydrogenation improves significantly this sensitivity. Similar tendency was revealed also for WM (Fig. 2, *b*, *d*). In particular, hydrogenation decreases the ultimate strength and yield strength of WM in the initial state by 6 %, while for operated WM – by 23 % and 12 %, respectively.

*Sensitivity of mechanical properties to WJ metal degradation depending on specimen orientation.* Strength characteristics of WJ evaluated in air on the differently directed specimens show that radially oriented specimens (across the pipe wall) are the most sensitive to the changes in WM after its long-term service (Fig. 3). However in the power-generating industry for testing of the metal state, longitudinal and tangentially oriented specimens are generally used (for WM there are specimens cut across the WJ axis or along beads overlapping direction). According to the obtained results these specimens are less suitable for this purpose. Therefore in order to estimate the state of the exploited WM, the radially directed specimens are recommended to be used.

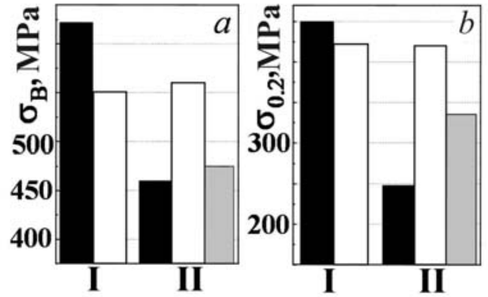



Fig. 3. Characteristics of strength in air for WM nonoperated (I) and operated 15Kh1M1F steel (II) welded joints determined on radially (black bars), longitudinal (light bars) and tangentially (grey bars) oriented specimens.

The impact toughness *KCV* of WJ is depends also on the specimen orientation (Fig. 4). In particular the *KCV* level of BM in initial state and after service, determined on radially directed specimens, is much lower to compare with longitudinally directed specimens. It is due to the metal texture along the pipe axis. Specimens orientation effect increases in BM after service and may be caused by delamination along segregative bands after metal exploitation. At the same time the *KCV* values for the WM are low-sensitive to the specimens orientation change (Fig. 4).

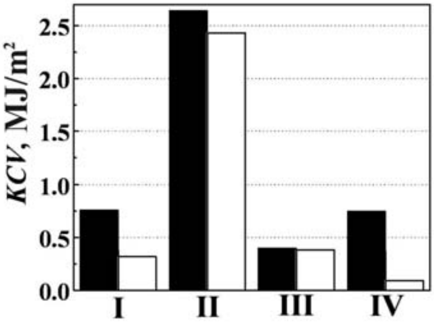



Fig. 4. Impact toughness of nonoperated BM (I) and WM (II) and operated WM (III) and BM (IV) evaluated on radially oriented *R-C* (light bars) and longitudinal *L-R* (dark bars) specimens.

Hence the presented results show more intensive degradation during service of WM as compared to BM. Also the possibility (due to electrolytic hydrogenation) to estimate the state of degraded metal from different zones of WJ using the integral mechanical properties was shown. The different sensitivity to the state of the operated WJ metal depending on specimens orientation was shown and peculiarities of fracture mechanism under hydrogen effect have been demonstrated.

*Crack growth resistance tests.* It was shown that in the initial state WM has higher static crack growth resistance – the critical value of *J*-integral $J_{1c}$ (Fig. 5). Thus, WM in initial state has better properties such as hardness, impact toughness, tensile properties and static crack growth resistance, to compare to BM in the initial state. As a result of exploitation the crack growth resistance of all WJ zones decreases and this confirms the decrease of this factor sensitivity to the change of the metal state due to exploitation of WJ zones (including BM). But the maximum decrease of $J_{1c}$ value (in 4.5 times) was for WM, thus proving once more the lowest stability of WJ mechanical properties due to high-temperature operation in hydrogenation environment. Moreover, unlike the integral mechanical factors of the metal state considering the change of this local parameter ($J_{1c}$) makes it possible to estimate not only the WM state but also the BM state after service.

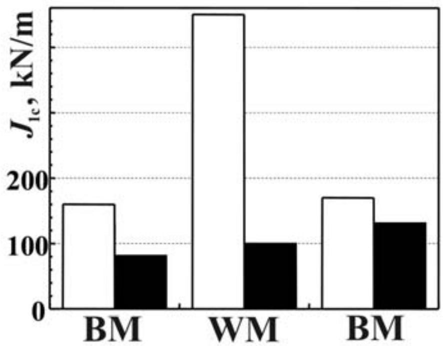



Fig. 5. fracture toughness $J_{Ic}$ of WJ metal in the initial state (light bars) and after service (dark bars) of the WJ metal of 15Kh1M1F steel. Specimens are oriented longitudinally.

Fatigue crack growth resistance tests at the threshold values of stress intensity factor (SIF) $\Delta K$ give higher fracture locality, compared to static crack growth resistance tests, and thereby are attractive for steel degradation analysis. As the mechanical factor of state of degraded WM the threshold value of the effective SIF $\Delta K_{th\,eff}$ range was used. The specimens were tested in the initial state, after ~$2\cdot10^5$ h operation on the steam pipeline and after degradation in laboratory conditions by thermocycling in hydrogen. The influence of hydrogen, absorbed during degradation, on this factor was evaluated. Specimens were hydrogenated by holding them for 2 h. in pure hydrogen at pressure 0.3 MPa and temperature 570 $^{o}$C. in this case it was considered that WM was saturated with hydrogen but due to the low exposure time under high temperature no changes in the metal occur. The $\Delta K_{th\,eff}$ value of the hydrogenated WM was compared to the corresponding values for WM after 2 h of vacuum outgassing.

The positive effect of hydrogen absorbed by WM on $\Delta K_{th\,eff}$ level in the initial state (Fig. 6 *a*) was revealed. This phenomenon agrees with known relationships of hydrogen effect on the effective fatigue crack growth resistance threshold of low-alloy and heat-resistance steels. Moreover for operated WM the $\Delta K_{th\,eff}$ values are lower than for the outgassed metal (Fig. 6 *a*).

A revealed negative hydrogen effect on the effective threshold of fatigue crack growth resistance of the exploited WM indicates its tendensy to hydrogen embrittlement and doubts its further service. Moreover the decrease of the $\Delta K_{th\,eff}$ level of exploited WM, compared to the nonoperated WM, more than in 3 times is the evidence of its very intensive degradation during service.

To substantiate the critical state of the degraded WM, the specimens from WJ have been tested after different number of thermocycles in pure hydrogen before and after outgassing. It was revealed that $\Delta K_{th\,eff}$ levels of hydrogenated and outgassed WM decrease with increase of the number of thermocycles in hydrogen.

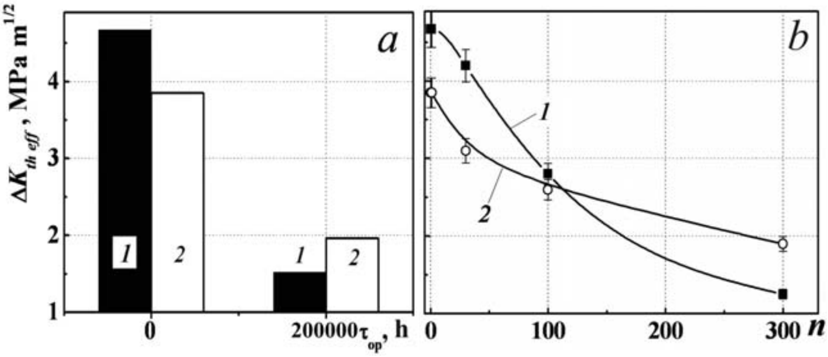



Fig. 6. Change of the effective fatigue crack growth resistance threshold $\Delta K_{th\ eff}$ of hydrogenated (*1*) and outgassed (*2*) WM versus operating time $\tau_{op}$ (*a*) and a number of thermocycles *n* in hydrogen (*b*).

The point of intersection of curves for hydrogenated and outgassed WM indicates such metal state at which positive effect of hydrogen on $\Delta K_{th\ eff}$ level changes to negative (Fig. 6 *b*). This state of degraded metal is suggested to be the critical because on it's reaching the WM became inclined to local hydrogen embrittlement. The correlation between operating time and number of thermocycles can be a ground for establishing a critical service time and residual lifetime of the steam pipeline.

Summarized results on the change of mechanical factors of WJ metal state after service were compared by their sensitivity to hydrogen degradation (Fig. 7). Practically all the most used mechanical properties are sensitive to WM state change after degradation. At the same time for BM only local parameters of fracture mechanics $J_{Ic}$ та $\Delta K_{th\ eff}$ are sensitive to the degradation. Furthermore for the same service time on the steam pipeline the sensitivity of these parameters to WM degradation is greater than sensitivity of BM almost 2-fold.

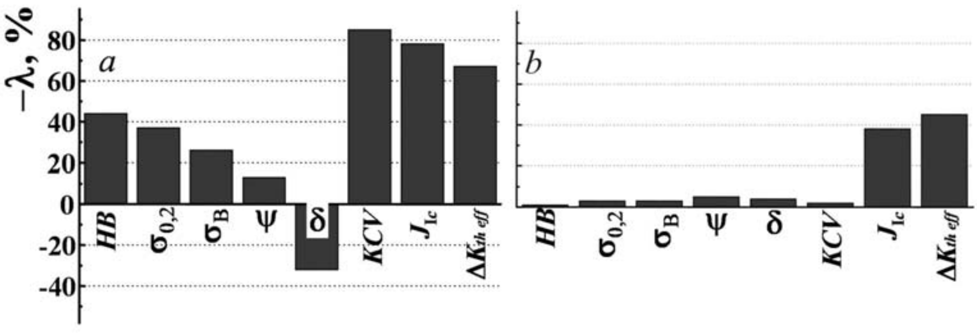


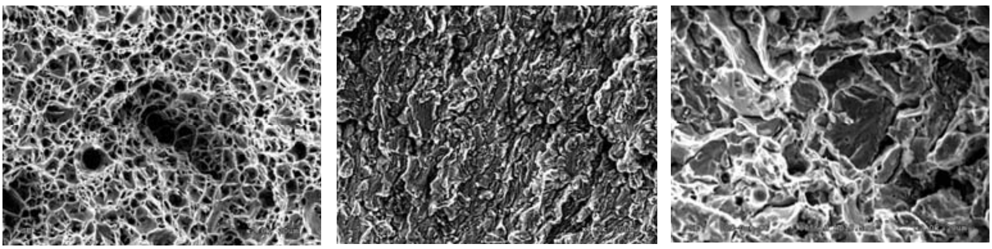

Fig. 7. Comparison of metal state mechanical parameters via sensitivity to high-temperature hydrogen degradation of WM (*a*) and BM (*b*). $\lambda$ – a relative change of corresponding factors due to exploitation.

Simultaneous decrease of the strength (resistance to ductile fracture) and both impact toughness and crack growth resistance (resistance to brittle fracture) of exploited WM is uncommon phenomenon. The low resistance to brittle fracture is inherent to the materials with high strength and hardness. Therefore the revealed abnormal change of the mechanical properties of WM appears due to degradation during service, whereas under the influence of any other known factors (thermal treatment, alloying, deformation) on the metal the tendency of these properties change should be contrary to the obtained one.

Simultaneous decrease of the strength and resistance to brittle fracture of WM after service is caused by ferrite grain size increase and results in the decrease of the degraded WM strength. This fact agrees well with the known dependence of the strength change versus the grain dimensions (Holl-Petch relationship). The grain-boundary carbides decrease a cohesive strength of the ferrite grains boundaries, and consequently the brittle fracture resistance of the degraded WM.

In addition to simultaneous decrease in strength and resistance to brittle fracture the atypical change of the plasticity parameters (elongation $\delta$ and reduction in area $\psi$) is inherent to degraded WM. Usually under the influence of other factors, the elongation $\delta$ and reduction in area $\psi$ are changing in a similar way and correlate with variation of brittle fracture parameters. For the degraded metal these plasticity parameters describe ambiguously the change of WM state after service degradation ($\delta$ is increasing and $\psi$ is decreasing). This fact makes impossible the simultaneous use of the quantities $\delta$ and $\psi$ as characteristics of the changes in the WM plasticity due to degradation. Different, in principle, changes in the characteristics $\delta$ and $\psi$, on the one hand, and the phenomenon of simultaneous decrease in the strength and resistance to brittle fracture, on the other, are the evidence of a specific correlation between the parameters of plasticity and other mechanical properties. In particular, the increase in $\delta$ for the operated WM agrees well with the its strength decrease, whereas the reduction in area $\psi$ correlates with the lowering of the resistance to brittle fracture. Here, we should also remember the well-known "competition" between the quantities $\delta$ and $\psi$ as the characteristics of the metal tendency to hydrogen embrittlement in the case of cylindrical specimens tension in gaseous hydrogen or under cathodic polarization. It is usually preferred to use the reduction in area, which is more sensitive to the hydrogen embrittlement of materials. Hence, the correlation of the parameter $\psi$ with the characteristics $J_{lc}$, and $\Delta K_{th\ eff}$ should be considered as the manifestation of WM degradation, which testifies to the increase in its tendency to hydrogen cracking and the danger of brittle fracture.

A low power-consuming of hydrogen cracking, which is possible under service conditions, is also corroborated by the microfractography of fracture surfaces of preliminarily hydrogenated specimens in tension (Fig. 8). If the classical ductile fracture by means of the formation of microvoids and their coalescence is realized in operated and nonoperated WM without hydrogenation (Fig. 8 *a*), then, after it, a mixture of ductile and the classical transgranular failure is observed in nonoperated WM and that with intergranular fracture in operated WM (Fig. 8 *b* and *c*). Hence, the last two types of fracture are the consequence of the embrittling action of hydrogen absorbed by the metal. At the same time, according to the generally accepted concepts on the power-consuming of fracture, exactly the intergranular fracture is considered as less energy-consuming. On the boundaries of ferritic grains, numerous traces of inclusions in the form of individual coarse pits or chains of fine pits are observed. They are the evidence of the loss of cohesive bonding between the matrix and inclusions under the action of hydrogen and, correspondingly, of the decrease in breaking strength along the grain boundaries.



*a* *b* *c*

Fig. 8. Fractography features of the fracture of specimens of outgassed WM from nonoperated (*a, b*) and operated for ~ $2 \cdot 10^5$ h (*c*) WJ, subjected to tension in air without (*a*) and after preliminary electrolytic hydrogenation (*b, c*).

## Conclusions

The changes of the mechanical properties of welding joints of low-alloy heat-resistant 15Kh1M1F steel from the power steam pipelines after long-term high-temperature degradation in hydrogenating environments have been investigated.

It is shown that unlike the base metal (BM) of steam pipeline, integral mechanical properties of which practically are insensitive to changes in metal state because of service, such properties as hardness, tensile strength and impact toughness are sensitive to high-temperature degradation of weld metal (WM). The degradation of WM was revealed to proceed more intensive than of BM. It is confirmed by the decrease of the integral mechanical properties of WM (except for relative elongation) and local ones, such as fracture toughness $J_{1c}$ and fatigue crack growth resistance (effective threshold of stress intensity factor $\Delta K_{th\ eff}$).

The anisotropy of WM mechanical properties change after degradation under service conditions was revealed. It is shown that electrolytic hydrogenation during tensile testing allow us to reveal the change of WM and BM state after its service using the integral mechanical properties.

Simulation of the WJ degradation, using the in-laboratory method of thermal cycling in hydrogen, enables the substantiation of the critical state of WM by the inversion effect of absorbed hydrogen on $\Delta K_{th\ eff}$ parameter; below this level WM becomes sensitive to hydrogen embrittlement. According to these results the method for assessment of the state of degraded WM, taking into account hydrogenation, can be developed.

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