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МЕХАНИЧЕСКИЕ И ТРИБОЛОГИЧЕСКИЕ ХАРАКТЕРИСТИКИ ГАЗОВЫДЕЛЕНИЯ ТРУБОПРОВОДНЫХ СТАЛЕЙ КАК ФУНКЦИЯ ЭЛЕКТРОЛИТИЧЕСКОГО ЛЕГИРОВАНИЯ ВОДОРОДОМ

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MECHANICAL AND TRIBOLOGICAL CHARACTERISTICS OF GAS-MAIN PIPELINE STEELS AS FUNCTION OF ELECTROLYTIC HYDROGEN DOPING

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An accelerated wear test with scanning dynamic load was developed to monitor the evolution of wear characteristics and frictional behaviour as function of operational lifetime and hydrogen charging. Hydrogen concentration in the steel specimens was determined using an original technique TriDes developed in ICMM-CSIC (Madrid, Spain) and based on mechanically stimulated gas emission in ultrahigh vacuum. Hydrogen charging before mechanical and tribological tests enhanced the difference in mechanical and tribological characteristics between new samples and the samples after long operation life. Therefore, hydrogen charging together with dynamic indentation and tribological testing can be used in the future for non-destructive control of submicrometer defects and deterioration of mechanical properties of construction steels used for gas pipes.

Keywords: gas main pipe steel, mechanical properties, hydrogen embrittlement

Introduction. Indentation and friction tests can be used for virtually non-destructive evaluation of operational microstructural damage of steel of gas-main pipes. Degradation of characteristics of structural materials usually occurs during their long-term operation. Therefore, the assessment of the operational conditions of constructions should not be focused only on the presence of macroscopic defects related to corrosion or mechanical damage, but also include the analysis of the degree of degradation of the material characteristics. So far the main activity in this area has been centred on the heat-resistant steels and alloys which operate at elevated temperatures. These steels undergo important microscopic structural transformations due to the effects of high temperature and hydrogen uptake, which processes are of special concern in power generation and petrochemistry [1].

Degradation of low-carbon steel in outdoor applications consists mainly in increase in hardness, elastic limit and ultimate stress, and significant decrease in fracture toughness and crack growth resistance [2]. Until recently it was generally believed that this degradation is related to deformational ageing, whereas the effect of structural transformations is negligible [3]. This belief is based on the analysis of gas-main pipes after operation during one to two decades. Presently, there are some evidences that different degradation processes may occur during even

longer operation life, between 30 and 50 years. Generation of dispersed microscopic faults in the material bulk is considered as the main reason for these degradation processes which lead to decrease in hardness, elastic limit and ultimate stress and even more significant decrease in fracture toughness and crack growth resistance [4]. In fact, the majority of accidents having significant economic, environmental and human impacts are considered being the consequence of these second degradation processes.

There are two principal mechanisms lying behind dispersed microscopic structural degradation of steels. The first one is related to the absorption of hydrogen as a result of cathodic electrochemical corrosion reactions of steels in aqueous solutions. The hydrogen content in pipes being in operation is typically 2 to 4 times higher than in the pipes stored during the same period time [4]. The second one is due to structural transformations induced by carbon migration from the grains to the intergranular boundaries, where carbide layers of nanometre thickness are formed. These carbide layers cause local embrittlement of the material and reduce the cohesion between the grains [5]. There are some experimental evidences indicating that hydrogen enhances carbon diffusion and promotes generation of microscopic faults under applied stress by the mechanism of hydrogen embrittlement [4]. For instance, there is a pronounced correlation between the decrease in fracture toughness of pipe steel, which is insensitive to hydrogen embrittlement, but sensitive to the microscopic structural faults and the increase in hydrogen content in this steel as results of operation [6]. It can be figure out from these results that hydrogen induces generation of dispersed microscopic structural faults in the steel.

Objectives. The existent methods of non-destructive evaluation are efficient for detection of macroscopic defects in gas-main pipes. However, they are not sensitive to dispersed microstructural faults. Other physical methods whereby the dispersed microscopic faults in the pipe steel can be evaluated, e.g., internal friction, suffer from technical and technological difficulties of in-situ analysis of the pipes. Therefore, indentation and rubbing, which can be used both for evaluation of plastic properties and fracture toughness of steels, are good candidates for prospective virtually non-destructive evaluation technique of operational degradation of gas-main pipes.

Experimental results and discussion. Two pipe steels of the same strength class have been used in this work: API X52 carbon steel and 17G1S (GOST 10705-80) analogous to DIN 1.0570. Samples were cut from the pipes which were stored or operated during approx. 30 years on two different gas-main pipes.

Long-term operation has only limited negative effect on standard mechanical characteristics of both steels (Table1, Fig. 1), but significant influence on the impact toughness KCV and fracture toughness J_i. It can be figured out from these results that operation causes local embrittlement of steel rather than general degradation of its plastic properties. It should be noted that steel 17G1S has higher strength and plasticity than X52 as can be inferred from the parameters KCV and J_i.

The results of wear tests for both steels showed that degradation due to operation had no significant effect on the depth parameter I_c and friction force F under static loading conditions (Table1, Fig.2).

However, the plasticity significantly decreased under these conditions. In contrast, under dynamic loading I_d increased, that was especially notable for X52 for which I_d increased on 42%.

Table 1

Mechanical and tribological characteristics of steels X52 and 17G1S

	HV	σ	ψ	δ	KCV	J_i	I_c	I_d	F_c	F_d	I^*_c	I^*_d	K^*_c	K^*_∂
X52 stored	1,83	475	72,9	22,7	177	86	12,8	25,6	14,5	3,9	9,1	31,5	0,173	0,380
X52 operated	1,6	460	62,5	20,9	55	37	12,9	36,7	15,3	4	13,1	39,6	0,076	0,274
17G1S stored	1,85	595	79	22,9	206	122	9,8	23,5	9,8	0,9	11,7	32,3	0,200	0,330
17G1S operated	1,69	547	71	20,8	138	89	11,7	32,9	9,7	1	14,1	36,6	0,100	0,330

***-parameters of steels determined after electrolytic hydrogen doping**

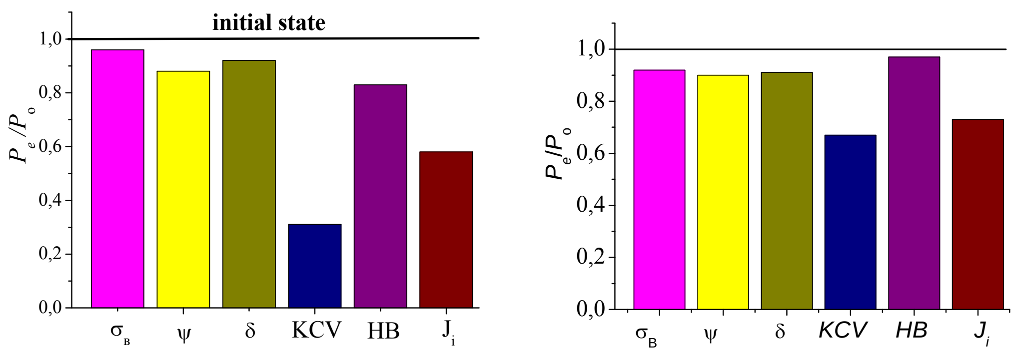

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Fig. 1. Ratios of various characteristics for steels obtained from the pipes being in operation and those stored without operation. Steel X52 (a) and 17G1S (b)

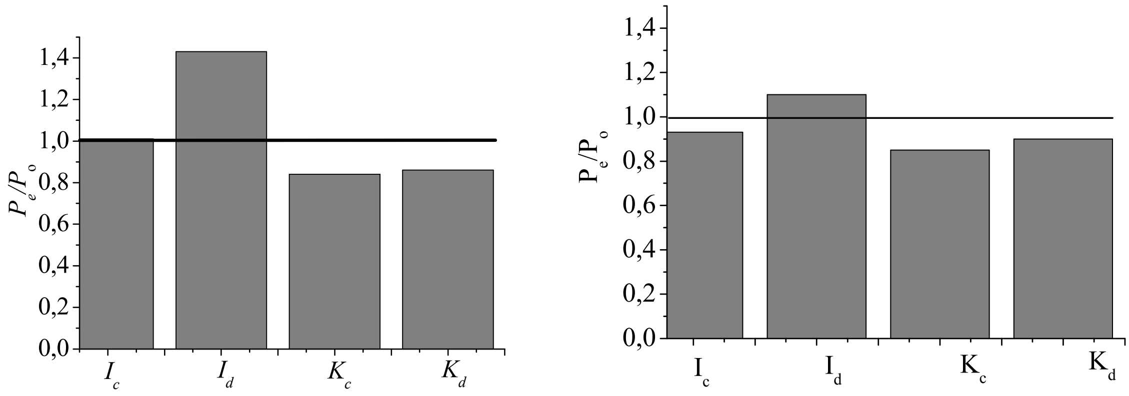

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Fig. 2. Ratios of the parameters I and K for steels obtained from the pipes being in operation and those stored without operation. Steel X52 (a) and 17G1S (b).

Coefficient of plasticity also decreased in the experiments with dynamic loading for steel being under operation. The following parameters were used for characterization steel degradation: plasticity coefficient, *K*; total depth of the wear track, *I*, being the sum of the plastic deformation under applied normal load and traction, I_p, and damage of the material due to fracture of local volumes, I_f. While operation had only minor effect on the wear of steels under static loading conditions, the components I_{dp} and I_{df} drastically increased under dynamic loading (Fig. 3).

Mass wear under dynamic loading was especially sensitive to the structural damage due to steel operation and increased on 60% and 150% for 17G1S and X52, correspondingly, as compared with the samples of stored steel pipes, which were not in operation. These results can, probably, be ascribed to decrease in fracture toughness due to specific stress distribution in the subsurface layer of steel which was in operation. Same mechanisms lie behind fatigue damage of steel. Another important problem is related to significant increase in the activation volume of deformation under dynamic loading that can result in the increase in probability of involvement in the process of plastic deformation of locally embrittled microscopic volumes.

Enhancement of damage of steel on microscopic scale as result of long-term operation is evident from the results of acoustic emission (AE) measurements during indentation of X52 (Fig. 4). Steel samples which were in operation are characterized by smaller number of AE sources, but up to four-fold higher amplitude of AE signals. This can be explained by the presence of locally embrittled microscopic volumes which hinder plastic deformation as can be figured out from lower values of ψ and δ. Higher rate of AE can be ascribed to different high-energy events related to fracture of embrittled zones which had not been observed for steel which was not in operation. The results of reciprocating wear test in high vacuum performed by alumina pin (Fig. 5) corroborate the above conclusions. For steel 17G1S the wear rate rapidly decreased at the beginning of sliding tests and almost stabilized after 100 cycles.

The effect of operation consisted in the increase of the wear on the initial stage, whereas the overall tendency was the same as for the stored steel. This behaviour can be ascribed to fracture component of wear, which increase after operation. In contrast, the wear rate of X52 did not stabilized and continued increasing with the number of cycles although with ever slower rate. This had to be due to the larger plastic component of X52.

By comparing the graphs in Figs.1 and 3 one can note that the wear parameter under dynamic loading I_{df} is more sensitive to operational degradation of steel than *KCV* or J_i. The results also indicate that steel X52 underwent severer degradation due to operation than steel 17G1S. These findings abundantly evidenced the perspectives of wear measurements under dynamic loading for non-destructive evaluation of degradation of pipe steel.

Previous studies revealed that irreversible deterioration of low-carbon steels occurs when steel is exposed to cathodic electrolytic hydrogen doping with the current density higher i = 5 мА/см^2. Therefore, in the present work the effect of hydrogen on steel degradation was studied in the range of current densities from 0,1 to 2.

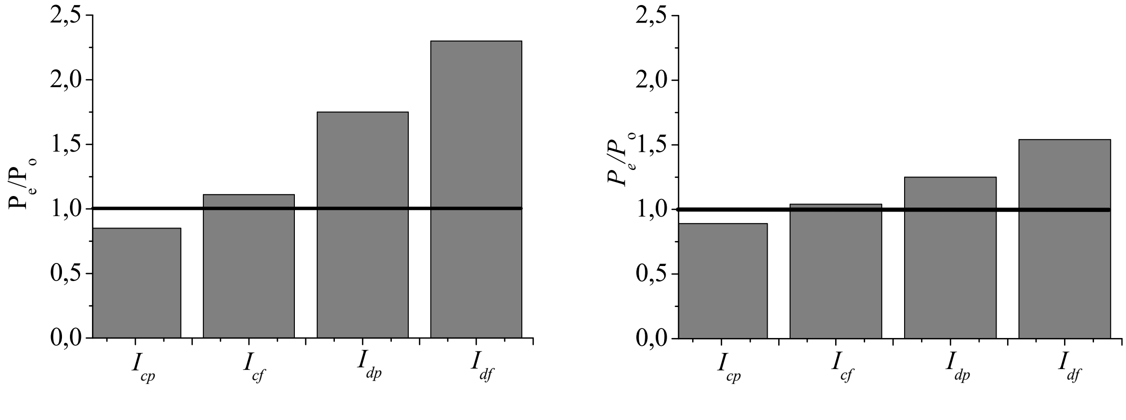


Fig. 3 Ratios of the parameters I_p and I_f for steels obtained from the pipes being in operation and those stored without operation. Steel X52 (a) and 17G1S (b)

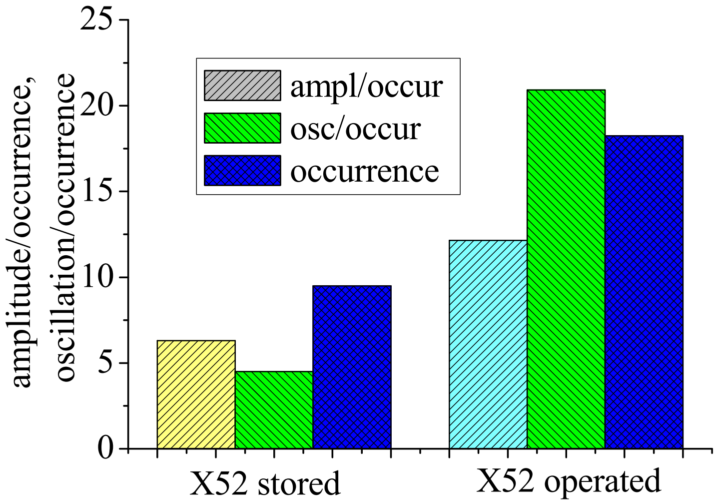


Fig. 4. Results of acoustic emission measurements during indentation of X52

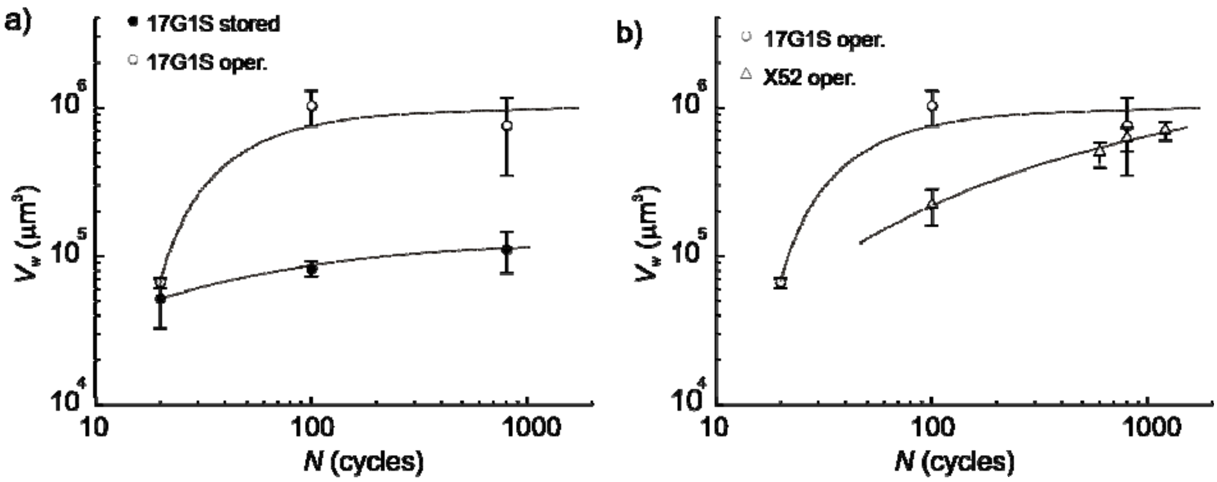
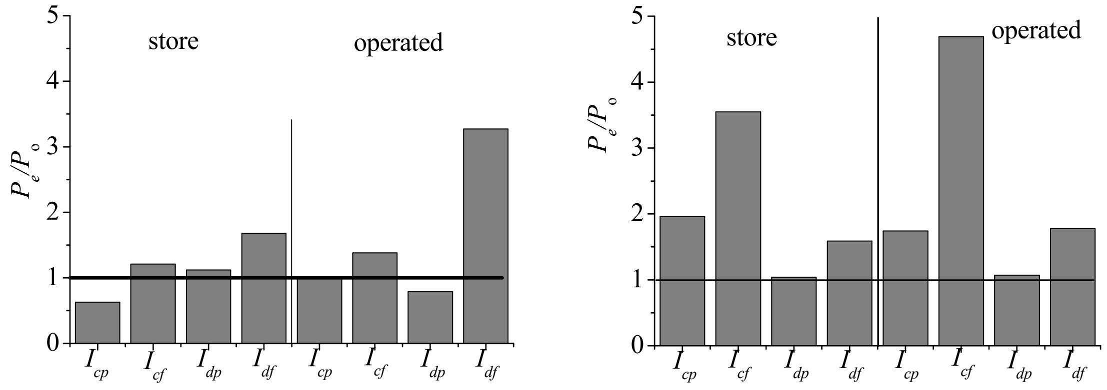


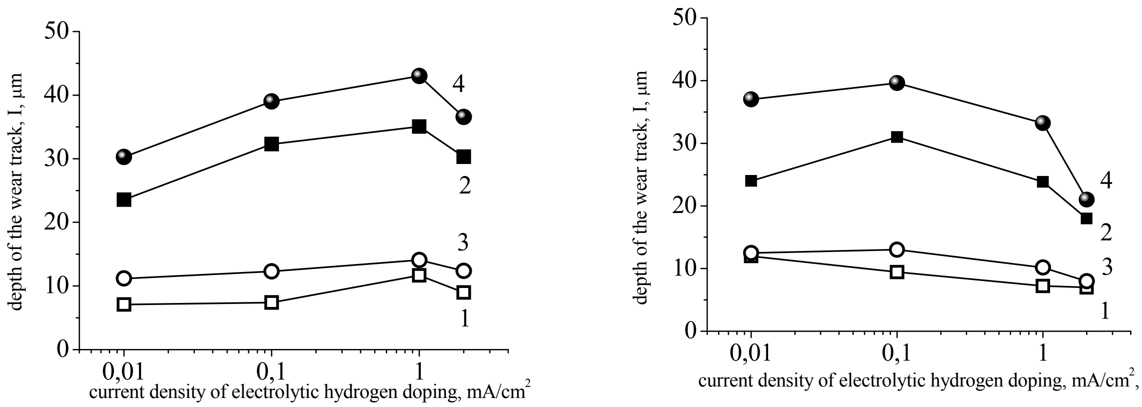
Fig. 5. Volume of worn material as function of the number of reciprocating sliding cycles



a **b**

Fig. 6. Effect of hydrogen doping on various parameters of steels: X52 (a) and 17G1S (b)

By doing so the reversible hydrogen embrittlement of steel related to diffusive or dislocation transport mechanisms could be studied. For the lowest studied current density (0,1мA/cм^2) the effect of hydrogen doping on the total depth of the wear track is very weak if any both under static and dynamic loading (Table 1, *I**, *K**). However, the plasticity of steel was significantly reduced due to hydrogen embrittlement even at such a low hydrogen concentration. This effect was especially notable under static loading. There are two possible mechanisms whereby hydrogen affects the wear rate of steels. The first one has to be related to the increase of the elastic limit due to dislocation blocking that leads to the increase of the wear resistance. Another one is due to hydrogen embrittlement that results in enhanced fracture of the topmost layer of the material especially under dynamic loading. The first and the second mechanisms are proper for X52 and 17G1S, correspondingly, as shown in Fig. 6.



a b

1,2 - store 3,4- operated

Fig. 7. Effect of current density during electrolytic hydrogen doping on the depth of the wear track for steels X52 (a) and 17G1S (b) under static (1,3) and dynamic (2,4) loading

Hydrogen doping caused small or negligible decrease in the plastic component of the depth of the wear tracks under both static and dynamic loading. However, the fracture component significantly increased. For X52 under static loading this increase was 20% and 50% for stored steel and steel being in operation, correspondingly. Under dynamic loading the effect of hydrogen doping was even more significant, especially for steel being in operation. Similar results were obtained also for 17G1S steel, although larger difference was observed under static loading. These findings indicate that steel 17G1S is more susceptible to hydrogen embrittlement. It should be mentioned though the fracture component of wear drastically increased, the total depth of the wear track increased 21% and 37% for X52 and 17G1S, correspondingly.

Hydrogen doping of pipe steel before friction test can significantly increase the sensitivity of the method for evaluation the degree of deterioration of steel due to operation. Dynamic loading is more sensitive for this purpose. However, the relationship between the parameters found from tribological tests and the hydrogen doping are nonlinear and very complex due to different mechanisms involved. The effect of hydrogen on the results of tribotesting must depend on chemical composition, structure and susceptibility for hydrogen embrittlement of steels. This is illustrated in Fig.7, which shows the effect of the current density on the depth of the wear track under dynamic and static loading. Variation of I with i follows the same tendency for both studied steels: at low current density it increases with the increase in i, whereas after certain value of i it decreases. Therefore, at low hydrogen concentrations hydrogen doping enhances wear process, whereas at higher H concentrations wear is hindered.

Conclusions. Degradation of steel during long-term operation in outdoor applications such as gas-main pipes relates with embrittlement of local microscopic volumes of the material rather than with general decrease of plasticity. Steel X52 experienced larger degradation than steel 17G1S.

Though plasticity coefficient decreased for both steels as result of operation, wear rate increased only under dynamic loading. Both components characterising wear rate: depth of plastic deformation, I_p, and wear due to mass loss related with fracture of local zones, I_f, increase under dynamic loading for steel being in operation. This effect was especially significant for I_f : 60% for 17G1S and 150% for X52. Structural degradation of steel on microscopic scale has been confirmed by measuring acoustic emission during indentation.

The parameter of wear under dynamic loading, I_{df}, is more sensitive for the degree of steel structural degradation than general toughness parameters *KCV* and J_i.

The effect of hydrogen doping on the total depth of the wear track was negligible under both static and dynamic loading, although plasticity coefficient significantly decreased that indicated hydrogen embrittlement.

Hydrogen doping can have dual effect on the plastic component on the depth of the wear track: increasing or decreasing one. However, the fracture component of the wear track significantly increased after hydrogen doping, which effect was more notable for steel being in operation. Authors kindly thank Shurygina Z., Mordel L., Tkachenko I. and Kozyrev D., (Frantsevich Institute for Problems of Materials Science of NASU) for assistance in indentation and tribology tests. This work has been partly supported by the grant of the Ministry of Economy and Competitiveness of Spain (IPT-2012-1167-120000) and FEDER.

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Грінкевич К.Е., Цирульник О.Т., Роман Е., Невшупа Р.А. Механічні та трибологічні характеристики газовиділення трубопровідних сталей як функція електролітичного легування воднем

Прискорене випробування зносу зі скануванням динамічного навантаження було розроблено, щоб стежити за розвитком характеристик зносу і тертя в період експлуатації і зарядки воднем. Концентрацію водню в сталевих зразках визначали за допомогою оригінальної методики TriDes, розробленої в ICMM-CSIC (Мадрид, Іспанія) заснованої на механічному стимулюванні газів у надвисокому вакуумі. Воднева зарядка до механічних і трибологічних випробувань підвищує механічні та трибологічні характеристики нових зразків порівняно із зразками після тривалого терміну експлуатації. Таким чином, воднева зарядка разом з динамічним навантаженням і трибологічним тестуванням може бути використана в майбутньому для неруйнівного контролю субмікронних дефектів і підвищення механічних властивостей конструкційних сталей, що використовуються для газових труб.

Ключові слова: газове виділення трубопроводної сталі, механічні властивості, воднева крихкість

Гринкевич К.Э., Цирюльник А.Т., Роман Е., Невшупа Р.А. Механические и трибологические характеристики газовыделения трубопроводных сталей как функция электролитического легирования водородом

Ускоренное испытание износа со сканированием динамической нагрузки было разработано, чтобы следить за развитием характеристик износа и трения в период эксплуатации и зарядки водородом. Концентрацию водорода в стальных образцах определяли с помощью оригинальной методики TriDes, разработанной в ICMM-CSIC (Мадрид, Испания), основанной на механическом стимулировании газов в сверхвысоком вакууме. Водородная зарядка до механических и трибологических испытаний повышает механические и трибологические характеристики новых образцов по сравнению с образцами после длительного срока эксплуатации. Таким образом, водородная зарядка вместе с динамической нагрузкой и трибологическим тестированием может быть использована в будущем для неразрушающего контроля субмикронных дефектов и повышения механических свойств конструкционных сталей, используемых для газовых труб.

Ключевые слова: газовоевыделение трубопроводной стали, механические свойства, водородная хрупкость

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