Low and high cycle fatigue of heat resistant steels and nickel based alloys in hydrogen for gas, steam turbines and generators applications

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Abstract. It has been established that, at some region of hydrogen pressure and strain rate exists a maximum influence of hydrogen on the plasticity, low cycle fatigue and cyclic crack resistance of Ni-Co alloys and high nitrogen steels. The drop of plasticity of the dispersion-hardening materials within the temperature range of intense phase transformations is caused by the localization of strains on the grain boundaries due to the intense redistribution of alloying elements in the boundary regions. Moreover, the increase in plasticity observed at higher temperatures is caused both by partial coagulation of hardening phases and possible dissolution of small amounts of finely divided precipitations. The effect hydrogen on short-term strength and plasticity, high- and low-cycle durability of 15Cr12Ni2MoNMoWNb martensitic steel, 10Cr15Ni27Ti3W2BMo austenitic dispersion-hardened steel, heat resistant 3,5NiCrMoV rotor steel, 04Kh16Ni56Nb5Mo5TiAl and 05Kh19Ni55Nb2Mo9Al Ni-base superalloys in range of pressures 0–30 MPa and temperatures 293–1073 K was investigated. In the case of 15Cr12Ni2MoNMoWNb steel and 04Kh16Ni56Nb5Mo5TiAl alloy the dependence of low-cycle durability (N) and characteristics of plasticity (δ and φ) on the hydrogen pressure consists of two regions. In the first region (low pressures), the N, δ and φ abruptly drops, and in the second, the negative action of hydrogen becomes stable or decrease negligibility.

1 Introduction

The production of turbine and generator equipment requires a wide usage of dispersive hardened heat-resistant Fe-Ni, Ni-Cr, Ni-Co alloys and high nitrogen steels. Elevated temperature steels and alloys are exploited at high temperatures steam (up to 973 K), hydrogen containing gas mixtures (up to 1173 K). Therefore one of the most important requirements for such steels and alloys is their resistance to hydrogen degradation at very high temperatures. In other words their ability to keep high level of mechanical and fatigue properties under the action of hydrogen in wide range of exploitation parameters. At the same time, steels and alloys are known to be rather sensitive to hydrogen embrittlement [1-6].

Power equipment on NPP and advanced FPP, transport and energetic gas turbines requires their modernization due to increasing of working parameters up to the super high, extreme level. The production of future turbine equipment requires a wide usage of dispersive hardened heat-resistant Fe-Ni and Ni-Co alloys. Heat-resistant steels and alloys are exploited at high temperatures steam (up to 973 K), hydrogen containing gas mixtures (up to 1073…1173 K). Therefore one of the most important requirements for such steels and alloys is their resistance to high temperature, high pressure gaseous environments. In other words their ability to keep high level of mechanical properties under the action of hydrogen in wide range of exploitation parameters. The serviceability of structures in hydrogen is, as a rule, estimated according to the results of testing at room temperature and life extension procedures has base on such approaches. However, the operating conditions of the equipment for hydrogen power engineering include cyclic loading of the products in hydrogen in fairly broad temperature ranges. In most cases, the influence of gaseous hydrogen on mechanical properties weakens as temperature increases and, according to the presented in, the upper temperature of embrittlement under the analyzed conditions was equal to 573 K. At the same time, we reveal a significant decrease in the plasticity of heat-resistant nickel alloys in hydrogen under a
pressure of 35 MPa at temperature 973 K. The aim of this investigation is to study the influence of high pressure hydrogen on the short-term strength and plasticity, low- and high-cycle durability of martensitic steel, austenitic dispersion-hardened steel, and Ni base superalloys at high temperatures.

2 Materials and experimental procedure

Static tensile tests were carried out on standard fivefold cylindrical specimens with working part diameter 5 mm by displacement rate \( V = 6.7 \times 10^{-5} \text{s}^{-1} \) on the original equipment. This type specimens for determination high-cycle durability submitted to cyclic loading on scheme “pure bending with rotation” at fixed strain amplitude with frequency 50 Hz at room temperature. The low-cycle durability tests for pure strain-controlled sign-preserving bending was found for the strain amplitudes \( \varepsilon = 1.6\% \) and a loading frequency of 0.5 Hz on polished plane specimens with a working part of 3x6x20 mm were carried out on typical equipment. We determined the influence of hydrogen under a pressure 30 MPa on the critical stress intensity factor (SIF) under a static load \( K_{c} \). For this purpose 50x60x20 mm specimens with a preliminarily induced fatigue crack were loaded in off-centre tension in a high-pressure chamber. The cyclic crack resistance (CCR) characteristics were determined in three-point bending of 160x40x20 mm beam specimens at a frequency of loading of 20 Hz and a coefficient of cycle asymmetry \( R = 0.22 \).

To determine the indicated mechanical characteristics in hydrogen, the working chambers were preliminarily evacuated, blownout with hydrogen, again evacuated, and filled with hydrogen up to a given pressure. At high temperatures, the specimens were held under the testing conditions for 30 min up to the attainment of thermal equilibrium. It has been established [1] that, at some values of hydrogen pressure and strain rate, which depend on the chemical compositions and structures of materials, maximum influence of hydrogen on the plasticity, low-cycle fatigue life, and static and cyclic crack resistance of martensitic steels and nickel alloys are achieved. In short-term tension, austenitic dispersion hardened steels are substantially embrittled by hydrogen after preliminary hydrogenation at elevated temperatures and upon attaining its content above 12 wppm, and the properties of hydrogenation specimens at room temperature in air and hydrogen are equal [1]. This is why we held a part of the specimens for 10 h in a hydrogen atmosphere under 623 K and 35 MPa. These regimes provide the hydrogenation of specimens to hydrogen contents of 3.2 wppm (15Cr12Ni2MoNMoWNb steel), 15 wppm (10Cr15Ni27Ti3W2BMo steel), 19 wppm (05Kh19Ni55Nb2Mo9Al alloy) and 20 wppm (04Kh16Ni56Nb5Mo5TiAl alloy). On the other hand during long term service in hydrogen or hydrogen containing gas structural material has been alloyed by hydrogen. For example stable high nitrogen steels P-900 (for retaining rings of NPP turbogenerators): 7...20 ppm; dispersive hardened steels (Ni23Mo1.5Ti3), (Ni27Mo1.5W2): 8...25 ppm; Ni-Cr-Fe alloys (Ni55Cr19Fe12Mo9Nb2) (for resistive face of combustion chamber of gas turbine), (Ni63Mo6Ti3), (Ni56Mo6Nb4), (Ni42Fe36Cr14Nb3Mo2) (for inlet gas turbine nozzle), Ni-Co alloys (Ni56Co15Cr9W6Al5Mo4, Ni64Cr14Co10Mo5Al3Ti3) (for gas turbine rotor disks and blades), which strengthened by \( \gamma' \) (Ni23Al12Ti, (stable up to 1373 K), \( \gamma''(\text{Ni})_3(\text{Al,Ti}) \) (stable up to 1373 K) phases: 8...30 ppm.

Hydrogenated and non-hydrogenated specimens were tested in helium and hydrogen under different pressures. The hydrogen concentration (Cu) was determined with a LECO TCH 600 instrument.

3 Results and discussion

The martensitic steels contain about 10% of residual austenite after the optimal thermal treatment in the form of thin layers between the plates of martensite and on the boundaries of the former austenitic grains. The chemical composition, heat treatment regimes and mechanical properties of investigated alloys in helium and in hydrogen under a pressure of 35 MPa are given in [1]. The fatigue properties of 15Cr12Ni2MoNMoWNb martensitic steel, 04Kh16Ni56Nb5Mo5TiAl, 10Cr15Ni27Ti3W2BMo and 05Kh19Ni55Nb2Mo9Al dispersion hardened alloys were investigated. The alloying with niobium, vanadium, titanium, aluminium and boron leads to the formation of the carbide TiC, borides Me3B2, and Ti, and was confirmed to be \( \gamma' \) (Ni23Al12Ti, (stable up to 1373 K), \( \gamma''(\text{Ni})_3(\text{Al,Ti}) \) (stable up to 1373 K) phases: 8...30 ppm. The action of hydrogen on the plasticity [1] and hydrogen embrittlement, which often leads to the formation of the carbide TiC, borides Me3B2, and Ti, and was confirmed to be \( \gamma' \) (Ni23Al12Ti, (stable up to 1373 K), \( \gamma''(\text{Ni})_3(\text{Al,Ti}) \) (stable up to 1373 K) phases: 8...30 ppm. The action of hydrogen on the plasticity [1] and hydrogen embrittlement, which often leads to the formation of the carbide TiC, borides Me3B2, and Ti, and was confirmed to be \( \gamma' \) (Ni23Al12Ti, (stable up to 1373 K), \( \gamma''(\text{Ni})_3(\text{Al,Ti}) \) (stable up to 1373 K) phases: 8...30 ppm. The action of hydrogen on the plasticity [1] and hydrogen embrittlement, which often leads to the formation of the carbide TiC, borides Me3B2, and Ti, and was confirmed to be \( \gamma' \) (Ni23Al12Ti, (stable up to 1373 K), \( \gamma''(\text{Ni})_3(\text{Al,Ti}) \) (stable up to 1373 K) phases: 8...30 ppm. The action of hydrogen on the plasticity [1] and hydrogen embrittlement, which often leads to the formation of the carbide TiC, borides Me3B2, and Ti, and was confirmed to be \( \gamma' \) (Ni23Al12Ti, (stable up to 1373 K), \( \gamma''(\text{Ni})_3(\text{Al,Ti}) \) (stable up to 1373 K) phases: 8...30 ppm. The action of hydrogen on the plasticity [1] and hydrogen embrittlement, which often leads to the formation of the carbide TiC, borides Me3B2, and Ti, and was confirmed to be \( \gamma' \) (Ni23Al12Ti, (stable up to 1373 K), \( \gamma''(\text{Ni})_3(\text{Al,Ti}) \) (stable up to 1373 K) phases: 8...30 ppm. The action of hydrogen on the plasticity [1] and hydrogen embrittlement, which often leads to the formation of the carbide TiC, borides Me3B2, and Ti, and was confirmed to be \( \gamma' \) (Ni23Al12Ti, (stable up to 1373 K), \( \gamma''(\text{Ni})_3(\text{Al,Ti}) \) (stable up to 1373 K) phases: 8...30 ppm. The action of hydrogen on the plasticity [1] and hydrogen embrittlement, which often leads to the formation of the carbide TiC, borides Me3B2, and Ti, and was confirmed to be \( \gamma' \) (Ni23Al12Ti, (stable up to 1373 K), \( \gamma''(\text{Ni})_3(\text{Al,Ti}) \) (stable up to 1373 K) phases: 8...30 ppm. The action of hydrogen on the plasticity [1] and hydrogen embrittlement, which often leads to the formation of the carbide TiC, borides Me3B2, and Ti, and was confirmed to be \( \gamma' \) (Ni23Al12Ti, (stable up to 1373 K), \( \gamma''(\text{Ni})_3(\text{Al,Ti}) \) (stable up to 1373 K) phases: 8...30 ppm. The action of hydrogen on the plasticity [1] and hydrogen embrittlement, which often leads to the formation of the carbide TiC, borides Me3B2, and Ti, and was confirmed to be \( \gamma' \) (Ni23Al12Ti, (stable up to 1373 K), \( \gamma''(\text{Ni})_3(\text{Al,Ti}) \) (stable up to 1373 K) phases: 8...30 ppm. The action of hydrogen on the plasticity [1] and hydrogen embrittlement, which often leads to the formation of the carbide TiC, borides Me3B2, and Ti, and was confirmed to be \( \gamma' \) (Ni23Al12Ti, (stable up to 1373 K), \( \gamma''(\text{Ni})_3(\text{Al,Ti}) \) (stable up to 1373 K) phases: 8...30 ppm. The action of hydrogen on the plasticity [1] and hydrogen embrittlement, which often leads to the formation of the carbide TiC, borides Me3B2, and Ti, and was confirmed to be \( \gamma' \) (Ni23Al12Ti, (stable up to 1373 K), \( \gamma''(\text{Ni})_3(\text{Al,Ti}) \) (stable up to 1373 K) phases: 8...30 ppm. The action of hydrogen on the plasticity [1] and hydrogen embrittlement, which often leads to the formation of the carbide TiC, borides Me3B2, and Ti, and was confirmed to be \( \gamma' \) (Ni23Al12Ti, (stable up to 1373 K), \( \gamma''(\text{Ni})_3(\text{Al,Ti}) \) (stable up to 1373 K) phases: 8...30 ppm.
comparison of the $K_{th}$ threshold values of and the cyclic fracture toughness $K_f$ of 15Cr12Ni2MoNMoWNb and 10Cr15Ni27Ti3W2BMo steels has shown, that on the temperature dependence of $K_f$ and $K_{th}$ of 15Cr12Ni2MoNMoWNb steel are absent the hydrogen embrittlement extrems. Hydrogen negative influence of the fatigue crack growth resistance characteristics of this steel, as a rule, essential and monotonic decrease with temperature increasing.

As the number of technology industries are increasingly used engine and vehicles with limited lifetime, due to the intensification of working parameters and decrease specific quantity of metal structures. In these structures allowed the emergence of strain s that exceed the yield stress of materials, i.e., the frequent plastic (little cycles) deformation. Taking into account the impact of variables elastic–plastic loading, high temperatures and corrosive gas environments on the mechanical properties of materials is essential to ensure the reliability of some energy products and aerospace engineering. Especially important is to assess the degree of hydrogen embrittlement, which often leads to catastrophic failure of structures [1, 2].

It is well known, that on the stainless steel surface exists the spinel thin coating. But thermally-induced degradation-relaxation kinetics of such structures composed of spinel $\text{Cu}_{0.1}\text{Ni}_{0.1}\text{Co}_{1.6}\text{Mn}_{1.2}\text{O}_4$ ceramics are structural inhomogeneities [7] and surface active environment (including hydrogen) play a decisive role in non-exponential kinetics of negative relative resistance drift. Crossover from stretched- to compressed-exponential kinetics in spinel-metallic structures is mapped on free energy landscape of non-barrier multi-well system under strong perturbation from equilibrium, showing transition with a character downhill scenario resulting in faster than exponential decaying.

The effect of hydrogen on yield stress and ultimate strength of investigated materials is negligible. In the case of 15Cr12Ni2MoNMoWNb steel and 04Kh16Ni56- Nb5Mo5TiAl alloy the dependence of low-cycle durability (N) and characteristics plasticity ($\delta$ and $\varphi$) on the hydrogen pressure consists of two regions. In the first region (low pressures), the $N$, $\delta$ and $\varphi$ abruptly drops, and in the second, the negative action of hydrogen becomes stable or decrease negligibility.

The action of hydrogen on the plasticity [1] and low-cycle durability of martensitic steels is identical: maximum at room temperature and decreases when temperature increases (Fig.1). At 673 K the mechanical properties of 10Cr15Ni27Ti3W2BMo steel specimens in helium and hydrogen is equal. As temperature increases from 293 to 473 K, the coefficient of influence of hydrogen on the low-cycle durability $b$ of non-hydrogenated specimens of 10Cr15Ni27Ti3W2BMo steel decreases from 0.86 to 0.22 (Fig.1, curves 2, H). At the same, for hydrogenated specimens, it remains constant within the range 0.2–0.22 up to 773 K (Fig.1, curves 2, H + H). At 473 K, the additional influence of preliminarily dissolved hydrogen becomes negligible, i.e., for low-cycle fatigue, this temperature is sufficient for the hydrogenation of stable dispersion-hardening austenitic steels from the atmosphere of hydrogen. In tension, when the maximum tensile stresses are localized at much larger distances from the specimen surface, this effect is attained for 973 K [1]. The degree of embrittlement of 10Cr15Ni27Ti3W2BMo steel somewhat decreases at 873 K. However, for both loading modes, the temperature interval of significant hydrogen degradation for austenitic steels is much larger than for martensitic steels m15Cr12Ni2MoNMoWNb (Fig.1, curves 1). Analogically, in whole temperature diapason 293–1073 K the 04Kh16Ni56Nb5Mo5TiAl alloy is more sensitive to hydrogen embrittlement than 05Kh19Ni55Nb2Mo9Al alloy (Fig.1, curves 3 and 4). In helium ultimate strength, reduction of area w and number cycles to failure N of 04Kh16Ni56Nb5Mo5-TiAl alloy (17–18% intermetallics) are essentially high than properties of 05Kh19Ni55Nb2Mo9Al alloy (8% intermetallics) [1]. Because of the considerable degradation of 04Kh16Ni56Nb5Mo5TiAl alloy in hydrogen under the pressure 30 MPa for all indicated characteristics 05Kh19Ni55Nb2Mo9Al alloy is better.

![Fig. 1. Temperature dependences of number cycles to failure N (e=1.6%) in helium (He), hydrogen under the pressure 30 MPa (H) and hydrogen under the pressure 30 MPa after preliminary hydrogenation (35 MPa H2, 623 K)](image-url)
10 h) (H + H) and coefficients of hydrogen influence \( b=\frac{N_{\text{He}}}{N_{H}} \) on 15Cr12Ni2MoNMoWNb (1), 10Cr15Ni27Ti3W2BMo (2) (a), 05Cr19Ni55Nb2Mo9Al (3) and 04Cr16Ni56Nb5Mo5TiAl (4) (b) alloys.

The additional effect of preliminary dissolved hydrogen on the properties of 15Cr12Ni2MoNMoWNb steel and 04Kh16Ni56Nb5Mo5TiAl alloy developed at hydrogen environment pressure least of 10 MPa. The parameters of loading and the modes of action of hydrogen for which the mechanical characteristics of the investigated alloys are minimum at 293 K can be formulated as follows: at the strain rate in short-term static tension in hydrogen \( V=6.7 \times 10^{-5} \) s\(^{-1}\); the frequency and amplitude of bending under the conditions of low-cycle fatigue \( v=0.5 \) Hz and \( \varepsilon=1.6\% \), and the pressure of hydrogen must be higher than 10 MPa. In the case of 10Cr15Ni27Ti3W2BMo steel and 05Kh19Ni55Nb2Mo9Al alloy the limit is absent and their serviceability is a monotonically decreasing function of hydrogen pressure. The ultimate hydrogen embrittlement of these materials achieved only after preliminary high temperature hydrogenation. Hydrogen decreases high-cycle durability of martensitic steels and Ni-base alloys, the degree of hydrogen effect increase with strain amplitude decrease. The additional effect of preliminary dissolved hydrogen is negligible for 10Cr15Ni27Ti3W2BMo steel (Fig. 2a) and is absent for 05Kh19Ni55Nb2Mo9Al alloy (Fig. 2b).

For 10Cr15Ni27Ti3W2BMo steel and 05Kh19Ni55Nb2Mo9Al alloy the limit is absent and the pressure of hydrogen must be higher than 10 MPa. Hydrogen decreases high-cycle durability of martensitic steels and Ni-base alloys, the degree of hydrogen effect increase with strain amplitude decrease. The additional effect of preliminary dissolved hydrogen is negligible for 10Cr15Ni27Ti3W2BMo steel (Fig. 2a) and is absent for 05Kh19Ni55Nb2Mo9Al alloy (Fig. 2b).

There is the strong dependence of the threshold stress intensity factor \( K_{\text{th}} \) on the frequency of cyclic loading (Fig. 3) for heat resistant 3,5NiCrMoV rotor steel [10, 11]. The tendency of monotonic decreasing of the \( K_{\text{th}} \) values with decreasing of frequency is observed both in air and hydrogen environment.

However this trend is significantly stronger for test in hydrogen. There is a strong dependence of...
fracture mechanics parameters on the values of yield stress of steels used for generators.

Fig.3. Ratio $K_{th}(\text{air})/K_{th}(\text{hydrogen})$ versus frequency of loading for steel 38KhN3MFA.

The assessment of hydrogen effect on these parameters with comparison with air can be made from the following diagrams [2, 10, 11, 14] (Fig.4): $K_{IC} = F_1(\sigma_{0.2})$ or $K_{JC} = F_1^*(\sigma_{0.2})$, $\Delta K_{IC} = F_2(\sigma_{0.2})$, $\Delta K_{th} = F_3(\sigma_{0.2})$. Here: $K_{IC}$ is a fracture toughness defined under static loading by standard method; $K_{JC}$ is a static fracture toughness defined on a base of J-integral; $\Delta K_{IC}$ is a cyclic fracture toughness defined from a diagram of fatigue crack growth; $\Delta K_{th}$ is a range of threshold stress intensity factor, which can be also defined from fatigue crack growth diagram.

Fig.4. Diagrams $K_{IC} = F_1(\sigma_{0.2})$ (a), $K_{JC} = F_1^*(\sigma_{0.2})$ (b), $\Delta K_{IC} = F_2(\sigma_{0.2})$, $\Delta K_{th} = F_3(\sigma_{0.2})$ (c) for steels: 1 – 3,5NiCrMoV; 2 – 8Mn8Ni4Cr; 3 – 18Mn4Cr; 4 – 18Mn18Cr on air (a) and after hydrogen saturation (b, c) (○ $K_{IC}$, ● $K_{JC}$).

But it is necessary to take into account the experimental results of the fatigue crack growth in specimens with rectangular cross sections which were weakened by sharp and blunt one-sided notches (for example the notch root $\rho = 0.2$; 5; 10 and 22.5 mm) [12, 13]. The tests were performed in the low- and high-cycle fatigue modes by imposing a constant value of the nominal load ratio $R = -1$; 0 and a moment amplitude $Ma = 15.84$ N·m. All the results of fatigue tests must be analyzed in terms of the parameter $\Delta K$ including the influence of the notch.

4 Conclusions

effect on properties of 10Cr15Ni27Ti3W2BMo austenitic dispersion-hardened steel and 05Kh19Ni55Nb2Mo9Al alloy achieved on hydrogenated specimens at hydrogen pressure above 10 MPa. Hydrogen decreases high-cycle durability of martensitic steels and Ni-base alloys, the degree of hydrogen effect increase with strain amplitude decrease. The temperature range of essential hydrogen degradation is a structure-sensitive factor: 293–623 K in the case 15Cr12Ni2MoNMoWNb martensitic steel, 293–973 K for 10Cr15Ni27Ti3W2BMo austenitic dispersion-hardened steel and 293–1073 K for Ni-base alloys.
There is the strong dependence of the threshold stress intensity factor $K_{th}$ on the frequency of cyclic loading for heat resistant 3,5NiCrMoV rotor steel. The tendency of monotonic decreasing of the $K_{th}$ values with decreasing of frequency is observed both in air and hydrogen environment. There is a strong dependence of fracture mechanics parameters on the values of yield stress of steels used for hydrogen cooling generators.

References