Fatigue 2010

The low-cycle fatigue of corrosion-resistant steels in high pressure hydrogen

A.I. Balitskii\textsuperscript{a*}, V.I. Vytvytskyi\textsuperscript{a}, L.M. Ivaskevich\textsuperscript{a}

\textsuperscript{a}Karpenko Physiko-Mechanical Institute, Lviv 79601, Ukraine

Received 5 March 2010; revised 12 March 2010; accepted 15 March 2010

Abstract

The dependences of low-cycle durability of 11 corrosion-resistant steels of the main grades on gaseous hydrogen pressure within the range of 0.1…35 MPa at 293 K have been obtained. Homogeneous austenitic steels as well as the steels with intermetallide strengthening possess the highest service ability in hydrogen. Ni–Al–Ti steels treated for maximum heat resistance have the durability in hydrogen which is proportional to the content of Ti/Al and Ti, and is also determined by the treatment conditions. Transition materials and steels with unstable austenite form a group of steels with medium sensitivity to hydrogen. The group of metals that are catastrophic embrittled in hydrogen includes high-strength martensitic-ageing and ferritic steels.

Keywords: low-cycle durability, corrosion-resistant austenite, high-strength martensitic-ageing and ferritic steels, hydrogen pressure, preliminary hydrogenation, embrittlement.

The pressure of gaseous hydrogen is one of the most significant factors negatively and unpredictably affecting the serviceability of stressed metals in the absence of occlusion (at room temperatures) \cite{1-5} under the conditions of reversible hydrogen embrittlement when the fracture process runs without any signs of chemical reactions, microstructural changes, transformations, and damage. Earlier \cite{2-5}, this phenomenon was studied by analyzing the behavior of selected types of steel, which does not give sufficient amount of data for generalizations. The systematic data on the behavior of corrosion-resistant Fe-materials are practically absent.

In what follows, on the basis of the data of low-cycle fatigue testing of 11 types of corrosion-resistant steel, we formulate some requirements to the structure and chemical composition of steels which could guarantee their high resistance to the action of hydrogen. We study the influence of the pressure of hydrogen on the low-cycle fatigue of steels with different phase compositions and types of hardening in order to determine some mechanical and structural parameters specifying the hydrogen resistance of steels.

To analyze the role of strength, structure, and types of hardening of solid solutions, we study several groups of materials (see Table 1 and Fig. 1), namely, four austenitic steels (\(\gamma\)) subjected to thermal treatment for solid solutions with different contents of austenite- and ferrite-forming substitutional elements in the base composition (\(\sigma_{0.2} \approx 200-500 \text{ MPa}\); in two steels with elevated content of manganese, the role of substitutional hardening element is played by nitrogen whose concentration varies within the range 0.15-0.34%), three dispersion-hardened austenitic steels (\(\gamma+\gamma'\)) in which the concentration of nickel is \(\geq 20\%\) (\(\sigma_{0.2} \approx 500-800 \text{ MPa}\)), three martensite-aged (MA) steels

\textsuperscript{*} Corresponding author
E-mail address: balitski@ipm.lviv.ua

\textcopyright 2010 Published by Elsevier Ltd. Open access under CC BY-NC-ND license.

\[\text{doi:10.1016/j.proeng.2010.03.253}\]
with intermetallic hardening and $\sigma_{0.2} \approx 900-1100$ MPa, and C0,08Cr17Ti ferritic corrosion-resistant steel with $\sigma_{0.2} = 260$ MPa.

The low-cycle loading of flat smooth specimens with a thickness of 2-3 mm by pure bending [2] was carried out in a IP-2VTD installation. A high-pressure unit with membrane compressor produced a pressure of 98 MPa in the working chamber. A specially designed procedure of preparation [4] of hydrogen experiments included the following operations: evacuation of the working chamber down to a pressure of 1.33 Pa followed by its filling with purified hydrogen (GOST 3022-70) up to a pressure of 6 MPa and hydrogen release into the atmosphere. This sequence of operations was repeated three times and then the working chamber was filled with hydrogen to the required pressure.

Table 1. Chemical and Phase Composition, Mechanical Properties, and Durability of Corrosion-Resistant Steels in Air and for $P_H = 35$ MPa

| No. | Steel Structure | $\sigma_{0.2}$, MPa | $\sigma_{0.2}$, MPa | $\phi$, % | $\psi$, % | $N_{air}$, cycles | $N_{H}$ ($P_H = 35$ MPa), cycles |
|-----|----------------|----------------------|----------------------|-----------|-----------|------------------|----------------------------------|
| 1.  | C0.08Cr11Ni12Ti2BA | $\gamma+\gamma'$ | 1180 890 30 46 | 3100 | 3100 | 2300 |
| 2.  | C0.00Cr19Ni23Nb2Ti | $\gamma$ | 550 220 48 50 | 1850 | 1850 | 1850 |
| 3.  | C0.06Cr14Mn20Ni10MoN | $\gamma$ | 810 510 62 73 | 3200 | 3200 | 1800 |
| 4.  | C0.04Cr12Ni36Ti3Al | $\gamma+\gamma'$ | 1110 820 31 51 | 2730 | 2730 | 1373 |
| 5.  | C0.06Cr12Mn20Ni5N | $\gamma$ | 800 420 54 62 | 2600 | 2600 | 1300 |
| 6.  | C0.04Cr11Ni83Mo2Ti1 (TT3) | $\gamma+\gamma'$ | 1180 770 21 24 | 1592 | 1592 | 1095 |
| 7.  | C0.08Cr18Ni10Ti | $\gamma+\delta$ | 610 320 64 61 | 1800 | 1800 | 600 |
| 8.  | C0.03Cr11Ni8Co4Mo2V | MA | 1100 1070 18 65 | 1700 | 1700 | 380 |
| 9.  | C0.08Cr17Ti | Ferrite | 507 360 34 66 | 800 | 800 | 70 |
| 10. | C0.02Cr11Ni11TiMo | MA | 1000 930 20 75 | 1300 | 1300 | 70 |
| 11. | C0.2Cr14Ni3Mo2W | MA | 1000 790 17 55 | 1000 | 1000 | 30 |
| 12. | C0.04Cr11Ni43Mo2Ti (TT1) | $\gamma+\delta$ | 1250 820 29 49 | 2563 | 2563 | 1736 |
| 13. | C0.04Cr11Ni43Mo2Ti (TT2) | $\gamma+\delta$ | 1250 820 29 49 | 2563 | 2563 | 1736 |

The amplitude of cyclic strains in the surface layers at a frequency of 0.5 Hz was equal to 1.6%.

The hydrogen resistance of the media was determined by using the coefficient of influence of hydrogen $\beta$ defined as the ratio of the number of cycles to failure in hydrogen to the number of cycles to failure in air. According to the values of their hydrogen resistance for $P_H = 35$ MPa and 293 °K, one can split the investigated materials into several groups. Thus, group I ($\beta = 0.5 \div 1$, $N = 1000 \div 2100$ cycles; see Fig. 1) contains low-strength highly plastic carbon- and nitrogen-free C0,00Cr19Ni23Nb2Ti steel in the state of solid solution practically insensitive to hydrogen and alloyed only with substitutional elements. This steel has low values of $\sigma_{0.2}$ and $\sigma_p$. Its low-cycle durability in air is also low (~ 1850 cycles). Group I also contains Ni-Al-Ti steels with intermetallic hardening and low-carbon nitrogen-hardened 14-10-20 and 12-5-20 steels. Group II ($\beta = 0.2 \div 0.4$ or $NH = 350 \div 800$ cycles) includes steels with unstable austenite, e.g., 18-10 steel and C0,03Cr11Ni8Co4Mo2V austenitic-martensitic steel with intermetallic hardening. Steels from group III (C0,02Cr11Ni11TiMo and C0,08Cr17Ti ferritic-aging steels and C0,08Cr17Ti ferritic steel) exhibit catastrophic embrittlement for high pressures of hydrogen.

The indicated distribution of materials according to their hydrogen resistance was checked under the conditions of combined action of adsorbed and absorbed hydrogen. The mode of occlusion was simulated by high-temperature hydrogenation: the specimens were heated in hydrogen under a pressure of 35 MPa to 773°K, held for 4 h, cooled down to room temperature, and tested for low-cycle fatigue in hydrogen at $P_H = 35$ MPa. It was discovered that preliminary high-temperature hydrogenation (PHTH) (Fig. 2) does not decrease the low-cycle hydrogen resistance (LCHR) of homogeneous (19-23, 14-10-20, 12-5-20, and 18-10) and MC steels (see Table 1. Nos. 10 and 11).

After PHTH, the durability of 11-43 (12) and 12-36 (4) steels becomes two and four times lower, respectively. Therefore, the homogeneous austenitic and MC steels have constant ultimate hydrogen durability at 293 °K independent of the temperature conditions and preliminary hydrogenation.
In materials with intermetallic hardening, where the phase boundaries play the role of hydrogen collectors, the LCHR depends on PHTH. To prevent negative consequences of the application of Ni-Al-Ni steels in high-pressure hydrogen, it is necessary to specify the corresponding temperature conditions fairly carefully.

In the dependences of LCHR on $P_H$, it is necessary to separate the properties and characteristics typical of all studied materials from the specific characteristic of individual structures. In general, the plots of the analyzed baric dependences are curves with two different sections corresponding low and high pressures. For low pressures, the durability of steels decreases, as a rule, more rapidly than under high pressures. The maximum decrease in serviceability is observed for $P_H < 6$ MPa. As the level of pressure increases further, the negative effect of hydrogen remain stabile.

Actually, the behavior of different materials is different under high pressures. All steels (except those hardened with the $\gamma'$-phase) have ultimate baric hydrogen resistance, i.e., the characteristic number of cycles to failure in hydrogen which remains constant as the pressure of hydrogen increases further. For Ni-Al-Ni steels, the indicated limit is absent and their serviceability is a monotonically decreasing function of $P_H$. Therefore, the baric limit of LCHR is a structure-sensitive factor. Thus, this limit exists for homogeneous MC and ferritic steels and is absent in the materials with $\gamma'$-phase.
As follows from Fig. 1, the \((\gamma + \gamma')\)-steels (Nos. 1, 4, and 12 in Table 1) are promising for application in hydrogen. They were studied after thermal treatment for the maximum heat resistance. The effect of aging in these materials appears as a result of the formation of coherent microstresses and general dispersion hardening controlled either by increasing the total amount of precipitations or by the level of stresses (by changing the parameter of incompatibility of the lattices of precipitations and the matrix). The lowest stresses are caused by the precipitations of the \(\gamma\) phase of \(\text{Ni}_{13}(\text{Al,Ti})\). The durability of the \(\gamma\)-steels in hydrogen increases with the ratio of contents of titanium and aluminum (\(\text{Ti} / \text{Al}\)) and the content of Ti (Fig. 3) specifying the composition and stoichiometry of intermetallic precipitations [6]. The increase in the indicated parameters leads to the following sequence of changes in the type of the second phase (bcc): \(\text{Ni}(\text{Al,Ti}) \rightarrow \text{Ni}_{2}\text{Ti} \rightarrow \text{Ni}_{13}(\text{Al,Ti})\) (fee) \(\rightarrow \text{Ni}_{3}\text{Ti}\) (hep).

Most likely, the parameters Ti and \(\text{Ti} / \text{Al}\) play, in this case, the role of indicators of the microstructural concentration of strains on the phase boundaries accompanied by the accumulation of hydrogen and damage to the metal. Thus, e.g., the influence of changes in the thermal treatment (TT) on the LCHR of 11-43 steel was discovered in [2]. As a result of simulation of the thermal conditions of soldering by step-by-step hardening (No. 13, TT2), the multiphase structure of steel (No. 12, TT1) transformed into a state close to a substitutional solution. As a result, the hydrogen resistance of steel became 1.5 times higher, i.e., equal to its level observed in air. After overaging (No. 6, TT3), this characteristic significantly decreases.

In comparing the LCHR of homogeneous steels alloyed with \(\text{C} + \text{N}\) and \(\text{C}\), we used the characteristics of nitrogen- and carbon-free refined \(\text{C}0.00\text{Cr}19\text{Ni}23\text{N}2\text{b}2\text{T}2\text{t}1\text{t}1\text{e}2\text{l}1\) steel (\(S < 0.003\%\), \(O_2 < 0.0008\%\), \(P < 0.003\%\)) in the state of solid solution as a reference point. Thus, for the indicated group of steels we simulated the behavior of the matrix \(\gamma\)-solution containing only substitutional elements. The relative influence of alloying with interstitial elements (\(\text{C}\) and \(\text{N}\)) was estimated by comparing with the LCHR of the substitutional solution. Since the substitutional elements weakly affect the strength of solid solutions as compared with the interstitial elements [6], the analyzed properties are weakly sensitive to changes in the concentrations of alloying elements within broad ranges of their concentrations [7]. The effect of hardening of the solution with nitrogen and carbon on the durability of steel can be different. Indeed, the durability of 18-10 steel with 0.08\% \(\text{C}\) in air is equal to the durability of 19-23 steel. At the same time, in hydrogen, its durability becomes 60-70\% lower. The 14-10-20 steel alloyed with nitrogen to 0.34\% at 0.04\% \(\text{C}\) has the same durability as the reference steel (its LCHR is \(\approx 1800\) cycles for much better static and fatigue characteristics in air). The comparison of the characteristics of two nitrogen-containing \(\text{C}0.06\text{Cr}12\text{Mn}20\text{Ni}5\text{N}\) and \(\text{C}0.06\text{Cr}14\text{Mn}20\text{Ni}10\text{MoN}\) Cr-Ni-Mn steels shows that their durability in hydrogen increases (from 1300 to 1800 cycles) with the concentration of nitrogen (from 0.15 to 0.34\%) and austenite-forming substitutional elements (Cr from 12 to 14\% in the presence of Ni and Ni from 5 to 10\%), i.e., as the stability of austenite increases. In the family of dispersion-hardening and homogeneous steels, the highest LCHR and, in fact, the complete absence of sensitivity to the action of the media are observed for substitutional solutions. In general, the procedure of solid-state hardening with nitrogen efficiently increases the LCHR of homogeneous austenitic steels.

Conclusions

On the basis of the data of testing of 11 corrosion-resistant steels of principal structural class established the dependences of low-cycle fatigue on the pressure of hydrogen within the range \(P_{\text{H}} = 0.1...35\) MPa at 293\(^\circ\)K. In the order of decrease in LCHR, the investigated materials can be arranged as follows: 1 austenitic steels with stabilized austenite and alloyed with nitrogen, \(\text{Ni-}, \text{Al-}, \text{Ti-}\) steels hardened with coherent \(\gamma\)-phase whose hydrogen resistance depends on the type of thermal treatment, 18-10 metastable steel, \(\text{C}0.03\text{Cr}11\text{Ni}8\text{Co}4\text{Mo}2\text{V}\) transient-type steel, martensite-aging and ferritic steels.

Hydrogen resistance of the first type of steels, 18-10 austenitic steel, and the last types of steels did not depend on the preliminary high-temperature hydrogenation, which results in the additional 2-4-folds of durability. The maximum decrease in serviceability is observed for PH < 6 MPa. As the level of pressure increases further, the negative effect of hydrogen remains stable.

The structure of a solid solution of homogeneous austenite alloyed containing only substitutional elements proves to be optimal in a sense of attainment of the maximum hydrogen resistant of corrosion-resistant steels. \(\text{Ni-Al-Ti}\) steels treated for maximum heat resistance have the durability in hydrogen which is proportional to the content of Ti/Al and Ti, and is also determined by the treatment conditions. By changing the mode of thermal treatment it is possible to increase the low-cycle hydrogen resistance of this type steels to the level of their durability in air.
As promising trends for the elevation of static and fatigue strength of materials in hydrogen is alloying of solid solutions with nitrogen, increasing of the degree of stability and restriction of the amounts of C, S, P, and O₂.

References

[1] O. S. Andreikiv, G. M. Nykyforchyn, and V. I. Tkachov, “Strength and fracture of metallic materials and construction elements in hydrogen-containing media,” in: Progress and Achievements [in Ukrainian], Karpenko Physicomechanical Institut of Academy of Sciences, Lviv (2001), pp. 248-286.

[2] V. I. Tkachev, V. I. Kholodnyi, and I. N. Levina, Serviceability of Steels and Alloys in Hydrogen [in Russian]. (1999).

[3] V. I. Tkachev, A. N. Romaniv, V. I. Vitvitskij, V. N. Kljuchnikov, and B. A. Agejev, "Experimental evolution of adsorption of hydrogen embrittlement of metals," in: Proc. of the Internat. School on the Physics of Ionic Solvatio [in Russian], Kiev (1983), p. 111.

[4] V. I. Tkachov, L. M. Ivas'kevych, and V. I. Vytvyts'kyi, "Methodical aspects of the evaluation of hydrogen resistance of steels," Fiz.-Khim. Mekh. Mater., 38, No. 4, 17-25 (2002).

[5] V. I. Tkachov, V. I. Vytvyts'kyi, and S. O. Hrebenyuk, "High-cycle fatigue of steels in high-pressure hydrogen," Fiz.-Khim. Mekh. Mater., 34, No. 1, 111-112 (1998).

[6] F. B. Pickering, Physical Metallurgy and the Design of Steels, Applied Sci. Publ., London (1978).

[7] E. A. Ulyanin, T. V. Svistunova, and F. L. Levin, Corrosion-Resistant Alloys Based on Iron and Nickel [in Russian], Metallurgiya, Moscow (1986).