HIGH-STRENGTH STEELS FOR OPERATION IN CRYOGENIC FUELS

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ABSTRACT

The analysis of the materials capable of operating in cryogenic fuels and their combustion products has been conducted. The requirements to the phase composition of corrosion-resistant carbon-free maraging steels, ensuring the combination of high strength (1000-1400 MPa), toughness values and hydrogen resistance at the temperatures from 17 to 500 K.

KEYWORDS

Maraging steel, cold brittleness, hydrogen brittleness, strength.

The works are being widely conducted presently for the development of engines and power plants, using cryogenic fuels (liquified natural and oil gas, hydrogen), which is associated with the shortage of oil and fuels made of it and due to the aggravating ecological situation and also due to the increasing demands of several branches of industry (aerospace) in the fuels with the improved heat of combustion and low-temperature service life. The selection of materials capable of operating in cryogenic fuels, especially at long-term service life is rather important problem among many problems arising in the process of these developments. This problem includes two aspects-cold brittleness and hydrogen brittleness.

The cold brittleness of structural steels and alloys with body centered cubic structure manifests itself in the decrease of ductility, impact toughness and cracking resistance at low temperatures. Heating to normal temperatures recovers the initial property level, if cooling didn't cause any changes in the phase composition. As a rule the effect of the time factor in this case is rather weak.

Hydrogen brittleness of the materials, as applied to the operating conditions of power plants, most frequently results in the decrease of ductility and characteristics of static and cyclic cracking resistance. The maximum manifistation of hydrogen brittleness is observed during the tests in the temperature range from 150 to 600 K. The embrittling effect is produced both by the external hydrogen media, and hydrogen, dissolved in the metal prior to testing. The amount of hydrogen, absorbed during the exposure in the water-containing medium, is increased with the operating temperature increase. It should be also noted, that hydrogenation at high temperature occurs not only in the hydrogen atmosphere but also in the atmosphere of gaseous hydrocarbons, dissociating on the metallic substrate with the release of hydrogen, capable of being diffused inside the metal. This process proceeds intensively at the temperatures above 800 K for methane. The increase of hydrogen effect duration during the tests or saturation sharply increases the embrittlement intensity. The highest danger as far as hydrogen embrittlement is concerned is the operation in the hydrogen atmosphere at the temperatures close to the room temperature after hydrogenation at high temperatures.

Thus, the embrittlement of the power plants various elements, operating with cryogenic fuels is governed by different mechanisms. For the materials used in cryogenic tanks, pipes, turbopump aggregates, operating at the temperatures close to the liquid hydrogen temperature (17 K) the decrease of their serviceability is associated with the cold brittleness phenomenon. For the components of heat exchanger, some elements of the burner, cooled structures, operating at higher temperatures (up to 500 K) the serviceability is defined by the total resistance to cold and hydrogen brittleness. For the components of the combustion chamber, turbine, nozzle, operating at high temperatures (up to 1000-1300 K) the most dangereous is hydrogenation at high temperatures and the operation at the transitional regimes at lower temperatures (300-700 K). However, it should be taken into account for the last case, that the material operates not in the atmosphere of gaseous hydrogen, but in the atmosphere of combustion products, the embrittling effect of which is much lower, compared to pure hydrogen.

Thus, from the viewpoint of the materials embrittlement, operating in the cryogenic fuels, the most dangerous is the operating temperature range from 17 to 500 K. The most expedient for these temperatures is the use of carbon-free maraging high-strength corrosion-resistant steels. Maraging steels ensure higher levels of strength and especially yield of the base metal and weldments both at normal and cryogenic temperatures, compared to austenitic steels widely used presently in cryogenic engineering. Besides, austenitic steels have lower technological efficiency in welding and are unsuitable for making large-size thin-walled structures (like tanks), due to high thermal linear expansion coefficient and significant distortion on thermal cycling. Maraging steels, having lower (by 1,5-2 times) thermal linear expansion coefficient, are the most promising material for such structures. Maraging steels are more technologically efficient and much cheaper, compared to high-alloy iron-nickel and nickel-base superalloys.

The change in the mechanical properties of high-strength martensitic EP866(15X16K5N2MUFAB) steel and high-alloy austenitic iron-nickel base - EP700(10X15N27T3M) alloy with the strength level of $\sigma_B = 1200$ MPa under the effect of cryogenic media and gaseous hydrogen are shown in Fig. 1 and 2. Fig. 1 shows, that EP866 steel with the pure martensitic structure is incapable of operating at low temperatures due to the sharp increase of sensitivity to stress concentrators. The strength of notched specimens σ_B^H is reduced at the temperature, lower than 150 K, and the impact toughness of the specimens with the fatigue crack KCT at T<220 K. Precipitation - strengthened iron-nickel-base EP700 alloy with the austenitic structure at cryogenic temperatures is practically insensitive to stress concentrators and doesn't reduce the toughness, compared to the room temperature. The tests of both materials under the effect of hydrogen atmosphere (the results are obtained together with A.A.Rogov) show (Fig.2), that they are rather sensitive to hydrogen brittleness. The brittleness temperature dependence $\beta = 1 - \psi_H / \psi_0$ (ψ_0 and ψ_H - are the initial reduction of area value and the value after the hydrogen effect) was

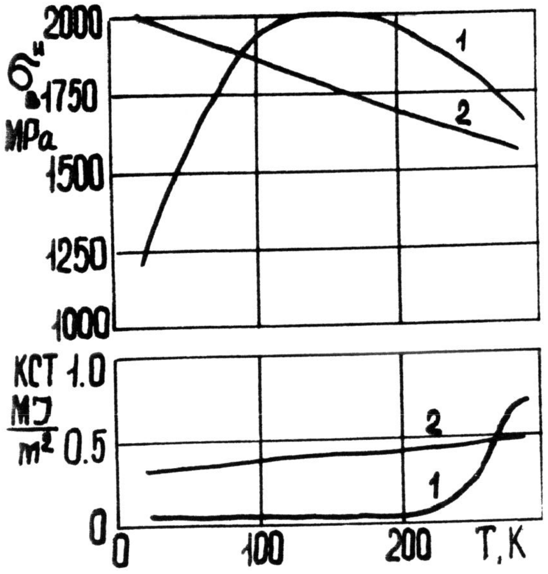

Fig. 1 Sensitivity to stress concentrators and toughness of EP 866 (1) and EP 700 (2).

defined at testing according to three conditions: 1 - tests of unsaturated specimens in hydrogen (T= 293 K, P= 15 MPa); 2 - tests in the air (T = 293 K) of the specimens, saturated in hydrogen (T= 673 K, P = 15 MPa, τ=10 hours); 3 - the test in hydrogen of saturated specimens. Martensitic EP866 steel is more sensitive to the tests in hydrogen atmosphere and is much lower sensitive to hydrogen saturation. Austenitic EP700 alloy, on the contrary, weakly responds to the tests in hydrogen atmosphere, but sharply reduces the ductility after hydrogen saturation, which is associated with hydrogen solubility in the austenitic matrix. The conducted analysis allows to suppose, that the mixed austenitic - martensitic structure can have minimum sensitivity to the effect of hydrogen and cryogenic temperatures, possessing the advantages of both martensitic matrix (lower hydrogen solubility), and austenitic one (low ductility decrease on testing in the gaseous hydrogen atmosphere and at cryogenic temperatures). The properties of the steels with mixed austenitic-martensitic structure can be controlled both by changing the phases ratio and their strengthening method. However, it should be taken into account, that the serviceability in the atmosphere of liquid and gaseous hydrogen should be ensured with high enough strength level ~ 1000 MPa. General requirements to high-strength corrosion-resistant maraging steels have been taken into consideration when developing the steels, operating in cryogenic fuels (Ya.M.Potak, 1972; C.R.Birman, 1974). They include the minimum content of interstitial atoms, gases and impurities; alloying with nickel in the amount of 8-10 %, increasing the martensitic matrix toughness, the molybdenium content of 1-2 % for preventing grain boundary precipitations during temper; alloying with chromium in the amount of 10-13%, ensuring the neccessary corrosion resistance. The principles of alloying and heat treatment ensuring high resistance to the effect of cryogenic temperatures and hydrogen atmospheres. The basic factors, defining the serviceability in these atmospheres are as follows: the amount and the distribution of the residual austenite; phase cold hardening of the martensitic matrix, the nature, amount and distribution of the strengthening phases.

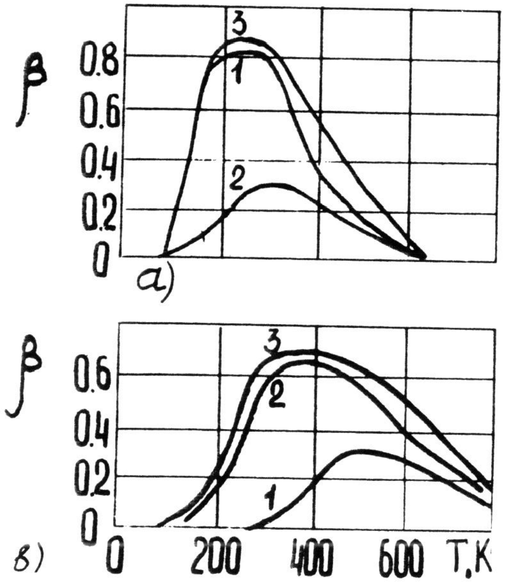

Fig.2 Embrittlement intensity for EP866(a) and EP700 alloy (b) on testing by the regimes 1, 2, 3.

The austenitic-martensitic phases relation can be controlled both by the steel alloying and the quenching temperature. The phase composition of low-carbon corrosion-resistant steels is defined with the sufficient accuracy by Potak-Sagalevich (Potak Ya.M., 1972) structure diagram for the equilibrium state of quenching from 1323 K. The mathematical processing of the experimental dependence of martensite fraction in the steel (α_M) on the chemical composition gives the relationship

$$\alpha_M = \exp[-5{,}68 * 10^4 * (\Sigma Ci * Ki)^{11{,}35}] \qquad (1)$$

where Ci- element weight fraction,

Ki - chromium equivalient of the first element (K_{Cr} = 1) in Potak-Sagalevich structure diagram.

The performed studies showed, that the equilibrium state of the austenitic-martensitic matrix, quenched from 1323 K does not give the optimum properties relationship. The quenching of carbon-free steels of this class from lower temperatures (1023 K) by 30-50 K exceeding the Ac_3 point gives the simultaneous strength and toughness increase at cryogenic temperatures. The low-temperature quenching efficiency includes not only the retention of considerable austenite quantity, but also obtaining phase cold - hardened fragmented banded substructure, consisting of alternating austenite crystals and rod-type martensite. The martensite fraction (α'_M) is defined for the quenching state from 1023 K for Cr-Ni-Co-Mo steels by the following relationship

$$\alpha'_M = \exp[-2{,}81 * 10^4 * (Ci * Ki)^{16}] \qquad (2)$$

In this case K chromium equivalents values significantly differ from the corresponding values of Potak-Sagalevich diagram. Ki factors values for carbon-free Fe-Cr-Ni-Co-Mo steels after quenching from 1323 K (Potak-Sagalevich coefficients) and after quenching from 1023 K are given in Table 1. Austenite content change in the steel changes simultaneously the strength level, toughness at the cryogenic temperatures and the sensitivity to hydrogen brittleness. The strength is decreased by every austenite percent, i.e. appoximately by 6 MPa with 20-50 % austenite content in the martensitic carbon-free matrix. The residual austenite effectively decreases the cold brittleness temperature (Tc.b.), the first 10-15 % austenite effect is particularly great. Further its effect is decreased. For carbon-free chromium-nickel steels tempered at 773 K to the strength level of σ_B~900 ÷ 1100 MPa the following relationship was obtained

$$Tc.b.\ (K) = 240 - 12 * A - 0{,}23 * A^2 \qquad (3)$$

where A - austenite volume fraction in percent (A < 30 %). The qualitative estimation of austenite effect on the hydrogen embrittlement resistance considerably depends on hydrogen effect nature. In the present paper the studies were carried out at sufficiently rigid hydrogen effect - the saturation in hydrogen atmosphere (P = 15 MPa) at 473 K for 100 hours and the tests in hydrogen atmosphere (P = 15 MPa) at the room temperature.

Table 1. Chromium equivalents values of Fe-Cr-Ni-Co-Mo martensite formation after different quenching temperatures.

Quenching temperature, K	Ki for the element			
	Cr	Ni	Co	Mo
1323	1,0	1,5	0,2	0,6
1023	1,0	2,5	0,8	1,0

The dependence of the embrittlement on the austenite content (A, %) and the strength level (σ_B, MPa) was studied (together with V.I.Vyshvanyuk) on the wide range of Fe-Cr-Ni-Mo melts with the austenite content of 8-73 % (the residue is martensite) and the strength level of 960-1140 MPa. The heat-treatment was carried out in the following way - quenching from 1023 K, temper at 773 K, two hours. The embrittlement was estimated by $\beta = 1 - \psi_H/\psi_0$ values (ψ_0 and ψ_H - the reduction of area values at the uniaxial tension at the room temperature, respectively, in the air and under the selected conditions of hydrogen effect). The following dependence was obtained by the regression analysis method:

$$\beta = -0,216 - 0,0444 * A + 0,00862 * \sigma_B + 0,00105 * A^2 - 0,00000689 * A^3$$

This dependence is given in Fig. 3 in the form of the diagram. From the diagram it transpires that the minimum embrittlement is observed at 25-30 % residual austenite content and the strength level raise increases the embrittlement intensity. In such a way, the optimum factor, from the viewpoint of hydrogen embrittlement, is 25-30 % residual austenite content, which simultaneosly ensures the sufficient toughness at cryogenic temperatures.

The considered group of alloys doest't contain the elements, causing the precipitation strengthening, in connection with which the strength level doesn't exceed 1000-1100 MPa. The strength level increase can be achieved by alloying with the elements, causing preicpitation strengthening. The study of

two alloying systems - with titanium and molybdenum along with cobalt showed, that the best reliability properties are ensured in the alloys with cobalt - molybdenum strengthening (Fig.4). The toughness at cryogenic temperatures in the alloys with Co-Mo strengthening with the strength level of 1200-1400 MPa is higher by 2-4 times, compared to the alloys, strengthened with Ti intermetallic compounds. The performed complex of studies showed, that the strength level in the steels of the second system is determined both by Mo and Co content. Molybdenum makes greater effect on strengthening, compared to Co, as it directly enters into the composition of the precipitating Fe_2Mo-phases under ageing. Cobalt decreases Mo solubility in the solid solution, accelerates its decomposition, increases the volume fraction of the precipitated phases. Simultaneously the size of the martensite rods and the diameter of strengthening phases are decreased. Based on the above-mentioned principles a number of carbon-free corrosion-resistant steels with the strength level of 1000 - 1400 MPa, and able to operate in the cryogenic fuel at the temperatures from 17 to 600 K have been de-

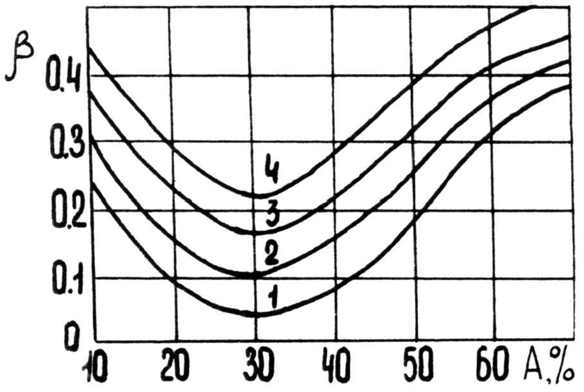

Fig.3 The effect of austenite on the embrittlement of Fe-Cr-Ni-Mo steels with σ_B = 960 MPa (1); 1020 MPa (2); 1080 MPa (3); 1140 MPa (4).

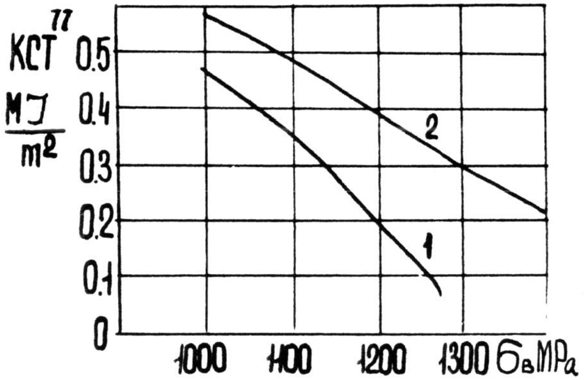

Fig.4. Cold brittleness of carbon-free maraging steels with different alloying methods. 1-steels with Ti-strengthening 2-steels with Co-Mo-strengthening.

veloped. The basic properties of these steels in comparison with the austenitic high-alloy EP700 steel are given in Table 2.

Table 2. Cryogenic steels.

Steel	Heat treatment condition	A %	Test temp. K	$\sigma_{в}$	$\sigma_{0,2}$	KCU	KCT	β
				MPa		MJ/m^2		
03X12N10MT (UNS-25)	Quenching, 1023 K. 2 times, temper 773 K.	30	293	1000	930	2.0	1.3	0,3
			77	1500	1350	1,5	0,8	
			20	1700	1550	1,1	0,4	
03X9N9K5M3 (UNS-49)	Quenching, 1023 K, temper 773 K.	15	293	1200	1170	1,8	1,1	0.25
			77	1650	1500	1,0	0,5	
			20	1900	1700	0,9	0,3	
03X10N9K7M3 (UNS-59)	Quenching, 1023 K. + (203 K) temper 773 K	25	293	1400	1300	1,8	1.3	0.35
			77	1850	1700	0,8	0,4	
			20	2100	1900	0,4	0,2	
10X15N27T3MR (EP 700)	Quenching, 1273 K ageing 1023 K. 16 hours, 923 K, 10 hours	100	293	1200	850	0.9	0.5	0.7
			77	1500	1000	0,8	0,4	
			20	1700	1150	0,7	0,4	

CONCLUSION

The optimum combination of the strength and reliability properties during service in cryogenic fuels at the temperatures from 17 to 500 K was obtained for the carbon-free maraging steels with the controlled phase composition, developed on the base of Fe-Cr-Ni-Co-Mo system.

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