HIGH-STRENGTH CORROSION-RESISTANT STEELS TOUGHNESS AFTER HEATING AT 623-773 K

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ABSTRACT

Fracture toughness of high-strength corrosion-resistant steels has been considered as the function of the duration and temperature of service heatings at 623-783 K. The analysis of various embrittlement mechanisms has been conducted, the methods for the estimation of kinetic parameters of the joint martensitic matrix decomposition processes have been proposed and realized on the personal computer. Temperature-time curves of the equal embrittlement values have been plotted for 01X12N8M2D2T steel by way of computations.

KEYWORDS

Martensite, chromium, solubility, strengthening, toughness.

The development of the modern branches of engineering required the development of technologically efficient high-strength steels, operating under all climatic conditions in the temperature range from 203 to 773 K. These steels should be easily welded in the thermally strengthened state and provide the weldment strength, close to that of the base metal strength. The basis for the development of such materials are poorly aged low-carbon corrosion-resistant martensitic steels (Ya.M.Potak, 1972). This class steels are used, mainly, at the temperatures not higher than 573 K, as the increase of the service temperature results in the solid solution decomposition and the decrease of the toughness and corrosion resistance. The nature, kinetics and interaction of the processes, observed in the temperature range of 573-773 K (recovery, precipitation of cementite, chromium carbides and intermetallic phases, delamination by chromium, stable austenite formation) define, to a great extent, the service reliability of these steels. The regularities of the

martensitic matrix decomposition processes and their effect on strengthening and embrittlement have been studied on test melts with the structure of carbon-free martensite (based on Fe-Cr-Ni systems with the additional alloying of some melts by 2 % Mo, 2 % Cu and 0.2 % Ti) and also on a number of commercial steels with the use of a complex of mechanical and physical analysis methods.

Two initial states have been considered - the quenched one, corresponding to the state of the weld and the near weld zone, and the quenched one with the subsequent temper, characteristic of the thermally strengthened base metal. As a rule, the temper for this class steels is carried out at high enough temperatures of 773-823 K, ensuring practically the completion of the recovery processes and the major part of carbonitride and intermetallic phases precipitation. In this case strengthening and embrittlement on subsequent long-term heatings at lower temperatures is, mainly, due to the solid solution delamination by chromium. In conformity with the Fe-Cr phase diagram (R.P.Elliot, 1970) the processes of Cr - phase formation, containing to 80 % Cr, are observed at the temperatures lower than 803 K, and the data on chromium solubility in iron at the temperatures of 573 -803 K are rather contradicting. The results of studying the chromium solubility limit in the martensitic matrix on the basis of Fe-Cr-Ni system are practically absent.

In this paper the study of chromium precipitation kinetics from the solid solution was, mainly, conducted by the resistometric method, which is rather sensitive to chromium content in the solid solution. It was found for the high-tempered condition of chromium-nickel martensite, that the value of the specific electrical resistance is increased by 2.2*10 Ohm*m with the increase of chromium content by 1 %, which allows to perform the qualitative estimation for the process of the phases (zones) precipitation, enriched in chromium. In the studied melts with the low content of interstitial atoms (< 0.01 % wt) the formation of carbonitrides is practically eliminated. It is shown in the paper, that the intensity and the maximum value of decrease at heatings after the initial temper are increased with the increase of Cr content in the steel. It was found by the authors, that rather long-term exposures (∼ 2000 hours) at 673 K the values ρ for all the melts with different Cr content become close, which can indicate the decomposition completion and the achievement of the chromium equilibrium concentration in the solid solution. The increase of heating temperature reduces the maximum value of decrease ρ, corresponding to the equilibrium state achievement, which characterizes the increase of chromium solubility with the temperature rise. The delamination by chromium is not observed at the heating temperatures above 803 K. After the embrittling

heatings the secondary heating at the temperature above 803 K results in the complete recovery of properties for all studied melts, which shows the complete solution of the phases (zones) rich in chromium, being precipitated at lower temperatures. The analysis of the obtained dependences for the maximum decrease (or increase) of ρ value at different heating conditions for the melts containing 9-13 % Cr, makes it possible to estmate the position of chromium solubility limit in the carbon-free iron-chromium-nickel martensite. The calculations show that the chromium concentration is 7.5; 8.5; 10.0 and 11.5 % wt at 623, 673, 723 and 773 K respectively.

The authors have performed the mathematical processing of the kinetic curves for ρ variation in accordance with equation (J.Christian, 1978)

$$\varepsilon = 1 - \exp(-K\tau^n),\qquad(1)$$

where K and n are constants; ε and τ are the extent and duration of the transformation, respectively. The transformation extent was calculated from the relationship

$$\varepsilon = \Delta\rho / \Delta\rho_{max},\qquad(2)$$

where $\Delta\rho$ and $\Delta\rho_{max}$ are the current and maximum values of ρ variation at heating.
In particular, it was obtained for the process of chromium precipitation from the solid solution, that at 623 K : K = 0.14; n = 0.26; at 673 K : K = 0.34; n = 0.25 at the activation energy Q = 0.58 kcal/mol, which is close to the activation energy of chromium volume diffusion.

The precipitation of the phases (zones) rich in chromium results in the material strengthening and embrittlement. The unambigous correlation is observed between the changes of electroconductivity (i.e. the transformation extent) and hardness HRC . With the chromium "removal" from the solid solution and the phases (zones) formation the hardness is increased. The precipitation of 1 % Cr increases the hardness aproximately by 3.5 HRC. The solution of the phases rich in chromium at high tempering temperatures results in the hardness decrease, respectively. Maximum strengthening on heating can be calculated according to the formula:

$$[\Delta HRC_\varrho]max = 3.5 \{[Cr] - [Cr]_\varrho\}.\qquad(3)$$

where [Cr] and [Cr]$_\varrho$ are initial and equilibrium (for the given heating temperature) chromium concentration in the solid solution, respectively. The decomposition of iron-chromium-nickel martensite, besides strengthening, results in the steel embrittlement. However, if strengthening is defined, mainly, by the matrix state, the number and dispersion of the phases, precipitated along the grain body, embrittlement is defined both by the grain body and the grain boundary state. Due to this fact the correct relation between the decomposition of

the martensitic matrix, strengthening and embrittlement can be obtained with the absence of the grain boundary state variation. In the paper the embrittlement was estimated by the variation of the cold brittleness temperature, Tc.b., determined as the temperature at which the fracture work of the specimens with the fatigue crack KCT is decreased by two times. The long-term exposures at 573-623 K for all the studied compositions and at 573-773 K for the melts alloyed with 2 % Mo don't result in the change of the grain boundaries state and lead to the increase of Tc.b. in accordance with the relationship:

$$\Delta \, Tc.b. = 14 * \Delta HRC_e = 49 * \Delta Cr. \qquad (4)$$

where HRC and Cr are the values of the increase in hardness and chromium quantity, precipitated from the solid solution. For the steels, containing no Mo, long-term heatings at the temperatures above 623 K result in the change of the grain boundaries, the etching ability of which is sharply increased. In this case the increase of Tc.b. value is much higher, than it was defined by the relationship 4, the discrepancy being the higher, the higher is carbon and nitrogen content in the steel. Thus, alloying of corrosion-resistant high-strength steels, used at elevated temperatures, with molybdenum is obligatory, and chromium content should be minimum, providing the required corrosion resistance of the steel.

Carbon-free steels, based on Fe-Cr-Ni -Mo system can ensure the strength level not more than 1000 MPa, which is not sufficient in some cases. The strength level increase is possible when alloying the base system with the elements, causing precipitation strengthening, such as Cu, Al, Ti, a.o. However, in this case the embrittlement intensity after the service heatings is increased, especially on the weld metal and the near weld zone of the weldments, not subjected to post -welding heat treatment. Hence, the prediction of the temperature-time serviceability zone for maraging corrosion-resistant steels is possible only when analyzing each decomposition mechanism separately and plotting the mathematical models, describing the process kinetics and its effect on strengthening and embrittlement. In the temperature range of 573-773 K different processes are superimposed on each other and it is rather difficult to separate them. The selection of the test melts alloying, the conditions of the initial heat treatment and studying methods allows in some cases to separate the kinetics of the individual process. As mentioned above, the temper at the high enough temperature, close to Ac_1, allows to analyze chromium precipitation processes out of the solid solution after long-term heatings by the resistometric and hardness methods. The analysis of copper and titanium precipitation out of the solid solution in the alloys, alloyed with these elements is possible for the alloys with low Cr content (less than 10 %) at the temperatures higher than its solubility limit (>673 K). At these temperatures the recovery processes occur quickly enough and stop at the early stages of precipitation strengthening. The selection of ageing and delamination processes by chromium can be carried out (on condition of their independence from each other) by differential kinetic curves plotting for the alloys, containing and not containing elements, causing precipitation strengthening.

However in most cases it was found to be impossible to separate the different transformations, particularly in complex-alloyed steels, where decomposition and solubility limits may not coincide with the ones obtained for simple test alloys. The mathematical methods of effects separation were developed and realized with the help of personal computers for these cases. It was accepted in the proposed model, that the considered processes occur independently from each other and the equation 1 is performed for each process. Besides, the transformation degree is believed to be proportional to the measured value change. Based on the experimental kinetic dependence of ΔX alloy particular property change (for example, specific electric resistance or hardness) being the total response for the phase and structure transformations in the alloy, the parameters Ki and n_i of equation 1 for i - process are calculated by nonlinear approximation methods. The calculation is carried out on the base of the relationship:

$$\Delta X = \sum \Delta Xi = \sum \Delta Xmax_i * [1-\exp(-Ki * \tau^{n_i})], \quad (5)$$

where $\Delta Xmax_i$ - the maximum change of the considered property when completing i - process. $\Delta Xmax_i$ value for every process can be obtained from the experiments with the test melts or calculated simultaneously with Ki and n_i parameters, if the mechanism of the i- process isn't changed in some temperature zone, so n_i value doesn't depend on T temperature and the following relationship is true for Ki:

$$Ki = Koi * \exp[-n_i * Qi/RT]. \qquad (6)$$

where R - universal gas constant.
Qi - activation energy of the i- process.
Koi - preexponential factor.
As a rule, the value of activation energy for decomposion processes corresponds to the activation energy of the chemical element diffusion or crystalline lattice fault and can be accepted either from the literature data or calculated on the base of the kinetic dependences for the considered process (n=const) at some temperatures on the base of the relationship for τ_ε time at the transformation degree ε = const:

$$\tau_\varepsilon = \tau_o * \exp (Q / RT), \qquad (7)$$

where τ_0 doesn't depend on the temperature. The values of n_i and K_i parameters for the delamination processes by chromium and the strengthening phases precipitation in steels, alloyed with copper and titanium (Table 1), were obtained by the combination of experimental and calculating methods.

Table 1. Kinetic parameters of martensite decomposition process.

Precipitations	T K	K	n	B
α - Cr	723	0,75	0,26	49
Cu	723	1,61	1,2	50
Ni$_m$ Ti$_n$	723	1,19	0,62	680
austenite	723	0,0007	1,1	-

Simultaneously, B_i coefficients, corresponding to cold brittleness temperature increase at 1 % wt element precipitation out of the solid solution are given in table 1. These coefficients were derived from the analysis of the cold brittleness temperature dependence on the decomposition degree for a number of test melts and commercial steels. For example, from the relationship 4 for chromium precipitation process out of the solid solution it is inferred that B_{Cr} = 49. The total increase of the cold brittleness temperature ΔT_Σ can be calculated from the relationship:

$$\Delta T_\Sigma = \Sigma \Delta T_i = \Sigma B_i * (C_i - C_{ei}) [1 - \exp(-K_i * \tau^{n_i}], \quad (8)$$

where C_i - the concentration of the i- element in the steel, C_{ei} - solubility limit of the i- element at the heating temperature.

As mentioned above, the considered phases (zones) the precipitation processes out of the solid solution result in the strengthening and the cold brittleness temperature increase. However, austenite formation stable at cooling to cryogenic temperatures is possible at long-term heatings in the temperature range of 723-773 K. Austenite interlayers between martensite crystals increase the steel toughness and respectively decrease the cold brittleness temperature. The measurement of the austenite quantity A (vol %) was performed by the magnitometric method and austenite formation kinetics was studied for Fe-12Cr-8Ni-2 Mo base system. Equation 1 kinetic parameters for this process at the temperatures of 723 and 773 K are given in Table 1. The dependence of the cold brittleness temperature change ΔT_A on the austenite content

is nonlinear and at A < 30 % is defined by the expression:

$$\Delta T_A = 0.23 A^2 - 12 A \quad (9)$$

The derived relationships allow to predict the temperature-time range of serviceability for the differently alloyed steels. The similar region is given in Fig. 1 for 01X12N8M2D2T (with 0,2 % Ti) complex-alloyed steel, in which the austenite in the initial state is absent.
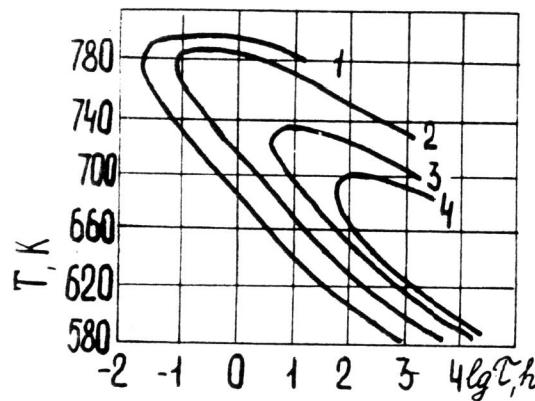

Fig.1 Temperature-time curves for the equal embrittleness values:
ΔT_Σ =100 K (1);
ΔT_Σ =200 K (2);
ΔT_Σ =300 K (3);
ΔT_Σ =400 K (4).

The UNS-16 (06X15N5MUFB) modification of thermal-resistant steel with the ultimate strength of σ_B^{293} = 1200 MPa and σ_B^{773} = 1000 MPa was developed on the base of the above-pointed conceptions for the operation at the temperatures of 203-773 K. Compared to the initial steel, chromium content was decreased from 15 to 13 %, which allowed not only to decrease the delamination intensity by chromium at the service heating, but also to increase nickel content, remaining in the martensitic class. This factor gave the possibility to suppress the ferrite formation entirely and to ensure the optimum quantity of the residual austenite (15-20 %), which allowed to increase the toughness with the satisfactory thermal resistance properties. Besides, it should be noted, that higher values of cracking resistance and corrosion cracking resistance is peculiar to the novel UNC-16Ya (06X13N7MUFB) steel both for the base metal and weldments, not subjected to heat treatment after welding. The comparison of UNS-16 and its UNS-16 Ya modification properties after the service heating at 723 K for 250 hours are given in Table 2. The starting heat treatment of both steels included the quenching from 1273 K and the temper at 793 K, 2 hours.

Table 2. The properties of UNS-16 and UNS-16Ya thermal resistant steels

No	Steel	Heating condition	Base metal properties		Weldments properties (heat treatment+welding)	
					Melting zone	Corrosion cracking resistance in salt-spray chamber 5%NaCl at 308 K
			K_{ic}^{203}	K_{iscc} in 3%NaCl	KCT^{203}	
			MPa $*$ m$^{1/2}$		MJ/m^2	MPa
1.	UNS-16	–	220	152	1,2	1000
		723 K,250 h	60	90	0,08	300
2.	UNS-16Ya	–	220	152	1,2	1000
		723 K,250 h	91	120	0,4	600

CONCLUSION

The basic processes, causing the embrittlement of low-carbon high-strength corrosion-resistant steels after long-term heatings at 623-773 K are the delamination by chromium and intermetallic phases precipitation. The maximum effects of the cold brittleness temperature increase at the exposures in the order of one thousand hours are observed at the temperatures of 673-723 K. The formation of residual austenite and cromium solubility increase at the temperatures of 723-773 K result in the embrittlement intensity decrease. On the base of the developed principles the steel, capable of operation for 250 hours at the temperatures to 773 K has been produced.

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