Mechanical Properties Degradation Modeling of Austenitic Chromium-Nickel AISI 304 Steel After Thermal Ageing

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Abstract. Austenitic chromium-nickel steel AISI 304 is used as a structural material for heat exchange equipment. Long-term operations result in degradation of mechanical properties of material due to formation of chromium carbides at grain boundaries. The influence of various thermal ageing modes of AISI 304 steel on mechanical properties with metal fragments of reactor plant on fast neutrons of RP BN-600 taken as an example after long-term operation has been investigated.

1. Introduction

Structural elements of fast neutron reactor plant equipment are operated at temperatures up to 550 °C for lengthy periods of time. One of the main structural materials for these elements is austenitic corrosion resistant AISI 304 steel, prone to thermal ageing that result in secondary phases (precipitates) [1].

There are number of publications [1-10] concerning changes in structure and mechanical properties of AISI 304 steel after thermal ageing at 500-800°C. Holomon parameter \( P \) [1] characterizing combined effect of temperature and duration of thermal ageing is widely used to compare the changes in properties and structure of steel after ageing in various conditions:

\[
P = T (5.15 + \log \tau),
\]

where \( T \) is ageing temperature in Kelvin; \( \tau \) is ageing duration in hours.

Most of the studies presented in literature are described as in-situ ageing [1-10]. They show that changes in steel structure depend on factors such as carbon content, the presence of \( \delta \)-ferrite and stresses. Characteristic structural changes concerning the isolation of excess carbide and intermetallic phases during ageing (without stresses) of 304H steel (C-0.05 ÷ 0.7%) are displayed in time-temperature-precipitation-diagrams [2, 3]. The results are given for a temperature range of 550 ÷ 800 °C and a duration of up to 100,000 hours (\( P \approx 4500 \div 9500 \)). The test samples were preliminarily subjected to austenizing annealing. Studies of the secondary phase generated by thermal ageing show that the main precipitate in the given range of \( P \) is \( M_{23}C_6 \)-type carbide. At the same time, at \( P \approx 8900 \), the \( \sigma \) phase [6] which is the most significant embrittlement factor in thermal ageing was found. Reduction of carbon, \( \delta \)-ferrite and stresses in steel accelerates formation of \( \sigma \)-phase, and therefore it can be detected at lower Holomon parameter \( P \) [1-8]. The combination of several factors generally has a synergistic effect. Thus, \( \sigma \)-phase was observed at \( P<7000 \) in steel (not subjected to austenization) with reduced carbon content.
C = 0.012% and initial δ ferrite content of 2.5% [6]. Together with the above precipitates, some authors also found Me₆C carbide [4] and the secondary α-phase [8, 11] in aged steel. During thermal ageing precipitate emissions reduce plasticity [2, 6, 9] and impact strength of steel [2, 8, 10] with practically constant properties. It has been shown that at carbide embrittlement the relative decrease of these characteristics was at the range of ~ 0.5 ± 0.6 from the corresponding values of the initial state [2, 8, 9, 10]. At transition to intermetallic embrittlement (with formation of σ-phase) they fell ~ to 0.15, which was close to the level of "complete ageing" for 316 steel and non-austenitized welds [1].

Along with the described studies of laboratory ageing in “Prometey”, works were carried out to assess changes in the structure and properties of austenitic steels after operational ageing of up to 170,000 hours as part of the RP BN-600 [12-14]. It has been confirmed that thermal ageing practically has no effect on the material’s yield strength and ultimate strength and has the greatest effect on ductility and toughness. The most representative data array are presented in the work [14] for 304 steel after operation as part of the intermediate heat exchanger (IHE) of RP BN-600 in the temperature range of 515–550 °C for 170,000 hours. Most of the obtained experimental data confirm that the relative decrease in ductility and toughness characteristics is at least ~ 0.5 ± 0.6 from the initial level. The exception is the mechanical properties studies results of pipe plate metal, in which Me₆C₆-type carbides almost completely fill grain boundaries that leads to a significant fraction of intergranular destruction and reduction of ductility and impact strength by less than 0.5 of the initial value. At the same time, the presented data [12-14] are obtained on a limited base of thermal ageing, while the design service life of RP BN-600 made of 304 steel can amount to 480,000 hours. Obviously, because of the time-limited period of research and/or engineering that justify the service life of the materials the experimental results can be obtained only by accelerated ageing at elevated temperatures. At the same time, it is necessary to ensure that the temperature and holding time are combined so that the process mechanism does not change during operational and accelerated ageing. It seems advisable to carry out material ageing at increased temperature in terms of the operating conditions to Holomon parameter values corresponding to the specified resource. In addition, there is a significant influence of the initial state of the metal on the thermal ageing rate [1-10, 14]. Therefore, in order to determine the possibility of extending the service life of RP BN it is advisable to use the natural material of the operating reactors.

This work studies the investigation results of the effect of accelerated thermal ageing on short-term mechanical properties of austenitic chrome-nickel 304 steel. Ageing acceleration was performed by two methods: post-ageing is performed by additional thermal ageing of metal after 170,000 hours in RP BN-600 at elevated temperature, and laboratory ageing of the same metal at elevated temperature in simulated initial state after additional heat treatment - austenization. All the precipitates formed during service life are dissolved during austenitization. In both cases, the natural metal of the RP’s fragments is investigated, and in case of post-ageing in order to speed up the process not only the increased temperature, but also the service lifetime are used.

2. Research materials and methods

The studies were carried out on 304 steel samples cut from shell and upper pipe board of the intermediate heat exchanger (IHE) of RP BN-600 after operation at 550 °C for 170,000 hours (O state). According to the process regulations, at IHE manufacturing the shell metal and the upper pipe board was heat treated (austenitized) at 1050 °C before installation. In order to simulate the initial state, some of the test samples were heat treated at the same temperature for 30 minutes to restore the structure and properties (OA state). Post-ageing of metal in O state was carried out at 700 °C during 31500 hours (OLPA state). Ageing of metal in OA state is performed at 700 °C during 35000 hours (OALA state). Periodic intermediate metal extraction was carried out to assess the kinetics of changing structure and properties during post-ageing and ageing. Metal states and thermal holding modes are given in Table 1; chemical composition of materials is given in Table 2.
Table 1. Conditions of analyzed steel.

| No. p/p | State      | Thermal holding mode                                                                 |
|---------|------------|--------------------------------------------------------------------------------------|
| 1       | (O)        | Operational ageing at $T = 550 \, ^\circ C$ for $170,000 \, \text{hrs}$             |
| 2       | (OLPA)     | Operational ageing + laboratory post-ageing at $T = 700 \, ^\circ C$ from $100$ to $31,500 \, \text{hrs}$ |
| 3       | (OA)       | Operational ageing + austenized heat treatment $T = 1050 \, ^\circ C$ - $0.5 \, \text{hr}$ |
| 4       | (OALA)     | Operational ageing + heat treatment ($T = 1050 \, ^\circ C$ - $0.5 \, \text{hr}$) + laboratory ageing at $T = 700 \, ^\circ C$ from $800$ to $35,000 \, \text{hrs}$ |

Table 2. Chemical composition of the tested 304 steel

| Fragment | C     | Cr     | Ni     | Mn     | Si     | S      | P      | Ti     |
|----------|-------|--------|--------|--------|--------|--------|--------|--------|
| Shell    | 0.08  | 17.7   | 9.5    | 1.48   | 0.56   | 0.007  | 0.016  | 0.09   |
| Pipe board | 0.09  | 17.8   | 8.9    | 1.36   | 0.63   | 0.008  | 0.010  | 0.05   |

Ageing was performed in laboratory furnaces. The furnace temperature was kept with accuracy $\pm 1 ^\circ C$. Impact bending tests were carried out on Charpy type V-notch samples. The tests were carried out at the most sensitive to heat-ageing temperature of + 20 °C.

3. Results and discussion

Figure 1-a shows time dependencies of impact strength ($T_{\text{test}} = 20 \, ^\circ C$) of the shell metal and the pipe board after post-ageing at 700 °C as well as the impact strength values obtained for state O. In this state the level of impact strength of the pipe plate metal is nearly twice lower than that of the shell metal, despite minor chemical differences in the composition. The 2-sectional time dependence of the strength during post-ageing is similar for both materials, with non-monotonic character. In areas up to 6000 hours, partial recovery of properties is observed with a maximum from 4000 to 6000 hours. At a longer time in the second post-ageing area, the strength value decreases to reach the "plateau" ($\tau = 8000 \div 31,500 \, \text{hrs}$), but does not reach the level in state O, remaining 1.2-1.5 times higher. At the same time, within the whole time span, the difference between the impact strength values of the shell metal and the pipe board are practically constant.

![Figure 1](image-url)
Such a non-monotonic nature of the impact strength time dependence seems is because of an in temperature increase to 700°C in laboratory conditions, resulting in growth of carbon solubility in the solid austenite solution as compared to the operating conditions. Therefore, the balanced concentration of chromium is changed. It is bigger in the first stage of the post-ageing than that at the austenite-chromium carbide boundary by the end of the operating period. This result in partial dissolution of carbides formed at grain boundaries and the increased impact strength during operation.

The suggested assumption is confirmed by thermodynamic and kinetic calculations of carbide formation reaction. For 18/12 type steel [15] the balanced carbon concentration was calculated from empirical equation (2) providing good correlation between the calculated and experimentally determined values.

\[
\lg[C]_1 = 7.71 - \frac{6672}{T(K)}
\]

where \( [C]_1 \) is the equilibrium concentration of carbon in the solid austenite solution for 18/12 type steel in ppm, \( T(\text{K}) \) is Kelvin temperature.

The balanced concentration of carbon \([C]_2\) for the tested composition of 18-9 type (Table 2) was calculated taking into account the change in the content of alloying elements as per the following (3):

\[
[C]_2 - [C]_1 = \frac{f^{\text{Si}}_C f^{\text{Cr}}_C f^{\text{Mn}}_C f^{\text{Ni}}_C}{f^{\text{Si}}_C f^{\text{Cr}}_C f^{\text{Mn}}_C f^{\text{Ni}}_C}
\]

where \( f^{\text{Si}}_C, f^{\text{Cr}}_C f^{\text{Mn}}_C, f^{\text{Ni}}_C \) are the relative carbon activity coefficients determined for 18/12 composition; \( f^{\text{Si}}_C, f^{\text{Cr}}_C f^{\text{Mn}}_C, f^{\text{Ni}}_C \) are the coefficients of relative carbon activity determined for 18/9 composition (Table 2). The values of relative carbon activity coefficients were calculated as per the dependencies given in [16].

As a result, the equilibrium concentration values, which amounted to 0.000133 wt.% and 0.00195 wt.% for 550 °C and 700 °C respectively were calculated as per the equations (1) and (2) for the pipe board.

With the values \([C]_2\) obtained from the material balance equation (4), the balanced constant of \( \text{Cr}_2\text{C}_6\) \( K_p \) (5) formation reaction was calculated

\[
\frac{[\text{Cr}]_v}{[\text{Cr}]_g} = \frac{C_{\text{Cr}} - C_{\text{Kr}}}{C_{\text{Cr}}}
\]

\[
k_p = \frac{1}{\frac{[\text{Cr}]_v}{[\text{Cr}]_g}}
\]

where \([\text{Cr}]_v\) is the concentration of chromium in the austenitic solution upon completion of the carbide formation reaction and getting the balanced carbon content \([C]_f\). \( C_{\text{Cr}} \) is the total chromium content in the steel, \( C_{\text{Kr}} \) is the chromium content in \( \text{Cr}_2\text{C}_6 \) carbide after bonding of the super balanced carbon in carbide. The obtained \( K_p \) allows to calculate the equilibrium concentration of chromium at the boundary of austenitic solution and carbide \([\text{Cr}]_g\) - the initial boundary condition of chromium diffusion from solid solution to the boundary of grain at which carbide growth occurs (6):

\[
[\text{Cr}]_g = (K_p [\text{C}]_s)^{\frac{1}{3}}
\]

Calculations carried out according to equations (4-6) for the metal of the pipe board showed that the values of chromium concentration \([\text{Cr}]_g\) in the austenitic solid solution at the carbide boundary were 3 wt.% and 7 wt%; for temperatures of 550 °C and 700 °C, respectively.

The rate of the chromium carbide formation reaction at a relatively low operating temperature is determined solely by the rate of chromium diffusion from the grain volume to the boundaries, since the volume diffusion coefficient of chromium is significantly less than the grain-boundary diffusion coefficient \( D^{\text{Cr}}_v = 1 \cdot 10^{-22} \, \text{m}^2/\text{s} \) and \( D^{\text{Cr}}_g = 3 \cdot 10^{-11} \, \text{m}^2/\text{s} \), respectively [17], and also significantly less than the diffusion coefficient of carbon in austenite \( D^{\text{C}}_v = 1 \cdot 10^{-15} \) [18]. So for kinetic calculations, a diffusion
model for a semi-limited body can be used, according to which the amount of chromium transferred to the boundary during the time \( \text{d} \tau \) is

\[
dC_r = 2S([C_r]^v - [C_r]^g)\left(D_v \frac{d \tau}{\pi}\right)^{1/2}
\]

where \( S \) is the boundary area per unit volume, coefficient 2 takes into account the two-sided diffusion of chromium to the boundaries. Calculations of carbide formation kinetics carried out taking into account changes in equilibrium concentrations \([C_r]^v\), \([C_r]^v\) and \([C_r]^g\) as carbon and chromium of their austenitic solution move to carbide. They showed that after 170 thousand hours of operation the reaction is far from complete and more than 0.06 % wt. of carbon remains in the solid solution of the metal of the pipe board. Calculations of the diffusion profile of chromium show a decrease in chromium content in the submicron layer near the grain boundary to values less than 7% wt. This fact also has experimental confirmation. In the work [14] the microstructure of the grain boundary regions of the metal of the pipe board after long-term operation was studied by electron backscattered diffraction (EBSD). Thin layers of \( \alpha \)-iron with reduced chromium content localized along the grain boundary near chromium carbide particles are obtained. It is obvious that during long-term operation, the diffusion of chromium from the boundary vicinities to the carbide formed at the grain boundary resulted in \( \gamma \rightarrow \alpha \) transformation.

Thus, the partial recovery of property values detected at the initial stage of post-ageing (up to 6000 hours) is due to the formation of a grain boundary zone depleted by chromium as a result long-term operational ageing at 550 °C and a significant increase in the equilibrium value \([Cr]^g\) with an increasing temperature up to 700 °C. These factors provide reverse diffusion of chromium from the grain boundary at the initial stage of post-ageing and partial dissolution of grainbordering chromium carbides formed during operation, resulting in partial increase of impact toughness. Examination of fractures of samples after impact bending tests in the state of O and OLPA (4000 hours), carried out in work [19], makes it possible to conclude that the number of carbides on the flat facets surface formed at destruction twin-boundaries is reduced. At the same time, a special role of twin-boundaries in austenitic 304 steel properties degradation in case of thermal ageing is noted.

Reduction of impact strength is due to the increase in the chromium content in the boundary vicinities caused by acceleration of diffusion at 700 °C from the bulk. Constant values in second section of impact strength time dependence is due to tend carbon content in austenite to equilibrium concentration \([C_r]^v\) at 700 °C (Figure 1).

The obtained time dependencies of impact strength as a result of laboratory ageing at a temperature of 700 °C for the test samples after austenizing heat treatment simulating the initial state (OALA state) show that the dependence monotonously comes to the "plateau" after 5000 hours of ageing at a 700 °C. Kinetic calculations of carbide formation allow to conclude that by this time carbon content decreases to equilibrium value \([C_r]^v\).

It should be noted that when the ageing duration increases to 35 thousand hours, there are no significant changes in impact strength which indicates the absence of other mechanisms leading to degradation of properties, in particular forming of intermetallic phases. This fact is confirmed by monotonic curves of dependencies Holomon parameter \( P \) – relative decreasing of impact strength due to ageing at wide range temperature-time conditions for shell and upper pipe board metals.

It should be noted that in all investigated states (O, OLPA, OALA) except for simulated initial state of OA, time dependencies of impact strength for metal of pipe board and shell are fundamentally different. The shell metal shows a significantly lower tendency to thermal ageing relative to the pipe board metal with practically close grain sizes and little difference in chemical composition. Obviously, there are structural state differences associated with steels melting technology that are indelible in high temperature austenitic heat treatment.
Figure 2. - Operation of impact strength of steel 304 shell (○, ▲) and upper pipe board (○, ●) of IHE RP BN-600 in states of OA and OALA; ○ – OA state; ▲, ● – OALA state.

Figure 3. – Relative changing of impact strength vs Holomon parameter P steel 304 shell (○, ▲) and upper pipe board (○, ●) of IHE RP BN-600

4. Conclusions
1. Two-stage heat exposure - operational ageing and post-ageing in laboratory conditions at temperature elevated to 700 °C non-conservative simulates long-term thermal ageing of steel 304 RP BN-600 operating conditions at 550 °C temperature. Extreme dependence of impact strength of steel 304 on time of post-ageing at temperature 700 °C is revealed. At the initial stage of post-ageing partial recovery of properties takes place with maximum in the range of 4000 ÷ 6000 hours, then values of properties decrease.
2. The increase in the impact strength of the 304 steel at the initial stage of post-ageing at a temperature of 700 °C is due to the incompleteness of the carbide formation reaction during operation and the formation of a chromium-depleted area near the grain boundary. Increasing the temperature to 700 °C increases the solubility of carbon in the austenitic solution and the cause reverse diffusion of chromium from the carbide into the solid solution, accompanied by partial dissolution of the grain boundaries carbides formed during operation.

3. In order to simulate long-term operational ageing of 304 steel it is adequately used data on ageing of metal of spent fragments of equipment in the state after austenitization (simulation of initial state) at temperature increased to 700. The results of tests in this state on a time basis of 35 thousand hours show that after a holding duration of more than 5 thousand hours there are no changes in the impact strength, which is due to the completion of the carbide formation reaction.

4. There is significance in the tendency to thermal ageing of metal fragments of heat exchange equipment at close grain sizes and insignificant difference in chemical composition.

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