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CARBIDE FORMING SPECIAL FEATURES AND FRACTURE MECHANISMS UNDER THE AUSTENITIC CHROMIUM-NICKEL 304 STEEL POST-LIFE AGEING

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Abstract. Post-life ageing of austenitic chromium-nickel 304 steel elements of the fast neutrons reactor equipment was carried out at a temperature above the operating conditions. The change in the short-term mechanical properties of the material was investigated. The relationship between the change in impact strength, fracture mechanisms and the morphology of carbide precipitates was revealed.

Keywords: post-life ageing; austenitic steel; mechanical properties; fracture mechanisms; microstructure; carbides precipitation.

1. Introduction

An operating temperature of the fast neutrons reactor equipment structural elements can be up to 550°C for a long time. Austenitic chromium-nickel 304 steel is one of the main structural materials for these elements. It is known that under these operating conditions, steel exhibits a tendency to thermal ageing, leading to degradation of the material properties [1].

There are a number of publications where changes in the mechanical properties and structure of 304 steel under the thermal ageing effect are considered [1-4]. The investigations were carried out both on metal aged under laboratory conditions [1, 2] and on metal after post-life ageing during 200,000 hours [3]. As shown in work [4], the 304 steel was studied in two states after operation in the intermediate heat exchanger (reboiler) of the fast neutrons reactor at 515-550°C for 170 thousand hours and after laboratory ageing at 700°C. It was confirmed that thermal ageing practically does not affect both to the yield strength and ultimate strength of the material. Thermal ageing most strongly affects to the ductility and impact resistance. These changes in the mechanical properties were associated with microstructural changes, in particular, with the $Cr_{23}C_6$ carbides precipitation on the grain boundaries, weakening the cohesive strength of the grain boundaries. The plasticity, toughness and crack resistance decreases, the temperature dependence of these properties changes and the tendency to cold-brittle appears under the ageing process.

The fast neutrons reactor design service life may be up to 480 thousand hours. Obviously, in a time-limited period of research and/or constructional design, experimental results which justify such a long service life of materials can only be obtained through accelerated ageing at elevated temperatures. It is desirable to provide such a temperature and holding time combination, so that a mechanism for changing the microstructure and properties at the accelerated ageing was the same for ageing under operating conditions. For the equipment life prediction, it seemed expedient to carry out the service equipment elements

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ageing at an elevated temperature, i.e. in fact, it is the ageing of material previously worked at operating temperatures, with the aim of longer service life modeling. In this case, the studies duration due to the operating exposure is reduced, and also, what is important, the full-scale metal of the equipment elements is investigated. The present work is devoted to the problem of the short-term mechanical properties changing and their correlation with fracture mechanisms of austenitic chromium-nickel 304 steel during the post-life ageing process.

2. Materials and methods

The investigations were carried out on a 304 steel samples cutting from the upper tube plate conical transition of the fast neutrons reactor reboiler after exploitation at a 515-550°C range temperature with a duration up to 170,000 hours. In the reboiler manufacturing formulae, the upper tube plate metal before the installation was heat-treated at a 1050°C. To simulate the initial state, some of the metal samples to be studied were heat-treated at the same temperature for 30 minutes in order to restore the properties. The chemical composition of the metal is shown in Table 1.

In laboratory furnaces at a temperature of 700°C, the ageing of metal after exploitation up to 15,000 hours was carried out.

Impact-bending tests were carried out on the Charpy V-notch specimens at the temperature of 20°C, which most sensitive to thermal ageing. The fracture patterns, local elemental and phase composition of precipitates investigations were carried out using a scanning electron microscope Vega II (Tescan).

Table 1. Chemical composition of the investigated steel.

Elements content, mass. %							
C	Cr	Ni	Mn	Si	S	P	Ti
0,09	17,8	8,9	1,36	0,63	0,008	0,010	0,05

3. Mechanical tests results

The impact resistance effects (T_{test} = 20°C) on the thermal ageing time at a T = 700°C are shown in Fig. 1. The initial point of this correlation corresponds to the impact strength value after exploitation. The impact resistance value in the simulated initial state is also presented for comparison.

The time dependence of the metal impact resistance under ageing process is nonmonotonic with a maximum in the range from 4000 to 6000 h. When thermal ageing time is more than 6000 h, the impact strength gradually decreases, asymptotically approaching to the metal impact strength values in the state after exploitation.

4. Fractographic investigations results

Fracture surface specimen images under impact loading after exploitation are shown in Fig. 2. The flat facets (Fig. 2-b), formed by the quasi-brittle fracture mechanism, are observed among viscous intergranular fracture points (Fig. 2-a).

The size of these facets without signs of plastic deformation is comparable with the size of the metal grain. At the same time a large number of facets located in a plane that is parallel to the macrocrack propagation. The flat facets are observed at the specimen fracture even visually when the light is reflected. In areas of viscous intergranular cup fructure, particles of a globular shape are observed. The X-ray spectral microanalysis of these particles allows to identify them as a chromium carbides.

The simulated initial state sample fractions are formed entirely by the viscous intercrystalline fracture mechanism.

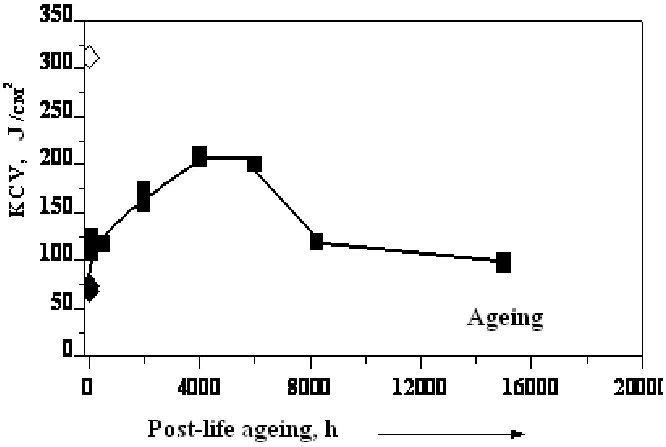

Fig. 1. "The 304 steel impact strength - the ageing time at a 700 °C" curve. T_{test} = 20°C. ◇ - simulated initial state after austenitization, ◆ - state after exploitation, ■ - post-life ageing.

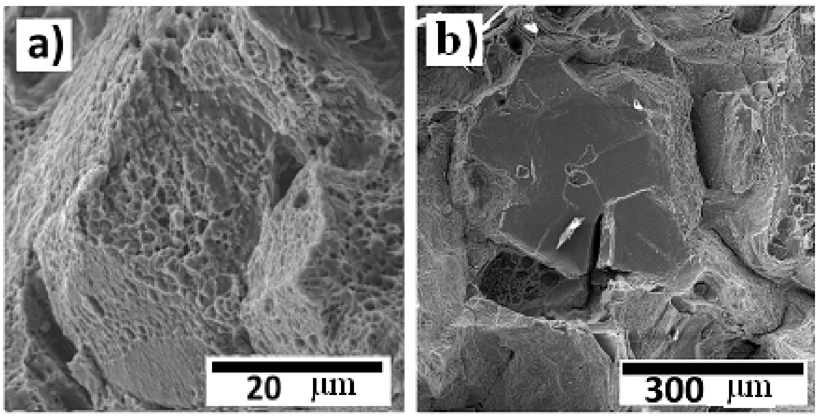

Fig. 2. The sample fracture surface under impact loading after exploitation: a) viscous intergranular fracture area; b) quasi-brittle intergranular fracture facets.

The sample surface fracture in the first stage of post-life ageing (τ = 4000 h) corresponding to the impact strength maximum (KCV = 207 J / cm^2) visually looks brushed. The fracture after impact loading is formed mainly by viscous intergranular fracture areas (Fig. 3-a). When the surface was studying in a scanning electron microscope, only individual quasi-flat areas with a traces of plastic deformation (Fig. 3-b) were detected. The depth of the plastic zone in such areas is somewhat smaller in comparison with the surrounding areas.

When ageing time increasing (τ = 15,000 h) and it is correspond to the "plateau" on the "impact resistance – post-life ageing time" curve, facets similar to those found for samples after exploitation (Fig. 2-b) were found on fractures.

Facets images on fractures after exploitation, as well as a quasi-flat areas on the sample fracture after 4000 hours of ageing, obtained at high magnification, are shown in Fig. 4. It was possible to reveal a continuous layer of lamellar particles covering the surface at the flat facets surfaces observed for low magnifications after the exploitation (Fig. 4a). On a quasi-flat area of the sample's fracture after ageing (τ = 4000), such particles do not form a continuous layer and it have smaller dimensions in the observation plane (Fig. 4b). For the facets after 15,000 hours of ageing, a continuous layer of lamellar particles, as for facets after exploitation, was again found.

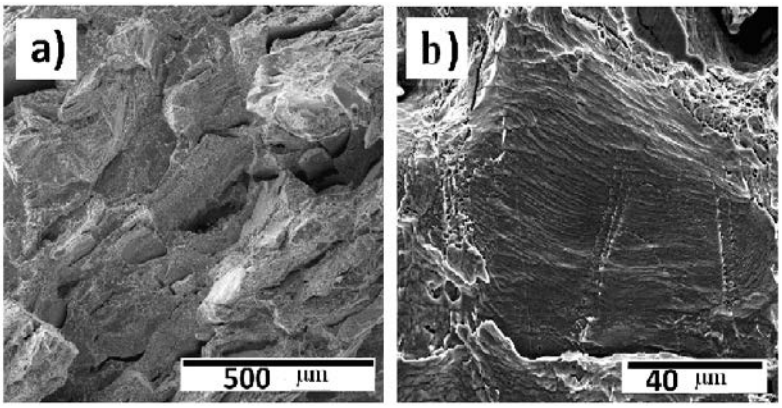

Fig. 3. Samples fracture surfaces under impact loading after post-life ageing process during τ = 4000 h: a) general form, b) quasiplane areas with a traces of plastic deformation.

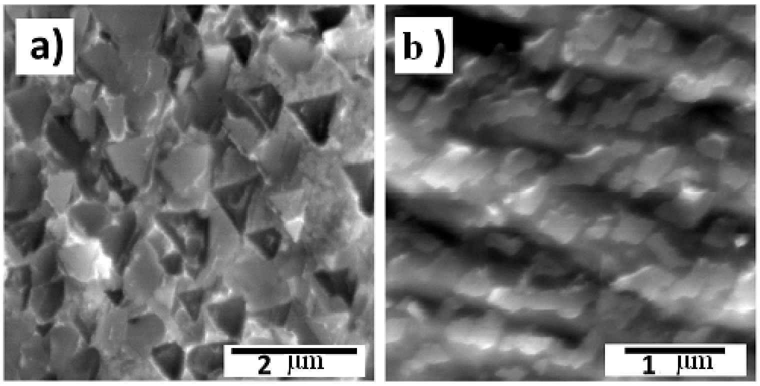

Fig. 4. The flat surfaces fractures images at high magnification: a) after exploitation, b) after post-life ageing (τ = 4000 hours).

X-ray spectral microanalysis (EDX) of the facets surfaces covered with a continuous layer of precipitates, carried out with a variation of the probe electron energy from 10 to 20 keV by the method of [5] made it possible to establish the presence of a chromium carbide layer with a thickness of 0.02 μm.

Identical areas separated by the crack development were identified by comparing the fractions of the two response halves of the sample from the material after exploitation. Images of such facets are shown in Fig. 5. With a low magnification, an imperceptible relief on the facets surface, formed when facets intersect with glide planes, is observed. It should be noted that the surface filled density by the lamellar particles within the frame of facet plane changes. The transition zone is shown in Fig. 5-c, there are few particles in the upper part of the figure, their dimensions are far less than the distance between the glide planes traces, and the lower part of the surface figure is filled with a continuous layer of lamellar particles. A similar picture is observed on the material formed during fracture, and the mutual arrangement of the areas densely filled with particles on both halves of the destroyed sample allows us to conclude that the crack developed in a thin layer of the lamellar particles of chromium carbide, and not along the carbide-metal interface (Fig. 5-a and 5-b). Identical thickness of the chromium carbide layer from both halves of the specimen fracture, equal to 0.02 μm, was detected using the EDX method. This indicates that the tear occurred approximately in the middle of the carbide layer, and its resulting thickness is 0.04 μm. When the facets surface observed with a large magnification, it is established that in the observation projection a significant number of the detected particles have the shape of an equilateral triangle (Figs. 4-a, 5-c), moreover, their sides orientation corresponding to the glide planes direction (Fig. 5-c).

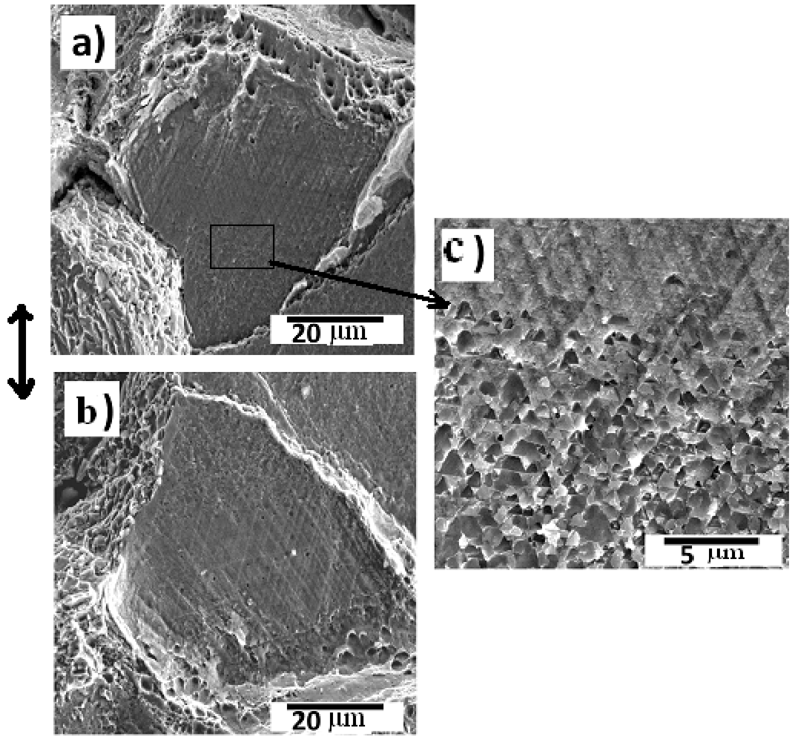

Fig. 5. The facets image of the two response halves (a, b) of the fractured sample after exploitation, and (c) – the transition zone between the areas with different carbide densities.

5. Discussion

The obtained results indicate that degradation of material properties under the thermal ageing of 304 steel occurs due to the formation of grain-boundary chromium carbides, which reduce the cohesive strength of the material. This corresponds to the results of previous studies on thermal ageing [1-4].

It is established that in the formation of globular carbides at the grain boundaries, the mechanism of viscous intergranular destruction due to the nucleation, growth, and association of pores is realized. The formation of a continuous layer of lamellar carbides leads to quasi-brittle fracture by the mechanism of interlayer separation, the crack developing within a thin layer of plate-like carbides. Fractografic studies have shown that changes in mechanical properties during the ageing are directly related to the fracture mechanisms that are being realized. Reduction of toughness and plasticity after a long exploitation is due to a change in the fracture mechanism from the viscous intragranular characteristic of austenitic steels to a viscous intergranular and, in part, quasi-brittle intergranular mechanism. An increase in the toughness at the initial stage of post-life ageing is accompanied by the absence of sections of quasi-brittle fracture (flat facets) observed on metal fractions in a state after exploitation. The decrease in the toughness at long post-life ageing times is associated with the appearance of newly facets of quasi- brittle fracture. In this regard, the question of the formation of plate-like carbides should be discussed in more detail.

Metals with FCC lattice, as a rule, retain the viscous transcrystalline nature of failure in a wide temperature range, only when the cohesive strength of the grain boundaries of such materials is weakened by various precipitates at low test temperatures; a transition to intergranular destruction, including quasi-brittle, can occur [4, 6]. Intergranular destruction is realized due to the specific interaction of the deformation bands with the grain boundaries, with sufficient plasticity of the FCC materials, the accumulation of the plastic deformation traces in the form of steps of inconsistency on the boundary surface occurs, and when the critical concentration of these steps is reached, destruction will occurs [6]. The presence of steps of discrepancy is clearly observed in the images of the facets of quasi-brittle fracture both for high and low magnifications (Fig. 5). On the other hand, of brittle behavior mechanisms of FCC steels with a high nitrogen content associated with the interaction of active and inactive glide planes have been described [7]. In the case of inhibition of active glide planes by interstitial impurities, in particular, by dissolved nitrogen atoms, when the active planes intersect the inactive tearing voltage in the direction perpendicular to the inactive plane, leading to quasi-brittle failure, can be formed.

On the obtained facet images at high magnification (Fig. 4-a), it is seen that the intersection of the layer of plate-like carbides on the facet surface by glide planes was accompanied by the cracks formation, so that the particles on the facet surface predominantly have the shape of an equilateral triangle. In the area of the facet covered with a less dense layer of carbides, the inconsistency steps (Fig. 5-c) are clearly observed. It can be concluded that the braking of glide planes when they intersect a layer of plate-shaped carbides, the formation of a separation surface along a weak spot, between layers of lamellar carbides led to a quasi-brittle development of the intergranular crack. Later, the crack spread along the boundary along the sections with less dense filling with carbides, but with the accumulated steps of inconsistency.

The specific shape of the plate-like carbide particles in the form of an equilateral triangle, seen on the facets, is evidently formed upon fracture as a result of the intersection of the carbide layer by the glide planes of the $\{111\}\gamma$ family. Plates of carbides in the form of an equilateral triangle, observed on the facet surface, are parallel to one of the faces of the tetrahedron formed by the planes of the $\{111\}\gamma$ family. The triangle would not be equilateral with another orientation of the facet plane relative to the active glide planes. It should be noted that, since in FCC materials the formation of twins occurs along the {111} family planes, an extended flat facet of quasi-brittle fracture is the double boundary. This leads to the fact that carbides of a specific plate form are formed on the twin boundary surface. The specific plate form of carbides was studied in detail by Beckith and Clark [8], who proved that in the presence of the orientation relation of the cube-cube:

$$\{100\}_{\gamma}||\{100\}_{M_{23}C_6}$$
$$\langle 010\rangle_{\gamma}||\langle 100\rangle_{M_{23}C_6}, \quad (1)$$

in the case of the conjugation of crystallite $Cr_{23}C_6$ with austenite substrate along the (111) plane, the maximum correspondence of the crystal lattice sites of the growing particle and substrate is reached, and the matching parameter of crystal lattices in this case approaches 0.99.

In this connection, when a germ is formed on the twin boundary, the orientation ratio is satisfied on both sides of the growing carbide. This is the reason for the specific platelet shape of the particle and this creates the conditions for the formation of a continuous layer of particles along the entire surface of the twin. At the intergranular boundaries, chromium carbides with globular shape predominate. Both types of particles reduce the cohesive strength, but the destruction of grain boundaries is accompanied by plastic deformation, since the globular particles do not cover the sections of the boundary with a continuous layer. On the fracture, they are usually located as a "cups" form on the surface (Fig. 2-a). Plastic deformation during fracture along these boundaries is absent when twin boundaries are densely filling with plate-shaped carbides (Fig. 2-a). The absence of quasi-brittle fracture on fractures after post-life ageing during 4000 hours, as well as a significant decrease in the filling density of quasi-plane surfaces with carbides, indicates about a partial dissolution of plate-like carbides (Fig. 4b). Apparently, in the transition from operating conditions to a post-life ageing at elevated temperatures, conditions for the dissolution of carbides are created, and this leads to a partial restoration of the steel properties. It can reasonably be assumed that the specific shape of the plate-like carbides leads to their faster dissolution as compared with a globular carbides, due to a much larger specific surface area. After a longer post-life ageing, the formation of lamellar carbides on the twin boundaries begins again, it leads to the appearance of facets of quasi-brittle fracture and, as a consequence, to the material degradation. Thus, the change in the process direction, the partial dissolution of the carbides in the first stage of post-life ageing, and the return to their growth with an increasing of ageing time, cause the formation of a maximum on the "impact resistance – post-life ageing time" curve.

It can be assumed that the presence of a significant chromium concentration gradient in the border regions after thermal ageing under operating conditions is a probable cause of partial dissolution of carbides in the first stage of post-life ageing. A prolonged holding at a relatively low temperature, from the point of view of the substitution element diffusion rate, as well as the reaction of carbide formation on the grain boundary, controlled by the slow diffusion of chromium, but with a very high equilibrium constant, provides the border zone formation depleted of chromium. A similar phenomenon is observed in tests for intergranular corrosion under conditions of provocation of carbide formation [9]. The dissolution will continue until the chromium concentration is equalized at the boundary of the carbide with the metal at equilibrium under these conditions; after this, due to the diffusion of chromium from the volume, the carbide growth process will begin again and will proceed at a higher rate because of the higher diffusion mobility of chromium. A rigorous justification of the hypothesis proposed requires detailed thermodynamic and kinetic calculations, which is beyond the scope of this article.

6. Conclusions

1. The nonmonotonic dependence of the toughness after post-life ageing at an elevated temperature at 700 °C of 304 steel, previously operated in heat exchanging equipment of fast neutron reactor at a range temperature up 518 to 550°C for 1700000 hours, was detected. Partial restoration of impact strength with a maximum in the range of 4000-6000 hours of attrition occurs at the initial stage of ageing, then the values decrease, asymptotically approaching the level for the metal after exploitation. Such post-life ageing of steel does not conservatively model its further operational ageing.

2. It has been shown that the partial reduction of impact strength at the initial stage of ageing is mainly due to the dissolution of lamellar chromium carbides on the twin boundaries and, as a result, by the removal of facets of quasi- brittle fracture on fractures.

3. It is shown that the specific plate form of carbides is due to the orientation relationship with the growth of carbides at the twin boundaries.

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