

Mechanism and Kinetics of Thermal Embrittlement of Austenitic Chromium-Nickel Steel during Long-Term High-Temperature Holding

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Abstract. This article describes a model of structural changes in austenitic chromium-nickel steel during long-term thermal soakings. The time for reaching equilibrium content of Cr_{23}C_6 carbide at a temperature of 600 °C is calculated. The calculation results are compared with experimental data on the kinetics of thermal embrittlement of steel at a temperature of 600 °C after thermal holding for up to 15000 hours.

Introduction

Long-term high-temperature operation under conditions of high diffusion mobility of alloying elements in steel leads to changes in the structure and, as a consequence, in the mechanical properties of structural materials. Periodic destructive testing of equipment elements of reactor facilities makes it possible to assess the residual level of properties at the time of testing. To be able to predict the level of mechanical properties during further operation (after destructive testing), it is necessary to predict the structural and phase transformations occurring in the material.

The purpose of this work is a computational and experimental assessment of the kinetics of the process of structural transformations and thermal embrittlement in austenitic steel grade 09Cr18Ni9 during long-term high-temperature holding.

Mechanism of thermal embrittlement and a description of the calculation model

To describe the mechanism of thermal embrittlement, it is necessary to establish the relationship of structural changes with a decrease in the characteristics of impact toughness over time.

Secondary phases in steel grade 09Cr18Ni9 during long-term high-temperature holding are formed in the following order. First, due to the limited solubility of carbon, it is released from the solid solution with the formation of chromium carbide Cr_{23}C_6 . This leads to the formation of areas with a low chromium content near the carbide precipitates. It is known [1] that chromium with its content in steel ~ 17% in combination with nickel, in contrast to its usual ferritizing action, strongly contributes to the formation of an austenitic structure as a result of complex interatomic interaction. Therefore, in zones depleted in chromium, austenite is transformed into ferrite (α). In this case, the excess nickel content by diffusion can pass into the forming G-phase.

To confirm the stated mechanism, an experiment was carried out on a metal with different carbon content: 0.07 and 0.09 wt. %. The samples were exposed to heat holding for various durations at a temperature of 600 °C, during aging, the content of the α -phase was determined (Fig. 1). In the material with a carbon content of 0.07 %, the α -phase was formed significantly less, which confirms the relationship between the precipitation of chromium carbide and the formation of the α -phase, since at a carbon content of 0.07 and 0.09 wt. %, the amount of Cr_{23}C_6 at a

temperature of 600 °C in an equilibrium state according to the data of thermodynamic modeling is also significantly different and amounts to 0.87 and 1.57 wt. % respectively.

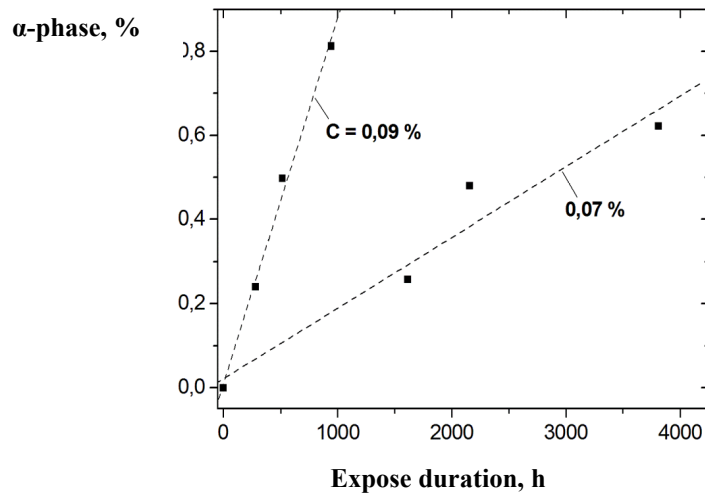


Fig. 1. Influence of carbon content on the kinetics of α -phase precipitation at a temperature of 600 °C.

Of the secondary precipitates found in steel, only chromium carbide has an embrittling effect. Therefore, the formation of chromium carbide will determine the kinetics of thermal embrittlement. The formation of particles of the carbide phase will proceed until the equilibrium content is reached at a given temperature. According to the results of thermodynamic modeling, the equilibrium content of Cr_{23}C_6 at a temperature of 600 °C is 1.57 %. Let's assume that all grains in the material structure are spherical and of the same size. Under these conditions, the process of carbide formation in each of the grains will proceed in the same way. In the range of operating temperatures, the carbide phase is formed mainly along the grain boundary. Fig. 2 shows a diagram of the formation of a layer of carbide with a thickness of δ along the grain boundary γ - austenite in the direction v from the boundary to the center of the sphere.

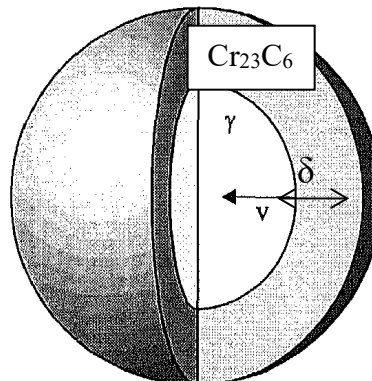


Fig. 2. Scheme of the growth of the carbide phase along the grain boundary of austenite.

The thickness of the carbide layer δ is related to the volume fraction by the following relationship [2]:

$$V^k = 1 - \left(\frac{d_\gamma - 2\delta}{d_\gamma} \right)^3, \tag{1}$$

where V_k is the volume fraction of the carbide phase, d_γ is the austenite grain diameter.

The calculation of the thickness of the layer of the carbide phase at each moment of time can be carried out on the basis of the analysis of the physical and mathematical model of chromium diffusion. A diagram of the growth process of the carbide phase, limited by chromium diffusion, is shown in Figure 3 [3]. There is a transition region between carbide and ferrite, but for simplicity, a sharp phase boundary is assumed in the scheme, at which the chromium concentration changes abruptly from the equilibrium value in ferrite (C_{Cr}^α) to a similar value in $Cr_{23}C_6$ carbide (C_{Cr}^k). At a considerable distance from the center of the new phase, the chromium concentration retains its initial value (C_{Cr}^γ).

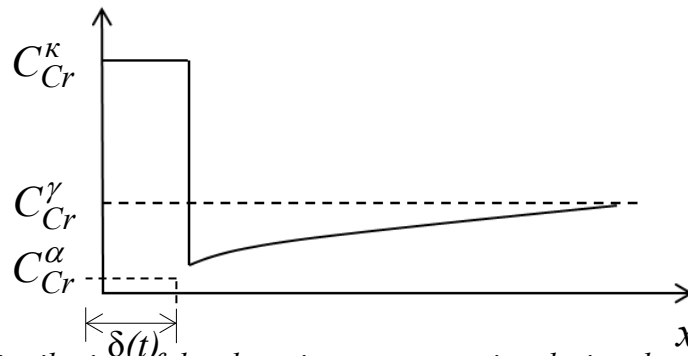


Fig. 3. Schematic distribution of the chromium concentration during the growth of the carbide phase layer [3].

The mathematical formulation of the growth problem for a layer of a new phase is given, for example, in [4]. The redistribution of chromium in the region $\delta(t) < x \leq \infty$ is described by the diffusion equation:

$$\frac{1}{D} \frac{\partial C}{\partial t} = \frac{\partial^2 C}{\partial x^2} \tag{2}$$

with the following boundary conditions:

$$\lim_{x \rightarrow \infty} C(x, t) = C_{Cr}^\gamma; \quad C(\delta(t), t) = C_{Cr}^\alpha; \quad C(x, t) = C_{Cr}^k, \text{ at } x < \delta(t); \quad \frac{\partial C(\infty)}{\partial x} = 0.$$

A mass balance must be observed on the surface of the new phase layer:

$$\left(C_{Cr}^k - C_{Cr}^\alpha \right) \frac{d\delta(t)}{dt} = D \left. \frac{\partial C}{\partial x} \right|_{x=\delta(t)} \tag{3}$$

Based on the solution of the indicated boundary value problem in [5], an expression was obtained for calculating the thickness of the new phase:

$$\delta(t) = 2 \sqrt{\frac{C_{Cr}^{\gamma} - C_{Cr}^{\alpha}}{C_{Cr}^{\kappa} - C_{Cr}^{\alpha}}} \sqrt{\frac{Dt}{\pi}} \quad (4)$$

$$t_p = \frac{\pi}{D} \left(\frac{d_{\gamma} \left(1 - \sqrt[3]{1 - V^{\kappa}} \right)}{2 \frac{C_{2p} - C_{Cr}^{\gamma}}{C_{Cr}^{\kappa} - C_{2p}}} \right)^2 \quad (5)$$

Results and discussion

For the calculation, the following values of the parameters included in the expression (5): $D_{Cr} = 8,1 \cdot 10^{-20} \text{ m}^2\text{s}^{-1}$ [6]; $d_{\gamma} = 66,5 \text{ }\mu\text{m}$; $C_{Cr}^{\gamma} = 14,76\%$; $C_{2p} = 0,1 * C_{Cr}^{\gamma} = 1,476 \%$; $C_{Cr}^{\kappa} = 81,95\%$. The time to reach the equilibrium content of Cr_{23}C_6 carbide at a temperature of $600 \text{ }^{\circ}\text{C}$, according to the calculation results, was 12164 hours. To verify the calculated data, an experiment was carried out, during which thermal soakings were carried out at a temperature of $600 \text{ }^{\circ}\text{C}$ for various durations, followed by determination of the impact toughness (Figure 4). The cessation of the precipitation of the Cr_{23}C_6 carbide leads to the stabilization of the values of the impact toughness. According to the calculation data, the time to reach the equilibrium carbide content is 12164 h, according to the experimental data, the thermal embrittlement process is stabilized at a holding time of 11000 h. Thus, the calculation results are in good agreement with the experimental data, the discrepancy is 11 %, while the calculated estimate shows a longer value of time reaching an equilibrium content of the carbide phase, therefore, it is conservative.

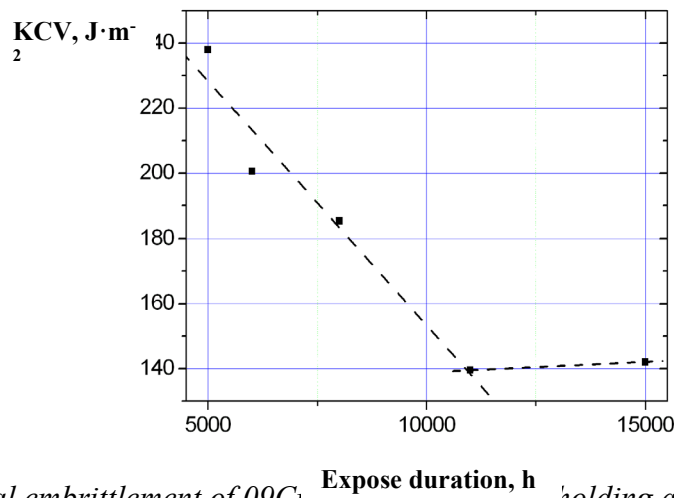


Fig. 4. Thermal embrittlement of 09Cr1 holding at a temperature of $600 \text{ }^{\circ}\text{C}$.

Summary

The time for reaching equilibrium content of Cr_{23}C_6 carbide at a temperature of $600 \text{ }^{\circ}\text{C}$ is calculated. According to the calculation data, the time to reach the equilibrium carbide content is 12164 h, according to the experimental data, the thermal embrittlement process is stabilized at a holding time of 11000 h. Thus, the calculation results are in good agreement with the experimental data, the discrepancy is 11 %, while the calculated estimate shows a longer value of time reaching an equilibrium content of the carbide phase, therefore, it is conservative.

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