

# Effect of impurities and grain boundaries on the kinetic characteristics of the radiation damage of iron and austenitic steels

**D Demidov<sup>1</sup>, E Smirnov<sup>1</sup> and A Tsepelev<sup>1,2</sup>**

<sup>1</sup>National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), 31 Kashirskoe highway, Moscow, 115409, Russia

<sup>2</sup>Institute of Metallurgy and Materials Science of the Russian Academy of Sciences (IMET RAS), 49 Leninsky pr., Moscow, 119991, Russia

**E-mail:** dmitrydem11@gmail.com

**Abstract.** Austenitic stainless steel AISI 304, 316 and similar in composition, are used to create many elements of the reactor core, such as fuel cladding of fast-neutron reactor. It is known that during the operation, they became subject to such type of radiation damage, as the vacancy swelling and radiation creep. In this paper, was analyzed the effect of alloying elements, impurities and their complexes with radiation defects (RD) on the characteristics of RD and radiation-enhanced diffusion (RED) Parameters of vacancy voids nucleation and growth processes were also studied on the example of Cr18Ni10T steel. Evaluation of the temperature dependence of steady-state concentration of RD for materials with different binding energy complexes "defect - impurity", the effective values of mutual recombination rate RD for materials complexes, influence the formation of impurity complexes and volume density of grain boundaries on the rate of growth of vacancy voids and radiation creep was conducted. The possibility of varying the characteristics of the complex defect - impurity and grain boundary size for the suppression of radiation creep and vacancy swelling was studied

## 1. Introduction

There exist a lot of ways of decreasing in the vacancy swelling and radiation creep of austenitic steels, but physically all of them are reduced to a decrease in the alloy concentration of point radiation defects (RD).

The first method consists in steel alloying of small amounts of alloying elements (AE) such as Ti, Zr, Si, Mo, Nb, whose atoms form the impurity complexes with vacancies, which reduces the concentration of free vacancies, and increases the radiation-enhanced diffusion (RED), promoting rapid recombination of point defects[1]. The second method is based on increasing the volume density of grain boundaries in the system (decreasing grain size) that give rise to a large amount of the unsaturating sinks for vacancies and of interstitial atoms [2].

## 2. The calculation part

To assess the role of impurities in reducing the concentration in the RD, it is necessary to use the model of radiation - enhanced diffusion in systems with impurities and the system of kinetic equations annealing RD in steels alloy with impurities [3, 4]:



$$\begin{aligned}
\frac{\partial C_v}{\partial t} &= K_0 - K_{iv} C_v C_i - K_{3v} C_v C_I + K_{4v} C_{vI} - K_{5v} C_v C_{iI} \\
\frac{\partial C_i}{\partial t} &= K_0 - K_{iv} C_i C_v - K_{3i} C_i C_I + K_{4i} C_{iI} - K_{5i} C_v C_{vI} \\
\frac{\partial C_I}{\partial t} &= K_{4i} C_{iI} + K_{4v} C_{vI} - K_{3i} C_i C_I - K_{3v} C_v C_I + K_{5i} C_v C_{vI} + K_{5v} C_v C_{iI} \\
\frac{\partial C_{vI}}{\partial t} &= K_{3v} C_v C_I - K_{4v} C_{vI} - K_{5i} C_v C_{vI} \\
\frac{\partial C_{iI}}{\partial t} &= K_{3i} C_i C_I - K_{4i} C_{iI} - K_{5v} C_v C_{iI}
\end{aligned} \tag{1}$$

Here  $K_0$  is the irradiation dose per second,  $K_{iv}$  is the recombination constant of interstitial atoms and vacancies,  $C_i$  is the concentration of interstitial atoms,  $C_v$  is the concentration of vacancies,  $C_I$  - concentration of impurity atoms,  $C_{iI}$ ,  $C_{vI}$  - the concentration of complexes "interstitial atom - impurity atom" and complex "vacancy - impurity atom, respectively.  $K_3$  and  $K_4$  are the rate constants of formation and decay of appropriate complexes, characterizing the recombination defect in the complex ( $i + vI \rightarrow I, v + iI \rightarrow I$ ). Description of radiation defects concentration depend on various temperatures, and the sink density values, generation rate of defects at different stages of annealing are given in [4, 5]. Annealing of radiation defects at high temperatures and substantial density of sinks is the main phenomenon, realized at the analysis of the RED in metals.

In accordance with [3], process of defects annealing at a time  $t = \tau_1 = \frac{1}{\sqrt{K_0 K_{iv}^{eff}}}$  completes when defects are accumulated in the process of mutual recombination, where

$$K_{iv}^{eff} = W[D_i + zC_I(D_v \exp \frac{E_{iI}^b}{kT} + D_i \exp \frac{E_{vI}^b}{kT})] \approx W D_i (1 + D_i \exp \frac{E_{vI}^b}{kT}) . \tag{2}$$

The next moment  $C_v$  increases and  $C_i$  decreases in proportion to the  $\sqrt{t}$  and from the time point

$t = \tau_3 = \frac{1}{K_{vs} C_s}$  there is an annealing steady state for which the solutions of the equations (5) with low concentration of sinks are [3 - 5]:

$$\begin{aligned}
C_v &= \sqrt{\frac{K_0 K_{is}}{K_{iv}^{eff} K_{vs}}} = \sqrt{\frac{K_0 D_i}{K_{iv}^{eff} D_v}} \\
C_i &= \sqrt{\frac{K_0 K_{vs}}{K_{iv}^{eff} K_{is}}} = \sqrt{\frac{K_0 D_v}{K_{iv}^{eff} D_i}} .
\end{aligned} \tag{3}$$

Solutions based on substantial concentration sinks are given later:

$$C_v = \frac{\rho D_i}{2D_{iv}} \left( \sqrt{\frac{4K_0 K_{iv}}{\rho^2 D_i D_v}} + 1 - 1 \right)$$

$$C_i = \frac{\rho D_v}{2D_{iv}} \left( \sqrt{\frac{4K_0 K_{iv}}{\rho^2 D_i D_v}} + 1 - 1 \right) \quad (4)$$

We consider grain boundaries as RD sinks and volume density (grain boundary size) will be varied. The volume density of grain boundaries meant by the ratio of the volume occupied by the grain boundaries to the volume of grains themselves in a dedicated unit volume.

To estimate the effect of alloying elements on the concentration of RD, let us consider their energy characteristics of the interaction with the RD. To do this for a large number of alloying elements and impurities found in austenitic steels, let us analyze the impact of the binding energy in "AE atom - vacancy" on the effective recombination coefficient RD, a decrease which should lead to a significant reduction in free-migrating vacancies.

In addition to increasing  $K_{iv}^{eff}$ , the role of the introduction of alloying elements is to bind a large number of free-migrating vacancies in the complexes which gives to changing their diffusion properties, prevents their accumulation in the pores and reduces the intensity of the climb of edge dislocations, responsible for the acceleration of the radiation creep

**Table 1.** Values of the volume density of grain boundaries and grain size [7]

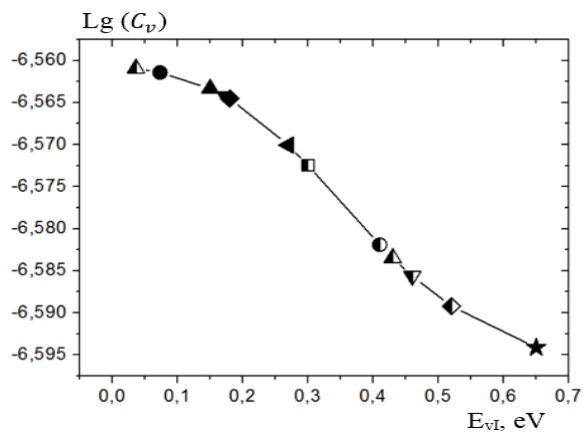
Volume density of grain boundaries ( $\kappa$ )	Grain size, $d$ (mm)	In figures 3, 5, 6
$10^{-1}$	$7,50 \cdot 10^{-1}$	1
$10^{-2}$	$7,50 \cdot 10^{-2}$	2
$10^{-3}$	$7,50 \cdot 10^{-3}$	3
$10^{-4}$	$7,50 \cdot 10^{-4}$	4
$10^{-5}$	$7,50 \cdot 10^{-5}$	5
$10^{-6}$	$7,50 \cdot 10^{-6}$	6

Later, we adducing vacancies concentration dependences on the binding energy in the complex "vacancy - AE atom", temperature, irradiation dose, AE concentration. From figures 1 – 4 it can be seen that the concentration of RD is significantly reduced with the increase in the binding energy of the complex "vacancy - atom AE" and with increasing volume density of grain boundaries.

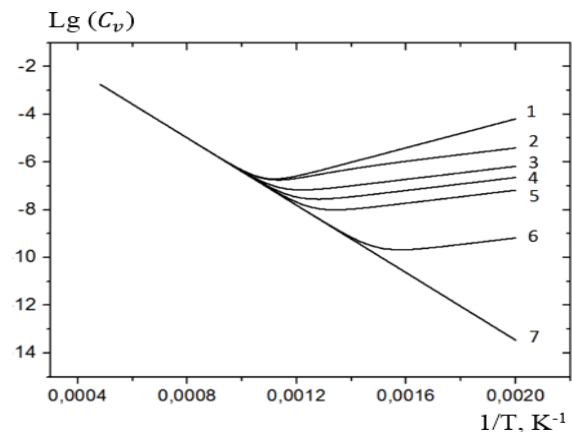
One can also note the constant exponential growth of RD recombination with an increase  $E_{v/}$ . Graphs of the complexes RD concentration, as well  $K_{iv}^{eff}$  dependences on the AE concentration are given at work [1].

Figures 5 and 6 shows that the increase in the volume density of grain boundaries significantly reduces the concentration of free-migratory vacancies in the system and, as a consequence, reduced the rate of growth of vacancy voids and radiation-accelerated creep. The constructed model confirms proven the linear dependence of these effects on the concentration of the RD system.

Also, a significant role to reduce these rates of increase in the binding energy is played in "AE atom - vacancy", as represented in figures 7 and 8. It can be seen that the increase of the binding energy not only reduces the rate of growth of pores and creep but displaces their highest values at higher temperatures.



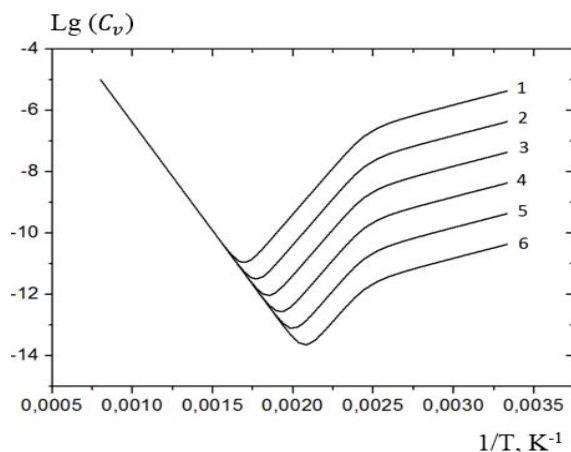
**Figure 1.** The vacancies concentration dependence in the binding energy of impurity complexes in austenitic steels. Temperature - 973 K. The rate of generation of RD:  $K_0 = 10^{-6}$  dpa/c,  $\kappa = 10^{-3}$ . AE concentration - 0.4 at. %.



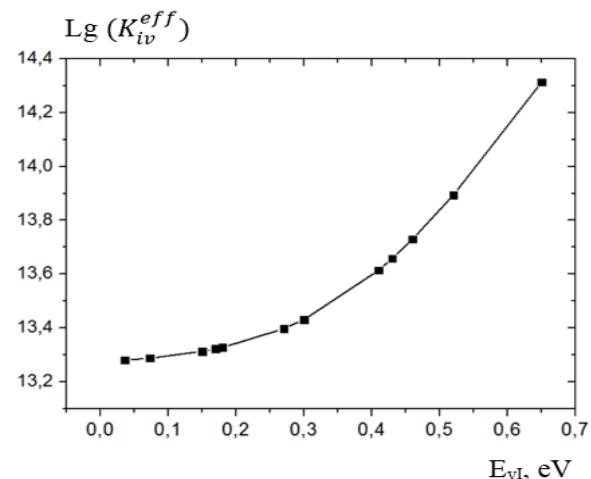
**Figure 2.** Temperature dependence of vacancies concentration. : AE – Ti,  $\kappa = 10^{-3}$ , 1 – without alloying;  $K_0 = 10^{-6}$ ; 2 –  $C_I = 0.01$  at. %,  $K_0 = 10^{-6}$ ; 3 –  $C_I = 0.3$  at. %  $K_0 = 10^{-5}$ ; 4 –  $C_I = 0.3$  at. %,  $K_0 = 10^{-6}$ ; 5 –  $C_I = 0.3$  at. % ,  $K_0 = 10^{-7}$ ; 6 –  $C_I = 0.5$  at. % ,  $K_0 = 10^{-6}$ ; 7– concentration of equilibrium vacancies.

The results obtained in this work, are in good agreement with the results of [8] and also take into account not reviewed in [6] the effect of temperature variation of the shear modulus, which is important to accurately determine the binding energy of the complex "vacancy - atom AE".

Consider the effect of the grain boundaries volume density on the vacancies concentration and complex "vacancy - atom AE" and the impact of the binding energy upon the recombination constant RD -  $K_{iv}^{eff}$ .



**Figure 3.** The vacancies concentration dependence on the temperature in austenitic steels for various bulk density of grain boundaries (table 2). AE - Ti, 0.4 at. % ,  $K_0 = 10^{-6}$  dpa /s.



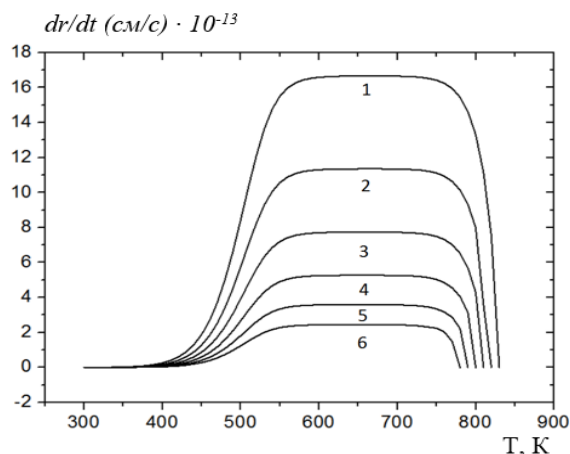
**Figure 4.** The constant recombination dependence of radiation defects on the binding energy in austenitic steels.  $T = 973$ ,  $K_0 = 10^{-6}$  dpa/s,  $\kappa = 10^{-3}$ .

We will consider the effect of the binding energy in the complex "AE atom - vacancy" and the grain boundaries volume density at the rate of vacancy pores growth and radiation creep speed. Let us estimate the values based on expressions (5) and (6), respectively [8]:

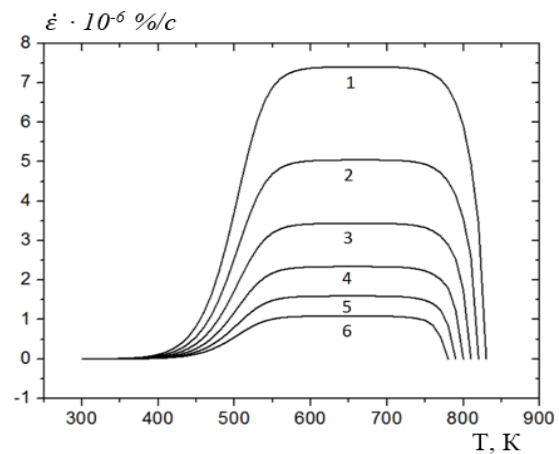
$$\frac{dr}{dt} = \frac{\Omega}{r_v} [Z_v D_v C_v - Z_i D_i C_i] \quad (5)$$

$$\dot{\varepsilon} = \frac{2\Omega L}{9} [Z_i D_i C_i - Z_v D_v C_v], \quad (6)$$

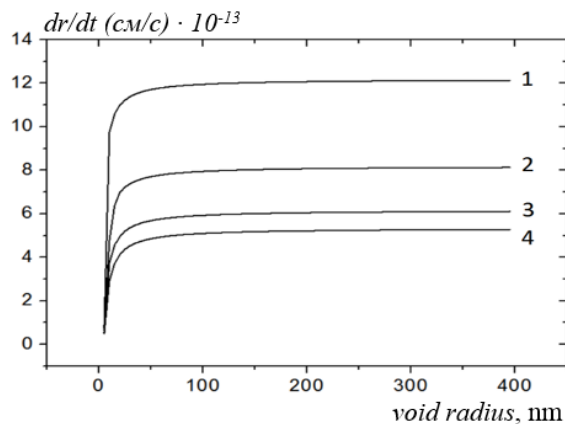
where  $Z_i$  and  $Z_v$  are preference factors,  $\Omega$  is the atomic volume,  $L$  is the bulk density of dislocations,  $r_v$  is the initial radius of the growing pores. The values of  $L$ ,  $Z_b$ ,  $Z_v$ ,  $r_v$ , are taken from work [8]:



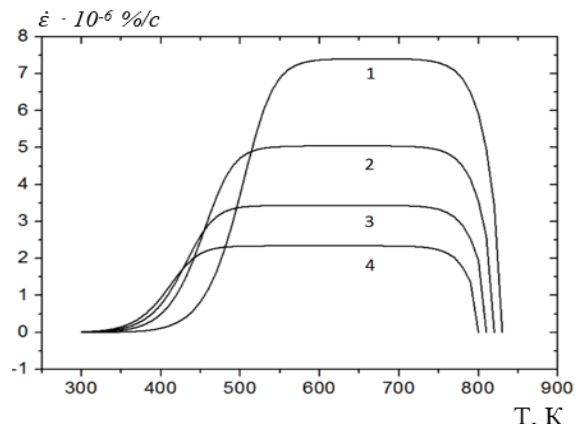
**Figure 5.** Curves are given different grain boundaries bulk density (table 1). AE - 0.4 at. % Ti.  $K_0 = 10^{-6}$  dpa /s. Dependence of vacancy pore growth rate in the austenitic steel pores on temperature.



**Figure 6.** Curves are given for different grain boundaries bulk density (table 1). AE - 0.4 at. % Ti.  $K_0 = 10^{-6}$  dpa /s. The velocity of the austenitic steel radiation creep on temperature.



**Figure 7.** Dependence of vacancy pore growth rate in the austenitic steel pores on pore radius.  $T = 800$  K. The concentrations of the alloying elements are equal to 0.4%.  $K_0 = 10^{-6}$  dpa / s.  $\kappa = 10^{-3}$ . 1 – alloying of P; 2 – alloying of S; 3 – alloying of Nb; 4 – alloying of Ti.



**Figure 8.** The velocity of the austenitic steel radiation creep on temperature. The concentrations of the alloying elements are equal to 0.4%.  $K_0 = 10^{-6}$  dpa/s.  $\kappa = 10^{-3}$ . 1 – alloying of P; 2 – alloying of S; 3 – alloying of Nb; 4 – alloying of Ti.

### 3. Conclusion

The paper analyzed the possibility of suppressing the vacancy swelling and radiation-accelerated creep of austenitic steels through the introduction of alloying elements and varying the volume density of

grain boundaries. It also analyzes the possibilities of varying the parameters of the alloying elements to reduce the concentration RD in the system.

It has been shown that there is an exponential decrease in concentration RD [1], by increasing the binding energy of the impurity complex and by increasing the concentration of the alloying element in the system. The influence of the radiation defects concentration and share grain boundaries on the vacancy rate of swelling and radiation creep is analyzed.

The dependences of the radiation creep rate and vacancy swelling rate for the various parameters of the alloying element and temperature have been given. The obtained dependences are in good agreement with the results of work [8]. It is shown that there is a significant decrease in these speeds by increasing the binding energy of the impurity in the complex and in the decrease in the average volume of grain.

### Acknowledgements

This work was performed within the framework of the Center of Nuclear Systems and Materials supported by MPhI Academic Excellence Project (contract № 02.a03.21.0005, 27.08.2013).

### References

- [1] Demidov D N and Smirnov E A 2015 15 *Int. Conf. on Rad. Phys. of Met. and All.: Int. ural seminar (Kyshtym)* **11** 15
- [2] Zelenskiy V F, Neklyudov I M and Chernyaeva T P 1988 *Radiation defects and swelling of metals* (Kiev: Naukova dumka) p 293
- [3] Akhiezer I A and Davydov L N 1985 ( Kiev: Naukova dumka) p 225
- [4] Smirnov E A 2013 *Metal Physics and Advanced Technologies* **35** (8), 1001–12
- [5] Novoselov A N , Smirnov E A and Shmakov A 2013 *Metal Physics and Advance Technologies* **35** (7) 1005-12
- [6] Faulkner R G and Song S–H 1996 *Mater. Sci. Technol.* **12** 904
- [7] Mehrer H 2007 *Diffusion in Solids* 645
- [8] Mansur L K and Yoo M H 1978 *J. Nucl. Mater.* **74** (2) 228