Effect of titanium doping on accumulation and annealing of radiation defects in austenitic steel 16Cr15Ni3Mo(0-1)Ti at low temperature (80 K) electron irradiation

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Abstract. The effect of titanium doping on accumulation and annealing of radiation defects was investigated in austenitic stainless steel 16Cr15Ni3Mo under low temperature (80 K) electron irradiation. Steel has been taken in the quenched, aged and separation of solid solution states. The data obtained on the accumulation of radiation defects and their evolution during isochronous annealing. The types of defects and its complexes and the activation energy of the processes taking place with their participation is identified. The mechanisms of radiation-induced processes and the effect of titan doping is discussed.

1. Introduction
Currently, the austenitic stainless steel is most widely used for the reactor internals elements. It is well known that limiting phenomenon of the radiation resistance of the reactor steels has become associated with radiation-induced structural and phase changes.

Radiation defects play an important role in processes of radiation damage of metals and alloys, radiation-induced structural phase transitions [1]. Atomic segregation may be homogeneous by volume of grains, but most are mixed. In the latter case, they are observed on clusters of point defects, dislocations, grain boundaries or interphase surfaces. Freely migrating defects (vacancies and interstitials) cause the following opposite effects:

1. Accelerating the evolution of real materials often are metastable towards equilibrium;
2. The emergence of phenomena associated with the induction of non-equilibrium processes in alloys: the formation of clusters of radiation defects and segregation until separation of the phases.

It is known [2], that addition in small amounts (0.2 - 1.0 wt.%) of titanium in the austenitic steels substantially reduce the vacancy swelling. In [3,4] has been suggested that the swelling is weakened by radiation-induced formation of dispersed precipitates γ’-phase. Research on the interaction of impurity atoms of titanium with radiation defects are presented in [4,5,6].

We have previously shown, that irradiation at elevated temperatures iron-nickel alloys, leads to an ordered solid solution separation. Doping of titanium leads to the suppression of the process and the formation of precipitates γ’-phase [6]. However, knowledge of the interaction of point defects with Ti atoms is very incomplete.

Vacancy clusters (VC) is formed during the free migration of vacancies and their interaction with each other and with the dopants. In this regard, the low-temperature electron irradiation and...
Postradiation isochronous annealing were used in this work to study the evolution of radiation defects and their interaction with each other and with the titanium atoms.

Purpose of work is to explore the effect of doping titanium on the accumulation and annealing of radiation defects and radiation-induced structural changes in the austenitic stainless steel.

2. Materials and methods

For investigation it was taken 16Cr15Ni3Mo austenitic stainless steel smelted in a vacuum induction furnace from high-purity components with titanium concentration of 0, 0.6, 1.0 wt.% Ti. Doping was carried out by adding the titanium to the melt. The concentration of carbon in the steel was 0.03 wt.%. Original state steel was obtained by annealing at 1323 K for 30 minutes, followed by quenching in water. The grain size after this treatment is 100-200 μm and a dislocation density about 10^7 cm^-2. According to X-ray and electron-microscopic data studied were single-phase austenitic steel.

The part of quenched samples were annealed at 923 K 5 hours to form γ'-phase precipitates. Using electron microscopy, scanning tunneling microscopy, it is shown that in aged steel γ'-phase are presented with size of 7-10 nm with concentration of (4×6)·10^16 cm^-3 (volume ratio of ~ 3%). Another part of the sample were annealed at 773 K 3 hours to form a separation of solid solution (SSS). 5 MeV electron irradiation was carried out on a linear electron accelerator at 80 K to fluence (1-4)·10^18 cm^-2. Measurement of residual resistivity at 4.2 K, carried by the standard four probe potentiometric method with sensitivity at the level of 0.01 nΩ×cm and an accuracy of 0.02%.

3. Experimental results

As mentioned above, studies were performed on samples in three states: quenched, annealed and aged to maximize the separation of the solid solution (SSS). To understand the states after heat treatment and structural-phase changes in the material it is performed isochronous annealing of non-irradiated steels.

**Figure 1.** The dependence of the residual resistivity of steels in the quenched state on isochronous annealing temperature.

**Figure 2.** The dependence of the the resistivity steels in quenched state electron-irradiated to different doses on isochronous annealing temperature. In the lower part of the figure - differentiated curves.
Figure 1 shows the changes in the electrical resistivity of steels in the quenched state at the isochronous annealing. It can be seen that the increase of annealing temperature leads to an increase in resistivity at 700 - 800 K, and at higher temperatures up to 950 K begins to decline in the resistivity and the alloy with 1% Ti below the reference value. This indicates the reduction of the titanium (and nickel) concentration in the solid solution. It should be noted an important feature, the maximum growth of the electrical resistivity is higher, the lower the concentration of titanium. At the isothermal annealing at 923 K in steel containing titanium, the formation of intermetallic precipitates such as Ni₃Ti, is shown by electron microscopy studies. To determine the processes occurring during isochronous annealing in this temperature range in the aged at 923 K samples were also carried isochronous annealing in the range 600-920 K.

These isochronous annealing showed that the growth of the resistivity in the 700-800 K with the subsequent downturn discovered earlier in the isochronous annealing of quenched samples, reproduced with the same dependence on the concentration of Ti. Thus, there are two observed at annealing processes - at 700-800 K and in the vicinity of 900 K and above. The increase in the resistivity at 700-800 K is associated with the processes of separation and approach to equilibrium state, as has been shown for the fcc alloys Fe-36% Ni [7]. With increasing temperature above 800 K in the investigated alloys it occurs the homogenization of austenitic solid solution and lowering resistivity in accordance with the equilibrium states. Thus, the presence of titanium in solid solution suppresses the thermal separation process, and decreases the equilibrium curve of the solid solution separation of stainless steel.

During the low-temperature electron irradiation at 80 K dose dependence of growth of residual electrical steels studied are linear at least up to a dose 10¹⁸ cm⁻². This reflects a continuation of the resulting radiation-induced defects.

In Fig. 2 it is presented the results of isochronous annealing of quenched samples irradiated by electrons. Dependencies obtained for steel with 1% Ti at different doses are practically identical. In the region of room-temperature electrical resistivity of the irradiated samples is not reaches the initial value. In the case of steel alloyed by 0.6% Ti exceeding of the value over the initial resistivity in the region of room temperature is maintained for more than steel with 1% Ti.

**Figure 3.** Resistivity dependences on the isochronous annealing temperature of steels annealed before electron irradiation at different temperatures. At the bottom part of the figure - differentiated curves.
Maximum value of annealing is at the first peak at 110-120 K. The second peak poorly defined, is about 170-180 K. The third peak of annealing is situated at 220-240 K. The amplitude of the first peak tends to increase with increasing dose and concentration of titanium. In the area of 220-240 with increasing temperature the resistivity decreasing of the steel with 0.6% Ti much less than of the steel with 1% Ti. The peak annealing, located at 240 K is well defined.

Figure 3 shows the data of isochronous annealing of steels annealed before irradiation at 773 K for maximum separation (SSS) or aged at 923 K for the formation of intermetallic precipitates. It can be seen that the peaks of the annealing substantially the same ones as in the case of quenched samples. The first peak of annealing almost the same amplitude and position on the temperature scale for all samples. The second peak is clearly visible only in the alloy without titanium. The third annealing peak in the area of 220-240 clearly visible on an alloy without titanium and is located near 240 K. In the region of room-temperature it is observed partial annealing, as well as in quenched samples.

With further increase in the annealing temperature it is observed an increase in resistivity at 350-400 K on all steels. However, the resistivity increase in the alloy without titanium substantially greater. The maximum value of the resistivity reaches at the samples annealed for SSS state, at 660 K, which is significantly lower than for the non-irradiated samples. At higher temperatures, at steels annealed for SSS the resistivity falls below the initial value. This drop is not to become at the steel with 1% Ti, annealed at 923 K, the electrical resistivity close to the initial level. These data indicate that during the annealing of the irradiated samples it is occure the further separation of solid solution and thus homogenization of a solid solution above 800 K, as well as for the unirradiated samples. Accordingly, this results in a decrease in the resistivity below the original values for samples annealed for SSS state.

4. Discussion
In this work were shown, that the increase in resistivity at low temperature irradiation (80 K) is linearly dependent on the radiation dose. This means that with increasing radiation dose is a linear growth of preserved concentrations of radiation-induced defects. It is possible that under irradiation it occurs the recombination of close pairs. Thus, dumbbell configuration of self-interstitials (SIA), unlike pure metals may be different: Fe-Fe, Fe-Ni, Fe-Cr, Ni-Cr, and others. From this follows that the migration energy of self-interstitials may be more high.

The activation energy of the processes corresponding to the detected annealing peaks may be estimated by known formula $E_A = kT_0 \ln(\nu \Delta t)$ [8], where $\nu$ - frequency of the Debye, $\Delta t$ - annealing time, $T_0$ - the peak annealing temperature. Evaluation provides for a peak at about 110 K (0.36±0.02) eV. For peak around 170 K estimation gives (0.55±0.05) eV. For a peak at 220-240 K estimation gives the activation energy of about (0.65±0.07) eV

Considering the annealing peak at 110-120 K which is broad and has a large amplitude can be assumed that it is associated with the annealing of self-interstitials on the sinks and vacancies. The presence of titanium leads to the formation of complexes SIA - Ti atom. Perhaps these complexes dissociate or migrate at 170 K. The third peak annealing at temperatures of 220-240 K is due to the migration of vacancies. And these vacancies in steels containing Ti react with the Ti atoms to form complexes vacancy-atom of Ti. Besides the vacancies annealed at sinks and form vacancy clusters (VC). On the formation of complexes indicates that this peak is clearly visible in the steel without titanium and 0.6% titanium. In the area of room-temperature dissociation of complexes and VC of small multiplicity and growth of VC greater degree of multiplicity occurs. This is indicated by the beginning of the separation of the solid solution, leading to an increase in resistivity. At higher temperatures of isochronous annealing dissociation of the remaining VC, which leads to further separation of the solid solution to temperatures near 700 K.

Thus we can say that radiation defects due to the interaction with the Ti atoms form a series of more complex defects compared to defects in non-alloy steel. Some of these types of defects have higher thermal stability.
5. Conclusion
The data obtained on the effect of Ti doping on the accumulation and annealing of radiation defects and radiation-induced structural phase changes in the austenitic stainless steel 16Cr15Ni3Mo (0-1) Ti at low temperature (80 K) electron irradiation.

1. At the non-irradiated alloys the impurity of Ti inhibits the thermal separation of the solid solution at 700-800 K. At temperatures above 850 K, the formation of the second phase (Ni₃Ti) occurs.

2. The accumulation of radiation defects at 80 K leads to a linear increase in resistivity with increasing radiation dose, which means saving generated point defects.

3. In the irradiated at 80 K alloys migration of self-interstitials, with an activation energy of 0.36 eV, to sinks and formation of complexes self-interstitials - Ti atom occurs in the temperature region 110-120 K. Dissociation of these complexes occurs near 170 K. The binding energy of complexes - 0.19 eV.

4. The migration of vacancies occurs at 220-240 K with an activation energy of 0.65-0.70 eV. Thus there are leads to formation of vacancy clusters and complexes vacancy - Ti atom. Dissociation of these complexes and vacancy clusters starts at around room temperature and occurs to 700 K. This results in a radiation-induced separation of the solid solution.

Obtained data indicate that radiation defects interact with titanium atoms and form a number of more complex defects compared to defects in the non-alloyed steel. Doping of titanium has an effect on radiation-induced processes.

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References
[1] Votinov S N, Prokhorov V I, Ostrovsky Z E 1987 Irradiated Stainless Steels Moskow, Science 128 p.
[2] Mariasz P J J. 1984 Nucl. Mater., 122-123 472
[3] Garner F A 1984 J. Nucl. Mater. 122-123 459
[4] Sagaradze V V, Pavlov V A, Alyab’ev V M, Goshchitskii B N, and others 1988, Fiz. Met. Metallov., 65 970-977.
[5] Perminov D A, Druzhkov A P, Arbuzov V L 2011 J. Nucl. Mater., 414, pp. 186-193.
[6] Arbuzov V L, Danilov S E, Kazantsev V A, and Sagaradze V V 2014 The Physics of Metals and Metallography, , 115, 10, 1017–10.
[7] Danilov S E, Arbuzov V L, Kazantsev V A 2011 Journal of Nuclear Materials 414 200–204
[8] Konobeevsky S T 1967 Influence of irradiation on materials, Moskow Atomizdat 402c.