Comparison of microstructure changes and irradiation induced growth of E635 alloy under neutron irradiation influence

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Abstract. Model samples of zirconium E635 alloy after rolling, annealing, quenching were subjected to reactor irradiation in BOR 60 up to a fluence ~ $10^{26}$ m$^{-2}$. The Mössbauer studies data on the state of iron in the original samples previously subjected to rolling, annealing and quenching, and on the irradiated alloy samples are given. It is revealed that in the initial samples iron is in different intermetallic compounds, and also partly in the solid solution. During irradiation the iron atoms move from one type of intermetallic compounds to another one and in to the solid solution. Data on the relative content of iron in different phases and compounds are compared with the results of irradiation-induced growth strain measurements. The correlation between irradiation-induced grows and iron atoms redistribution in alloys is found.

1. Introduction
Radiation growth of zirconium alloys is one of the important phenomena in the operation of nuclear reactors. To establish the mechanisms of irradiation-induces growth the complex investigations of many alloy parameters must be carry out as before irradiation and also after irradiation. The phase composition changing must be studded too. The necessary information about the origin and evolution of secondary phases and redistribution of elements in the alloy matrix during thermomechanical treatment, as well as information about the phase transformations under the influence of reactor irradiation can be obtained by Mössbauer spectroscopy. This is possible because iron and tin contained in alloy compositions have Mössbauer isotopes. This method allows study the phase composition of alloys with low content of alloying elements. Mössbauer spectroscopy data on iron redistribution in alloys and data on radiation growth are analyzed to find correlation between them.

2. Materials and methods
The alloy of type E635 (Zr-1.2% Sn-0.34% Fe-1.0% Nb-0.03 ÷ 0.05% O) is chosen for investigations. Model alloy samples were prepared with introduced Mössbauer isotopes $^{57}$Fe and $^{119}$Sn. The alloy composition and method of preparation are chosen close to the composition and method of preparing of industrial alloys. As the heat treatments the quenching, recrystallization and annealing of rolled samples and quenching are used. Before being placed in the fast neutron reactor BOR-60, all the
samples were autoclaved to create a protective oxide film to prevent the penetration of hydrogen in a sample from lithium in the reactor tests, since such a procedure is carried out with real samples.

To investigate changes in the microstructure during irradiation, samples were taken after the first stage of irradiation (up to fluence of \((2 \div 3) \times 10^{25} \text{ m}^{-2}\)) and after the great irradiation (up to fluence of \(11 \times 10^{25} \text{ m}^{-2}\)), which corresponds to a dose of approximately 20 displacements per atom (dpa). Mössbauer studies of quenched, rolled and annealed samples were performed before irradiation and after each of the two stages of irradiation. The technique of sample preparation, modes of radiation tests and Mössbauer studies described in [1, 2].

The data about the phase composition changes of the samples during irradiation obtained by transmission electron microscopy (TEM) and irradiation-induced growth were compared in previous paper [2]. Mössbauer spectroscopy allows obtaining more accurate data on the quantitative change in the phase composition of the samples [1]. That’s why it is necessary to consider new data. In this paper quantitative data on the phase composition of the irradiated samples obtained by Mössbauer spectroscopy are used for comparison.

### 3. Analysis of results

The detected by Mössbauer spectroscopy iron containing phases and compounds and the distribution of iron among these phases and compounds in the alloy E635 [1], as well as relevant data about the irradiation-induced growth (IIG) [2, 3] are summarized in table.

| Treatment | Phase, compound | Before irradiation | 1-step of irradiation | IIG (1%) | 2-step of irradiation | IIG (2%) |
|-----------|-----------------|--------------------|----------------------|----------|----------------------|----------|
| Annealing | S.s. Fe in α-Zr | –                  | 32 ± 2               | 0.06     | 29 ± 2               | 0.11     |
|           | Zr,Fe           | 1.3 ± 1.0          | 35 ± 3               | 37 ± 2   |                      |          |
|           | Zr(Nb,Fe)₂      | 75.7 ± 2.0         | 16 ± 2               | 17 ± 2   |                      |          |
|           | (Zr,Nb)₂Fe      | 23 ± 2             | 17 ± 4               | 17 ± 2   |                      |          |
| Rolling   | S.s. Fe in α-Zr | –                  | 34 ± 2               | 0.04     | 30 ± 2               | 0.18     |
|           | Zr,Fe           | 1.9 ± 1.5          | 11 ± 2               | 38 ± 3   |                      |          |
|           | Zr(Nb,Fe)₂      | 81 ± 2             | 33 ± 3               | 16 ± 2   |                      |          |
|           | (Zr,Nb)₂Fe      | 17.1 ± 3           | 22 ± 2               | 16 ± 3   |                      |          |
| Quenching | S.s. Fe in α-Zr | 13 ± 2             | 30 ± 2               | 0        | 34 ± 5               | -0.01    |
|           | Zr,Fe           | 21 ± 2             | 38 ± 4               | 15 ± 4   |                      |          |
|           | Zr,Fe           | 30 ± 2             | –                   | –        |                      |          |
|           | Zr(Nb,Fe)₂      | 8 ± 2              | 16 ± 2               | 30 ± 2   |                      |          |
|           | (Zr,Nb)₂Fe      | 28 ± 2             | 16 ± 2               | 21 ± 5   |                      |          |

In most cases the presence of three or more microphases were revealed in the alloy with a sufficiently low error. The relative concentrations of individual phases varied from 1.3 to 81% of the total iron content in the alloy. These concentrations were changed under irradiation and the changes in the 1-st and 2-nd stages of irradiation were revealed in different ways. Solid solution was represented by some feature. It was practically absent in annealed and cold worked (rolled) samples, but it was manifested in noticeable quantity after irradiation. Another feature is the disappearance of one of the phases in the quenched sample after irradiation.

Irradiation-induced growth strain values for all the samples did not exceed 0.18% for all types of thermomechanical treatments. Additionally, with increasing rolling deformation the irradiation-induced growth increases. In quenched samples the irradiation-induced growth was virtually nonexistent; by the way, the texture was not observed.
The change of the relative concentration of phases, in which iron is in a different quantitative ratio with other chemical elements, indicates the redistribution of alloying elements between the second phase particles and the solid solution in the alloy under irradiation. Apparently, there is a relationship between the evolution of microstructure and irradiation-induced growth. It is believed that the irradiation-induced growth of zirconium is due to two factors: the alignment of oriented loops and climb of dislocations stimulated by irradiation [4]. The direction of flow of point defects during irradiation may occur due to the formation of a large number of opposite point defects and care for their dislocation and other drains. These streams can be weakened by increasing mutual recombination of point defects by radiation.

We can assume that the role in creating or preventing directed flows of point defects plays the process of atoms redistribution. The received data are considered from this point of view.

At the initial stage of irradiation there is a significant redistribution of the iron atoms: intermetallic compounds Zr(Nb,Fe)$_2$ are destroyed in rolled and annealed samples and in quenched samples and iron goes from compounds (Zr,Nb)$_2$Fe and Zr$_2$Fe into solid solution and into compound Zr$_3$Fe, and in the quenched sample into Zr(Nb,Fe)$_2$. In the annealed sample there are more phase content changes compared to rolled samples. An interesting fact is that: after the first radiation exposure step the irradiation-induced growth of annealed samples higher than that of the rolled.

After the second stage of irradiation the phase composition of annealed sample varies slightly, but in the rolled sample the concentration of compound Zr$_3$Fe increases due to decay of compounds Zr(Nb,Fe)$_2$ and (Zr,Nb)$_2$Fe. We would note that the phase compositions of the annealed and rolled samples after the second step of irradiation are the same. In quenched samples there are the processes of iron atoms redistribution which are in the reverse to rolled sample.

Thus, in rolled samples the redistribution of atoms can facilitate the formation of the directed flows of point defects, whereas in the annealed sample at the second irradiation stage such processes are practically absent. Best irradiative properties of the annealed samples in comparing with the rolled those during the second stage of irradiation can be explained by absence of the atoms redistribution processes. Slightly worse results of irradiation-induced growth strain of annealed samples in the first stage of exposure can be explained by more intensive process of atoms redistribution.

As to quenched alloys, it is necessary to take into account their essential difference from rolled and annealed alloy in a phase composition. This difference is particularly evident in the presence of a large number of non-equivalent state of the iron atoms. Metastability of these states leads to a large number of competing processes of redistribution of atoms under irradiation, which may contribute to the recombination of point defects and prevent the formation of directed streams of point defects.

4. Conclusion
1. Quantitative Mössbauer data on the iron phases and compounds redistribution in rolled, annealed and quenched samples of E635 alloy before and after two stages of radiation exposure compared with the irradiation-induced growth strain value.
2. The assumptions about the possible correlation of atom redistribution and irradiation-induced growth are made: processes of atoms redistribution in rolled and annealed samples contribute to the formation of directed streams of point defects. So annealed samples have the worst irradiation-induced growth strain value at the first stage of irradiation due to more intensive process of redistribution of atoms, while in the second stage of irradiation, they showed better radiation characteristics and virtually no redistribution of atoms.
3. The presence a large number of metastable non-equivalent states of the iron atoms in quenched samples result in a large number of competing processes of atom redistributions under irradiation, which may lead to recombination of point defects and prevent the formation of directed streams of point defects.
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