Phase changes of iron near surface layers under argon ion irradiation

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Abstract. Mössbauer spectroscopy data on Ar⁺ ion irradiation influence on iron state are analyzed. It was shown the formation of new iron phases under Ar⁺ ion interaction with surface of zirconium alloy samples with iron and without iron layers. The appearance of paramagnetic phase in the surface layers was detected. Transformations of intermetallic compounds in zirconium alloys was established. Much changes are found in near surface layers.

1. Introduction
One of the main problems of nuclear power production is at present the safe maintenance of nuclear reactors with increasing reactor service time and fuel burnout rate. Raising the corrosion stability of zirconium alloys is important for the solution of this problem. This deals with creation of modern materials. The main priorities of modern materials is the development of new methods to increase the performance of metallic materials. Reliability, durability and efficiency of parts and components of systems and mechanisms are largely determined by their surface properties. In particular, to improve the corrosion resistance and to improve the tribological characteristics of products it is often sufficient and economically advantageous the modification of only the surface layers. Therefore, the challenge now is focused to obtain the necessary structural and phase states and properties of the surface layers of the material. To do this, we must study the changes in the structural and phase state in the surface layers after Ar⁺ ion radiation. Mössbauer spectroscopy allows us to study the thin surface layers, so it can be used to solve these problems. The aim of the article is to show the changes in phase compositions of zirconium alloy under Ar⁺ ion irradiation by Mössbauer spectroscopy.

2. Experimental
The used Mossbauer spectrometer operated in the mode of constant acceleration. ⁵⁷Co (Cr) was used as a source of resonant radiation. Isomer shifts are given relatively of α–iron. Conversion electron Mössbauer spectra (CEMS) were registered with proportional counter [1, 2]. The fitting of spectra is carried out using Univem MS. The scheme unit for production of iron films and irradiation with argon ions is shown in Figure 1.

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Irradiation by Ar+ ions have been made using the installation, forming a beam of Ar+ ions with Gaussian distribution of the ions energy in the range of 3.5 - 15 keV, with an average energy of 10 keV and the ion flux density \( j = 15 - 20 \mu \text{A} \cdot \text{sm}^{-2} \). Doze of irradiation was in the range of (0.1-5)*10^{18} \text{ion*cm}^{-2} \ [1].

The thickness of iron layer was determined by gravimetric and photometric methods. The experimental error is 20 nm.

3. Results and discussion

Results of the Mössbauer investigations are shown in Figures 2, 3 and Tables 1, 2. CEMS spectrum of 57Fe layer (thickness 50 nm) can be fitted by superposition of lines of quadrupole splitting of paramagnetic phases (Figure 2 a, b) such as Fe2O3, Fe3+, Fe2+. During obtaining iron layer on any substrate by iron evaporation the lines of Fe2O3 in paramagnetic state appeared in the beginning of this process. Before irradiation the low intensity lines of α-Fe are visible in the spectra (Figure 2a). After irradiation these lines are not visible. The spectra parameters are given in Table 2. The irradiation results in disappearance of α-Fe and increasing of Fe2O3 quantity in paramagnetic state.

Existence of lines of quadrupole splitting of Fe2O3 paramagnetic phase can be explained by formation of iron nanoparticles on the surface and their interaction with air components and thin oxide.

**Figure 1.** Schema of iron layer preparation and irradiation by Ar+ atoms.

**Figure 2.** CEMS spectra of 50 nm 57Fe layer on surface of E635 before (a) and after (b) irradiation by Ar+ ions. \( E = 10 \text{ keV}, \) dose 5*10^{17} cm^{-2}.

**Figure 3.** CEMS spectra of 500 nm 57Fe layer on surface of E635 before (a) and after (b) irradiation by Ar+ ions. \( E = 10 \text{ keV}, \) dose 5*10^{17} cm^{-2}.
layer on surface of zirconium alloy. Existence of iron paramagnetic phases with valence state Fe\(^{3+}\), Fe\(^{2+}\) has not good explication at this stage of research. One can suppose an interaction with thin oxide layer ZrO\(_2\) which is always formed on surface of zirconium alloys. Irradiation by Ar\(^+\) ions changes the phase composition in the surface layers both for thin (50nm) and thick (500nm) iron films (Tables 1 and 2).

**Table 1.** Mössbauer spectra parameters of \(^{57}\)Fe in 50 nm layer.

| Phase | S, % | IS, mm/s | QS, mm/s | W, mm/s | H, T |
|-------|------|----------|----------|---------|------|
| Before irradiation | | | | | |
| Fe\(_2\)O\(_3\) | 69.3 | 0.38±0.02 | 0.83±0.02 | 0.58±0.03 | |
| Fe\(^{2+}\) | 14.3 | 0.38±0.02 | 1.42±0.02 | 0.64±0.03 | |
| Fe\(^{3+}\) | 7.0 | 0.85±0.02 | 1.90±0.02 | 0.45±0.02 | |
| \(\alpha\text{-Fe}\) | 10.6 | 0.03±0.02 | 0.03±0.02 | 0.30±0.02 | 32.80±2.37 |
| After irradiation | | | | | |
| Fe\(_2\)O\(_3\) | 81.2 | 0.24±0.02 | 0.87±0.02 | 0.54±0.03 | |
| Fe\(^{2+}\) | 13.2 | 0.28±0.02 | 1.48±0.02 | 0.45±0.02 | |
| Fe\(^{3+}\) | 6.2 | 0.90±0.02 | 2.06±0.02 | 0.55±0.02 | |
| \(\alpha\text{-Fe}\) | - | - | - | - | |

**Table 2.** Mössbauer spectra parameters of \(^{57}\)Fe in 500 nm layer.

| Phase | S, % | IS, mm/s | QS, mm/s | W, mm/s | H, T |
|-------|------|----------|----------|---------|------|
| Before irradiation | | | | | |
| Fe\(_2\)O\(_3\) | 33.2 | 0.43±0.02 | 0.81±0.02 | 0.65±0.03 | |
| Fe\(^{2+}\) | 13.3 | 0.38±0.02 | 2.25±0.02 | 0.69±0.03 | |
| Fe\(^{3+}\) | 7.2 | 0.90±0.03 | 2.25±0.02 | 0.67±0.02 | |
| \(\alpha\text{-Fe}\) | 47.3 | 0.02±0.02 | 0.00±0.02 | 0.90±0.02 | 33.1±0.2 |
| After irradiation (information to depth 300 nm) | | | | | |
| Fe\(_2\)O\(_3\) | 37.2 | 0.30±0.02 | 0.82±0.02 | 0.75±0.03 | |
| Fe\(^{2+}\) | 5.2 | 0.26±0.02 | 1.97±0.02 | 0.75±0.02 | |
| Fe\(^{3+}\) | 20.2 | 0.85±0.02 | 2.25±0.02 | 0.65±0.02 | |
| \(\alpha\text{-Fe}\) | 38.1 | 0.02±0.02 | 0.00±0.02 | 0.90±0.02 | 33.1±0.2 |
| After irradiation from surface (to depth ~20 nm) | | | | | |
| Fe\(_2\)O\(_3\) | 43.2 | 0.31±0.02 | 0.83±0.02 | 0.74±0.03 | |
| Fe\(^{2+}\) | 10.1 | 0.39±0.02 | 2.21±0.03 | 0.75±0.04 | |
| Fe\(^{3+}\) | 14.2 | 0.92±0.02 | 2.06±0.02 | 0.69±0.02 | |
| \(\alpha\text{-Fe}\) | 33.3 | 0.02±0.02 | 0.00±0.02 | 0.90±0.02 | 32.7±0.2 |

There is decreasing of \(\alpha\text{-Fe}\) content for thick layer (500 nm) and its disappearing for thin layer (50nm). The nearer the surface the lower \(\alpha\text{-Fe}\) content (Table 2 column 2). The increasing of paramagnetic phase Fe\(_2\)O\(_3\) from 33% to 43 % is detected (Table 2). The increasing of the share of Fe\(^{2+}\) ions is accompanied with simultaneous decreasing of the Fe\(^{3+}\) share. The changes of the share are approximately equal. This can be explained by influence of zirconium. Comparing the parameters of CEMS spectra for different iron layer thicknesses (Tables 1 and 2) we can see some regularity in the behavior of the isomer shift and large changes of the values of quadrupole splitting under irradiation influence. The irradiation results in the decreasing of isomer shifts magnitudes from 0.38 to 0.24 mm/s for 50 nm layer and from 0.43 to 0.31 mm/s for 500 nm layer. This can be explained by large changes in electron density on the iron nuclei. The decreasing of isomer shift of Fe\(_2\)O\(_3\) paramagnetic phase indicates an increase in the density of s-electrons at the nucleus. As there are no significant changes in the magnitudes of QS for Fe\(_2\)O\(_3\) paramagnetic phase, so there are no significant changes in surrounding of iron atoms in this phase. Part of iron ions is in Fe\(^{2+}\) and Fe\(^{3+}\) states. The magnitudes of
QS of these phases containing iron in paramagnetic states such as Fe$^{2+}$ and Fe$^{3+}$ are abnormally high. There is no any regularity in the behavior of QS (Tables 1, 2). As follows from high magnitudes of QS, great distortions of crystal structure presenting in these phases containing iron in paramagnetic Fe$^{2+}$ and Fe$^{3+}$ states results in increasing of electric field gradient and consequently in the increase of the QS magnitudes. As to the alpha-iron spectra parameters, there are significant changes in their contents under irradiation and non-significant changes in magnitudes of IS, QS, $H_{\text{eff}}$. The latter can be explained by fluctuation in atoms surrounding caused by irradiation in this magnetic phase.

We can state that the second and fifth lines of alpha-iron spectra do not correspond to the law of intensities 3:2:1 for chaotic distribution of the magnetic moments in the sample or layer (Figures 3). When the vectors of magnetic moments are perpendicular to surface the intensities of 2-d and 5-th lines decrees or disappear. So in iron layers on zirconium alloys the vectors of magnetic moments are preferentially orientated perpendicular to surface, while in pure iron their preferential orientation is usually parallel to surface [3]. The significant magnitudes of line width ($W=0.45-0.90 \text{ mm/s}$) (Tables 1, 2) for all phases are due to different surroundings of iron atoms in the layers.

4. Conclusion

Thus, Mössbauer spectroscopy allows us to obtain data on the iron atoms state in the surface layers of different thicknesses. It was found that the iron layers have a heterogeneous structure as different phases or compounds. Iron layers have different phase composition depending of iron layer thickness. There are paramagnetic phases such as Fe$_2$O$_3$, Fe$^{3+}$, Fe$^{2+}$ and magnetic phase as $\alpha$-Fe in the iron layers. The phase composition is changed under irradiation, in particular the quantity of $\alpha$-Fe decreases, while the quantity of paramagnetic phase Fe$_2$O$_3$ increases. These compounds are no uniformly distributed through the thickness of the layers.

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