Mössbauer spectroscopy possibilities in investigation of the phase changes in alloy near surface layers under plasma, optic and ion irradiation influence

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Abstract. In this paper Mössbauer spectroscopy data on optic, plasma and ion irradiation influence on iron state are analyzed. It was shown the formation of new iron phases under plasma interaction with surface of steel samples. The appearance of paramagnetic austenite phases up to 20 microns from surface was found. The laser irradiation of thin Fe layers on V and Al layers on iron samples results into formation of solid solutions of these elements. The influence of ion irradiation with Ar+ on phase changes on surface of alloys is shown.

1. Introduction
One of the 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. To obtain the needed characteristics of used construction details, sometimes it is enough to change the surface properties. Therefore, the aim of many investigations is focused on obtaining the necessary structural and phase states and properties of the surface layers of the material. To do this, it is necessary to study the changes in the structural and phase state occur in the surface layers after laser irradiation, plasma exposure and ionizing radiation. Mössbauer spectroscopy allows us to study the thin surface layers, so it can be helpful to solve these problems. The aim of the article is to review and show the Mössbauer spectroscopy possibilities in study of Nano structural and phase state changes of iron in the alloys which have been exposed to the influence of the laser, ion and plasma irradiation.

2. Experiment
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 metallic iron. Conversion Electron Mössbauer Spectra (CEMS) were registered with proportional counter. The fitting of spectra is carried out using Univem MS. Laser irradiation has been used for modification of near surface regions of the samples. The films of iron-57 and Al with thickness 200 nm on, respectively, vanadium and iron substrates were used as samples for investigations. The layers have been obtained by thermal evaporation of iron and aluminum at vacuum ~0.0013 Pa. The laser with wavelength of =1.06 microns

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and pulse duration of 30 nano seconds was used. The details of experimental technique are described in paper [1].

The Ar$^+$ ions irradiation has been made using the installation, forming Ar$^+$ beam with Gaussian distribution of the ions energy in the range 3.5 - 15 keV, with an average energy of 10 keV and the ion flux density $j = 15 - 20 \, \mu\text{A/cm}^2$. The dose of irradiation was in the range of (0.1 -5) *10$^{18}$ ion * cm$^{-2}$ [2]. The cold worked zirconium alloy zircaloy-2 (Zry-2) was used for irradiation.

For studying of plasma influence the steel samples were prepared in the form of discs with a diameter of ~20 mm and thickness of 3–5 mm. The high-temperature pulsed plasma flux of $q = 0.85 \, \text{mW/cm}^2$ at a pulse duration $\tau = 20 \, \text{ms}$ was used. Working installation and surge chamber were previously evacuated to a pressure ~ 10$^{-1}$ Pa, and then the chamber was filled with plasma gas (nitrogen $p = 36 \, \text{Pa}$) [3]. The energy content of the stream varies from 10 to 50 kJ [3].

3. Results and discussion.

3.1 Laser irradiation

Results of the Mössbauer investigations are shown in Figures 1, 2. Before laser irradiation the spectrum consists of the lines of hyperfine splitting of alpha-iron (Figure 1a) (only 1 and 6 lines are shown) with hyperfine magnetic field $H_{\text{eff}} = 33.0 \pm 0.3 \, \text{T}$. After laser irradiation the shape of CEMS spectrum is changed. The first and six lines show the superposition lines of hyperfine magnetic splitting of the magnetic phases (Figure 1b) with 3 hyperfine magnetic fields $H_{\text{eff1}} = 33.0 \pm 0.3 \, \text{T}$, $H_{\text{eff2}} = 29.8 \pm 0.3 \, \text{T}$ and $H_{\text{eff3}} = 27.8 \pm 0.3 \, \text{T}$. According to results in paper [4], the solid solutions of Al in Fe are formed under laser irradiation. The intensities of lines with $H_{\text{eff1}} = 33.0 \pm 0.3 \, \text{T}$ correspond to the share of iron without Al atoms in nearest neighborhood, lines with $H_{\text{eff2}} = 29.8 \pm 0.3 \, \text{T}$ and $H_{\text{eff3}} = 27.8 \pm 0.3 \, \text{T}$ correspond to the coordination spheres containing 1 and 2 Al, respectively. It means that the laser irradiation mixes Al atoms with iron and initiates formation of solid solutions (SS).

![Figure 1](image1.png)

**Figure 1.** CEMS spectra of iron layer and iron layer under Al after irradiation by laser beam.

![Figure 2](image2.png)

**Figure 2.** Spectra of iron layer on vanadium substrate before and after laser irradiation and after annealing.

The same laser irradiation were exposed on iron film on vanadium substrate. The CEMS spectrum is shown in Figure 2. The shape of initial spectrum (Figure 2a) presents the shape of alpha iron spectrum with $H_{\text{eff}} = 33.0 \pm 0.3 \, \text{T}$. The intensities of second and fifth lines are greater than that of first and sixth lines. It means that majority of magnetic moments on the surface are oriented parallel to surface. After the laser influence, the spectrum shape is changed. In its central part the large line of
The paramagnetic phase is appeared (Figure 2b). In addition to lines of hyperfine magnetic splitting of alpha-iron the lines of hyperfine splitting of another magnetic phases are detected in this spectrum too. Fitting gives parameters of these lines such as $H_{eff_2} = 29.8 \pm 0.3$ T and $H_{eff_3} = 27.8 \pm 0.3$ T (IS$_1 = 0.00 \pm 0.01$ mm/s, IS$_2 = 0.00 \pm 0.01$ mm/s). Approximately the same results are obtained after annealing of the same type specimen (Figure 2c). Comparing these results allows us to make the conclusion that the laser irradiation results in formation of SS of V in Fe. The spectrum parameters of the central part are as follows IS = 0.00±0.01 mm/s, QS = 0.00±0.01 mm/s. Comparing them with parameters known for V-Fe alloys [5] we conclude that the central line of paramagnetic phase belongs to intermetallic compound Fe-V, and the lines of hyperfine magnetic splitting belong to SS of V in Fe. So the laser irradiation and annealing provides the same changes, i.e. formation of the intermetallic compound Fe-V and SS of V in Fe.

3.2 $Ar^+$ irradiation

Influence of ion irradiation by ions $Ar^+$ is shown in the Figure 3. Much changes are visible in CEMS spectra (Figure 3d). In transmission geometry the intensity of lines of intermetallic compound $Zr(Fe, Cr)_2$ in the form (C14) decreases relatively to intensity of lines of intermetallic compound $Zr(Fe,Cr)_2$ in the form (C15). Comparison of lines intensities in the CEMS spectra (Figure 3a, 3b) shows that part of $Zr(Fe, Cr)_2$ in the form (C14) was transformed to the compound $Zr_3Fe$.

![Figure 3](image.png)

**Figure 3.** Spectra of $^{57}$Fe in the zirconium alloys (Zry-2) in transmission mode: a) before irradiation, b) after irradiation, in CEMS mode: c) before irradiation, d) after irradiation.

3.3 Plasma irradiation

Interaction of plasma with surface of steel results in the phase changes in the nearest neighbor layers. This follows from analysis of CEMS spectra of initial specimen of steel and those after plasma influence (Figure 4). The spectrum of the initial steel specimen consists of lines of hyperfine magnetic splitting (HMS) of 3 magnetic phases (Figure 4a).

The values of IS = 0.00±0.02 mm/s, the values of magnetic fields are $H_{eff_1} = 33.0 \pm 0.1$ T, $H_{eff_2} = 30.4 \pm 0.2$ T, $H_{eff_3} = 27.5 \pm 0.5$ T. After the interaction they are equal to $H_{eff_1} = 33.6 \pm 0.1$ T, $H_{eff_2} = 30.4 \pm 0.2$ T, $H_{eff_3} = 28.1 \pm 0.5$ T. Before the interaction the line of paramagnetic phase (IS = 0.28±0.03 mm/s, A = 61%) is detected. After the interaction the lines of great intensity (IS = 0.07±0.05 mm/s, A = 14.1%) and low intensity (IS = 0.28±0.03 mm/s, A = 41%) are visible in the central part of the spectrum. Existence of three sextets can be explained by formation solid solutions of doping atoms, for example, Cr or another atom.
These doping nonmagnetic atoms such as Cr or Ni decrease the magnitude of $H_{\text{eff}}$. Sextet with $H_{\text{eff}}=33.0 \pm 0.1$ T is explained by existence of iron without another atom in nearest neighborhood, the other two ($H_{\text{eff}2}, H_{\text{eff}3}$)–by existence of iron states with coordination spheres containing one or two nonmagnetic atoms. So Mössbauer spectroscopy allows us to detect changes in structure of near surface layers and appearance of paramagnetic (possibly austenite) phase and to estimate the relative concentration.

4. Conclusion

Mössbauer spectroscopy is applied to investigations of the influence on surface layers of laser irradiation, irradiation by Ar$^+$ ions and interaction with plasma. It was shown:

a) Laser irradiation of Al films on Fe and Fe films on V results in formation of solid solutions of Al and V atoms in iron and formation of intermetallic compound Fe-V;

b) Irradiation by Ar$^+$ ions of zirconium alloys (E635) results in transformation of intermetallic compound Zr(Fe, Cr)$_2$ in the form (C14) to compound Zr$_3$Fe;

c) Plasma influence on surface of steel results in formation of paramagnetic austenite phase.

Acknowledgments

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