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Mössbauer Spectroscopy of Radiation — Induced Processes in Metallic Systems

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Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/60748>

Abstract

Nuclear power engineering development is held back by both the nuclear reactor safety reasons and the problems related to creating materials suitable for using in the reactors. These materials must be resistant to radiation, able to stand high temperatures, and stable to the corrosive environments. In this work, the general regularity of the interstitial atoms and vacancy interaction with impurity substitutional atoms of ^{57}Co (^{57}Fe) in bcc lattice metals has been systematically investigated for the first time. The electron states and structure of "impurity-interstitial" atom, "impurity-vacancy" systems, and their mössbauer parameters are defined. For the first time, by the Mössbauer effect study, the complexes annealing stages from isochronal annealing temperature have been defined. The mössbauer impurity atoms vibrations rms amplitude values and their binding energy are determined. It has been experimentally established that atom mobility considerably increases in radiation-damaged zones created by high-velocity charged particles, fission fragments, or ionized displaced atoms. The compound dumbbell state in bcc metals was investigated, and it was shown that unlike fcc metals, in the bcc metals the considerable quadrupole splitting was revealed, which enables us to separate them on different interstitial configurations around ^{57}Co impurity. It was also established that non-cubic charge distribution around a mössbauer atom leads to the electric field gradient that causes the nuclear levels hyperfine splitting owing to quadrupole interaction.

Keywords: Mössbauer effect, positron spectroscopy, point defects, irradiation by nuclear particles, isochronal annealing, quadrupole splitting, "impurity-interstitial" complexes, "impurity-vacancy" complexes

1. Introduction

Most of the materials that are being used in innovative technologies have complex composition, structure, and phase. They can be seriously affected by the irradiation of nuclear particles with high energy. Irradiation causes an excess formation of defects at an atomic level. The defects of structure can accelerate diffusion processes in materials and create centres of allocation of new phases in alloys. Moreover, if nuclear reactions appear by irradiation processes, there are more changes in the internal structure of materials. As a result, the new structural units appear, which are absent in the original matrix. The most important processes that occur at the interaction of high-energy radiation with a solid are ionization, the displacement of lattice atoms from their sites, and the occurrence of fission products from nuclear reactions. Ionized atoms are quickly neutralized in metals with high electroconductivity. As a result of the elastic collision with bombarding particles, the lattice atom can obtain energy E_p that may exceed the threshold of displacement energy E_d . Then, the atom leaves its initial place in the lattice. If the knocked-out atom has enough energy, it goes through several interatomic distances to a complete stop, which shows the formation of a pair-displaced atom and a vacancy. For most solids, E_d has a value of about 20-30 eV. If E_p is not much more than E_d , then during each collision, only one pair of such defects is formed. For large E_p , two or more "vacancy-interstitial atom" pairs are formed.

If irradiation is created by heavy particles, the energy E_p obtained by the lattice atom can be very large. Then, the average distance between collisions can be equal to the interatomic distance. In these conditions, every atom on the way of the primary knocked-on atom moves from its place. As a result, an area of strong lattice distortion appears. This area is called displacement spike. Primarily, a knocked-on atom can appear at very high temperatures. This is called thermal spike area. However, fission fragments can cause stronger local damages. The thermal and displacement spikes can occur in materials that were affected by irradiation in the reactor or the irradiation by heavy particles, except in large cascade displacements.

The most important characteristic of the collision is the energy, which is transmitted to the impinged atom. This energy that can change from zero in collisions at small angles to a maximum $E_{p\max}$ at elastic head-on collision is given by

$$E_{p\max} = 4Em / (M + m)^2,$$

where E and m – energy and mass of incident particle, M – mass of the target atom.

This ratio is used for nonrelativistic particles such as neutrons, protons, etc. For electrons with energy of the order of MeV, relativistic effects need to be considered. Then, this formula is modified:

$$E_{p\max} = 2E(E + 2m_e c^2) / Mc^2,$$

where, m_e – rest mass of electron, c – speed of light.

The minimum energy $E_{\min}$ needed for E_d energy transmission is equal to

$$E_{\min} = (M + m)^2 E_d / 4Mm.$$

This reasoning is not applicable for electrons and gamma-rays. In the case of electrons, the $E_{\min}$ value is large, and there is a need to consider relativistic mechanics:

$$E_d = 2E_{\min} [E_{\min} + m_e c^2] / 4Mc^2$$

Gamma-rays do not directly displace atoms. They transmit their energy to the electrons of the atom. During collision with the lattice atoms, they lead them to displacement. Minimal energy of gamma rays, which is required for the displacement of atoms, is determined from the relation:

$$E_d = 2E_{e\min} [E_{e\min} + m_e c^2] / Mc^2$$

When materials are irradiated by reactor neutrons or heavy particles with high energy, the crystal lattice undergoes a huge number of elementary damages. With this, free energy of the system increases, and activation energy of the system decreases. These processes are related to the movement of atoms and defects. As a result, a mobility of atoms and defects increase. Depending on the physical parameters of the material, nuclear, and other factors, their complexes of vacancies and interstitials may be formed. These formations under certain conditions can lead to the formation of dislocation loops.

At a sufficiently high temperature, defects undergo a series of transformations. Some of them cancel each other out. Another part of the defects can reach the surface of the metal or grain boundaries. If defects are absorbed by dislocation, they cause the pinning of the latter. If absorbed defects are too many, they move along the dislocation line. When they come together, they form the teeth, inhibiting the movement of dislocations. As a result of the absorption of defects, dislocation is the pinning and hardening of the material.

Experimental methods for direct observations of structural defects on the atomic level have undergone significant developments. They include the direct resolution of individual atoms on a field ion microscope, determination of the atomic configurations of point defects by x-ray diffusion scattering, Mössbauer and positron spectroscopy, and others. Field-ion microscope is used to study the phenomena on the crystal's surface. The X-ray diffusion scattering is very useful to study clusters, which are formed from point defects and vacancies. Positron annihilation is sensitive to single vacancies and their clusters. The Mössbauer spectroscopy is sensitive to changes in the energy shift of the nuclear levels. These changes lead to the hyperfine

interactions. In the Mössbauer spectrum, it is detected by several parameters such as the isomer shift, quadrupole, and magnetic hyperfine splitting, as well as the value of the Mossbauer effect probability.

This work presented the results of the studies of metals and their alloys by nuclear gamma-resonance spectroscopy and x-ray structural analysis. In order to carry out these works we have designed and developed a set of tools. The Mössbauer effect study requires spectrometer, electric vacuum samples, annealing furnaces, helium and nitrogen cryostates, installation for samples' hardening, and devices for low-temperature irradiation and measurement.

2. The Mössbauer effect essence

The Mössbauer effect is a physical phenomenon observed in solids. It consists of the emission of a gamma-ray by a radioactive atom, without any loss of energy, for this atom must be in a bound state. Then, the gamma ray emitted at the expense of the recoil effect of the atom nucleus is also in the bound state. This discovery was made in 1958 by the German physicist Rudolf Mössbauer and won the Nobel Prize in Physics [1]. In his work, he used the radioactive nuclide osmium-191 which undergoes β -decay with the radioactive iridium-191 formation.

Nuclear-gamma resonance spectroscopy, which is based on the use of the Mössbauer effect, is one of the unique methods in nuclear-physical experiments. The scope of the application of the method extends from about nuclear and atomic phenomena and structures to a wide range of analytical problems, including the study of the short- and long-range order in solids. High sensitivity to the bare shift of the energy level of the nucleus allows it to apply to the study of the defect structure of metals. In this case, the Mössbauer atom, emitting and absorbing resonance gamma rays, serves as a probe. With the help of specially designed experiments, sensitivity to iron-containing materials can be reduced to $\sim 10^{-4}$ at.%. Information about the object under study is contained in the Mössbauer spectra. Among these, we must be able to extract the parameters characterizing the state of the environment and the resonance atoms in the crystal lattice. The most important of these are the probability (value) of the Mössbauer effect and the width of the spectral line splitting. In practice, the magnitude of the effect is evaluated by the relation:

$$\varepsilon = \frac{I_{\infty} - I_0}{I_{\infty}} = \frac{N_{\infty} - N_0}{N_{\infty}},$$

where, I_{∞} , N_{∞} – the intensity of the radiation passing through the absorber at the source momentum, when the resonance absorption is virtually absent; I_0 , N_0 the same with full overlapping emission and absorption.

In connection with the registration of gamma-rays in an environment where the solid angle of detection $\Omega \ll 4\pi$, instead of parameters I_{∞} and I_0 , are limited to the counters N_{∞} and N_0 , respectively. Typically, the center of gravity in the abscissa of the spectrum does not coincide

with the zero point value of the velocity. This shift can be dismissed as a positive and a negative side, which is called the isomer shift. The reason for this shift is the Coulomb interaction of the nucleus with radius R and its electron shell. The extent of this interaction is estimated by the change in the potential energy of the nucleus and is determined by the density $|\psi(0)|$ electrons of s-level:

$$\Delta E = -\frac{2}{3} \pi Z e^2 |\psi(0)|^2 \cdot \langle R^2 \rangle,$$

where Z – the atomic number of the nucleus, e – electron charge, and $\langle R^2 \rangle$ – the mean square radius of the nucleus.

However, the core radius in the ground state is different from the radius of the excited state. In addition, the density of s-electrons at the nucleus of the source and absorber can be different. In view of these factors for the isomer shift, it is possible to write a more acceptable formula in terms of velocity:

$$\delta = K \cdot \frac{\Delta R}{R} \cdot \Delta |\psi(0)|^2$$

where K – a constant determined by isotope used, $\Delta |\psi(0)|^2$ – the difference between the electron densities of s – levels of the source and absorber, and $\Delta R/R$ – radius of the nucleus relative change at the transition from the excited state to the ground state.

The difference in density $\Delta |\psi(0)|^2$ occurs due to differences in valence of s-level. Consequently, the isomer shift contains information about the chemical bond. Since this value is relative, you must always specify the origin (usually relative to a standard absorber – the potassium ferrocyanide).

The width of the nuclear transition is determined by the Heisenberg uncertainty relation. Its value is sufficiently small. Therefore, there is a spectral width at half height used. It is the sum of the corresponding parameters of the line source r_s and absorber r_a . The experimental spectrum is always wider than that amount. The line broadening is stipulated by several causes, such as the nuclei environment heterogeneity, presence of inclusions, final thickness of the source, and absorber, lines hyperfine splitting, etc. On the Mössbauer, spectra magnetic and quadrupole splitting can be observed. The first splitting occurs when the resonant core is in ground or the excited state has a magnetic moment, while the core has an effective magnetic field. Quadrupole splitting arises from the interaction of the electric quadrupole moment of the nucleus with the gradient of the inhomogeneous electric moment. As a result of this interaction (e.g., in an excited state), the nuclei ^{57}Fe level, with the spin $I_a = 3/2$, splits into two sublayers. In the ground state, quadrupole moment is absent, and there is no splitting. Under these conditions, instead of a single line in the spectrum, there are two adjacent lines. They are called doublets. The distance between them is proportional to the electric field gradient (EFG)

and is recorded as the measure of this index. Thus, in all changes in Mössbauer's parameters, there is always a relationship between the characteristics of the nucleus and the properties of the object studied.

In Mössbauer experiments, the principle of the Doppler shift of gamma-ray energy by periodic motion of the source or absorber relative to the other is used to measure the absorption spectrum. If the experiments on the transmission of gamma-ray, then the absorber is investigated and the Doppler shift is provided by the source movement. In this case, the geometry of the experiment is called absorptive. When an object under study is the source itself, the movement is subjected to the absorber and the source remains stationary. The geometry of the experiment is then called emissive. The sensitivity of this method for Mössbauer atoms is four-five orders higher in magnitude than in absorption. The choice of mode is determined by experimental conditions. The mode with constant acceleration is basic in the majority of Mössbauer measurements. In this case, the relative velocity of the source and the absorber changes linearly at a predetermined interval $(-V \div +V)$.

Since some of the investigated materials (e.g., Mo) did not have their Mössbauer isotope, the process of creating a source for emission investigations was realized in the following way. First, radioactive cobalt chloride solution $^{57}\text{CoCl}$ is transferred onto the surface of the pre-annealed material and evaporated. Upon reaching the required activity, samples were thermodiffusion annealed in a hydrogen atmosphere at a high temperature. As a result, chloride solution was completely reduced to metallic cobalt. The ^{57}Co atoms embedded in a matrix occupy regular lattice sites, which is evidenced by obtaining a symmetric single resonance line for such materials and the absence of the electric field gradient at the nuclei. Mathematical processing of the experiment of the Mössbauer effect study spectra aims to obtain physical parameters that determine the shape of the resonance line. For sufficiently thin samples with a high range precision, the Lorentzian type can be described:

$$L(X) = a / \left[1 + 4 / b^2 (x - c)^2 \right]$$

where b – the half-width, c – the center of gravity position, and a – the amplitude of the resonance spectrum.

When processing, each experimental spectrum is represented as a superposition of several such Lorentzians. The primary means of adjustment has been selected with the least squares method. This method describes precisely enough the resonance line shape with fitting quality assessment by χ -square criterion [2]. Between the parameters of the resonance when removing the degeneracy in the magnetic, electric fields, there are certain connections. Hence, components of the experimental spectrum can be divided into a number of characteristics. The isotope ^{57}Fe can introduce three types of components: single peak (degenerate line), quadrupole doublet (removal of degeneracy on the interaction of the ^{57}Fe nuclear quadrupole moment with electric-field gradient), and sextet that arises in the splitting of the resonance line in a magnetic field.

To the fitting operation, performing a special program ALFA has been developed. It is intended to use the average power of the personal computer. Besides the mandatory background value N_{∞} , the varying parameters are as follows: for single peak-center position – the line width and amplitude; for doublet-center position – amplitude and width of the components in pairs 1 and 6, 2 and 5, and 3 and 4; and for the position of center of gravity – quadrupole and magnetic splittings. As a result, the spectrum processing are extracting parameters of lines and components, χ -square, the sum of the deviations of the theoretical values $N_T(v)$ from the experimental $N_i(v)$, a confidence interval for obtained fitting, and some others as appropriate.

The Mössbauer effect study spectroscopy can help us to determine the hyperfine structure and energy shifts of γ -line on ^{57}Fe nuclei in solids. Shifts are caused by the interaction of nucleus with electric and magnetic fields. They form externally to the nucleus charges [2, 3]. In Mössbauer spectroscopy, energy of hyperfine interaction does not depend on methods of measurement. It is determined by the product of two values. One of this corresponds to the nucleus or external field characteristic, while another one determines the parameters of nucleus. If it is needed to determine nucleus characteristics, the values of field that affect the nucleus need to be known. If the moment of nucleus is known, then we can determine the values of internal fields in solids.

In practice, energy shifts of γ -line is determined by an experiment in the position of the resonance Mössbauer spectrum with respect to any of the samples. This is expressed in mm/s. The calibration spectra is performed to change into eV. For this purpose, the metallic iron Fe or the potassium ferrocyanide – $(\text{Na}_2[\text{Fe}(\text{CN})_5\text{No}] \cdot 2\text{H}_2\text{O})$ with standard ^{57}Co source in Cr were used. Quadrupole and magnetic moments of excited states of Mössbauer's nuclei and changes of charge's distribution radius in some nuclei were determined with the help of the Mössbauer effect study method. These characteristics of nuclei cannot be obtained with the help of other methods that is why they represent a scientific interest in nucleus physics. The method of the Mössbauer effect study is successfully applied to measure internal fields and electric density on the nuclei. This direction in the Mössbauer effect study spectroscopy is very important. Mössbauer nuclei can be introduced into a very large number of different compounds and groups of metals. In cases when the compounds are studied for absorption, along with the absorption method, one can also use the emission measurement technique on the basis of the Mössbauer effect. The Mössbauer effect study spectroscopy allows to study hyperfine interactions at extremely low concentrations of impurities. Thus, the Mössbauer effect study spectroscopy is a powerful tool for the study of hyperfine interactions in both single crystal and polycrystalline, and in the compounds.

3. The Mössbauer effect probability

The probability of the Mossbauer effect is determined by the dynamic properties of crystals. In crystals, atoms stay in oscillatory movement with respect to the equilibrium position. These fluctuations depend on the masses of the atoms and force constants. The latter are an important characteristic of the interaction between them. They determine the macroscopic properties of

the crystal, as heat capacity and elastic characteristics. Probability of effect f is defined for a monatomic cubic crystal by the formula:

$$f = \exp(-4\pi^2 \langle x^2 \rangle / \lambda^2),$$

where, $\langle x^2 \rangle$ – mean square thermal displacements of atoms in the direction of the γ -ray radiation.

The probability of recoilless process will be greater if the wave length λ of the radiation is larger compared with the square root of the mean square displacement. The stronger the atom is bound in the crystal, the greater the probability of the Mössbauer effect. For determination, $\langle x^2 \rangle$ is needed to set up the absolute value of f . Thus, it is necessary to take into account the various factors that influence the measurement results. A simpler method of determining f is the measurement of the relative values of f in studies of the temperature dependence of this quantity.

4. The isomer shifts

The expression of the isomer shift can be obtained for a system consisting of a nucleus with charge distribution $\rho(r)$, which is in the electric field produced by the electron cloud $e/\psi(r)^2$, where, $\psi(r)$ – the wave function of the electrons. Electrostatic interactions are determined through

$$V = \int \rho(r) \varphi(r) dr$$

where $\varphi(r)$ – electrostatic potential of the electron shell. It should satisfy the Poisson equation

$$\frac{\partial^2 \varphi}{\partial x^2} + \frac{\partial^2 \varphi}{\partial y^2} + \frac{\partial^2 \varphi}{\partial z^2} = -4\pi e \rho(r)$$

In practice, the shift in the emission line is determined relatively to the absorption line. At this time, the source and absorber are in different chemical states.

This value is the isomer shift. It is determined by two factors: the change in the density $\rho(r)$ which is created by electrons in resonant nuclei in different compounds, and in the charge distribution, the change at the nucleus transition from the ground to the excited state. If the source and absorber are composed of different chemical compounds, the maximum difference of the absorption line is not at zero source velocity relatively to the absorber, and at some velocity is determined from $\delta E = v \frac{E}{c}$,

or

$$v = \frac{\delta E \cdot c}{E} = \frac{4\pi f e^2 r^2 c}{5E} \left(\Psi^2(o) - \Psi_{11}^2(o) \right) \frac{\delta r}{r},$$

where, $\delta r = r_B - r_o$ – the nucleus excited and ground stated radiuses difference.

Positive velocity corresponds to the motion of the source to the absorber $\frac{\delta r}{r}$ and expressed through

$$\frac{\delta r^2}{r^2} = (r_B^2 - r_o^2) / r^2$$

The electron charge density at the nuclei of $\varphi^2(o)$ is determined by s-electrons of various shells. Small contributions can also give $p_{1/2}$ electrons.

5. Quadrupole interaction

As a result of the quadrupole interaction in Mössbauer spectrum, it shows a hyperfine structure. Its individual components correspond to γ -transitions between split levels. For ^{57}Fe spin of the excited state 3/2 and the ground state 1/2. These hyperfine structures have the form of the doublet. Doublet is due to the splitting of the upper level into two states with 3/2 and 1/2. The ground state with spin 1/2 is not split (Fig. 1). Each level is shifted by the amount

$$W_{3/2} = +e^2 q Q / n \text{ and } W_{1/2} = -e^2 q Q / n,$$

where, Q – quadrupole moment of the nucleus.

There is a degree of deviation from the distribution of the averaged charge density of the nucleus in the $m = 1$ state from the spherical symmetry where, q – quadrupole interaction constant or the electric field gradient. The value of the quadrupole interaction depends on the product of the quadrupole moment and the electric field gradient.

The distance between the doublet components determines the quadrupole interaction constant. If the quadrupole interaction energy does not exceed the width of the nuclear level G , then instead of the individual components we can observe a broadened line:

$$\Delta E = W_{3/2} - W_{1/2} = \frac{e^2 q Q}{2}$$

Figure 1. Quadrupole splitting of ^{57}Fe

The asymmetry of the hyperfine structure transition intensity occurs at the presence of a preferred direction. It is given by a magnetic field or electric field gradient.

6. Magnetic hyperfine structure

The magnetic hyperfine structure appears in the spectrum as a result of the interaction of the nucleus dipole moment μ with its magnetic field $\mathbf{H}$. This field is generated by its own atom electrons (the Zeeman effect) or by external sources. The magnetic structure is always absent at the nuclear levels whose spins are zero. In the Mössbauer effect, the γ -transitions between the two nuclear levels are observed. Any of these levels can have a magnetic hyperfine structure. Each γ -quantum corresponds to a transition from a magnetic level of the excited state of the nucleus to the ground state sublevels. The selection rules are defined by radiation multipolarity. The respective energy levels are described in terms of:

$$E_M = \mu_n H m_I / I = g \mu_n H m_e,$$

where, μ_n – nuclear magneton; g – gyromagnetic ratio; $m_I = I, I-1, \dots, -I$.

Picture of the splitting of the excited levels $I = 3/2$ and the ground state $I = 1/2$ is widely used in the Mössbauer effect study spectroscopy. The upper level is split into four sub-layers, and the bottom is split into two sub-layers. Between the upper and lower levels, there are six transitions. They are allowed by the selection rules. The lines of the magnetic structures are arranged relative to the center of the spectrum. For these lines to be well resolved, the magnetic interaction value must be greater than the natural line width (Fig. 2).

Figure 2. Magnetic hyperfine splitting of ^{57}Fe spectrum

The method of nuclear gamma-resonance spectroscopy based on the Mössbauer effect, due to the high sensitivity and the small shifts of the energy level of the nucleus, has been used successfully for the study of the defect structure of metals. In this case, all the information about the state of the defect region is extracted using the Mössbauer atoms emitting or absorbing resonance gamma-rays. In recent papers on the use of the Mössbauer effect to study of point radiation defects interaction with substitutional impurity atoms on the basis of the Mössbauer isotope, ^{57}Fe has appeared [4].

7. The Mössbauer effect study spectrometers

Experiments to investigate the state of the impurity atoms in metals before and after irradiation by different particles were carried out on the Mössbauer effect study spectrometers. Schematic diagram of the spectrometer is shown in Figure 3.

Figure 3. Schematic diagram of the Mössbauer effect study spectrometer

It consists of a γ -radiation source, an absorber as a sample under study, a detector, and a storage device. The absorber imposed some movement velocity v relative to the source of γ -rays. Consequently, there is a Doppler shift in the absorption line relative to the emission line. By varying the rate of absorption, one can obtain the intensity of radiation transmitted through the absorber from the absorber velocity. This relationship represents the absorption spectrum. The nuclei of the Mössbauer isotope in the source and in the absorber may be in the same state and chemical environment. Then, when the value of the absorber relative velocity $v = 0$, the γ -rays resonant absorption occurs. By increasing the source or absorber velocity, the emission and absorption lines overlapping area is gradually reduced. At a certain value of the velocity v , resonance condition is completely broken. In the process of the Mossbauer absorption the integration occurs over the area of absorption and emission lines. Then. the experimental line width determined as $G'_{\text{exp}} > G_{\text{source}} + G_{\text{absorption}}$.

8. Irradiation by neutrons and charged particles

The VVR-K nuclear reactor of the Nuclear Physics Institute of the RK Nuclear Centre was used for irradiation of samples by neutrons. On the average, 2.5 neutrons were fitted in one fissionable nucleus in the nuclear reactor at ^{235}U fission. The neutrons' energy was distributed in the 0.1-15 MeV interval:

$$n(E)dE = \sqrt{\frac{Z}{\pi e}} \text{sh} \sqrt{Ee^{-E}} dE$$

The neutrons energy average value in the nuclear reactor channel was about 2 MeV. Consequently, collisions with surrounding atoms slow down the neutrons and decrease their energy. Therefore, they are much slower. The neutrons play a significant role in the creation of radiation defects in crystals. The samples' temperature are in the 80⁰ C limits at the neutrons' irradiation.

The samples' irradiation by the charged particles was conducted on U-150 isochronous cyclotron of the Nuclear Physics Institute of the RK Nuclear Centre. At charged particles irradiation, the generation rate of radiation defects in metals is high by several orders than at the neutrons' irradiation. Thus, by the beam intensity regulating, it can receive, for a short time. such a damage rate which corresponds to a long-term neutron irradiation. The major portion of the bombarding particles energy is spent, meanwhile, on the sample radiation heating. Consequently, the target temperature increases to a few hundred centigrade degrees against the beam intensity. In order to prevent the annealing of radiation defects, we perform intensive cooling of the target during irradiation with the temperature of cooling that reaches that of liquid nitrogen.

9. The Mössbauer spectra processing and analysis

For the useful information extraction from complex Mössbauer spectra and its interpretation, it is necessary to apply computer processing methods. Generally, the resonance of the Mössbauer line by Lorenz curve description is presented at an acceptable accuracy:

$$L(x) = \frac{a}{1 + \frac{4}{\gamma^2}(x - c)^2}$$

where, a – amplitude; γ – half-width; and c – the resonance line center of gravity position. For the experimental spectra fitting by the Lorenzian set, the least squares method is used, that is the following functional is minimized:

$$F(A) = \sum_{i=1}^n \omega \left[N_{i_{\text{th}}} - N(A, x_i) \right]^2$$

where, A is the varying parameter of adjustable function; x_i are the velocity values in the i_{th} -channel; $N_{i_{\text{th}}}$ is a count in i_{th} -channel of analyzer; ω is the weighting factor (usually equal to 1); and N is a number of dots of the experimental spectrum. Taking into account the relations between the Mössbauer spectrum, individual parameters can reduce the number of variable parameters.

10. The Mössbauer effect at the point defects in the hardened molybdenum investigation

The sufficient vacancy concentration in metals can be obtained by the hardening method. The vacancy formation energy in metals is less than interstitial atoms formation energy [5]. At heating up to the melting temperature, a considerable quantity of vacancies appears in metals, and their concentration is determined by following expression:

$$n = \exp\left(-\frac{E}{kT}\right),$$

where, E – vacancy formation energy; T – heating temperature; k – Boltzmann constant.

At high-speed hardening, 10^4 - 10^6 degree/s is succeeded to preserve the considerable part of vacancies non-equilibrium concentration in metals. The Mössbauer effect study permits to observe the selectively of vacancies, divacancies, and small clusters with ^{57}Co Mössbauer impurity atoms interaction. To this effect, the virgin sample with ^{57}Co impurity heats up to 1200°C temperature in 10^{-7} torr vacuum. Subsequently, they rapidly cool with 10^4 degree/s velocity.

The observation of a single vacancy interaction with ^{57}Co impurity atom permits to determine the overpatching around impurity atoms and hyperfine interaction parameters. Simultaneously, the root-mean-square amplitude of Mössbauer impurity atoms vibrations in substitution lattice sites, before and after vacancies capture, has been determined. Thus, the experimental works on hardening are very important for the Mössbauer spectra definition and identification. The spectra measurements are carried out at a room temperature on the installation, with uniform acceleration, while using a resonance detector with the FeAl converter. As can be seen (fig.4) in the ^{57}Co in molybdenum spectra, the additional defect line appears after hardening. The spectra processing permits to determine the individual spectrum components. They consist of an undisplaced line corresponding to ^{57}Co states in substitution lattice sites and quadrupole doublet. The last of ^{57}Co state connected with divacancy is determined. The line half-width is $\Gamma=0.34$ mm/s, the single line isomer shift is $\delta=-0.24$ mm/s, the quadrupole doublet isomer shift is $\delta=0.13$ mm/s relatively to the undisplaced line, and the quadrupole splitting value is $\Delta E=0.90$ mm/s.

The quadrupole doublet positive isomer shift relates to the electron density of 4s electrons on the nuclei decreasing by 20%. Meanwhile, the environment symmetry on ^{57}Co Mössbauer nuclei is disturbed and the electric-field gradient appears. Its interaction with the nucleus quadrupole moment is brought to hyperfine splitting on the emission spectra appearing. Consequently, the "defect" line which was described by the quadrupole doublet appears in the spectra. In order to determine activation energy of the vacancies related to ^{57}Co impurity atoms we have conducted isochronal annealing of the samples in the vacuum equal to 10^{-7} torr.

Figure 4. The Mössbauer emission spectra of ^{57}Co in molybdenum before (a) and after (b) hardening

The dependence of the "defect" line square relationship to the spectrum general square ($\Delta S/s$) from isochronal annealing temperature is determined (fig.5).

Figure 5. The molybdenum isochronal annealing after hardening

$\Delta s/s$ parameter at a temperature interval from room temperature up to 300° C, shows a negligible change. Above of this temperature, a drastic decrease occurs. The "defect" line completely disappears at 980°C temperature. The vacancies migration activation energy is determined by the following equation:

$$E_a = kT_0 \ln(\nu k/\alpha E_a),$$

where, $\nu=10^{13} \text{ s}^{-1}$ –Debye frequency; $k=2.6 \cdot 10^{-5} \text{ eV/K}$ –Boltzmann constant; T_0 –mean temperature; and $\alpha= \Delta(T^{-1})/\Delta t$ –design coefficient.

The vacancy migration activation energy obtained value is 2.2eV in molybdenum. It is seen that at temperatures above 400° C, the $\Delta s/s$ value is decreased. It is connected with the ^{57}Co impurity part associated with vacancies in the "impurity-vacancy" complexes decreasing. In temperatures above 400° C, these complexes begin to break down. The unallocated vacancies, migrate in the regular sinks. The free interstitial atoms return to the regular lattice sites.

Velocity, mm/s.

Figure 6. The Mössbauer spectrum of ^{57}Co in niobium: before (a) and after (b) hardening

11. ^{57}Co impurity atoms interaction with vacancy defect in niobium

The Mössbauer spectrum of impurity ^{57}Co atoms state in niobium after hardening was a single symmetrical circuit with $\delta=-0.15\text{mm/s}$. The standard sample of potassium ferrocyanide served

as an absorber. The line width of Mössbauer spectrum was made up $\Gamma=0.30$ mm/s. The samples were annealed in 10^{-6} mm. of mercury column vacuum at 1200° C temperature. The hardening was conducted in vacuum oil. After the hardening, an additional "defect" line appeared in the right of the spectrum (fig. 6). The parameters of this line are best described by the quadrupole doublet with the width equal to $\Gamma=0.45$ mm/s. The isomer shift is equal to $\delta=0.18$ mm/s relatively to the undisplaced line. The quadrupole splitting is $\Delta E=0.96$ mm/s. The positive isomer shift of the quadrupole doublet in the emission spectrum testifies reduction of the electron density on the nuclei of Mössbauer impurity. The quadrupole splitting appearance indicates symmetry disturbance around the impurity atoms' environment. Consequently, on the nuclei of the Mössbauer atoms, the electric-field gradient appeared. Such changes connected with ^{57}Co impurity are caused by vacancies. The impurity content in niobium did not exceed 10^{-6} in %.

The dynamic behavior of the ^{57}Co impurity by the isochronal annealing method in temperature interval has been investigated up to 1000° C (fig.7). The $\Delta s/s$ parameter does not change up to 300° C temperature. Therefore, in this temperature interval, the "impurity-vacancy" complexes are the stable. At 750° C temperature, the Mössbauer emission spectrum is recovered thoroughly up to its initial state. With the annealing temperature growth, the single vacancies are left step-by-step as the ^{57}Co impurity atoms and crystal lattice is recovered up to its initial state. The vacancy migration energy in niobium made up in accordance with literary data [6], 1.8 (4) eV.

Figure 7. Isochronal annealing of hardened niobium ($\frac{\Delta s}{s}$)

12. Defects interaction with impurity atoms in molybdenum irradiated by electrons and neutrons

The interaction of defects with impurity atoms is one of the fundamental mechanisms in the field of metal radiation damage. The particular investigations by the instrumentality of electrical resistance measure showed that impurity atoms can efficiently capture the migrate interstitial and bring the annealing stage to decay or absolute suppression [7, 8]. This problem

finds its confirmed experiments with molybdenum irradiated by electrons. The required concentration of vacancy and interstitial atoms in the sample of Mo^{57}Co at the temperature of 100K, was created by electron irradiation ($E=3\text{ MeV}$) to up to $1.07 \cdot 10^{19} \text{cm}^{-2}$ fluence. At this temperature, interstitial in molybdenum are mobile but vacancy remains stationary. Therefore, interstitial can proceed recombination with vacancies if they are captured by ^{57}Co impurity atoms. After irradiation at spectrum positive Doppler velocity, a sharp "defect" line and additional convexity from the left side of the substitution line appears (fig.8b). This indicates their accessory to the quadrupole doublet with large splitting (fig.8c).

Defect line	1	2	3	4	5
σ , mm/s	0, 48	0, 45	0, 45	0, 47	0, 47
E , mm/s	1, 82	1, 14	1, 48	0, 81	0, 39

Table 1. Values of the "defect" lines centers shifts

The Mössbauer spectrum can decompose on 4 quadrupole doublets with about $+0.46\text{ mm/s}$ central shifts relative to the substitution line (1-4 lines). The evidence of these lines was obtained from annealing experiments after the fast neutrons' irradiation at 4.6K (fig.9). The configuration 1 most clearly appeared after annealing at 124K. After annealing at 214K, it disappeared and line 3 are dominated. This process is connected with the reorientation of the defect in configuration 1 to configuration 3 [9]. The successive annealing at higher temperatures is accompanied by the captured interstitial release. The defect line 3 becomes unstable. On III (470 K) stage, the defect line 4 appeared clearly on the spectrum (fig.9e). At the same time, the fifth component with small quadrupole splitting appear (line 5, table 1). The annealing above stage 3 brings new defect lines appearing and disappearing in 1-5 configurations. The new lines are characterized by half of centre shift, as compared with 1-5 defect lines. The full annealing of the irradiated samples is completed in stage 5 at about 1300K temperature.

Thus, the direct evidences of interstitial atoms capture in Mo^{57}Co system around ^{57}Co impurity atoms have been found. Five variants of defect lines have been found with well-defined shear centre. They have different electric-field gradients. All 5 combinations were at the expense of the captured single, double or triple interstitials [10]. The observed stage 3 of the configuration existed at the expense of large cluster defects generated on ^{57}Co impurity atoms.

The substitutional impurities are always present in metals in small quantities. They constitute a significant part at the crystals' defect structure formation. The radiation defects' physical-mechanical properties are dependent on their configuration and electron structure.

The molybdenum polycrystal, with 99.98% purity, irradiated by reactor neutrons investigations, has been carried out by emission and absorption method. In the first event, the radioactive ^{57}Co was used as an impurity atom, and in the second event, stable isotope of ^{57}Fe was used for absorption experiments, where the samples enriched by ^{57}Fe isotope up to 60% were used. The ^{57}Co samples in the Mössbauer spectra were at a symmetrical circuit, with

Velocity, mm/s.

Figure 8. Mössbauer spectra of ^{57}Co in Mo, absorber ^{57}Fe in Pd: a) before irradiation; b) after electron irradiation, $E=3$ MeV at 100K temperature up to $1.078 \cdot 10^{19} \text{cm}^{-2}$ doses; c) after substitution line deduction.

$\delta=0.30(3) \text{mm/s}$ isomer shift relatively to a standard absorber (fig.10a). The absorption spectra measurement was conducted employing a ^{57}Co cosource in copper.

The conversion electrons resonance counter on the basis of FeAl was used as a detector. The irradiations of samples were conducted in the 10^{22} - 10^{23} neutron/ m^2 fluence interval. The emission spectra of irradiated samples change in accordance with the Mössbauer nuclei state in substitution lattice points. In the positive part of the spectrum, the additional "defect" line appears (fig.10 b, c, d) and the principal line is widened. In the sample spectra on absorption, if it is irradiated up to $5 \cdot 10^{22}$ neutron/ m^2 doses along with undisplaced line, it may be separated in addition of at least two quadrupole doublets (Fig.11). These quadrupole doublets have different isomer shift relatively to the undisplaced line: $\delta_1=0.13(3) \text{mm/s}$ and $\delta_2=0.46(3) \text{mm/s}$. The quadrupole splitting values are $\Delta E_1=0.75(3) \text{mm/s}$ and $\Delta E_2=0.82(3) \text{mm/s}$ respectively. At fluences above $5 \cdot 10^{22}$ neutron/ m^2 , the third quadrupole doublet with $\delta_3=0.46(3) \text{mm/s}$ and $\Delta E_3=0.82(3) \text{mm/s}$ parameters appeared in the spectra. With the irradiation doses increasing, the total intensity of the additional line increased and principal line position did not change. The sample spectra on ^{57}Fe absorption in molybdenum after irradiation also changed. Along with the principal lines, the "defect" line appeared in the negative part relative

Figure 9. The Mössbauer spectra of ^{57}Co in Mo, irradiated by electrons with $E=3$ MeV ($T=4.2$ K): a) after electron irradiation up to $1.07 \cdot 10^{19} \text{ cm}^{-2}$ doses at 100 K temperature, b) after fast neutrons irradiation up to $6.9 \cdot 10^{18} \text{ cm}^{-2}$ doses at 4.6 K temperature, c) after isochronal annealing at 214 K, d) 371 K, e) 460 K and f) 768 K

to the undisplaced line. It has been described by two quadrupole doublets: $\delta_1 = -0.11(3)$ mm/s and $\delta_2 = 0.76(3)$ mm/s. The quadrupole splitting values of these doublets were $\Delta E_1 = 0.95(3)$ mm/s and $\Delta E_2 = 0.72(3)$ mm/s, respectively.

The "defect" line appearance in the sample spectra after irradiation signifies the radiative single defects captured by the Mössbauer impurity atoms. The present stage of the residual electrical resistance measurement after irradiation corresponds to the migration of the interstitial type radiation defects in molybdenum [11]. The interstitial atoms connected with ^{57}Co impurity atoms in molybdenum formed the stable dumbbell shaped configuration.

These complexes have been annealing at higher temperature as compared with the free interstitial atoms. In emission spectra, such complexes appear in two configurations and in only one configuration – in absorption spectra. In addition, the neutron irradiation leads to the appearance in the absorption spectra of yet another impurity state of cobalt atom. It is characterized by the quadrupole doublet with $\delta = 0.13(3)$ mm/s isomer shift. A doublet with

Figure 10. The emission Mössbauer spectra of ^{57}Co in molybdenum before (a) and after irradiation at doses: 10^{22} (b), $5 \cdot 10^{22}$ (c) and 10^{23} (d) neutron/ m^2 . The calculated spectrum decomposition are indicated by the dotted line.

such parameter has been detected in the samples subjected to hardening. Thus, these complexes can relate to the connection with vacancies cobalt impurity atoms. Therefore, the simultaneous formation of "impurity-interstitial" and "impurity-vacancy" complexes are possible in molybdenum samples after irradiation. The most likely orientations of ^{57}Co impurity atoms and interstitials mixed dumbbells are directed along $\langle 110 \rangle$ and $\langle 111 \rangle$ axis (fig. 12).

The isochronal annealing has allowed to determine the annealing stages of "impurity-interstitial" and "impurity-vacancy" complexes. In fig.13, the isochronal annealing results of the samples irradiated by neutrons of up to 10^{22} (a), $5 \cdot 10^{22}$ (b) and 10^{23} (c) m^{-2} fluences are presented. In the temperature interval of up to 600K, the $\Delta S/S$ relationship remains constant. At an annealing temperature of above 600K, the vacancies become free from fixed sinks and begin to migrate along the crystal. In the case of "impurity-interstitial" complexes encountered, the vacancies are annihilated with these complexes. The Mössbauer impurity atoms become free and recover in the lattice points. The Mössbauer impurity atoms' environment symmetry are recovering. At 950K temperature, the irradiated sample spectrum is completely recovered to the initial state.

Velocity, mm/s.

Figure 11. Spectra of ^{57}Fe absorption in molybdenum before (a) and after (b) neutrons irradiation up to 10^{21} neutrons/ m^2 doses

Figure 12. The orientation direction of mixed dumbbell in molybdenum lattice: a- $\langle 110 \rangle$ and b - $\langle 111 \rangle$

13. The point defects atomic configuration in the chromium irradiated by high energy protons

The atomic configurations of irradiated metals with bcc lattice have been investigated commonly by numerical methods with molecular dynamics methods [12]. The current metal electron theory is qualitative. It rightly describes the peculiarities of interatomic interactions.

Figure 13. The molybdenum samples isochronal annealing curves, irradiated by different neutrons doses

But quantitative adjectives of these interaction receptions present a considerable difficulty. Therefore, the ^{57}Co impurity atoms' interaction with interstitial point defects in chromium was investigated here by the emission method. The initial Mössbauer spectra of samples consist of symmetrical single lines. The line width is $\Gamma = 0.28 \text{ mm/s}$, the Mössbauer effect value is $\epsilon = 23\%$, and isomer shift $\delta = 0.07 \text{ mm/s}$ relatively to the standard absorber.

The sample irradiation has been realized by 10MeV protons at $10^{21} - 3 \cdot 10^{22} \text{ m}^{-2}$ fluences. The sample Mössbauer spectra have been measured at liquid nitrogen temperature. After irradiation, the absorption line becomes asymmetrical. The spatters on the line wings are observed. The spatters' appearance is testified that the "defect" line spectrum consists of more than one quadrupole doublet (fig.14). Along with a single substitution line, the additional "defect" line described by three quadrupole doublets has been observed (Tabl.2).

Parameters	1	2	3	4
$\delta, \text{ mm/s}$	0, 07	0, 45	0, 43	0, 38
$\Delta E, \text{ mm/s}$	0	1, 14	1, 48	0, 86
$\epsilon, \%$	2000%	82	34	56

Table 2. Defect" line with quadrupole doublets

The first line corresponds to the substitution line of ^{57}Co nuclei in chromium regular lattice site. The presence of a single line and absence of quadrupole doublets indicate ^{57}Co environment symmetry by matrix atoms. The large values of the observed shows that the Mössbauer effect probability in chromium is very high.

The other spectra components correspond to quadrupole doublets. They characterize the different stages of cobalt in irradiated chromium defect structure. The new three quadrupole doublets appearance in the spectrum is probably stipulated by the three different complexes formation. They correspond to the Mössbauer "impurity-interstitial" atom mixed dumbbells structure. These dumbbells are formed as a result of interstitial capture by Mössbauer atoms.

There is a high probability of the formation of the above configurations. However, the dumbbells along [110, 111] and [100] directions are energy-optimal. The three quadrupole decomposed lines appearance in the Mössbauer spectra can attribute to these mixed dumbbell three configurations. The equal shift ($\delta=0.45$ mm/s) of doublet lines is indicated on their centres' location in the regular lattice sites. The quadrupole splitting large value is probably stipulated by the electric-field gradient at the expense of the considerable displacement of impurity and interstitial atom from the equilibrium position.

Velocity, mm/s

Figure 14. Emission Mössbauer spectra of ^{57}Co in chromium, irradiated by protons at fluences: a) $5 \cdot 10^{21}$, b) $7 \cdot 10^{21}$, c) $3 \cdot 10^{22} \text{ m}^{-2}$

The mixed dumbbell configurations splitting value in chromium is six times higher than in aluminium. The Mössbauer impurity atoms in aluminium represent an interstitial dumbbells structure. The ^{57}Co impurity atoms can pass from one position to another. We thereby can witness a generation of the equivalent configurations in most likely directions in the fcc structure.

Such behaviour of ^{57}Co impurity atom in aluminium is confirmed by the Mössbauer effect for the "defect" line decreasing from 0.9 up to 0.2, which is described by one quadrupole doublet.

14. The point defects interactions in neutrons irradiated tungsten, vanadium, and chromium

The majority of bcc structure metals are the perspective materials in the nuclear technology and space engineering. Among them, the molybdenum and niobium are the most investigated in details [13-18]. It has been established that the point defects generated in crystal structure, after irradiation, interacted between themselves like impurity atoms. The Mössbauer nuclei application as impurity atoms allow to consider the electron state and structure of the "impurity-interstitial" and "impurity-vacancy" complexes. For the molybdenum and niobium cases, the "impurity-interstitial" complexes have a dumbbell configuration. Their Mössbauer parameters depend on the bombarding particles type, energy, and irradiation temperature [12, 19, 20]. For annealing temperature interval of 300-900K in molybdenum, three different configurations of "impurity-interstitial" complexes have been determined. They are moving from one state to another against irradiation conditions and bombarding particles type. From the spectra analysis we can distinguish several annealing stages of the "impurity-interstitial" systems. In the temperature range of 300-550 K, the state, which corresponds to the quadrupole doublet, with the following parameters $\delta=0.13\text{mm/s}$ and $\Delta E=0.75\text{mm/s}$, is stable. At the annealing temperature of about 450K, a new state occurs along with the aforementioned. It is characterized by the quadrupole doublet with $\delta = 0.46 \text{ mm/s}$ and $\Delta E = 0.82 \text{ mm/s}$. At a higher temperature of 800K, another state with $\delta= 0.46 \text{ mm/s}$ and $\Delta E= 1.01 \text{ mm/s}$ appears on the Mössbauer spectra. All these complex states are completely annealed at temperatures higher than 1150 K, and the sample Mössbauer spectra recover up to the initial state [21, 22]. In niobium, the bound states of impurity atoms with interstitials and vacancies formation occur by an analogous scheme, but the Mössbauer spectra parameters have their peculiarity [23, 24]. However, some questions on this problem, connected with radiation defects interaction with impurity centers are still not answered. To address this problem, initial samples of the polycrystalline foils by ~99.99% cleanness have been used. Preliminarily, the samples undergo a high-temperature annealing at 1500 K and the vacuum of 10^{-8} torr in the course of 20 hours. This is followed by the ^{57}Co radioactive isotope spread on the sample surface by electrolysis in about 3-5 hours. As an isotope source, the $^{57}\text{CoCl}_2$ radioactive solution has been used. The emission spectra is measured by a resonance detector on the basis of the $^{57}\text{FeAl}$ alloy. Potassium ferrocyanide was used as a standard absorber.

In the initial state, the radioactive ^{57}Co impurity atoms are located in tungsten substitution sites. Their concentration does not exceed $10^{-6} \%$. At such concentrations, the impurity atoms do not interact among themselves. They also do not influence the crystal structure. Therefore, all derived information reflect the processes taking place in crystal as a consequence of radiation point defects interaction with ^{57}Co impurity atoms. Such method application allows to identify the different stages which are formed by the Mössbauer atoms capture on interstitial atoms and vacancies.

The initial spectra of all investigated samples correspond to the single Lorentz symmetrical circuit (fig.15). This indicates the absence of electric-field gradients on the Mössbauer nuclei. The Co^{57} isomer shifts in W, V, and Cr are observed respectively with 0.41 mm/s , 0.08 mm/s ,

and 0.07 mm/s relatively to the potassium ferrocyanide. The sample irradiation was conducted by fast neutrons at a temperature lower than 80°C. The neutrons fluence reached 10^{23} neutron/m². All spectra were measured at room temperature on the Mössbauer installation with uniform acceleration. The sample isochronal annealing was conducted in 10^{-4} torr vacuum. In the irradiated sample spectra along with the substitution line, we can observe the appearance of the additional "defect" line (Fig.15). Processing of the spectra enabled us to distinguish two different quadrupole doublet lines in W, besides the substitution line. These doublets can be provided by the defect structure formation nearby of the Mössbauer impurity atoms. The first quadrupole doublet with $\delta = -0.15$ mm/s isomer shift and $\Delta E = 0.80$ mm/s quadrupole splitting, probably, characterize the "impurity-vacancy" complexes state. The negative isomer shift indicates the decrease of electron density of complexes. On Co^{57} nuclei we can observe an appearance of the electric-field gradient.

Figure 15. The ^{57}Co in W Mössbauer spectra before (a) and after irradiation (b) by neutrons up to fluences: 10^{22} (b), $2 \cdot 10^{22}$ (c), $5 \cdot 10^{22}$ (d), $7 \cdot 10^{22}$ (e), 10^{23} (f). The spectra after undisplaced line deduction are shown in (k)

The second quadrupole doublet shows a positive isomer shift. It shifted on $\delta = 0.45$ mm/s relatively to the substitution line. The quadrupole splitting of the present doublet is equal to $\Delta E = 1.14$ mm/s. This doublet appearance is probably stipulated by the Mössbauer impurity atoms interstitial capture. The latest have become more active readily at irradiation temperature. As a result of the interaction, the ^{57}Co impurity atoms are displaced from crystal lattice sites and generated "impurity-interstitial" bound states of the dumbbell configuration. By computer simulation data in desired conditions, the most likely direction of the mixed dumbbell is along the $\langle 110 \rangle$ axis. Such assumption is confirmed by the electron density increasing on the Mössbauer nuclei. The electric-field gradient appeared on ^{57}Co nuclei. On the

right of Fig.15, the spectra after substitution line deduction are shown (k). At 800 K isochronal annealing, the "impurity-vacancy" complexes are annealed completely and in their place, the other "defect" line appears. It is described by the third quadrupole doublet with $\delta = 0.43$ mm/s and $\Delta E = 1.14$ mm/s parameters.

At the mentioned temperature, the interstitial atoms become free from the different traps and crystal structure irregularities. The activation energy of interstitial atoms migration in tungsten makes up 0.19 eV. The migrating interstitial atoms are recombined with vacancies in meeting with the "impurity atom-vacancy" complexes and the impurity atoms released. The latter further return to the regular crystal lattice. In addition, a part of the interstitial atoms are, probably, interacted with impurity atoms. Consequently, the new formation which presents also the "impurity atoms-interstitial" bound states are formed.

Velocity, mm/s.

Figure 16. The ^{57}Co Mössbauer spectra in V, irradiated by neutrons up to 10^{23} neutron/m² fluence after the substitution line deduction at different isochronal annealing temperatures

The "defect" line with positive isomer shift appearance in the Mössbauer spectra of vanadium samples after isochronal annealing at 800K temperature is confirmed of this assumption (fig. 16). Such "defect" line is well described by the quadrupole doublet with $\delta=0.41$ mm/s relatively to the substitution line and $\Delta E = 1.48$ mm/s. The calculation analysis has shown that such states corresponds to the dumbbell configuration along $\langle 111 \rangle$ axes. At a further increase on isochronal annealing temperature, the relative area under the spectrum decrease, but δ and ΔE values do not change. The "defect" lines in the spectra are completely annealed at 1200K temperature. The Mössbauer "impurity-interstitial" atom complexes annealing at temperatures above 1200K is probably realized by the single vacancies releasing, migration and their recombination with interstitial atoms. The vacancies migration activation energy is 1.3 eV in vanadium.

The chromium irradiation is at the same conditions. In the Mössbauer spectra, along with undisplaced line, the one 'defect' line also appears. It is described by one quadrupole doublet with $\delta=0.38$ mm/s and $\Delta E=0.86$ mm/s. Such quadrupole doublets are relevant for the tungsten samples also. Thus, one can assume that in metals with bcc structure, after neutrons irradiation, both "impurity-vacancy" and "impurity-interstitial" complexes are formed. In the Mössbauer spectra, the quadrupole doublets with electric-field gradients large values on ^{57}Co nuclei are appearing.

15. Investigation of recoil nuclei states in molybdenum, are generated by protons and α -particles irradiation

The recoil nuclei are generated as a result of the elastic and inelastic interactions of incident particles with target atoms, and the investigation of their states is a quite relevant problem of the radiative study of materials. The Mössbauer effect application allows to investigate the recoil nuclei states in crystals after irradiation. A new formed nuclei as a result of nuclear reactions can correspond to the Mössbauer radionuclide. Then, it can register selectively with such recoil nuclei by emission spectroscopy [25, 26]. By absorption and emission spectra comparison for these nuclei, it is possible to determine the state of the primary knocked-on atom (PKA). It is known that the atom displacement from the lattice minimum energy is equal about 25 eV. The recoil nuclei energy at (n, γ) -reactions may reach to a value of some 100 eV. At (d, p) -reactions, the recoil nuclei energy may reach no more than 10 MeV. Even so, the atom leaves its initial position in the crystalline lattice site. The stored energy is used for elastic collisions with other atoms. Over 10^{-12} s time, the PKA energy decreases below the displacement threshold energy. The life time of the Mössbauer level is considerably greater (10^{-7} s for ^{57}Fe) than the PKA stopping time. Therefore, the Mössbauer effect offers the unique opportunity for the PKA new location detection. At the same time, its immediate environment and electron state can be determined.

To study this effect, the experiments are conducted on polycrystalline molybdenum samples with 99.98% purity. The two sets of samples, enriched up to 80% by ^{57}Fe isotope, were prepared. The isotopes are deposited on the molybdenum samples surface by $2 \cdot 10^{-3}$ Pa vacuum coating. The enriched ^{57}Fe evaporated layer thickness constitutes 0.2 mg/cm² and native iron -20 mg/

cm². The evaporated layer enriched by ⁵⁷Fe samples was irradiated by protons with the energy of 50 MeV to up to 4.2·10²¹m⁻² fluence. The sample with native iron were irradiated by α-particles with 50 MeV energy, up to 2.7·10²¹ m⁻². Liquid nitrogen was used for cooling, so that the samples temperature at irradiation do not exceed 100K. The beam current density was 8·10⁻³A/m². The samples' spectra before irradiation corresponded to sextet. The spectrum parameters corresponded to the native iron spectra parameters (fig. 17, 18). The absorption spectra did not change after irradiation. In the emission spectra along with the sextet, a single symmetrical line appears (fig.17a, 18a). The ⁵⁷Co Mössbauer nuclei in irradiated samples are generated by ⁵⁷Fe(p, n)⁵⁷Co and Fe(α, p2n)⁵⁷Co nuclear reactions. The recoil nuclei mean energy at elastic interaction is defined by following equation:

$$\langle E \rangle = M_1 m E_0 / (M + m)^2,$$

where, m – bombarding particle mass; M – target nucleus mass; M₁ – the nucleus mass obtained after nuclear reaction; E₀ – the bombarding particle energy.

The recoil mean energy <E> at elastic collision of impinging particles with target atoms is shown in Table 3. Below, the corresponding path lengths in iron and molybdenum are presented.

Particles	Energy, MeV	Recoil nuclei mean energy, eV	Path length, μm	
			Fe	Mo
Protons	10	389	5·10 ⁻⁴	5·10 ⁻³
α-particles	50	506	7·10 ⁻⁴	7·10 ⁻⁴

Table 3. Recoil energy and ranges in Fe and Mo at elastic interactions of impinging particles with target atoms

The ⁵⁷Fe enriched iron layer thickness is 0.15 μm and native iron's is 0.71 μm. The recoil nuclei with 5-7Å free path length incipient at elastic collisions remains on iron matrix. The ⁵⁷Co Mössbauer radionuclides are generated consequently by ⁵⁷Fe(p, n)⁵⁷Co and ⁵⁶Fe(α, p2n)⁵⁷Co nuclear reactions. Therefore, the sextet appears in the absorption spectrum and corresponds to the ⁵⁷Fe spectrum. The model which is described [27] has been used for recoil nuclei mean energy calculation at inelastic interaction. The mean energy values of the particles inelastic interactions with target atoms are given in Table 4.

Particles	Energy, MeV	Mean recoil energy, эВ	Path length, μm	
			Fe	Mo
Protons	10	0, 16	0, 43	0, 04
α-particles	50	3, 16	0, 93	1, 88

Table 4. Recoil energy and ranges in Fe and Mo at inelastic interactions of impinging particles with target atoms

It is seen that the recoil nuclei path length in the targets are comparable with the iron evaporated layer thickness. Therefore, the part of ^{57}Co nuclei penetrates into the target substrate. In emission spectra, a symmetrical line appears along with the sextet (fig.17, 18). It is characterized by the ^{57}Co impurity atom state in molybdenum crystalline lattice. It is stipulated, thereby that at inelastic interactions, the Mössbauer nuclei obtain the energy sufficient for the matrix lattice penetration.

Figure 17. Absorption (a) and emission (b) spectra of ^{57}Fe , is evaporated on molybdenum surface after protons irradiation. Emission standard spectrum of ^{57}Co in Mo (c) taken from [28].

By Mössbauer spectra character, one may assume that the ^{57}Co isotope atoms predominately occupy the substitution sites in the molybdenum crystalline lattice lines, broadening what is probably stipulated by the fast hardening at ^{57}Co recoil nuclei slowing down and with the thermal spikes formation in the substitution region. The sextet appearance in the emission spectra after irradiation is characterized by the ^{57}Fe atoms state in matrix of metallic iron. The calculations have shown that the recoil mean energy for ^{57}Co atoms is 016 MeV at 10MeV protons irradiation and 3.16 MeV at α -particles irradiation. The recoil nuclei path length in target constitutes 0.04 and 1.80 μm , respectively [28].

The nuclei recoil means that energy is in the 400-500eV range. The path length of the nuclei recoil in molybdenum is about $(5-7) \cdot 10^{-4} \mu\text{m}$. Such nuclei recoils must remain practically and completely in the range of the evaporated iron layer on the molybdenum samples surface.

16. The Mössbauer spectroscopy of magnetic nanoparticles

Currently, the research activities and development of new diagnostic and medical technology in oncology appears as one of the important areas in medicine [29]. In spite of the sweeping

Figure 18. Absorption (a) and emission (b) spectra of the native iron, evaporated on molybdenum surface after α -particles irradiation. Standard emission spectrum of ^{57}Co in Mo (c) taken from [26, 28]

progress in modern medicine and biology development, cancer remains as an intractable disease which has taken million of humans life yearly. Each 30 seconds, one oncological patient in the world dies. The traditional treatment mode application such as the radiotherapy, surgical, chemotherapeutical, and other methods are limited by the difficulty of accessing the tumor, propagation of the cancerous cells to the whole of the body, and lack of selectivity of these methods against cancerous cells. Although radiotherapy is the unique means in fight against cancer, it very often affects the sound tissue.

In this section, the brand-new innovation technique on the basis of marked magnetic nanoparticles application has been proposed for use. This method of cancer therapy differs from standard therapy methods, whereby metal nanoparticles can be delivered directly to the cancerous cells. Hereupon, it is possible to make a direct impact on the malignant tumor without damage to the neighbouring healthy cells. The different magnetic nanomaterials production is present as a practical interest. It is stipulated, thereby that during nanodimensional state transition, a number of fundamental properties are changed. The nanoparticles are possessed by a highly-developed active surface and by a high absorptive capacity respectively. Because of their small dimensions they are comparable with cells, viruses, proteins and DNA dimensions. The nanoparticles can approach, interact and connect with the biological object. Nano-dimensional materials on the base of ferrites are very important and in disperse aqueous and non-aqueous solvents. Currently, investigation and engineering applications of the broad-spectrum of magnetic nanoparticles on the base of Co, Fe, and Ni metals, ferric oxides, MgFe_2O_4 , CoFe_2O_4 , MnFe_2O_4 , LiFe_5O_8 , and CoPt, FePt, MnAl, SmCo_5 etc., have been investigated [30].

In Fig.19, the scheme of the magnetic nanoparticles target delivery, diagnostics, and controlled hyperthermia are shown. The main point of the proposed method is in the following. Due to the fact that the nanoparticles can function both on tissues and cells levels, they can undergo endocytosis or phagocytosis. Consequently, the nanoparticles are absorbed by cells. In the course of this process, the magnetic nanoparticles can penetrate over the cytoplasmic membrane and in some cases in the nuclear membrane also.

Figure 19. The magnetic nanoparticles transportation scheme for the diagnostics and therapy

As summarized above, the magnetic nanoparticles are finding increased applications in oncology. Owing to newly developed drugs, free transportation by the intended users and the malignant tumor destruction with minimal side effect and minimal damage to surrounding tissues are also finding increasing applications. To achieve this goal nanoparticles obtaining the special biological markers are necessary to be designed, in possession of specific properties characterized by the different tumors. They correspond to the magnetic nanoparticles and antibodies special mixtures which identify the tumor location and penetrate in it. Since the nanoparticles are penetrated in the tumor structure, it is necessary to excite them by high-frequency magnetic fields.

Under this magnetic field, the whirling currents appear in the nanoparticles, which causes local heating. By the magnetic field intensity change, it is possible to enhance the nanoparticles temperature and consequently change the pathology region temperature. As the malignant tumor temperature increases to up to 43°C and higher these malignant tumors are disintegrated

and later on disappear completely [31]. Currently, the perspective in oncology magnetic nanoparticles on the ferric oxide base (hematite, magnetite, and maghemite) were approved by the Food and Drug Administration (FDA) in the many countries of the world.

The Mössbauer spectroscopy can give valuable information on ferric oxide nanoparticles super paramagnetic behaviour. The Mössbauer effect study enables us to control the hyperfine structure and the electron state of a magnetic nanoparticles on the base of ^{57}Fe nuclei ferric oxides. By researching results, the surface layer thickness can be calculated also. In addition, the initial samples, which are used at magnetic nanoparticles synthesis, are sufficiently and accurately identified. The Mössbauer spectroscopy can give selective information about the inside and surface properties of the nanoparticles. As an example, the hematite, magnetite, and their aggregation with FeO and natural iron Mössbauer spectra are given below (fig.20). One of the important problem at the ferric oxides particles synthesis process is the FeO, hematite – Fe_2O_3 , magnetite – Fe_3O_4 and maghemite – $\gamma\text{-Fe}_2\text{O}_3$ phases identification and separation. If the FeO has a cubic crystal structure and the hematite has a corundum-type structure, that both magnetite and maghemite have the spinel type structure, thus, is not distinguishable by the x-ray method. As shown by Fig.20, the hematite spectrum consists of one sextet. Also, the line is widened.

Figure 20. The Mössbauer spectra of the ferric oxides– hematite Fe_2O_3 , magnetite Fe_3O_4 , their aggregation (Fe_2O_3 , Fe_3O_4) with FeO and natural iron

The line broadening denotes that the spectral line represents a superposition of two unresolved lines, which cause the respective states of the ^{57}Fe atoms isotope. The magnetite spectrum corresponds to two clearly defined sextets for the ^{57}Fe atom states located in the octahedron

and tetrahedron sublattices with the spinel structure. On the sample spectra, which possessed all the ferric oxides components, the separate components are good and visible. The last spectrum corresponds to the pure metallic iron.

17. Conclusion

- In this work, the general regularity of the interstitial atoms and vacancy interaction with impurity substitutional atoms of ^{57}Co (^{57}Fe) in bcc lattice metals have been systematically investigated for the first time. The electron states and structure of "impurity-interstitial" atom, "impurity-vacancy" systems, and their Mössbauer parameters were defined.
- The irradiation influence on complexes on the base of ^{57}Co impurity atoms and interstitials formation stages, the dependence of electron state, internal crystalline electric fields from dose and irradiation energy of neutrons, fission fragments and accelerated charged particles were investigated. In the investigation, the Mössbauer impurity atoms vibrations rms, amplitude values, and their binding energy were defined.
- For the first time, through the Mössbauer effect study, the complexes annealing stages from isochronal annealing temperature have been defined. The processes of Mössbauer ^{57}Co impurity atoms thermal diffusion in bcc metals has been investigated. In iron-beryllium and iron-titanium laminated systems, the phase formation, which depends on the beryllium concentration in titanium and also on the temperature of isochronal annealing, was investigated. Using different experimental methods, the peculiarities of the impurity atoms accumulation process at high dose ion implantation in molybdenum have been shown.
- It has been experimentally established that the atoms mobility considerably increases in radiation damaged zones created by high-velocity charged particles, fission fragments, or ionized displaced atoms. As a consequence of the interaction of radiation defects with impurity atoms, their electronic states, nearby environment, and hyperfine structure of nuclear levels undergo changes. These were selectively registered by the Mössbauer spectroscopy method.
- The systematical investigation of point radiation defects with substitutional impurity interaction were performed. The "impurity-interstitial" complexes' stability temperature interval is indicated and their annealing stages have been determined. The Mössbauer parameters of the compound dumbbells composed of impurity and interstitial atoms have been determined. The technology of gamma radiation Mössbauer source production for emissive investigation is reinvestigated.
- In the fcc metals, the efficiency of the method was demonstrated on Al on impurity ^{57}Co atoms. Unlike the fcc metals, the bcc metals' considerable quadrupole splitting has revealed the ability to separate them on different interstitial configurations around ^{57}Co impurity. By following the process of formation and decay of these configurations after irradiation by different particles, as well as after isochronal annealing, it becomes possible to obtain important information about the defects' mobility and "impurity-defect" complexes state.

- - It has been established that non-cubic charge distribution around a Mössbauer atom leads to the electric field gradient. This causes the nuclear levels' hyperfine splitting, at the expense of quadrupole interaction, which emerges as two adsorption lines in case of ^{57}Fe . Quadrupole splitting is proportional to the electric field gradient on Mössbauer nuclei. As a result of systematic investigations on Al^{57}Co diluted alloys, it has been shown that one can observe the interstitial atom captured by ^{57}Co impurities directly by the appearance of an additional "defect" line in the Mössbauer emission spectrum.
- In the course of investigating radiation processes in metallic systems, the basic idea about atoms displacement mechanisms and defects stability was developed. The diffusion mechanism of the interstitials movement models was realized. Also, the impurity atoms role in the process of formation of "impurity-interstitial" complexes was studied.
- As a result of systematic investigations on Al^{57}Co diluted alloys, we have shown the interstitial atom captured by ^{57}Co impurities directly by the appearance of an additional "defect" line in Mössbauer emission spectrum.
- At the same time, for the purposes of its application to transportation of medicinal products to the fields of cancerous cells focused in human, the Mössbauer spectroscopy capability for nanoparticles properties was thoroughly investigated.

Acknowledgements

The authors would like to thank Dr. Umarov T.F. and Ospanov Y.O. for their useful help.

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