USE OF NUCLEAR PHYSICS METHODS FOR INVESTIGATION OF SHORT-RANGE ORDERING AND DEFECTS IN IRON BASED SIMULATING ALLOYS

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Abstract.
Changes of short range ordering and electron density were investigated by nuclear gamma-resonance and positron annihilation methods in simulating alloys containing tungsten, chromium, molybdenum and vanadium, used as doping additions. Change of the short-range ordering parameter sign was detected in alloys containing vanadium as the doping element. Different ordering was also observed in binary and ternary iron alloys. It was shown that dislocations were the basic defects in materials after rolling.

Keywords: Mossbauer effect, short-range ordering, electron density, positron annihilation, defect

1. Introduction. Actuality of the problem

Creation of alloys with improved radiation stability is of great importance in modern nuclear engineering. The results of recent experiments [1,2] have shown that the alloys with short-range ordering are characterized by relatively high mobility of atoms and defects at their boundaries resulted in
conservation of the atomic structure in the basic volume, where a number of point defects are generated and recombining. This process is called self-organizing of the irradiated alloys. It maintains radiation stability of materials. Self-organizing of structure takes place at the expense of damaging in shift cascades and future restoration of short-range ordering nanodomains parameters. Development of methods sensitive to short-range ordering is of significant interest in connection with this. One of the most sensitive methods of short range ordering study is Mossbauer spectroscopy [3-5] based on resonance absorption of photons without recoil, which is sensitive to the shortest neighborhood of iron-57.

It is useful to know the electron structure and defects distribution for obtaining complete information on the alloy properties. One of the most sensitive methods allowing to obtain these characteristics is positron annihilation method, which is based on determination of characteristics of gamma-radiation generated in the annihilation of positrons and giving the possibility both to determine changes of electron density and to reveal the accessibility of the electrons to the core or to conductivity zone. It must be emphasized that characteristics of positron annihilation show to be sensitive to the pulse distribution of the electrons, which are located far from nuclei.

It is necessary to mark that since positron annihilation takes place both on conductivity electrons and on core electrons the method of positron lifetime measurement allows to determine integral electron density and Doppler effect or photons angular distribution - to identify the concentration of core and conductivity electrons.

It should be noticed that experiments on study of the properties of iron based dilute alloys using Mossbauer spectroscopy and positron annihilation have been carried out up to date (see ref. [7,8]). Alloys with high chromium concentration were investigated in ref. [9]. There is no short-range ordering study in these works. Changes of electron density and defects properties in binary and ternary iron alloys were studied in ref. [10]. It was supposed that the positron was captured during its staying in non-defective region. This time is to be comparable with total positron lifetime in matter. Thus an experiment on determination of the annihilation mechanism is needed to be carried out at different temperatures and strains. Using these methods detailed study of short-range ordering and defects generated at it is possible.

2. Investigation methods and techniques.

2.1 Preparation of the samples

Samples for investigation were binary and ternary iron based alloys doped by chromium, vanadium, molybdenum, tungsten and a small amount of other impurities, annealed at 730 °C during 30 h. An additional cold deformation till 50 mcm was made for MS. The samples content is shown in
The previous thermo-mechanical treatment was homogenization at 1150 °C, tempering at 750 °C during 150 h, cold deformation till 110 mcm, annealing at 730 °C during 30 h. The samples content is also shown in table 1.

There were three parties of samples. Experimental samples of the first party were iron binary alloys containing 2-8% Cr or V, samples of the second party were alloys containing small amount (1%) of tungsten or molybdenum instead of chromium. Ternary alloys contained 8% of Cr and were studied in ref. [4,10].

The samples of the third party were iron alloys doped by 9% chromium after thermal treatment without rolling to 50 mcm. Temperature and regime of annealing were varied: one sample was annealed at 900°C during 1 hour, the other- at 730°C during 150 hours. Results are shown in tables 2, 4.

Table 1. Content of the samples of the second party samples

| Name    | Cr | Mn | Cu  | Mo | Ni  | W | V |
|---------|----|----|-----|----|-----|---|---|
| FeW     | 0.17 | 0.14 | 0.22 | -  | 0.12 | 0.84 | -  |
| FeMo    | 0.16 | 0.12 | 0.21 | 0.82 | 0.1 | 0.02 | -  |
| FeCr    | 8.67 | 0.23 | 0.2  | -  | 0.09 | 0.02 | -  |
| FeCrMo  | 8.5  | 0.19 | 0.2  | 0.88 | 0.12 | 0.02 | -  |
| FeCrW   | 8.72 | 0.21 | 0.19 | -  | 0.1  | 0.87 | -  |

2.2. Investigations of short range ordering

Mossbauer spectroscopy (MS) using Co-57 nuclei as the radiation source was used for determination of short range ordering peculiarities in iron based alloys with different doping additions. Transmission technique was chosen because of its sensitivity. Sensitivity of this method was proved by experiments with binary iron alloys doped by chromium and vanadium impurity with fixed concentration.

Spectra of Fe-Cr Fe-Cr-M alloys were measured by the Mossbauer spectrometer MC-1104Em using propagation geometry at room temperature, $^{57}$Co$^*$ (Cr)being the source of photons. Fitting was carried out using Uni- vem MS program [11].

MS lets to obtain information on nuclear physics parameters, which are determined by inter-atomic distance and sorts of the shortest neighborhood (SN) of iron atoms. The shortest neighborhood results in exchange and magnet-crystalline interactions, magnetic fields on iron, nuclei impurities distribution and change of Mossbauer spectra inter-atomic interactions parameters such as hyperfine magnetic field $H_{ef}$ and isomeric shift $\delta$. Magnetic field $H_{ef}$ and isomeric shift $\delta$ are determined corresponding to additive linear influence model [5] as:

$$H_{ef}(n, m) = H_0 + n\Delta H_1 + m\Delta H_2$$

$$\delta(n, m) = \delta_0 + n\delta_1 + m\delta_2$$
$H_0$ and $\delta_0$ are the magnetic strength on the nuclide and the isomeric shift in pure iron; $\Delta H_{1,2}$ and $\Delta \delta_{1,2}$ are contributions to magnetic field strength and to isomeric shift of each atom of the first and the second coordination spheres, $n$ and $m$ are numbers of atoms in the first and the second coordination spheres.

Different neighborhood results in generation of additional lines in the Mossbauer spectra of the alloys, the lines having different values of $H_{ef}$ and $\delta_0$ corresponding to different chemical shortest neighborhood (SN) with different amount of impurity atoms $n$ and $m$ in the first and the second coordination spheres. Thus one can determine the effective concentration and sort of the impurity from Mossbauer experimental spectra.

MS also allows to calculate in accordance to [4-6] the average parameter of short-range ordering (SRO) $\alpha$, which characterizes the deviation of experimental distribution of impurity atoms, surrounding the matrix atom from statistical as well as the local parameter of impurity atoms $B$ surrounding the atoms of sort $A$ within one coordination sphere provided short-range ordering. This parameter may be obtained using formula:

$$\alpha = 1 - \frac{N_i^{AB}}{NC_A C_B} = 1 - \frac{P_i^{AB}}{P_A} = 1 - \frac{P_{AB} j}{C_B j} = 1 - \frac{\sum n P(n)}{C_B j},$$

where $P(n)$ is the experimentally determined number of $A$ matrix atoms positions in the generalized coordination sphere with different number of impurity atoms $B$ in SN, $C_A$ is the total concentration of the matrix $A$ atoms in the solution, $C_B$ is the total calculated concentration of $B$ impurity atoms in the solution ($C_A + C_B = 1$), $j$ is the total coordination number, for BCC lattice ($j=14$). Concentration probabilities of position generation of matrix atoms in binary alloys with different number of impurity atoms provided disordering distribution may be specified by binomial law [5,6].

It may be considered that there is only one sort of impurities, which acts as all impurities of different chemical elements in the solid solution, forming the short-range ordering with the same short-range ordering parameter and total concentration.

If $\alpha=0$, the atoms are located chaotically and there is a classical solid solution, if $\alpha>0$ solid solution stratification takes place, if $\alpha<0$ then there is short- range ordering...

Iron is in ferromagnetic state in the samples under investigation, so the spectra are superposition of sextets of lines responsible to different chemical neighborhood (the first and the second coordination spheres) in the solid interstitial $\alpha$-solution.
Values of probabilities of different number of impurities - location for the samples under investigation (table 2) and the impurities included into the solid interstitial α-solution, were calculated for \( SN \) taking into account formula (3) and the upper limitation on concentration and provided their statistical distribution (see table 2).

**Table 2. Statistical probabilities of different partial spectra**

| Name of the 9-sample | Content of the basic doping elements | Statistical probability of the partial spectrum |
|----------------------|--------------------------------------|-----------------------------------------------|
|                      | Number of the nearest neighbors 0 1 2 3 4 5 |                                               |
| FeW                  | 0.89% W                               | 88.24 11.09 0.65                              |
| FeMo                 | 1.06% Mo                              | 86.14 12.92 0.90                              |
| FeCr                 | 9.75% Cr                              | 23.78 35.97 25.26 10.92 3.24 0.70             |
| FeCrW                | 10.1% (Cr+W)                           | 22.52 35.43 25.87 11.63 3.59 0.81             |
| FeCrMo               | 10.11% (Cr+Mo)                         | 22.49 35.41 25.89 11.65 3.60 0.81             |
| FeCrV                | 14.49 (Cr+V)                           | 11.17 26.51 29.20 19.79 9.22 3.13             |

We consider the value that is enough for the line reliable identification in the Mossbauer spectrum to be 1%, 2-6 line sextets, responsible for non-equivalent \( SN \) of iron in the solid solution with different amount of impurity atoms 0, 1, 2, 3, 4 и 5 may be found in dependence on the impurity concentration. Results of fitting are shown in fig.1,2
Partial isomeric shifts of Fe environments, mm/s

The number of impurity atoms surrounded by Fe

A

Average isomeric shift, mm/s

B
Figure 1. Dependence of partial isomeric shift (A) and partial magnetic field on iron-57 (C) on the number of shortest neighbors (SN) and the average values on impurity’s concentration (B and D)*.
Figure 2. Dependence of itinerant field strength on impurity concentration

Figure 3. Dependence of the short-range ordering parameter on impurity content
Figure 4. Dependence of the short-range ordering parameter (A) and areas’ ratio (B) on the sample content

Dependences of isomeric shift and itinerant field on the number of SN are shown in figures 1 and 2. Dependences of these main Mossbauer characteristics on impurities concentration are shown in figures 1b and 1d for better visual-
ization. Linear dependence of isomeric shifts and effective magnetic field on the number of impurity atoms in iron SN, observed for all samples is significant. This linear dependence is also observed in the dependence of magnetic field strength on impurity concentration.

Peculiarities of Mossbauer parameters changes were observed for Fe-Cr-V sample as well. It is seen that ordering (α<0) is more significant at low impurity concentrations (~1 at%). Thus short-range ordering takes place at low concentrations of the doping element. Such behavior of the short-range ordering parameter was observed in [4] as well. The tendency of short-range ordering is higher in tungsten and molybdenum alloys and is lower in chromium and vanadium alloys provided comparable concentrations (see fig.3,4); α>0 for Fe-Cr-V sample, that means stratification of the solid solution. The short-range ordering parameter monotonously grows from -0.25 to -0.03, i.e. practically to zero, within the concentration interval 2-9% at doping by chromium. It must be destroyed at concentrations of the order of 10%. The solution becomes nearly homogenies. The behavior of dilute alloys with vanadium as a doping element is more complicated within the up-mentioned concentration interval; α is negative in alloys at low concentrations, it changes its sign, so the solid solution must be stratified. α remains positive at 8% vanadium concentration, although it has a maximum at 6%. α is negative in binary alloys, but its module is significantly less than at doping by chromium (see fig.3). If tungsten or molybdenum are added to the iron-chromium alloy then the short-range ordering is stabilized. It should be marked that the module of α is small, i.e the solid solution becomes more homogenies.

The second and third Mossbauer spectrum lines areas ratio is 2 provided domains chaotic orientation and 0 if they are oriented along the rolling axis. This effect is most clearly observed in ternary alloys doped by molybdenum. It is necessary to mark that effect of increase of magnetic moments along the rolling axis is opposite to the effect of reduction of magnetic moments number perpendicular to the rolling plane. (see fig.4). In this alloy the ratio is nearly 1.5, that means preference of the rolling direction.

2.3. Investigation of electron density and defects

Investigations of electron changes were carried out using positron annihilation (AP) with positrons lifetime detection, since this technique is the most sensitive to changes of integral electron density. The experiments, confirming usefulness of our ideas were described in [4.10]. The instrumentation used in these experiments was a standard ORTEC lifetime spectrometer with time resolution 260 ps. $^{22}$Na was used as the positron source. We base on properties of positrons shown in table 3, results of experiments are shown in table 4.

It is necessary to take into account the contribution of annihilation in the source of e+ when fitting the experimental spectra. It can be measured with sufficient accuracy using the repair sample and calibration measurement if the sample has
known lifetimes. Then measuring the average lifetime in this sample one can
determine the part of background photons. In this work the background annihila-
tion lifetime is 400 ps, its contribution is 14%.

Table 3. Positron lifetimes in iron defects

| Defect           | Positrons’ lifetime, Ps | Vacancies size, Å | Clusters radii, Å |
|------------------|-------------------------|-------------------|-------------------|
| Fe – bulk        | 110                     |                   |                   |
| Fe-dislocations  | 165                     | 1.3               | 1.7               |
| Fe-monovacancy   | 175                     | 1.41              |                   |
| Fe divacancy     | 197                     |                   | 1.6               |
| Fe-3 vacancy     | 232                     | 1.9               |                   |
| Fe-5 vacancy     | 262                     | 2.2               |                   |
| Fe-6 vacancy     | 304                     | 2.6               |                   |

Table 4. Experimental results of research binary and ternary of the Fe-rich alloys

| Alloy       | t1 / error, ps | t1 / error, % | t2 / error, ps | t2 / error, % | Thermal treatment                                      |
|-------------|----------------|---------------|----------------|---------------|--------------------------------------------------------|
| FeW         | 166/1          | 97.1/0.9      | 412/12         | 2.9/0.6       | Annealing at 730° C during 30 h, tempering after first rolling (110 mcm) at 730° C during 150 h everywhere |
| FeMo        | 164/1          | 97.2/0.5      | 465/11         | 2.7/0.5       |                                                        |
| Fe2%Cr      | 165/1          | 80.1/0.6      | 520/12         | 19.9/0.6      |                                                        |
| Fe 4%Cr     | 165/1          | 79.5/0.6      | 515/8          | 23.5/0.6      |                                                        |
| FeCr 6%     | 163/1          | 78.8/0.6      | 510/13         | 21.2/0.6      |                                                        |
Here $t_1$ and $t_2$ are short and long lifetimes, $I_1$ and $I_2$ - amplitudes of the corresponding components.

It is necessary to emphasize that really only two types of defects can trap positrons: dislocations and clusters. Nevertheless, experiments with all samples showed that most of positrons were trapped by vacancies, associated with dislocations, and clusters. They may be trapped practically immediately after slowing down in the sample, this corresponds to their absence in the non-defect region. The probability of annihilation in such dislocations is nearly 97.1% in alloys with tungsten and molybdenum. This 97% probability of positrons trapping into dislocations is retained for all ternary alloys under investigation. The value of cluster trapping probability reaches nearly 0.2 in binary chromium and vanadium alloys.

Experiments in work [12] showed that annealing at 730°C did not take place: 72% of positrons were captured by dislocations, 28% - by clusters. There are only 6 vacancies in such clusters (see tabl. 3). Their size can be estimated in the manner described in [10]. It is 2.6 A. Our data are in qualitative correspondence to those shown in tabl. 3. Positrons are not trapped by dislocations and small clusters after annealing at 900°C since they are destroyed. The short component is nearly the bulk lifetime in Fe-9%Cr. But there is an alternative explanation, which was proposed in [12] basing on electron microscopy data. This alloy has a multi-phase structure, and the short lifetime component may be the result of positrons trapping into vacancies associated with dislocation after generation of chromium enriched interface regions in interface. Trapping into these defects may be responsible for the short lifetime component. The long one may be associated with annihilation on boundaries.

3. Conclusions

1. Investigations of ordering for iron alloys doped by chromium, vanadium, molybdenum and tungsten were carried out by transmission Mossbau-
er spectroscopy. Itinerant magnetic field strength and isomeric shift were measured. Dependence of these parameters on the number of nearest neighbors was obtained for different impurity concentrations and sorts of impurity atoms for binary and ternary alloys based on iron.

2. Calculation of the short-range ordering parameter basing on Mossbauer experiments were carried out. The impurity interval for ordering and stratification was determined. It was shown that in binary FeV alloys ordering changes to stratification at V concentration higher than 4%. At higher concentrations the solid solvation approaches to homogenies.

3. Study of structure defects was carried out for different thermo-mechanical treatment. It was shown that positron lifetime corresponded to trapping into dislocations and clusters, dislocation trapping being the main samples. Samples of Fe9%Cr were studied at different regimes of annealing. It was shown that annealing took place at 900°C, although it was only during 1h.

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