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

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Abstract

The changes of short range ordering and electron density were investigated by means of the nuclear gamma-resonance and the positron annihilation spectroscopies in model alloys containing tungsten, chromium, molybdenum, and vanadium used as dopants. The change of the short-range ordering parameter sign was detected in alloys containing vanadium. Different ordering was also observed in binary and ternary iron alloys. It was shown that dislocations were the main defects in these materials after rolling.

Keywords: *Mossbauer effect; Short-range ordering; Electron density; Positron annihilation; Defect*

1. Introduction.

The 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 resulting in the 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. The self-organizing of the structure takes place at the expense of damaging in shift cascades and future restoration of short-range ordering nano-domains parameters. The development of the 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 the resonance absorption of photons without recoil, which is sensitive to the nearest environment 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 the positron annihilation method, which is based on the 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 accessory of the electrons to the core or to conductivity zone. It must be emphasized that the characteristics of the positron annihilation show to be sensitive to the pulse distribution of the electrons which are located far from the nuclei.

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

It should be noticed that the experiments on the 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]). The alloys with high chromium concentration were investigated in ref. [9]. There is no short-range ordering study in these works. The changes of electron density and defects

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properties in binary and ternary iron alloys were studied in ref. [10]. It was supposed that the positron was captured during its staying in the non-defective region. This time is to be comparable with the total positron lifetime in the matter. Thus an experiment on the determination of the annihilation mechanism is needed to be carried out at different temperatures and strains. Using these methods the detailed study of the short-range ordering and defects generated at it is possible.

2.Investigation methods and techniques.

2.1 Preparation of the samples

The samples for the 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 table 1. 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 content of the samples is also shown in table 1.

There were three parties of samples. The experimental samples of the first party were iron binary alloys containing 2-8% Cr or V, the samples of the second party were alloys containing small amount (1%) of tungsten or molybdenum instead of chromium. The 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. The temperature and the regime of annealing were varied: one sample was annealed at 900°C during 1 hour, the other- at 730°C during 150 hours. The results are shown in tables 2 and 4.

2.2. Investigations of short range ordering

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

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

MS allows obtaining information on nuclear physics parameters, which are determined by inter-atomic distance and the 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 δ. Magnetic field H_{ef} and isomeric shift δ are determined corresponding to additive linear influence model [5] as:

$$H_{ef}(n, m) = H_0 + n\Delta H_1 + m\Delta H_2 \quad (1)$$

$$\delta(n, m) = \delta_0 + n\delta\Delta_1 + m\,\delta\,\Delta_2 \quad (2)$$

H_0 and δ_0 are the magnetic strength on the nuclide and the isomeric shift in pure iron; $\Delta H_{1,2}$, $\Delta\delta_{1,2}$- 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 the generation of additional lines in the Mossbauer spectra of the alloys, the lines having different values of H_{ef} and δ_0 and 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 the sort of the impurity from Mossbauer experimental spectra.

MS also allows calculating in accordance to [4-6] the average parameter of short-range ordering (SRO) *a*, which characterizes the deviation of the experimental distribution of the impurity atoms,

Table 1. *Composition of the samples of the second set*

Composition of the elements, mass. %							
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	-
Fe-Cr-V	8.4	-	0.12	-	0.6	-	4.51

surrounding the matrix atom from statistical as well as the local parameter of the impurity atoms *B* surrounding the atoms of sort *A* within one coordination sphere provided short-range ordering. This parameter may be obtained using the formula:

$$\alpha = 1 - \frac{N_i^{AB}}{NC_iC_AC_B} = 1 - \frac{p_i^{AB}}{C_B} = 1 - \frac{P_{AB}j}{C_Bj} = 1 - \frac{\sum_{n=1}^{j} nP(n)}{C_Bj} \quad (3)$$

where *P(n)* is the experimentally determined number of *A* matrix atoms positions in the generalized coordination sphere with a 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), The concentration probabilities of position generation of the matrix atoms in binary alloys with a 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 the 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 α=0, the atoms are located chaotically and there is a classical solid solution, if α>0 solid solution stratification takes place, if α<0 then there is a 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 a-solution

The values of probabilities of different number of impurities – the location for the samples under investigation (table 2) and the impurities included into the solid interstitial a-solution were calculated for *SN* taking into account formula (3) and the upper limitation on concentration, and provided their statistical distribution (see table 2).

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 a different amount of the impurity atoms 0, 1, 2, 3, 4 и 5 may be found in the dependence on the impurity concentration. The results of the fitting are shown in fig.1, 2

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

The 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); a>0 for Fe-Cr-V sample, which 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 the concentrations of the order of 10%. The solution becomes nearly homogeneous 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

Table 2. *Statistical probabilities of different partial spectra*

Name of the samples	Content of the dopants	Probability of the partial spectrum					
	Number of the earest 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
FwCrMo	10.11%(Cr+Mo)	22.49	35.41	25.89	11.65	3.6	0.81
FeCrV	14.49(Cr+V)	11.17	26.51	29.2	19.79	9.22	3.13

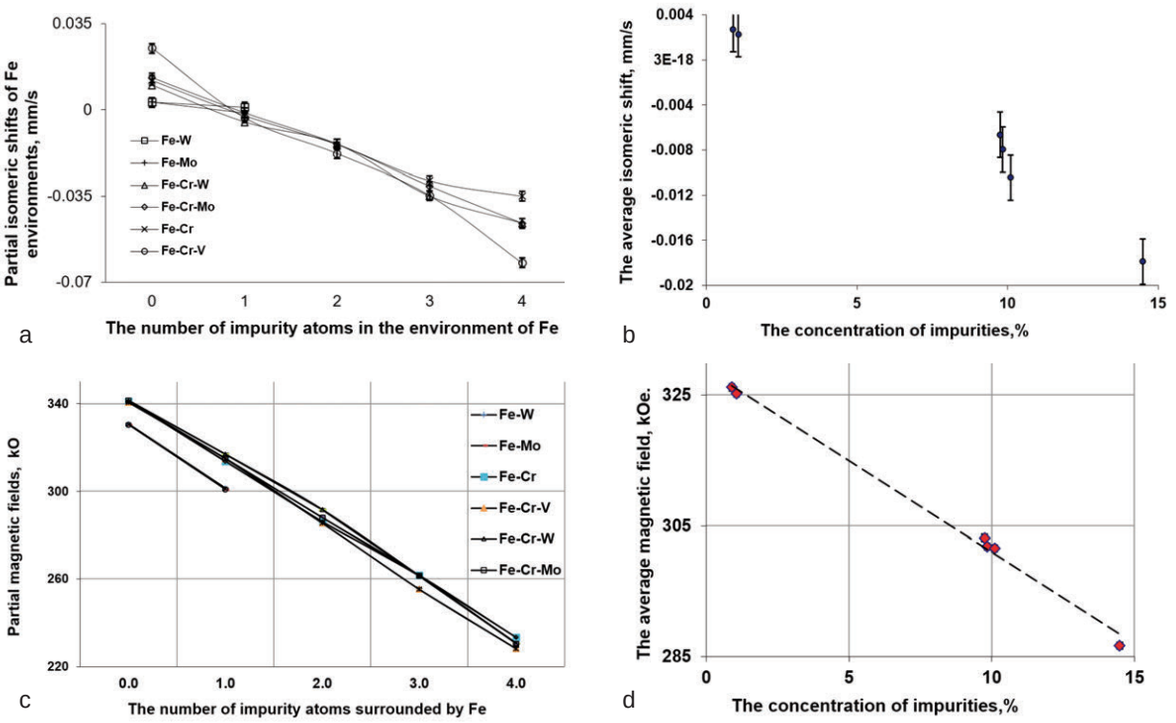

Figure 1. *Dependence of partial isomeric shift (a) and partial magnetic field on iron-57(c) on the number of shortest neighbors (SN) and the average values on impurity's concentration (b and d)**

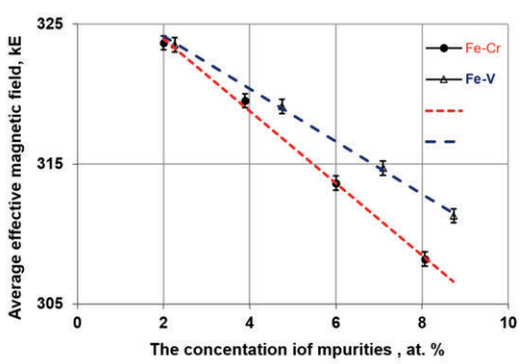

Figure 2. *Dependence of itinerant field strength on impuritny concentration*

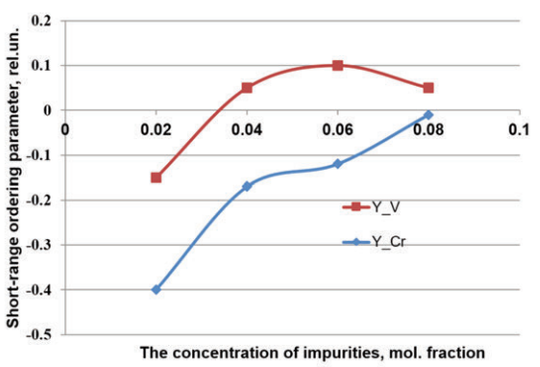

Figure 3. *Dependence of the short-range ordering parameter on impurity content*

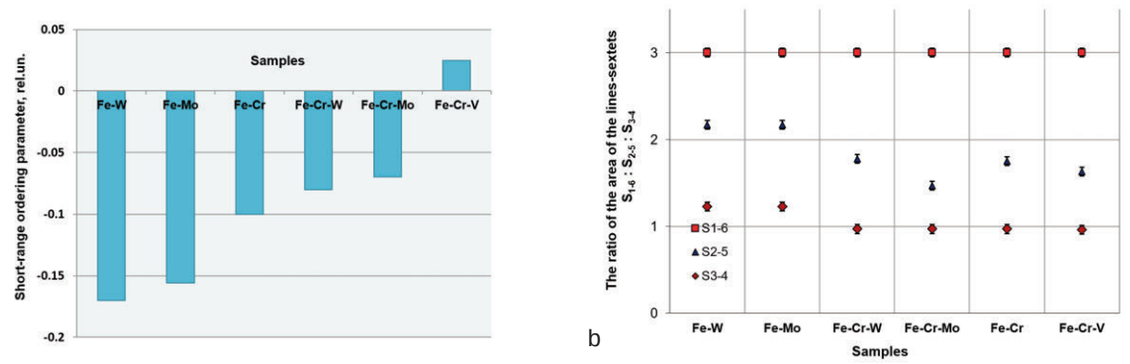

Figure 4. *Dependence of the short-range ordering parameter (a) and areas' ratio (b) on the sample content*

more homogeneous .

The second and the 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 the effect of the increase of magnetic moments along the rolling axis is opposite to the effect of the reduction of magnetic moments number perpendicular to the rolling plane(see fig.4). In this alloy the ratio is nearly 1.5, which means the preference of the rolling direction.

2.3. Investigation of electron density and defects

The investigations of the electron changes were carried out using the positron annihilation spectroscopy (PAS) with positrons lifetime detection, since this technique is the most sensitive to changes of integral electron density. The experiments confirming the usefulness of our ideas were described in [4, 10]. We used in these experiments a standard ORTEC lifetime spectrometer with the time resolution 260 ps. ^{22}Na was used as the positron source. We base on properties of positrons shown in table 3, the results of experiments are shown in table 4.

It is necessary to take into account the contribution of the annihilation in the source of e+ when fitting the experimental spectra. It can be measured with sufficient accuracy using the reference samples with the known positron lifetimes.. Then by measuring the average lifetime in tthese samples one can determine the source correction, i.e. fraction of positrons annihilating within

Table 3. *Positron lifetimes in iron defects*

Defect	Positrons' lifetime, ps	Vacancies size, Å	Clusters radii, Å
Fe–bulk	110	1,.3	1.3
–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	*I*1 / error, %	*t*2 / error, ps	*I*2 / 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	
Fe4%Cr	165/1	79.5/0.6	515/8	20.5/1	
FeCr 6%	163/1	78.8/0.6	510/13	21.2/0.6	
FeCr 8%	164/1	79.6/0.6	511/10	20..4/0.6	
FeCrMo	164/1	97.2/0.7	432/60	2.8/0.7	
Fe V2%	166/2		510/10	21.5/0.7	
Fe V 4%	164/1	78.2/0.6			
Fe V 6%	163/1	80.0/0.6	510/12	20.0/0.6	
Fe V 8%	169/1	82.1/0.5	556/13	17.9/0.5	
-FeCrV	163/1	97.1/0.7	417/60	2.9/0.7	
Fe 9%Cr	115/2	913	495/27	9.5/0.5	Annealing,at 900°C, 1 h
Fe 9%Cr	160/4/	72//3	315/13	28/3	Annealing at 730^{0}C, 150 h

the e+ source. In this work tthe source correction was 14% and it was described by one exponential function with the lifetime 400 ps.

It is necessary to emphasize that really only two types of defects can trap positrons: dislocations and vacancy clusters. Nevertheless, the experiments with all the samples showed that most of the positrons were trapped by vacancies, associated with dislocations, and clusters. They are trapped practically immediately after positron slowing down in the sample. The probability of e+ annihilation trapped in dislocations is nearly 97% in alloys with tungsten and molybdenum. This 97% probability of positrons trapped in 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.

The experiments [12] showed that annealing at 730^0C did not take place: 72% of the positrons were captured by dislocations, 28% - by the vacancy clusters. There are only 6 vacancies in such clusters (see table 3). Their size can be estimated in the manner described in [10]. It is 2.6 Å. Our data are in qualitative correspondence to those shown in table 3. The positrons are not trapped by the dislocations and small clusters after the annealing at 900°C since they are disappeared. The short component is close to the bulk lifetime in Fe-9%Cr, but there is an alternative explanation which was proposed in [12], based on the electron microscopy data. This alloy has a multi-phase structure, and the short lifetime component may be the result of the positrons trapping into the vacancies associated with the dislocations after generation of chromium enriched interface regions. Positron trapping into these defects may be responsible for the short lifetime component. The long-lived may be associated with the positron annihilation on the boundaries.

3. Conclusions

1. Investigations of the ordering for the iron alloys doped by chromium, vanadium, molybdenum, and tungsten were carried out by the transmission Mössbauer spectroscopy. Itinerant magnetic field strength and isomeric shift were measured. The 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 iron-based alloys.

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

3. The study of structural defects was carried out for different thermo-mechanical treatments. It was shown that the observed positron lifetime corresponded to e+ trapping on dislocations and vacancy clusters. The samples of Fe9%Cr were studied at different regimes of annealing. It was shown that the annealing took place at 900°C, although it was only for 1h.

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KORIŠĆENJE METODA NUKLEARNE FIZIKE ZA ISPITIVANJE KRATKOROČNOG PORETKA I DEFEKATA U LEGURAMA ZASNOVANIM NA GVOŽĐU

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Apstrakt

Promene kratkoročnog poretka i gustoće elektrona ispitivani su metodama nuklearne gama-rezonance i anihilacije pozitrona u legurama koje sadrže tungsten, hrom, molibden i vanadijum kao dodate primese. Promena parametara kratkoročnog poretka otkrivena je u legurama koje su sadržale vanadijum kao primesu. Različit poredak primećen je i u binarnim i trojnim legurama gvožđa. Pokazalo se da su dislokacije glavni defekti u materijalu posle valjanja.

Ključne reči: *Mesbauerov efekat; Kratkoročni poredak; Gustoća elektrona; Anihilacija pozitrona; Defekt*