

A study of thermodynamic properties of dilute Fe-Ru alloys by ^{57}Fe Mössbauer spectroscopy

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Abstract The room temperature Mössbauer spectra of ^{57}Fe were measured for $\text{Fe}_{1-x}\text{Ru}_x$ solid solutions with x in the range $0.01 \leq x \leq 0.08$. The obtained data were analysed in terms of short-range order parameter (SRO) and the binding energy E_b between two ruthenium atoms in the studied materials using the extended Hryniewicz-Królas idea. The extrapolated value of E_b for $x = 0$ was used to compute the enthalpy of solution H_{FeRu} of Ru in Fe matrix. The result was compared with corresponding values given in the literature which were derived from experimental calorimetric data as well as with the value resulting from the cellular atomic model of alloys by Miedema. It was found that all the H_{FeRu} values are negative or Ru atoms interact repulsively. At the same time, the Mössbauer data were used to determine values of the short-range order parameter α_1 . For the as-obtained samples in which atoms are frozen-in high temperature state, close to the melting point, the negative α_1 values were found. The findings indicates ordering tendencies in such specimens. On the other hand, in the case of the annealed samples where the observed distributions of atoms should be frozen-in state corresponding to the temperature 700 K, the $\text{Fe}_{1-x}\text{Ru}_x$ alloys with $x \geq 0.05$ exhibit clustering tendencies (a predominance of Fe-Fe and Ru-Ru bonds), which manifest themselves by positive values of the calculated SRO parameter. The clustering process leads to a local increase in ruthenium concentration and nucleation of a new ruthenium-rich phase with the hcp structure.

Keywords Mössbauer spectroscopy · Short-range order · Iron alloys · Enthalpy of solution

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1 Introduction

It has been proved that the ^{57}Fe Mössbauer spectroscopy is a useful tool for the study of short-range order (SRO) as well as interactions of impurity atoms in iron alloys [1–10]. This technique is especially powerful when the impurity neighbours of the Mössbauer probe have a sufficiently large effect on the hyperfine field generated at the probe, to yield distinguishable components in the Mössbauer spectrum attributed to different configurations of the probe neighbours. From the data given in the literature (see [11] for example) it follows that there are many binary iron systems suitable for the studies mentioned above. Worth noting is the fact that the impurity interactions are simply related to the enthalpy of solution of the impurity elements in iron [12]. The enthalpy as well as SRO parameter are widely used in developing and testing different models of binary alloys and methods for calculating the alloy parameters [13–15]. Moreover, the Mössbauer spectroscopy findings in some cases can be unique i.e. impossible to obtain with other methods, in particular the calorimetric ones. It can happen because the Mössbauer studies provide information about enthalpy of solution at relatively low temperature, below the Curie temperature whereas the calorimetric investigations are performed for samples at relatively high temperatures, above the Curie temperature, at which influence of magnetic interactions on thermodynamic properties of studied alloys cannot be observed. Additionally, the Mössbauer studies concern iron alloys in low-temperature α (bcc) phase in contrast to high-temperature calorimetry where most of iron systems under investigation are in γ (fcc) phase [3, 16].

In this paper the Fe-Ru iron based alloys were investigated by ^{57}Fe Mössbauer spectroscopy in order to determine the SRO parameter and the enthalpy of solution H_{FeRu} of Ru in α -Fe matrix [12]. According to our knowledge in the available literature there is no experimental data concerning the short-range order in Fe-Ru alloys. Moreover, the values of enthalpy of solution of Ru in Fe were estimated only for liquid phase at 2700 K and for γ -Fe matrix at 1600 K [17].

2 Experimental details and results

2.1 Samples preparation and measurements

The samples of $\text{Fe}_{1-x}\text{Ru}_x$ alloys with x in the range $0.01 \leq x \leq 0.08$ were melted in an arc furnace under an argon atmosphere and quickly cooled down to the room temperature. The weight losses during the melting process were below 0.2 % so the compositions of the obtained ingots were close to nominal ones. In the next step ingots were cold-rolled to the final thickness of about 0.04 mm and then the foils were annealed in vacuum at 1270 K for 2 h. After that they were slowly cooled to room temperature during 6 h.

The room temperature measurements of the ^{57}Fe Mössbauer spectra were performed in transmission geometry by means of a constant-acceleration POLON spectrometer of standard design, using a 50 mCi ^{57}Co -in-Rh standard source with a full width at half maximum (FWHM) of 0.24 mm/s.

2.2 Data analysis

Each measured spectrum was fitted with a transmission integral for a sum of different six-line patterns corresponding to various hyperfine fields B at ^{57}Fe nuclei generated by different numbers of Fe and Ru atoms located in the first coordination shell of the probing

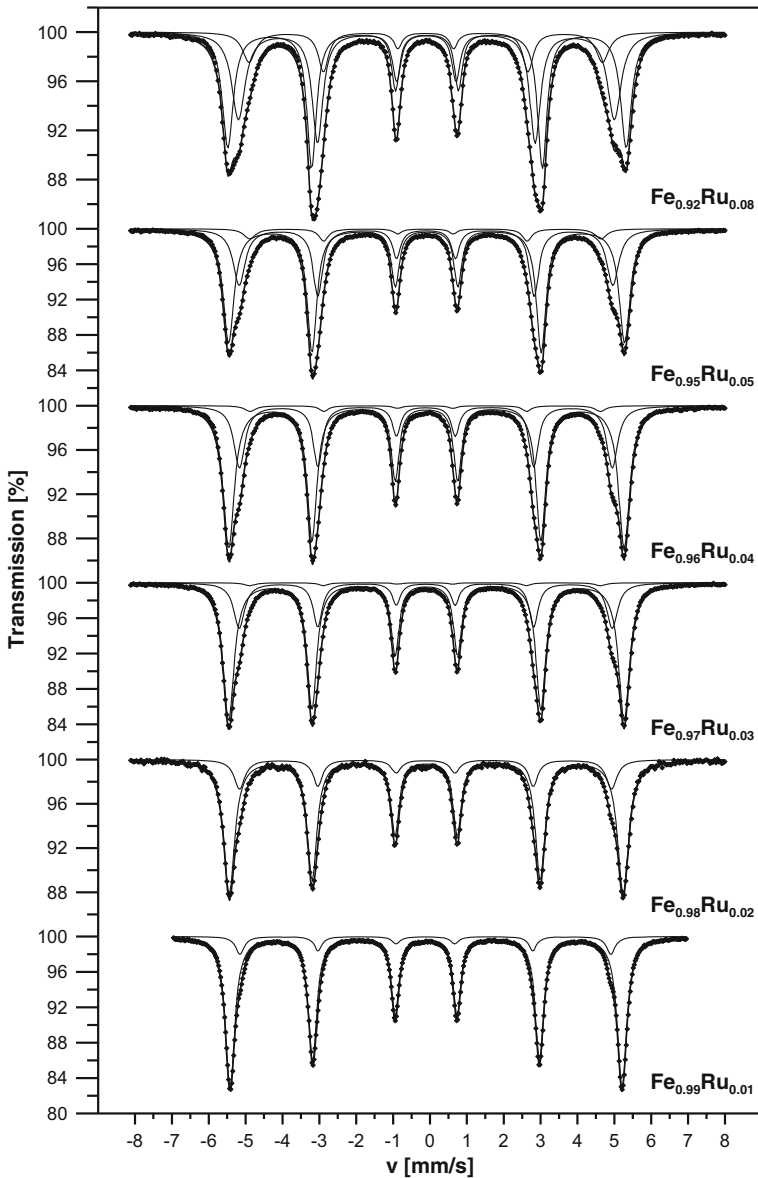


Fig. 1 The ^{57}Fe Mössbauer spectra for the Fe-Ru alloys measured at room temperature before the annealing process at 1270 K, fitted with Zeeman sextets

nuclei. The number of fitted six-line patterns depends on concentration of Ru in the samples and was two for $x = 0.01$ and three for $x = 0.08$. The fitting procedure was done under the assumption that the influence of Ru atoms on B as well as the corresponding isomer shift IS on a subspectrum, is additive and independent of the atom positions in the first coordination shell of the nuclear probe. In other words it was accepted that for each subspectrum

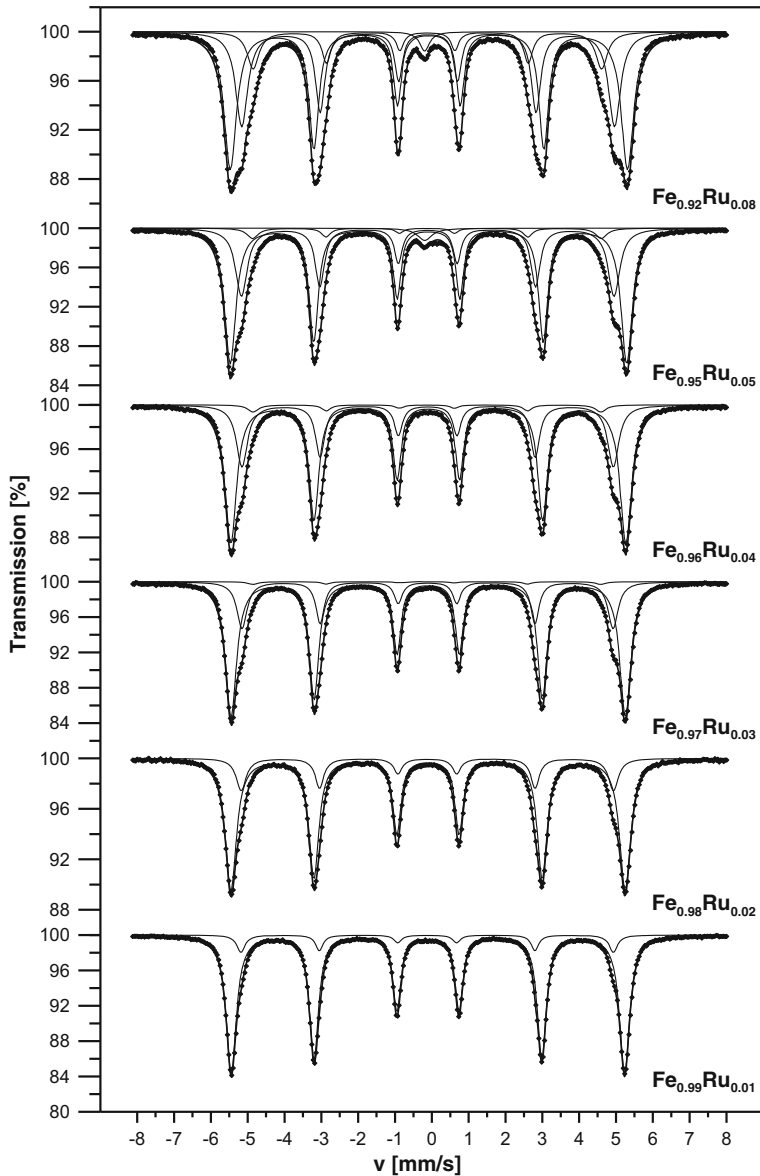


Fig. 2 The ^{57}Fe Mössbauer spectra for the Fe-Ru alloys measured at room temperature after the annealing process at 1270 K, fitted with Zeeman and single-line components

the quantities B and IS are linear functions of the number n of Ru atoms located, in the first coordination shells of ^{57}Fe . The functions can be written as follows:

$$\begin{aligned} B(n) &= B_0 + n\Delta B, \\ IS(n) &= IS_0 + n\Delta IS, \end{aligned} \quad (1)$$

Table 1 Some parameters of the assumed model fitted to the ^{57}Fe Mössbauer spectra measured for annealed $\text{Fe}_{1-x}\text{Ru}_x$ alloys. Values of the isomer shift IS_0 are reported relative to the corresponding value for $\alpha\text{-Fe}$ at room temperature

x	B_0 [T]	ΔB [T]	IS_0 [mm/s]	ΔIS [mm/s]
0.01	33.10(1)	-1.77(3)	0.003(1)	-0.022(3)
0.02	33.17(2)	-1.85(3)	0.005(1)	-0.020(3)
0.03	33.18(2)	-1.96(3)	0.011(2)	-0.019(3)
0.04	33.24(2)	-1.99(3)	0.014(2)	-0.019(3)
0.05	33.36(2)	-2.01(3)	0.018(2)	-0.021(3)
0.08	33.42(2)	-2.05(3)	0.029(2)	-0.021(2)

where ΔB and ΔIS stand for the changes of B and IS with one Ru atom in the first coordination shell of the Mössbauer probe. At the same time, we assume that the quadrupole splitting QS in a cubic lattice is equal to zero. Moreover, in spectra obtained for alloys after the annealing process with $x \geq 0.05$, the non-magnetic components were observed. These additional subspectra were accounted for by one paramagnetic singlet (IS relative to $\alpha\text{-Fe} = -0.087(12)$ mm/s). In authors opinion, the origin of non-magnetic subspectra is connected with the limited solubility of ruthenium atoms in the iron matrix and the nucleation of additional paramagnetic Ru-rich phase with hcp structure [18]. The fits obtained under these assumptions are presented in Figs. 1 and 2. The estimated parameters of the hyperfine field and isomer shift obtained for annealed Fe-Ru alloys are listed in Table 1.

The effective thicknesses $T_A(n)$ related to components of each spectrum for studied samples could be expressed as follows:

$$T_A(n) = \sigma_0 t_A N f c(n), \tag{2}$$

where σ_0 is the maximal cross section for nuclear γ resonance absorption, t_A denotes the thickness of the absorber, N stands for the total number of resonant absorbing atoms ^{57}Fe per unit volume, $c(n)$ describes the fraction of absorbing atoms corresponding to the component under consideration and f is the Lamb-Mössbauer factor. Assuming that the Lamb-Mössbauer factor does not depend on the configuration of atoms in the surroundings of the ^{57}Fe nucleus, the fraction $c(n)$ can be easily calculated using the $T_A(n)$ values as in such case

$$c(n) = \frac{T_A(n)}{\sum T_A(n)}. \tag{3}$$

The computed $c(n)$ values were used to find parameters $c(0)$, $c(1)$ and $c(2)$ being the total intensities of those components of a spectrum which are related to the existence of zero, one and two ruthenium atoms in the first coordination shell of nuclear probes ^{57}Fe . These parameters are presented in Fig. 3 together with calculated probabilities of finding zero $p(0)$, one $p(1)$ and two $p(2)$ Ru atoms in the first coordination shell of an Fe atom in the random bcc $\text{Fe}_{1-x}\text{Ru}_x$ alloy. In disordered (random) alloys, the probability $p(n)$ of local configuration of impurity atoms in the first coordination shell of ^{57}Fe nucleus is described by the binomial distribution:

$$p(n) = \frac{N!}{n!(N-n)!} x^n (1-x)^{N-n}, \tag{4}$$

where N denotes the coordination numbers of the first shell. In the case of $\text{Fe}_{1-x}\text{Ru}_x$ alloys with the x range of $0.01 \leq x \leq 0.08$ where atoms are distributed in the bcc lattice, $N = 8$.

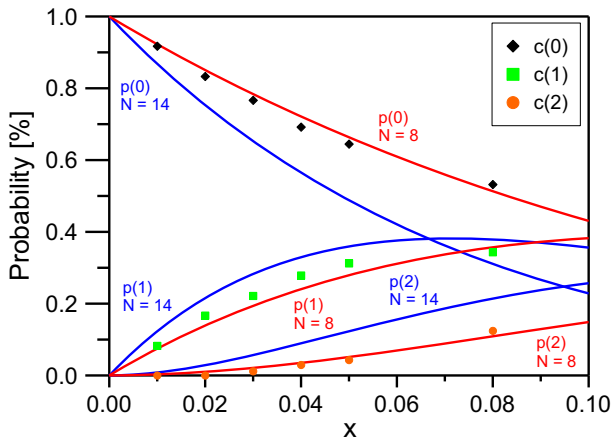


Fig. 3 Total intensities of those components of a spectrum which are related to the existence of zero $c(0)$, one $c(1)$ and two $c(2)$ Ru atoms in the vicinity of nuclear probes ^{57}Fe in the $\text{Fe}_{1-x}\text{Ru}_x$ alloys after the annealing process. The lines describe probabilities of finding zero $p(0)$, one $p(1)$ and two $p(2)$ Ru atoms in the first ($N = 8$ red lines) and two first ($N = 14$ blue lines) coordination shells of an Fe atom in the random bcc $\text{Fe}_{1-x}\text{Ru}_x$ alloy

To be sure that considered above model of spectrum is correct, the experimental parameters $c(0)$, $c(1)$ and $c(2)$ were compared with those resulting from the second possible model of the spectrum which assumes that Ru atoms located in the two first coordination shells of ^{57}Fe probes influence the values of B and IS almost in the same way ($N = 14$ in equation (4)). As one can see in Fig. 3, the second model is unlikely.

2.3 The binding energy of two Ru atoms in Fe matrix

The binding energy E_b for pairs of Ru atoms in the annealed materials was calculated using obtained $c(1)$ and $c(2)$ values. The calculations were performed on the basis of the modified Hryniewicz-Królas formula [3, 19], where E_b is expressed by:

$$E_b = -kT_d \cdot \ln[(1 + 2 \cdot c(2)/c(1)) \cdot (c(2)/c(1)) \cdot (1 + 2 \cdot p(2)/p(1))^{-1} \cdot (p(2)/p(1))^{-1}]. \quad (5)$$

In (5), k is the Boltzmann constant and T_d denotes the “freezing” temperature for the atomic distribution in a sample; $T_d = 700(50)$ K [7] in the case of the annealed sample. Worth noting is a fact that, in case of annealed $\text{Fe}_{1-x}\text{Ru}_x$ samples with $x \leq 0.02$, $c(2) = 0$. At the same time, for the alloys with $x \geq 0.05$, the Mössbauer spectra reveal coexistence of two different phases, ferromagnetic Fe-rich with bcc structure and paramagnetic Ru-rich with hcp structure. It means that the modified Hryniewicz-Królas model can be easily used to estimate the proper values of E_b for annealed $\text{Fe}_{0.97}\text{Ru}_{0.03}$ and $\text{Fe}_{0.96}\text{Ru}_{0.04}$ alloys only as they are one-phase bcc systems with know value of x ; the E_b values are 0.049(8) eV and 0.023(4) eV, respectively. In the next step we found the extrapolated value of the binding energy E_b for $x = 0$. The $E_b(0) = 0.13(4)$ eV. The obtained positive values of binding energy in $\text{Fe}_{1-x}\text{Ru}_x$ alloys with $x \leq 0.04$ suggest that interaction between two Ru atoms in iron matrix is repulsive.

Table 2 An enthalpy H_{FeRu} [eV/atom] of solution of ruthenium in iron

Calorimetric data, liquid (2700 K) [17]	Calorimetric data, γ -Fe (1600 K) [17]	Miedema's model [13]	This work α -Fe (700 K)
-0.19	-0.19	-0.20	-0.50(14)

2.4 An enthalpy of solution of ruthenium in iron

The $E_b(0)$ value was used to compute the enthalpy H_{FeRu} of solution of Ru atoms in α -Fe matrix. The calculations were performed on the basis of the Królas model [12] for the binding energy according to which

$$H_{\text{FeRu}} = -z \cdot E_b(0)/2 \tag{6}$$

where z is the coordination number of the crystalline lattice ($z = 8$ for α -Fe). The value of H_{FeRu} is presented in Table 2 together with corresponding values derived from calorimetric experiments [17] as well as calculated using the cellular atomic model of alloys developed by Miedema [13].

2.5 Short-range order parameter

In the $\text{Fe}_{1-x}\text{Ru}_x$ alloys with the x range $0.01 \leq x \leq 0.08$ where atoms are distributed in the bcc lattice, the total number of atoms located in first coordination shell of an atom is equal to 8. In the real alloys the distribution of impurity atoms is generally different from statistically predicted by binomial distribution (see Fig. 3). This deviation from the random state can be quantitatively described by SRO parameter and Mössbauer spectroscopy is a very useful tool for determination of the parameter since the hyperfine field B and isomer shift IS are influenced by the number of impurity atoms in the first coordination shell of ^{57}Fe probe. The value of the SRO parameter for the first coordination shell in bcc lattice can be computed with the following formula [9]:

$$\alpha_1 = 1 - \frac{\langle n \rangle}{8x}, \tag{7}$$

where $\langle n \rangle = \sum_{n=1}^8 nc(n)$ is the average number of Ru atoms in the first coordination shell of ^{57}Fe Mössbauer probe. The values of the SRO parameter α_1 in the $\text{Fe}_{1-x}\text{Ru}_x$ alloys calculated from Eq. 7 are presented in Fig. 4. As one can see, the negative α_1 values found for the samples before annealing process indicate ordering tendencies (a predominance of Fe-Ru bonds) in the as-obtained samples in which atoms are frozen-in high temperature state, close to the melting point. In the case of samples after annealing process where the observed distributions of atoms should be frozen-in state corresponding to the temperature 700 K, the negative values of α_1 samples with $x < 0.05$, also indicates ordering tendencies. In terms of interactions it means that the interaction between two Ru atoms is repulsive, which confirms our previous findings in Section 2.4. At the same time, the annealed $\text{Fe}_{1-x}\text{Ru}_x$ alloys with $x \geq 0.05$ exhibit clustering tendencies (a predominance of Fe-Fe and Ru-Ru bonds), which manifest themselves as positive values of the calculated SRO parameter. The strong clustering process leads to a local increase in ruthenium concentration and nucleation of a new ruthenium-rich phase with hcp structure. Taking the above into account, the solubility limit of Ru in Fe at 700 K is close to 5 at. % which is at variance with the value reported

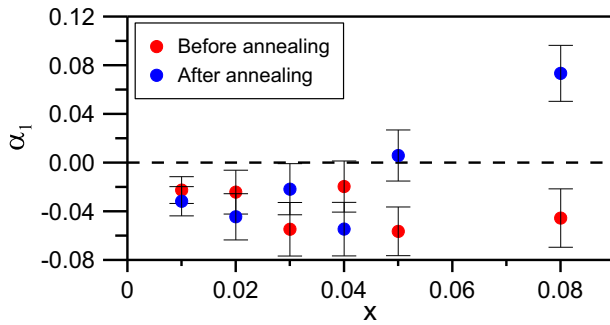


Fig. 4 The SRO parameter α_1 as a function of fraction x of Ru atoms in the $\text{Fe}_{1-x}\text{Ru}_x$ alloys

in Ref. [18] (2 at. %). Moreover, a comparison of results obtained for samples before and after the annealing process suggests that the rapid cooling in the arc furnace results in a single-phase Fe-Ru alloys, whereas the annealing process with subsequent slow cooling to room temperature leads to precipitation of a ruthenium-rich phase with hcp structure for the $\text{Fe}_{1-x}\text{Ru}_x$ samples with $x \geq 0.05$.

3 Conclusions

The results obtained in this study give rise to the following conclusions:

1. The obtained values of binding energy between two Ru atoms in Fe-Ru alloys suggest that interaction between Ru atoms in the studied materials is repulsive, when concentration of ruthenium atoms is relatively small, not exceeding about 4 at. %.
2. The estimated value of enthalpy H_{FeRu} of solution of Ru in α -Fe is $-0.50(14)$ eV/atom. This result differs from corresponding data derived from calorimetric experiments and Miedema's cellular atomic model of alloys. The disagreement between calorimetric findings and our result may be caused by different state of examined alloys. Calorimetric data for instance, was taken for samples at 1700 K where Fe-Ru alloys are in paramagnetic γ phase whereas our Mössbauer study concerns the alloys in ferromagnetic α phase with atomic distributions corresponding to the temperature about 700 K (below Curie temperature).
3. The negative values of SRO parameters α_1 obtained for as-obtained samples of iron-based Fe-Ru alloys indicate ordering tendencies. It means that Ru dissolves well in Fe at high temperature, close to the melting point. On the other hand for the annealed $\text{Fe}_{1-x}\text{Ru}_x$ alloys the sign of α_1 changes with x – from negative to positive. In the higher impurity concentration region the positive values of the SRO parameter, provide clustering tendencies which may cause the limited solubility of Ru in Fe and the nucleation of a new ruthenium-rich phase with hcp structure. The presence of this paramagnetic phase in annealed $\text{Fe}_{0.95}\text{Ru}_{0.05}$ and $\text{Fe}_{0.92}\text{Ru}_{0.08}$ alloys was revealed with the ^{57}Fe Mössbauer spectra presented in Fig. 2.
4. Finally, in view of the fact that the majority of presented results were obtained for the first time and due to importance of the data it is necessary to confirm our findings by other experimental techniques and theoretical calculations. In particular, X-ray diffraction measurements could confirm precipitation of ruthenium-rich phase with

hcp structure in annealed $\text{Fe}_{1-x}\text{Ru}_x$ samples with $x \geq 0.05$ as well as could provide evidence in support of the predominance of Fe-Ru bonds in the as obtained state.

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