

PHASE ANALYSIS OF IRON CONTAINING CORROSION PRODUCTS AT NPP SECONDARY CIRCUIT USING MÖSSBAUER SPECTROMETRY

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1. Introduction

Steam generator (SG) is generally one of the most important components at all nuclear power plants (NPP) with close impact to safe and long-term operation. Material degradation and corrosion/erosion processes are serious risks for long-term reliable operation. The variability of the properties and the composition of the corrosion products of the stainless Cr-Ni and mild steels in dependence on the NPP operating conditions (temperature, acidity, etc.) is of such range that, it is impossible to determine the properties of the corrosion products for an actual case from the theoretical data only. Since the decontamination processes for the materials of the VVER-440 secondary circuits are in the progress of development, it is necessary to draw the needed information by the measurement and analysis of the real samples [1].

⁵⁷Fe Mössbauer spectroscopy (MS) is a powerful analytical technique for its high sensitivity to changes in the atomic configuration in the near vicinity of the probe isotopes (in this case ⁵⁷Fe). MS measures hyperfine interactions and these provide valuable and often unique information about the magnetic and electronic state of the iron samples, the local crystal symmetry at the iron sites and structural defects [2].

2. Experimental details

Six filter deposits from NPP Dukovany were analysed using MS. All samples were measured at room temperature in transmission geometry using a ⁵⁷Co(Rh) source. Calibration was performed with α -Fe. Hyperfine parameters of the spectra including spectral area (A_{rel}), isomer shift (IS), quadrupole splitting (QS), line width (Γ), as well as hyperfine magnetic field (B_{hf}), were refined using the CONFIT fitting software [3], the accuracy in their determination are of ± 0.5 % for A_{rel} , ± 0.04 mm/s for IS, QS and Γ , and ± 0.5 T for B_{hf} . Hyperfine parameters for identified components (haematite, magnetite, hydroxide) are taken from [4].

3. Results

All measured spectra contains iron in magnetic and also in paramagnetic phases. Magnetic phases contain iron in form of nonstoichiometric magnetite $Fe_{3-x}M_xO_4$, where M_x represents impurities and vacancies which substitute iron in octahedral (B) sites. Another magnetic fraction is haematite α - Fe_2O_3 .

Paramagnetic fractions are presented in the spectra by quadrupole doublets. Their parameters are close to hydroxides (FeOOH) or small, so-called superparamagnetic, particles of iron oxides or hydroxides with the mean diameter of about 10 nm (fig.1). All MS parameters of measured spectra are listed in tab.1.

It should be noted that there is no problem to distinguish among different magnetically ordered phases when they are present in a well crystalline form with low degree (or without) substitution. Both the substitutions and the presence of small superparamagnetic particles make the situation more complicated [5]. In such cases, it is necessary to perform other supplementary measurements at different temperatures down to liquid nitrogen or liquid helium temperatures without and with external magnetic field [6].

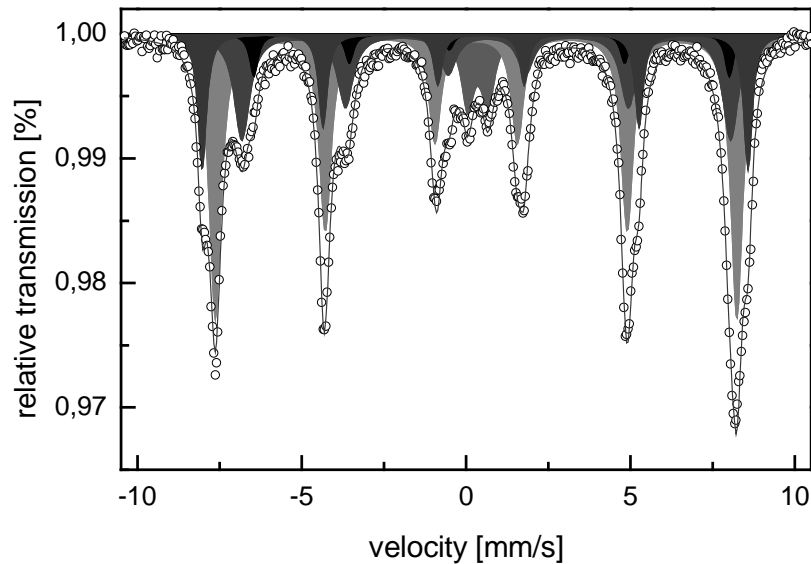


Fig.1: Mössbauer spectrum of sample 2.

Major fraction in all samples consists of magnetically ordered iron oxides, mainly magnetite. Magnetite crystallizes in the cubic inverse spinel structure. The oxygen ions form a closed packed cubic structure with Fe ions localized in two different sites, octahedral and tetrahedral. The tetrahedral sites (A) are occupied by trivalent Fe ions. Tri- and divalent Fe ions occupying the octahedral sites (B) are randomly arranged at room temperature because of electron hopping. At room temperature, when the electron hopping process is fast, the Mössbauer spectrum is characterized by two sextets. The one with the hyperfine magnetic field $B_{\text{hf}} = 48.8$ T and the isomer shift $IS = 0.27$ mm/s relative to α -Fe corresponds to the Fe^{3+} ions at the tetrahedral A sites. The second one with $B_{\text{hf}} = 45.7$ T and $IS = 0.65$ mm/s is the $\text{Fe}^{2.5+}$ - like average signal from the cations at octahedral B sites. Fe^{2+} and Fe^{3+} are indistinguishable due to fast electron transfer (electron hopping), which is faster (~ 1 ns) than the ^{57}Fe excited state lifetime (98 ns). The magnetite unit cell contains eight Fe^{3+} ions and eight Fe^{2+} and Fe^{3+} ions, 16 in total at the B sites, therefore, the intensity ratio $\beta = I(\text{B})/I(\text{A})$ of the two spectral components is a sensitive measure of the stoichiometry. Assuming that the room temperature ratio of the recoil-free fractions $f_{\text{B}}/f_{\text{A}}$ for the B and A sites is 0.97, the intensity ratio β for a perfect stoichiometry should be 1.94 [7]. In non-stoichiometric magnetite, under an excess of oxygen, cation vacancies and substitutions at the B sites are created. The vacancies screen the charge transfer and isolate the hopping process. For each vacancy, five Fe^{3+} ions in octahedral sites become trapped. In the Mössbauer spectrum these trapped Fe^{3+} ions at the octahedral sites and Fe^{3+} ions at tetrahedral sites are indistinguishable without applying an external magnetic field. Therefore, in the spectrum of non-stoichiometric magnetite, intensity transfer from the $\text{Fe}^{2.5+}$ to Fe^{3+} -like components is observed. Therefore, the intensity ratio β decreases markedly with the oxidation process, until the stoichiometry reaches the γ - Fe_2O_3 phase. In our samples the intensity ratio β is far from 1.94 (for perfect stoichiometry), varies from 0.47 up to 0.83. On the other hand, B sites of the magnetite exhibit broad, asymmetric line shape.

Tab. 1. *MS parameters of measured spectra.*

Sample	component	A _{rel} [%]	IS [mm/s]	QS [mm/s]	B _{hf} [mm/s]	Γ [mm/s]
1	haematite	27	0,34	-0,19	51,7	0,28
	A magnetite	42	0,30	-0,05	49,4	0,47
	B magnetite	22	0,63	0,00	45,8	0,65
	hydrooxide	9	0,33	0,58		0,50
2	haematite	16	0,36	-0,18	51,6	0,32
	A magnetite	49	0,30	-0,01	49,3	0,45
	B magnetite	23	0,62	-0,02	46,2	0,58
	B magnetite	5	0,71	0,14	45,0	0,31
	hydrooxide	6	0,36	0,62		0,47
3	haematite	18	0,37	-0,18	51,7	0,36
	A magnetite	41	0,29	-0,01	49,2	0,38
	B magnetite	16	0,52	-0,06	47,0	0,55
	B magnetite	9	0,88	0,17	46,3	0,42
	B magnetite	9	0,60	0,04	45,7	0,33
	hydrooxide	8	0,36	0,64		0,56
4	haematite	23	0,37	-0,13	51,4	0,39
	A magnetite	47	0,31	0,02	49,3	0,42
	B magnetite	6	0,47	-0,04	46,8	0,30
	B magnetite	4	0,67	-0,10	46,3	0,24
	B magnetite	14	0,64	0,14	45,1	0,54
	hydrooxide	6	0,33	0,66		0,47
5	haematite	15	0,37	-0,13	51,8	0,34
	A magnetite	55	0,29	-0,02	49,3	0,43
	B magnetite	10	0,80	0,14	47,3	0,32
	B magnetite	7	0,48	-0,03	46,9	0,32
	B magnetite	9	0,70	0,11	44,4	0,47
	hydrooxide	3	0,33	0,67		0,44
6	haematite	19	0,37	-0,15	51,7	0,33
	A magnetite	57	0,31	-0,01	49,5	0,48
	B magnetite	7	0,53	-0,01	46,7	0,36
	B magnetite	12	0,70	0,05	45,5	0,50
	hydrooxide	5	0,32	0,61		0,50

These observations can be explained by high level of impurities at B sites, probably Cr and Ni, since base steel material contains significant amount of these elements [8]. In order to cover broad, asymmetric line shape of B sites, more than one sextet (1-3) was used in fitting model for B sites (fig.2, tab.1).

4. Conclusion

Six filter deposits from NPP Dukovany were analysed using MS. All measured spectra contain iron in magnetic and also in paramagnetic phases. Magnetic phases contain iron in form of nonstoichiometric magnetite (64-81%) and haematite (15-27%), these phases are represented by sextets with corresponding MS parameters. Paramagnetic fractions are

presented in the spectra by quadrupole doublets. Their parameters are close to hydroxides or superparamagnetic particles of iron oxides or hydroxides (3-9%).

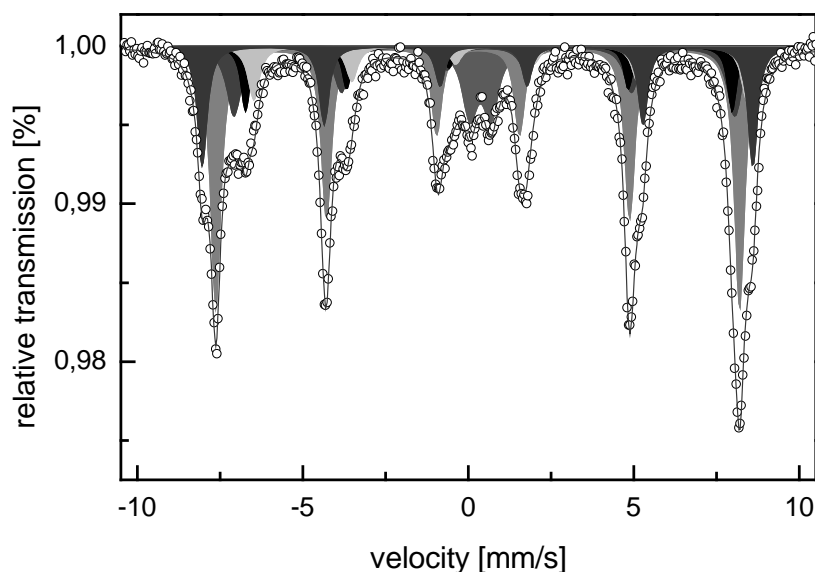


Fig.2: MS spectrum of sample 3, B sites of magnetite are fitted with 3 sextets.

For stoichiometric magnetite, the intensity ratio β should be 1.94. In our samples the intensity ratio β is far from 1.94, varies from 0.47 up to 0.83. Also, B sites of the magnetite exhibit broad, asymmetric line shape. This can be explained by high level of impurities at B sites, probably Cr and Ni, since base steel material contains significant amount of these elements.

Our results confirm good operational experiences and suitable chemical regimes (reduction environment) which results mostly to creation of magnetite (on the level 64% or higher) and small portions of haematite and hydroxides. Additional analyses should be performed in order to better describe and explain nonstoichiometry and impurities observed in magnetite in future work.

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