EXAMINATION OF CORROSION LAYERS IN FEED WATER DISPERSION BOX USING MÖSSBAUER SPECTROSCOPY

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1. Introduction

The variability of the properties and the composition of the corrosion products of the stainless and mild steels in dependence on the conditions (temperature, acidity, etc.) is of such range that, in practice, 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 water-cooled reactor (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 specimens. After five year operation one feed water dispersion box and corresponding distributing pipelines were replaced by new ones in the steam generator (SG) 35 of NPP Bohunice with the aim to analyse their overall stage and corrosion products on the surface. Mössbauer spectroscopy can be useful tool in investigation of corrosion layers [1], therefore it was used in backscattering geometry to identify surface layers of the feed water dispersion box.

2. Experimental details

Two pieces of material were cut off from the feed water dispersion box in order to create samples for backscattering Mössbauer spectroscopy. The samples were measured at room temperature using constant-acceleration Wissel mössbauer spectrometer with the ^{57}Co(Rh) source in backscattering geometry. The isomer shifts were determined relative to natural iron. Hyperfine parameters of the spectra including spectral area (A_{rel}), isomer shift (IS), quadrupole shift/splitting (QS), line width (Γ), as well as hyperfine magnetic field (B_{hf}), were refined using the CONFIT fitting software [2], the accuracy in their determination are of ±1 % for relative area, ±0.02 mm/s for isomer shift, quadrupole shift/splitting, and line width, ±0.5 T for hyperfine field correspondingly.

3. Results

Results from previous analysis [3] confirmed that during operation time a weak oxidation surroundings was in the observed SG35 after 5 years of operation.

Magnetically ordered components of the spectra were formed by two sextets, where Sextet A corresponds to the Fe^{3+} ions in tetrahedral (A) sites and Sextet B corresponds to Fe^{2+} and Fe^{3+} ions in octahedral (B) sites in magnetite spinel structure (fig.1, 2). No traces of other types of magnetically ordered corrosion products were found.

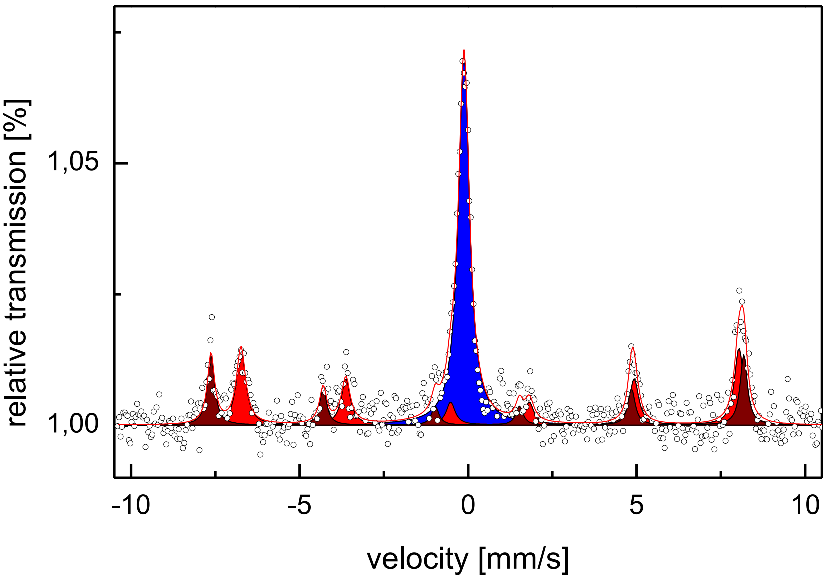

Fig.1. MS spectrum of sample 1. Dark red component represents A-sites of magnetite (Sextet A), red component represents B-sites of magnetite (Sextet B), blue component represents austenitic base material of the feed water dispersion box.

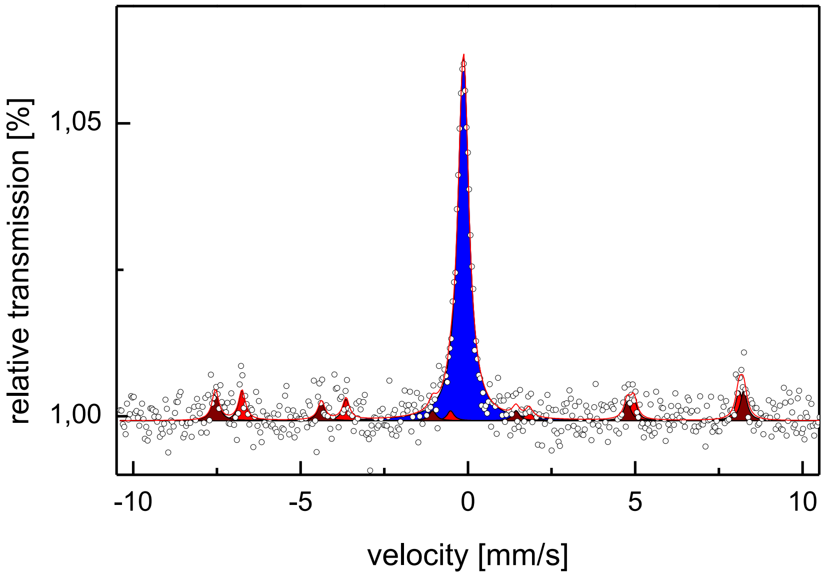

Fig.2. MS spectrum of sample 2. Dark red component represents A-sites of magnetite (Sextet A), red component represents B-sites of magnetite (Sextet B), blue component represents austenitic base material of the feed water dispersion box.

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 an 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_{hf} = 49T 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_{hf} = 46 T and IS = 0.65 mm/s is the $Fe^{2.5+}$ - like average signal from the cations at the octahedral B sites. Fe^{2+} and Fe^{3+} are indistinguishable due to a 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 β = I(B)/I(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_B/ f_A for the B and A sites is 0.97 [4], the intensity ratio β for perfect stoichiometry should be 1.94. 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 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. It should be noted that in our samples the intensity ratio β is far from 1.94 (for perfect stoichiometry), it is 1.48 for sample 1 and 1.07 for sample 2.

In central part of the spectra one can observe dominant singlet feature, which can be assigned as austenitic stainless steel, a base material of the feed water dispersion box.

Tab. 1. MS spectral parameters of sample 1 and 2.

	Component	A_{rel} [%]	IS [mm/s]	QS [mm/s]	B_{hf} [T]	Γ[mm/s]
sample 1	A-magnetite	21	0.27	0.00	49.1	0.26
	B-magnetite	31	0.65	0.00	45.9	0.32
	austenite	48	-0.12	-	-	0.40
	Component	A_{rel} [%]	IS [mm/s]	QS [mm/s]	B_{hf} [T]	Γ[mm/s]
sample 2	A-magnetite	14	0.27	0.16	49.0	0.25
	B-magnetite	15	0.67	0.02	46.2	0.24
	austenite	71	-0.13	-	-	0.40

4. Conclusion

Mössbauer spectroscopy in backscattering geometry was performed on two samples from the the feed water dispersion box in order to analyse corrosion layers at its surface.

In both samples the only form of identified corrosion product is magnetite, it forms 51% of the spectral area of sample 1, and 29% for sample 2. Rest of the spectral areas can be assigned as austenitic stainless steel, a base material of the feed water dispersion box. No traces of other types of magnetically ordered corrosion products were found.

Acknowledgement

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