

## Local and electronic structure of tribological materials: XANES analysis

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**Abstract.** Tribological materials from the wheel and the wheel chock of a railway train were studied. The samples were taken from new and used wheels and wheel chock. Experimental x-ray absorption near edge spectra (XANES) spectra above the Fe L<sub>2,3</sub> edges show the variations in the shape of the Fe L<sub>2,3</sub> edge fine structure, that correspond to the formation of Fe oxidized layer during the process of dry friction. Elemental analysis shows the large variations of element's distribution along the surface within 10 nm depth of damaged sample.

### 1. Introduction

Train is the safest transport. A big work was made to minimize the possibility of crash. But there still some problems that make a lot of harm to railway men. One of them is connected with brake blocks. Nowadays soft materials for brake blocks are preferable, such as composites. They consist of graphite, synthetic rubber, aluminum oxide and sulfur compounds. Such contents significantly increase the lifetime of wheel but lead to unexpected consequences. During exploitation specific defects arise, because composite materials are aggressive for steel [1]. These defects arise from redistribution of temperature fields [2] on the wheel rim under friction. So, radial cracks, metal dislocations appear and wheel can derail [3].

In order to investigate, what chemical reactions take place during the process of friction, the x-ray absorption spectra of corresponding materials were measured. This methodic was already successfully applied to exploration of complex chemical interactions between additives in engine oil and metallic surfaces [4]. Development of a stable tribolayer has been suggested to result in decreases in the wear rate and coefficient of friction for the unlubricated sliding of metals [5]. Process of direct friction of nanoparticles was already studied by TEM [6], where the importance of interdiffusion between wearing surfaces was shown. Here we apply the XANES spectroscopy for analysis of tribolayer formation during dry friction experiments of composite brake block and rail wheel.

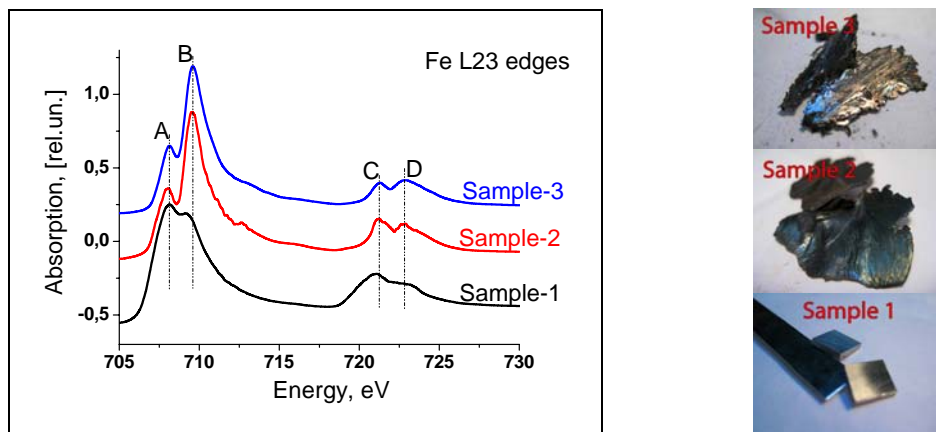
### 2. Experiment

The samples from dry friction experiment are shown on the right panel of Figure 1. Sample1 is the pure steel from the wheel far from its surface (the composition of steel is ~0.6% C, ~0.3% Si, ~1% Mn and the remainder is primarily Fe). Sample2 and Sample3 are damaged steel during friction process of steel with brake block. High temperature and pressure in tribological contact lead to the adhesive transfer of wheel material to the brake block. Sample2 is the damaged wheel material, taken from the brake block, while Sample3 was taken from the damaged surface of a wheel. Damaged steel after

friction has scaled structure like mica. Millimeter-sized scales were carefully subtracted from the samples shown in Figure1 for XANES experiments. Spectra were recorded at Russian-German beam line RGLB in high vacuum chamber. All samples were maintained on copper sample holder and a good conducting contact was provided between sample and sample holder. Total electron yield (TEY) signal from the sample was used for measurements. Size of x-ray beam in experiment was about  $50 \times 100 \mu\text{m}^2$  with energy resolution on the Fe L2,3 edge  $E/\Delta E \sim 5000$ . Elemental analysis of the samples was carried out by means of laser induced breakdown spectroscopy (LIBS) [7].

### 3. Results and discussion

Figure1 shows the Fe L2,3 XANES spectra for initial state of steel and steel after the dry tribological test with composite material of brake block. We can clearly identify the wear effects on the steel that occur during the test. Relative intensities of peaks A and B identify the chemical state of Fe atoms [8] within thin layer near surface. Signal from the Fe L2,3 edge TEY measurements comes from the depth about 300nm, thus observed changes in XANES spectrum result from the reaction that take place in the layer within 300nm from the surface. Sample-2 and Sample-3 have almost identical spectra with small changes in relative intensities of features C and D.



**Figure 1.** XANES spectra above the Fe L2,3 edges for the initial state of the wheel steel (Sample-1), damaged steel after friction test, adhered to the brake block (Sample-2) and damaged steel after friction test, left on the wheel (Sample-3)

Table 1 shows the elemental analysis for Cr, Ni, Cu and Mn for the studied samples. Amount of these elements tells us how steel state is changed during its exploitation. This information is additional to the information about Fe atoms chemical state, analyzed with x-ray absorption spectroscopy. One can notice that Sample3 was extremely inhomogeneous, which can be seen from intervals for fractions. Thus we have studied different points on a sample to find out does it sensitive to heterogeneity of the surface, but the XANES spectrum above the Fe L2,3 edge was insensitive to these changes. This fact authenticates that elemental content's variations occurs on the small depth (several nanometers of sensitive depth for laser induced breakdown spectroscopy [10]), because sensitive depth for TEY mode of measurements on the Fe L2,3 edge is several times larger.

**Table 1.** Fractions of Cr, Ni, Cu and Mn atoms in samples.

	Cr(%)	Ni(%)	Cu(%)	Mn(%)
Sample1	0.25	0.2	0.17	1.2
Sample2	0.1	0.38	0.17	3
Sample3	0.03-0.25	0.02-0.5	0.03-0.13	0.6-2.8

Figure 2 shows the comparison of reference materials spectra with our samples.

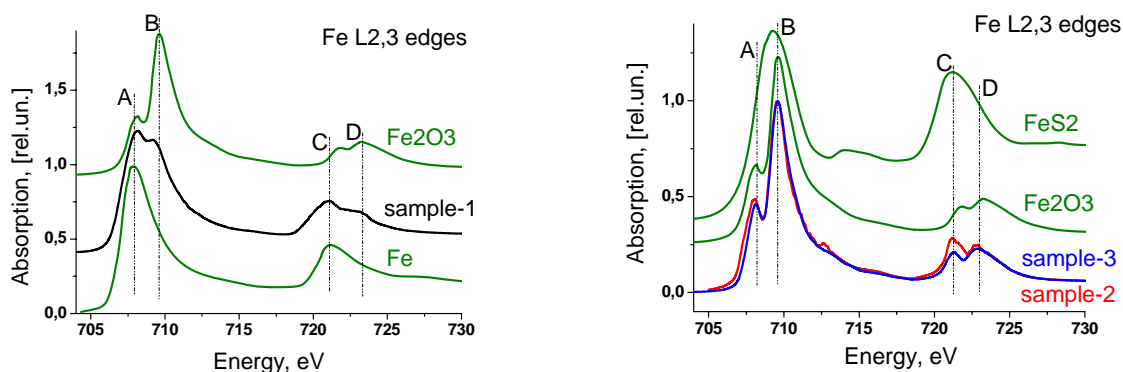


Figure 2. XANES spectra above the Fe L2,3 edges for the Sample-1 (left panel) and Sample-2, Sample-3 (right panel). Spectra of reference materials are shown in green color. Energy positions of peaks A,B,C,D are the same as on Fig.1

Left panel of Figure 2 reveals the fact that surface of initial steel, named as Sample-1, has an oxide layer. Thus XANES spectrum of Sample-1 is the superposition of pure Fe and Fe<sub>2</sub>O<sub>3</sub>. As a result of friction process a wheel is heated to high temperature and its surface has a contact with the air, so more and more Fe atoms oxidize, that can be seen from the relative intensities of features A and B on the right panel of Figure2. Some of scales from damaged wheel adhere to the brake block. We suppose that certain fraction of Fe atoms react with sulfur atoms of composite material, that diffuse into the wheel material due to high temperature from volume of brake block. But the concentration of Fe-sulphur compounds in Sample-2 and Sample-3 is small, that can be seen from right panel of Figure 2 (only spectrum for FeS<sub>2</sub> is shown that is most likely to be formed). The calculations of Fe L2,3 edges within multiplet theory [9] are in progress now.

#### 4. Conclusions

Tribological materials from the wheel and the wheel chock of a railway train were studied. Experimental x-ray absorption near edge spectra (XANES) spectra above the Fe L2,3 edges show the variations in the shape of the Fe L 2,3 edge fine structure – thus, indicating the formation of damaged area within 300 nm below the surface. Elemental analysis shows the large variations of element's distribution along the surface within 10 nm sensitive depth for LIBS of damaged sample. This reveals the fact of highly heterogeneous nature of tribological layer, formed during the process of dry friction of wheel steel and composite material of brake block.

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