MÖSSBAUER SPECTROSCOPY SYSTEM WITH INCREASED PERFORMANCE AND FLEXIBILITY – UTILIZATION IN MATERIAL RESEARCH

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1. Introduction

Measurement efficiency of the modern spectroscopy systems is determined by the quality of the hardware used to acquire signals and by the software used to analyse data. Up-to-date systems process data with zero data amount loss. In this paper, a new concept of Mössbauer spectrometer used for material research is presented.

Mössbauer spectrometer consists of spectrometric bench (radioactive source, velocity transducer, sample holder, and gamma-ray detector), measurement hardware, and control application. The Mössbauer effect is based on recoilless nuclear emission and resonant absorption of gamma-rays in the sample. The Mössbauer spectra acquisition is performed by gamma-ray intensity measurement together with radioactive source motion control causing the Doppler shift of the gamma-ray photons [1,2]. Mainly the synchronization between the detector signal acquisition and the source velocity motion processes is of crucial importance in this system. High precision execution of the detector signal analysis and the source movement control tasks is reflected in the quality of the system. The spectra accumulation process is based on the periodical summation of the appropriate data from each repetitive movement period for hours or days.

Employing Virtual Instrumentation (VI) concept (implemented in LabVIEW programming environment) for developing measurement instruments, a unique Mössbauer spectrometer has been built [3–8]. Besides the commercial products, we use other own developed units (gamma-ray detectors, signal amplifiers, velocity transducers...). For many years, we apply the VI concept in the design of our spectrometers, and with new functions, techniques, and processes implemented in LabVIEW, the system is improved continually.

The improved Mössbauer spectrometer measurement system offers a new approach to Mössbauer spectrometer construction. By detailed analyses and optimization we designed a high-performance system, which is generally able to save the measurement time. VI solution significantly increases the system performance and flexibility reflected in easy customisation for using cryostats, furnaces and other equipment necessary for a complex sample analysis.

2. Mössbauer Spectroscopy

Transmission Mössbauer Spectroscopy (TMS) is used for structural, phase, and magnetic characterization of mostly iron containing samples (commonly Fe, Sn, Ni, Zn, Eu etc.). Mössbauer Spectroscopy (MS) is a highly element selective method and in details it provides determination and quantification of phase composition of samples including amorphous and nanocrystalline; determination of valence and spin states of iron atoms, differentiation of structure positions of iron atoms, stoichiometry examination of cation

substitution; magnetic state determination and local configuration of magnetic moments of the atoms; measurement of temperature dependences, measurement in external magnetic field; determination of magnetic properties including temperatures of magnetic transitions; and study of mechanism and kinetics of reactions in solid phase, phase transformations. The spectrometric bench for room temperature TMS measurements is presented in Figure 1.
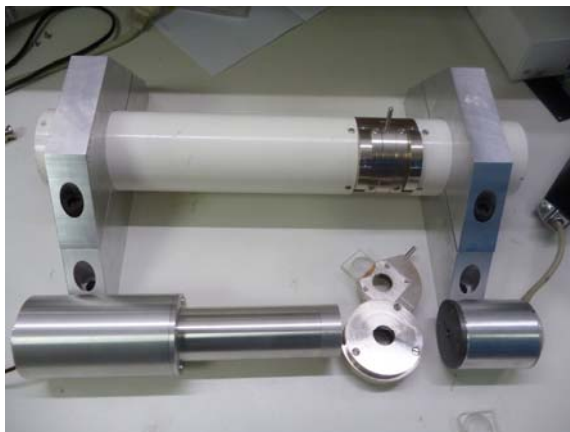

Fig.1: *Mössbauer spectrometric bench for room temperature measurements.*

This compact bench allows performing a precise analysis of the samples in TMS mode. The main parts include a gamma-ray detector, sample holder with collimators and velocity transducer.

Conversion Electron Mössbauer Spectroscopy (CEMS) and Conversion X-ray Mössbauer Spectroscopy (CXMS) are a pair of methods, which help investigate Mössbauer radiation in the backscattering geometry. Considering the energy losses during non-elastic collisions in the examined material is the scope of conversion electrons, or conversion X-ray radiation (originating from the sample surface of ~300 nm, resp. 1–10 μm thickness). Therefore, this technique is suitable for studying thin films and surface phase composition of the materials. The spectrometric bench for room temperature CEMS/CXMS/TMS measurements is presented in Figure 2.

Fig.2: *Mössbauer spectrometric bench for room temperature CEMS/CXMS/TMS measurements.*

All methods act as supporting methods in physics of materials, nanotechnology, metallurgy, chemistry, archaeometry, geology, and mineralogy.

If cryostats and furnaces are included, it is possible to analyse samples at different conditions, such as low temperatures (from 1.5 up to 300 K) and high temperatures (up to

1000 °C, with a possibility of inert atmosphere) and under an external magnetic field of up to 8 T (in the low temperature mode) [8]. The samples can be in the form of powder as well as thin films (plates). In the case of bigger compact samples, a backscattering mode of Mössbauer spectroscopy can be applied for characterization of the surface of the sample.

3. An experimental study with the CEMS mode

As a representative example of power of ^{57}Fe Conversion Electron Mössbauer Spectroscopy, we present a task to determine residual amount of austenite (gamma-Fe(C) phase) in the sample of stainless steel. Austenite is used to be formed during a manufacture of stainless steel and its higher content can affect mechanical properties of the sample. The sample was too thick to analyse it by conventional TMS, therefore CEMS was used. With respect to expected homogenous phase composition within the whole volume of the sample, CEMS measurement could provide a characterization of all the sample, despite the data were collected only from a thin surface layer (less than 300 nm). The CEMS spectrum, represented by experimental points, overall fits, and individual fitted components, is depicted in Figure 3. Table 1 provides a summary of the values of the Mössbauer parameters and assignments of individual components.
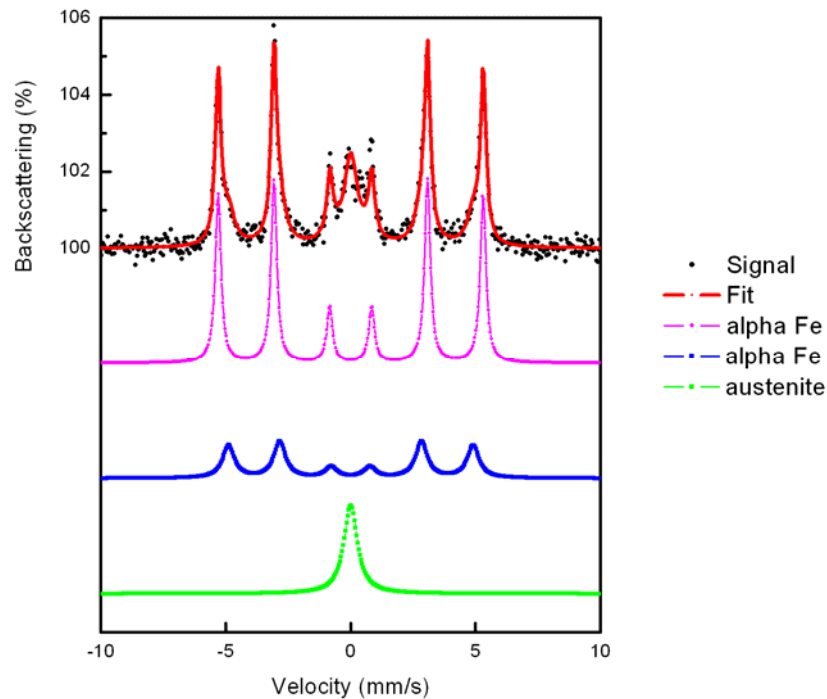

Fig.3: *Mössbauer (CEMS) spectrum of stainless steel sample.*

Tab. 1. *Mössbauer parameters and relative contents of components identified in the CEMS spectrum.*

Phase	component	Mössbauer parameter				
		A (%) ± 0.5	δ (mm/s) ± 0.01	ΔE_Q (mm/s) ± 0.01	B_{hf} (T) ± 0.3	Γ (mm/s) ± 0.01
alpha-Fe	sextet	59.7	0.00	0.00	33.0	0.27
alpha-Fe	sextet	24.9	0.01	0.01	30.5	0.57
austenite	singlet	15.5	0.00	-	-	0.65

In Table 1 δ is the isomer shift, ΔE_Q is the quadrupole splitting, B_{hf} is the hyperfine magnetic field, Γ is the linewidth, and A is the area of the subspectrum. The results show that Mössbauer spectroscopy is able to discern and quantify two different alpha zero valent iron (alpha-Fe) based phases in the stainless steel. These two phases are represented by two sextets with almost the same values of isomer shift and quadrupole splitting but differing in the hyperfine magnetic field. In addition to the major (alpha-Fe) phases, there are about 15.5% of gamma-Fe, which is expected to be in a solid mixture with carbon forming the austenite phase. X-ray powder diffraction could also give a quantification of austenite phase, however, not so precisely like Mössbauer spectroscopy.

4. Discussion

Main advantage of the presented concept is utilization of measurement hardware type. In this case, Windows-based computer, high-speed digitizer, and function generator are used to realize signal acquisition. A control application performing data analysis and spectra accumulation with user friendly application was then developed. The main application is hardware-platform independent, since it is usable with USB, PCI, PCIe, PXI, and PXIe modules used for signal acquisition, and is able to apply it in different Mössbauer techniques (TMS, CEMS, CXMS, other backscattering, etc.).

The control application was optimized for reaching zero dead-time of measurement by implementation of parallel data processing and by using of fast pulse processing algorithms in the MCA mode of the digitizer.

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