

IDENTIFICATION OF SURFACE LAYERS OF EARLY MEDIEVAL AGE AXE¹J. Dekan^{2,*}, M. Miglierini^{*}, D. Staššiková-Štukovská[‡]^{*}*Department of Nuclear Physics and Technology, Slovak University of Technology, Faculty of Electrical Engineering and Information Technology, Ilkovičova 3, 812 19 Bratislava, Slovakia*[‡]*Institute of Archaeology, Slovak Academy of Sciences, Akademická 2, 949 21 Nitra, Slovakia*

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We have used Mössbauer spectrometry for a study of an iron axe. Two experimental techniques were applied: (a) non-destructive measurements performed in backscattering geometry, and (b) identification of small pieces of surface covering substance which has accidentally disintegrated with the investigated axe. These measurements were performed at room and also at low (77 K) temperature. Presence of corrosion products including goethite, magnetite and lepidocrocite was confirmed.

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1 Introduction

Mössbauer spectrometry is a sensitive tool for identification of even subtle amounts of iron, iron oxides, and hydroxides. Owing to this feature, Mössbauer spectrometry finds a broad involvement in the investigation of archaeological artefacts [1]. It is employed for material analysis as well as for technological studies. The material analysis helps not only with the characterization of ancient objects from the point of view of the materials used but it often enables to identify the technical treatment or the manufacturing of the objects.

The review work of Stievano *et al.* [2] provides a description of development of Mössbauer effect method to the investigation of archaeological artefacts in Italy from 1980 on. It summarises some examples on the characterisation of clays and ceramic minerals comprising analysis of firing techniques, characterisation of less common materials of archaeological interest such as paintings (ochres) and other iron containing species. Applications of Mössbauer spectrometry to the study of ancient glasses helps in the elucidation of the pre-industrial glass manufacture technology [3].

Mössbauer spectrometry was found useful in the identification of iron-containing minerals in the investigation of corrosion products on the Delhi iron pillar [4] or on an Etruscan axe [5].

This work reports on the results of investigations of an ancient axe, which was unearthed on a territory of the archaeological excavation site near the village Borovce (Piešťany district, Slovakia). Special emphasis is put on the identification of Fe-containing phases.

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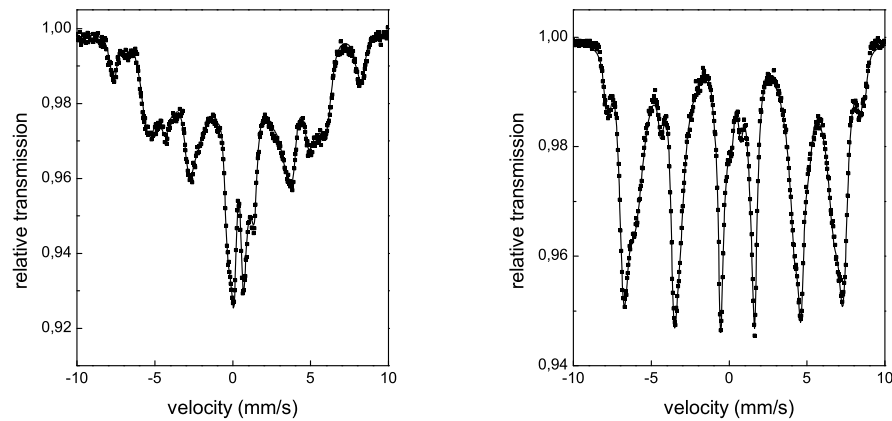


Fig. 1. Mössbauer spectra of sample A recorded at 300 K (left) and 77 K (right).

2 Experimental details

^{57}Fe Mössbauer spectrometry was employed in transmission geometry at room (RT: 300 K) and liquid nitrogen (LNT: 77 K) temperature as well as in backscattering geometry using a $^{57}\text{Co}(\text{Rh})$ source. Calibration was performed by a $\alpha - \text{Fe}$ foil and isomer shift values are given relative to the Mössbauer spectrum of $\alpha - \text{Fe}$ taken at RT. Evaluation of hyperfine parameters was done by the help of the CONFITA fitting program [6].

We have analyzed specimens taken from the surface of the iron axe. Two sets of samples were investigated. Sample *A* was prepared from surface corrosion fragments which were mechanically ground into fine powder. Sample *B* was a compact piece of surface covering substance (dimensions about $4 \times 4 \times 5 \text{ mm}^3$) which has accidentally disintegrated with the investigated axe. Sample *B* was incorporated into a holder made from epoxy resin. The inner part of sample *B*, which was originally in direct contact with the body of the axe, was polished for the sake of backscattering Mössbauer effect mode. A thin foil (about $250 \mu\text{m}$) was cut from sample *B* and measured in transmission geometry.

3 Results and Discussion

3.1 Sample A - powdered corrosion fragments

Examples of transmission Mössbauer spectra of the powder sample *A* recorded at RT and LNT are shown in Fig. 1. Mössbauer spectra are decomposed into four components. Two sextets of absorption lines are ascribed to A- and B-sites of magnetite (Fe_3O_4). At low temperature these two sextets are unresolved. The broad spectral components were reconstructed by distributions of

Tab. 1. Mossbauer spectra parameters including relative area, A, isomer shift, IS, quadrupole shift, QS, and hyperfine magnetic field, B, of sample A recorded at 300 K up and 77 K (bottom).

Component	A [%]	IS [mm/s]	QS [mm/s]	B [T]
A-magnetite	10	0.3	0	49.4
B-magnetite	2	0.51	0	45.82
goethite	74	0.1 ÷ 0.39	-0.28 ÷ -0.18	22.6 ÷ 35.91
lepidocrocite	14	0.38	0.57	
Component	A [%]	IS [mm/s]	QS [mm/s]	B [T]
A-magnetite	2	0.4	0	51.88
B-magnetite	6	0.34	0	50.14
goethite	88	0.4 ÷ 0.47	-0.24 ÷ -0.1	33.3 ÷ 43.85
lepidocrocite	4	0.44	0	0.59

hyperfine magnetic fields and according to the spectral parameters they are assigned to goethite (α – FeOOH). The central doublet represents lepidocrocite (γ – FeOOH). Magnetite, goethite, and lepidocrocite are products of corrosion [7] and the observed parameters are listed in Table 1.

It should be noted that no traces of the basic material, i.e. metallic iron were revealed. This was more or less expected because the powder sample *A* was prepared from small fragments that belonged to the surface rust and the whole surface is heavily corroded. It should be noted that the investigated material comes from Early Medieval Age and was exposed to the surrounding environment for about 1000 years.

3.2 Sample B - bulky piece of substance covering the surface of the iron axe

Sample *B* was investigated by the help of two Mössbauer effect techniques. First of all, a backscattering mode which enables examination of bulky, *i.e.* non-transparent (for gamma radiation) objects was applied. This technique provides information by means of de-excited gamma photons emitted by resonant iron atoms located in the depth of several tens of micrometers under the surface of the tested sample.

Collection of experimental data in backscattering geometry is extremely long lasting (several days). On the other hand, there is no need for special sample preparation and the investigated object can be examined as it is. To improve the statistics of measurement we have cut a thin disc from the piece of sample *B* embedded in an epoxy holder. Mössbauer spectra of sample *B* obtained by both experimental techniques are illustrated in Fig. 2. Mirror-like patterns confirm structural identity of the bulk (transmission spectrum in Fig. 2a) and surface (emission spectrum in Fig. 2b) regions. In both spectra, a presence of goethite (α – FeOOH) and lepidocrocite (γ – FeOOH) was identified. The corresponding Mössbauer parameters exhibit only minor deviations (within experimental error). Because no other spectral component was found in sample *B* we can conclude that this piece of surface covering substance is in fact very old rust.

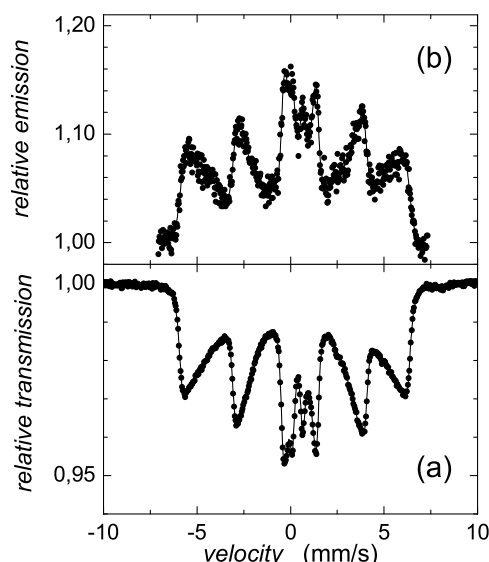


Fig. 2. Room temperature Mössbauer spectra of the sample B recorded in (a) transmission and (b) backscattering geometry.

4 Conclusion

We have investigated fragments of iron axe from Early Middle Age found in the grave No. 221 in the archaeological excavation site near Borovce (Piešťany district, Slovakia). Two types of samples were examined: debris of surface rust and a compact piece of surface covering substance.

With the aim to shed some light on the origin of the surface layers of the iron axe we have employed Mössbauer spectrometry for identification of iron-containing phases. Room and liquid nitrogen temperature experiments were performed in transmission as well as backscattering geometry. The obtained results confirm presence of corrosion products such as magnetite, goethite, and lepidocrocite in both types of samples. No traces of other phases were revealed. The results of Gauzzi *et al.* [5] from the study of Etruscan axe show that the axe is constituted mainly of goethite as oxidation product and traces of ancient metal are no longer detectable. Taking our results into account a conclusion can be proposed that the investigated pieces of the iron axe are products of long-lasting corrosion and were not applied to the surface of the axe by intention.

Nevertheless, it should be noted that Mössbauer spectrometry is sensitive only to substances which contain at least fractions of atomic percent of iron as either a constitution element or as an impurity. Having this in mind we shall continue this research by examining other parts of the surface as well as the body of this archaeological artefact. To support the results obtained by Mössbauer spectrometry also additional analytical methods should be employed.

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