

Mössbauer study of oxide phase distributions in rust formed on steel constructions near the Black Sea in Sochi

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Abstract The phase composition of the intermediate oxide layers formed on elements of steel structures at different positions relative to the sea water of the Black Sea near Sochi are investigated. The differences of the phase composition of these oxide layers are shown, depending on the location of the design details in relation to the sea and the abundancies of certain types of oxides in the studied layers are discussed.

Keywords Mossbauer effect · Steel corrosion · Phase analyze

1 Introduction

The corrosion of steel constructions near the Black Sea in the Sochi region is interesting from scientific and applied technical point of view. There are many buildings and constructions, which were built more then 50 years ago and also buildings constructed recently for the Olympics in 2014. These buildings are at different distances from the seawater. Some of the structures are washed by sea water during storms, while other parts are exposed to the vapors of sea air and sea spray. On the surface of steel structures oxide films are formed whose growth and phase composition depends on the degree of impact such as the intensity and duration. It is interesting to investigate the influence of the sea atmosphere on steel constructions and buildings that are disposed in different places relative to the sea in distance

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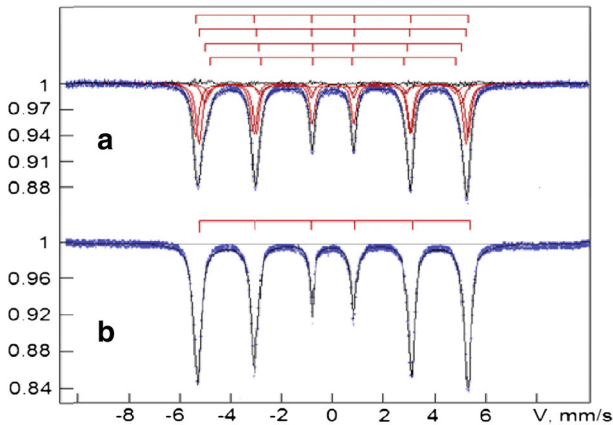


Fig. 1 Mossbauer spectra of: (a) the alloy under study, and (b) alpha-iron

and orientation during such a long time. Mössbauer spectroscopy is used for the identification of the nature of the oxides, as well as of the fraction of each of them in the corrosion products of steel structures on the beach of the Black Sea near Sochi. Such information is necessary to understand the nature of corrosion processes and to evaluate the residual life-time. Such information will be useful to develop methods and techniques to improve the durability of steel.

The oxide films, formed on steel structures under influence of sea atmosphere during more than 50 years, are investigated in this paper. For the investigations samples were taken from structures that were in periodic contact with water, and also samples from structures that were under the influence of sea wind only. Bearing columns made from steel were chosen as structures. These square columns supported sun beds on a beach. This paper is the continuation of previous investigations [1].

2 Sample preparation and experimental methods

Samples were taken from different parts of the steel structures. The total thickness of the corrosion layers varies between 2.5 and 3.0 mm. The corrosion products were scraped from middle layers (~1.5 mm deep). Absorbers with thickness $\sim 30 \div 50$ mg/cm² were prepared from the scraped products using known technology [2]. Mössbauer measurements were performed using a ⁵⁷Co(Cr) source with a spectrometer in transmission mode. The spectrometer was calibrated with an α -Fe foil spectrum at room temperature. All spectra are obtained at room temperature. The spectra were fitted using programs UnivemMS, MSTools [3].

3 Results and discussion

The spectrum of the metal part on of the steel structure is shown in Fig. 1 a. and spectrum of alpha-iron is shown in Fig. 1 b. The spectra of oxide films are shown in Figs. 2 and 3 and the results of their fitting in Fig. 4.

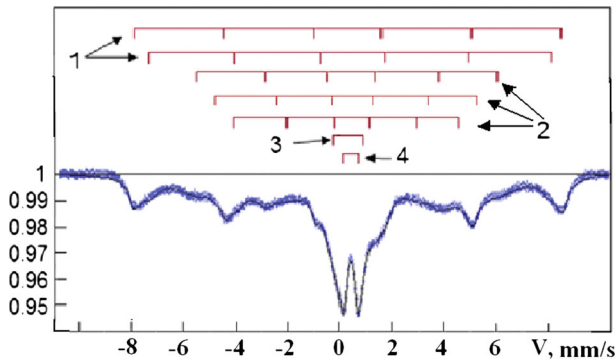


Fig. 2 Mössbauer spectra of the corrosion products formed on a detail of a construction element that was located at the distance of 10 m from sea. Oxides were scraped from the middle layer of the side looking at the sea ($T = 298\text{ K}$). 1 - $\gamma\text{-Fe}_2\text{O}_3$, 2 - $\alpha\text{-FeOOH(m)}$, 3 - $\beta\text{-FeOOH}$, 4 - $\gamma\text{-FeOOH} + \alpha\text{-FeOOH(s)} + \gamma\text{-Fe}_2\text{O}_3\text{(s)}$

The analysis of the spectrum of the original carbon steel (taken from one element of construction) (Fig. 1.a) and alpha iron (Fig. 1 b) shows that the used steel has a complex structural-phase state. The complexity is due the long time influence of the sea atmosphere and the deformation stress and, probably, the influence of the alloying elements. This conclusion follows from the fact that in spectrum Fig. 1 a in addition to the lines of pure iron, having a value of the hyperfine magnetic splitting $H_{\text{eff}} = 33.0\text{ T}$, there are lines with lower values of H_{eff} , than for alpha-iron. This may be caused by the replacement of some iron atoms by other elements in the alloy under study (such as Mn, Si, P, S .Cr, Ni, Cu) or by the presence of defects as vacancies and dislocations in the nearest neighborhood of the iron atoms.

The analysis of the oxides present in the spectra (Figs. 2 and 3) shows that they are a superposition of lines belonging to hyperfine magnetic splittings of magnetic phases and lines of quadrupole splittings of paramagnetic phases. The Mössbauer spectra parameters obtained in papers [1, 4] were used for fitting. For the identification of phases and compounds Mössbauer spectra parameters such as values of the hyperfine magnetic field H_{eff} , quadrupole splitting QS, isomers shift IS and areas of spectra lines are used.

One can see that the lines of the magnetic phases are broadened and changed in intensity. This means that the compositions of the iron compounds are not uniform in the oxide film and that the compound distribution depends on the distance to the sea. The spectra in Figs. 2 and 3 were therefore fitted to iron components having broadened Lorentzian lines. The fit parameters agreed with those published by Filippov [1] and Cook [4–6]. In the investigated oxide films the following compounds of iron are identified: $\gamma\text{-Fe}_2\text{O}_3$ (maghemite), $\alpha\text{-FeOOH}$ (goethite) (m), $\gamma\text{-FeOOH}$ (lepidocrocite), $\alpha\text{-FeOOH}$ (goethite) (s) ($IS=0.38 \pm 0.02\text{ mm/s}$, $QS=0.58 \pm 0.02\text{ mm/s}$), $\beta\text{-FeOOH}$ (akaganeite) ($IS=0.56 \pm 0.02\text{ mm/s}$, $QS=1.58 \pm 0.02\text{ mm/s}$) (where m-massive, s- superparamagnetic). In the central part of the spectra (Figs. 2 and 3) paramagnetic compounds such as $\alpha\text{-FeOOH}$ (s), γFeOOH ($IS=0.38 \pm 0.02\text{ mm/s}$, $QS=0.62\text{-}0.99\text{ mm/s}$) and $\gamma\text{-Fe}_2\text{O}_3$ are introduced without identification of their relative components.

The spectrum of the sample located at a distance of 10 m from the sea (Fig. 2) has distinctions in the ratio of the separate compounds of iron in comparison with those of the sample located closer to seawater (Fig. 3). These differences between the spectral shapes in

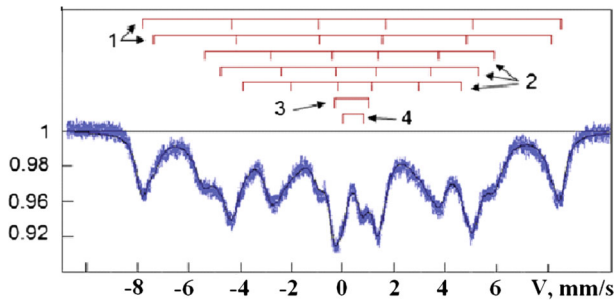


Fig. 3 Mössbauer spectra of corrosion products formed on a detail of a construction element that was in periodic contact with seawater during storms. Oxides found in the middle layer of this sample: 1 - $\gamma\text{-Fe}_2\text{O}_3$, 2 - $\alpha\text{-FeOOH(m)}$, 3 $\beta\text{-FeOOH}$, 4 $\gamma\text{-FeOOH} + \alpha\text{-FeOOH(s)} + \gamma\text{-Fe}_2\text{O}_3\text{(s)}$

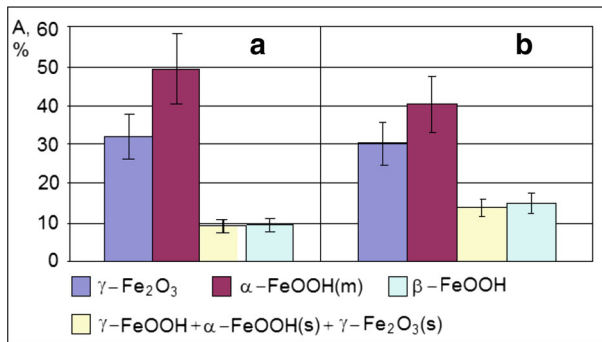


Fig. 4 Diagram of the phase distribution in the middle depth of the oxide layer of the samples which are : (a) in periodic contact with seawater; (b) at the distance of 10 m from sea (side looking at sea)

Figs. 2 and 3 show the influence of the distance from the seawater on corrosion processes in steels.

Doublets correspond to phases such as lepidocrocite ($\gamma\text{-FeOOH}$), akaganeite (βFeOOH) and possibly superparamagnetic phases goethite ($\alpha\text{-FeOOH(s)}$) and maghemite ($\gamma\text{-Fe}_2\text{O}_3\text{(s)}$). With increasing distance from the sea, the amount of magnetic goethite and phases corresponding to doublets have increased.

Since doublets are mainly caused by the presence of lepidocrocite and akaganeite, we can conclude that superparamagnetic goethite and magnetite phases, corresponding to a particle size of the order of $8\div 15$ nm and promoting the formation of a protective layer, exist only in very small amounts in the oxide layer of the sample in the vicinity of seawater. This means that the protective layer does not exist in this part of the construction. The active destruction process of the material continues at this point

With the increase of distance from the sea there is an increase of doublet areas in the spectrum (Figs. 2, 3 and 4). This fact confirms the existence of phases forming a protective layer, for example $\alpha\text{-FeOOH(s)}$. The nanophase goethite is known to be critical in the formation of the protective patina on weathering steel [4]. As our steel contains some amounts of silicon, nickel, copper and chromium it is possible to create a protective layer in the corrosion products formed on a detail of a construction that was located at the distance of 10 m from sea.

Thus it is possible to confirm that basic research of corrosion in steel constructions exposed to the external environment is possible. The study of the influence of corrosion products on steel requires an accurate identification of corrosion products and a determination of the weight fraction of each phase. Mossbauer spectroscopy allows to study the corrosion coating and unambiguously identify various oxides, because each phase has a unique set of hyperfine parameters. The weight proportion of each oxide can be determined through the area of the Mössbauer spectra components.

4 Conclusion

The influence of the Black Sea water and atmosphere on details of steel beach constructions was investigated.

In the oxide films from the surface of these constructions the presence of the phases Fe^{2+} and Fe^{3+} in different types of compounds such as $\gamma\text{-Fe}_2\text{O}_3$, Fe_3O_4 , (α -, β -, γ -) FeOOH in magnetic and superparamagnetic states are observed.

The relative concentrations of the various oxide compounds in investigated layers are determined.

It is found that on structures that were in periodic contact with water, a protective layer was not created, in contrast to sides of structures located at 10 m from the sea, where in a middle depth superparamagnetic $\alpha\text{-FeOOH}$ (goethite) can create a protective layer.

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