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Investigation of Corrosion Inhibitors by Nuclear Quadrupole Resonance Relaxometry Method

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ABSTRACT: The changes taking place with the corrosion-resistant coating, but not the state of the surface subjected to corrosion are investigated in this paper in contrast to traditional approaches. We used the method of nitrogen relaxometry NQR and multi-exponential inversion of decay of longitudinal and transverse components of the nuclear magnetization is applied for the first time for this purpose. The results of experimental studies of changes in the distributions of spin-spin and spin-lattice relaxation of crystallite powder of sodium nitrite and urotropin, the mixture of which is used as a corrosion inhibitor of ferrous metals are considered.

1 INTRODUCTION

There is a very large number of ways to protect the materials from corrosion. If you analyze all the compounds that are used in various countries for protection of ferrous alloys corrosion by volatile compounds, we can see that they all contain sodium nitrite or nitrite ions belonging to the other substances.

Protective properties of sodium nitrite $NaNO_2$, found for a long time allowing to use it as an inhibitor of the atmospheric corrosion of metals, for their preservation and storage, flushing conduits, etc. The protective effect of the inhibitors is due to their molecules or ions adsorbed on the metal surface and the corrosion rate is reduced catalytically.

To protect ferrous metals against atmospheric corrosion in the Russian Federation, for example, is widely used inhibited wrapping paper that contains an inhibitor UNI (a mixture of sodium nitrite and hexamine), (GOST 16295-93 1993). Sodium nitrite - a non-volatile inhibitor, urotropine - volatile and low toxicity inhibitor. Due to direct contact (sodium nitrite) and release fumes (urotropine) anticorrosive paper protects the packaged goods from corrosion.

One can use viscous solutions of sodium nitrite for long term storage. This is a contact inhibitor deposited on the surface of the object. An adding of sodium nitrite into the aqueous solutions, that is a substance increasing the viscosity significantly increases the efficiency and lengthens the time for the shields when storing products in any climatic conditions.

This prevents drying of a solution of sodium nitrite and falling of salt crystals from the surface of the metal and reduces the refluxing solution due to liquefaction at high humidity.

However, sodium nitrite, being a good inhibitor for steel, destroys the solder, i.e., in systems containing a number of heterogeneous electrochemical attitude of metals and alloys (steel, zinc, brass, solder, cast iron, aluminium), cannot be applied singly.

In the paper (Hassan et al. 2013), sodium nitrite was studied as an inhibitor for the protection of reinforcing steel in concrete from corrosion. The purpose of this study was an attempt to understand the mechanism by which sodium nitrite contributes to reducing the rate of corrosion on the surface of carbon steel, depending on pH and the presence of chloride in the system. In the literature (Rosenberg & Gaidis 1979) it have suggested that nitrite undergoes a chemical reaction with the divalent iron:

$$2Fe^{+2} + 2OH^- + 2NO_2^- \rightarrow 2NO + Fe_2O_3 + H_2O \qquad (1)$$

This reaction forms the barrier film of oxide Fe_2O_3 on the metal surface. The film protects from corrosion. The corrosion rate largely depends on the pH of the solution. The presence of chlorides increases the reaction rate of corrosion by acting as a catalyst. Nitrite ions act as inhibitors by increasing the rate of the barrier iron oxide film formation. Increasing temperature leads to the desorption of adsorbed sodium nitrite on the surface of the steel and reduces the effectiveness of the inhibitor.

The aim of this work was to study changes in the relaxation times distribution of nuclear quadrupole resonance (NQR) in microscopic inhibitor after its contact with the surface of inhibited black metal. This approach is original since the change of the metal surface state by corrosion in the presence of inhibitor is usually investigated.

2 EXPERIMENTAL STUDY

We have used nuclear quadrupole resonance as a research method because relaxation times, spectrum and shape of the NQR lines are very sensitive to small changes in the environment of the nuclei. Unlike nuclear magnetic resonance (NMR), nuclear quadrupole resonance frequencies are determined by the electric interactions, so the method allows not indirectly, but directly to study the electric field at the nuclei of atoms. NQR spectroscopy data are of fundamental importance for understanding the changes in the electronic distribution, the observation of physical phenomena occurring in crystals at the micro level.

Relaxation times express molecular dynamics, as well as provide information about the microstructure of matter. For homogeneous samples the signals of nuclear quadrupole resonance recedes by the same exponent. In this case, only the relaxation time can be precisely determined by a linear approximation. The relaxation time distribution is continuous for more complex samples, molecular crystals with impurities micropowders, porous media due to various intermolecular and many exponential inversion is required for definition of the relaxation times distribution.

Longitudinal NQR relaxation times are defined by spin-lattice interaction with the transfer of energy from the nuclear spins to mobile lattice, relaxation of the transverse nuclear magnetization depends on the spin-spin interactions and due to the inhomogeneities of crystallite lattice. Magnetization of the nuclei in the different materials differing in density, molecular structure and mobility in dependence on the environment is restored to the individual time constant. NQR signals relaxation in solids are very dependent on the degree of ordering in the sample. Amorphous samples generally relax faster than crystalline samples.

It was found previously that the longitudinal and transverse relaxation times of nuclei in the fine particles are reduced in comparison with the corresponding samples in large samples. It is assumed that this is caused by magnetization diffusion from the bulk to the crystallite surface. It is known that the phonon spectrum of atoms at the crystal surface differs from atoms in the bulk, due to the high concentration of lattice defects, dislocations, amorphous character, caused by plastic deformation during the milling process, or the influence of the environment surrounding the crystal. The result is a strong connection of the surface spins with the lattice due to fluctuations caused by the increased number of degrees of freedom.

Experimental measurements were performed on the NQR spectrometer Tecmag Apollo with TNMR software (Fig. 1). The pulse sequence recovery inversion 180° – τ – 90° was used to measure the spin-lattice relaxation time. Carr - Purcell - Meiboom - Gill (CPMG) sequence was used to measure the spin-spin relaxation time T_2. T_2^* relaxation time was measured from the shape of the Hahn echo signal. Finally, the sequences with spin-locking pulse of variable duration was used to measure the spin-lattice relaxation in the rotating coordinate system $T_{1\rho}$. All pulse sequences are well known and require no special description.

The program RILT (Regularized Inverse Laplace Transform) was used for the inversion of the Laplace transform described in the Iari-Gabriel Marino work (Marino 2004). The desired array of relaxation time distribution *f(T)* is the inverse Laplace transform of the time signal exponential decays measured by an array of *S(t)*. Array is calculated by the regularization using the least squares method. In the process of calculation was used from 50 to 200 iterations. Inversion of the Laplace transform have been used effectively by us previously (Sinyavsky et al. 2014, Dolinenkov et al. 2014) in the study of micro-composite and porous materials and phase transitions.

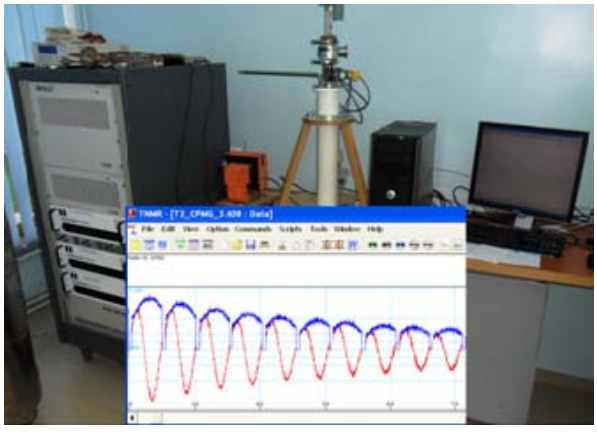

Figure 1. Tecmag - Apollo NQR spectrometer and interface of TNMR software.

The method of sample preparation was following. Small shavings of iron was placed in a saturated aqueous solution of inhibitor UNI (50% $NaNO_2$ and 50% $C_6H_{12}N_4$) for a 1.5 month. After that, the solution was evaporated, crystallized powder was dried and ground in a mortar. Iron particles were removed with a magnet. NQR measurements of the sample in the presence of metal particles are impossible due to the fall of the quality factor of the working circuit of spectrometer sensor. All measurements were performed at room temperature T = 297 K.

3 RESULTS AND DISCUSSION

Studies have allowed to establish that the 14N NQR line width of the urotropine in the sample in contact with the iron powder, practically unchanged compared with the control sample (770 ± 20 Hz). The same is true for sodium nitrite, width for the line ν- = 3.603 MHz is in the range of 280 ± 30 Hz for test and control samples.

The relaxation times distribution of the spin-lattice T_1 in urotropine and sodium nitrite in the UNI inhibitor after contact with iron and in the control samples are shown in Fig. 2 and Fig. 3, respectively. Distributions are of a multimodal nature even for a control sample, which was not in contact with the iron. The times distribution T_1 in the samples of pure urotropine and pure sodium nitrite are single-bimodal, in accordance with the theoretical model of the magnetization diffusion shown in the article (Sinyavsky 2014). It is shown in the paper that the modal distribution of relaxation times is determined by the value of the diffusion coefficient of the nuclear magnetization distribution and local inhomogeneities near the surface of the crystallite. Apparently, mutual influence of $NaNO_2$ and $C_6H_{12}N_4$ on the surface of the crystallites of both substances leads to multimodality. However, as can be seen from Fig. 2-3 time distribution T_1 in urotropine and for the relaxation times distribution T_1 in the sodium nitrite significant changes are observed then inhibitor is in the contact with iron. This is most likely due to change of the atoms mobility on the surface of the crystallites. If the mobility of the atoms on the surface of the solid body is higher, then likely spin relaxation time on the surface is shorter. It seems, that processes of spin-spin diffusion have an important role in the relaxation times distribution, leading to the transfer of magnetization from the mass of crystallite on the surface.

In the literature, so far of the research results of changes occurring on the surface of the crystal inhibitor by contact with the surface of ferrous metal, there is no.

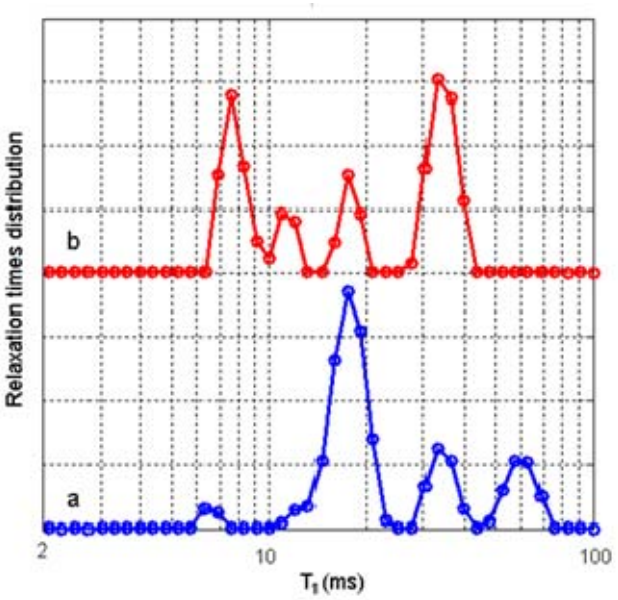

Figure 2. Distribution of spin-lattice relaxation times ^{14}N NQR in NMT of UNI inhibitor: a - control sample, b - is the sample after contact with iron.

There are three peaks in the spin-spin relaxation times distribution in investigated sample and in control sample of UNI inhibitor (Fig. 4), in contrast to pure sodium nitrite the time distribution T_2 is bimodal (Sinyavsky et al. 2014). The peak in the region of 100 ms is not shifted in comparison with the control sample and is caused, apparently, by the effect of urotropine to the surface of $NaNO_2$ crystals that crystallize from aqueous solution in the presence of $C_6H_{12}N_4$. The influence of iron oxide Fe_2O_3 on the surface of the sodium nitrite crystals leads to the shift of both short peaks.

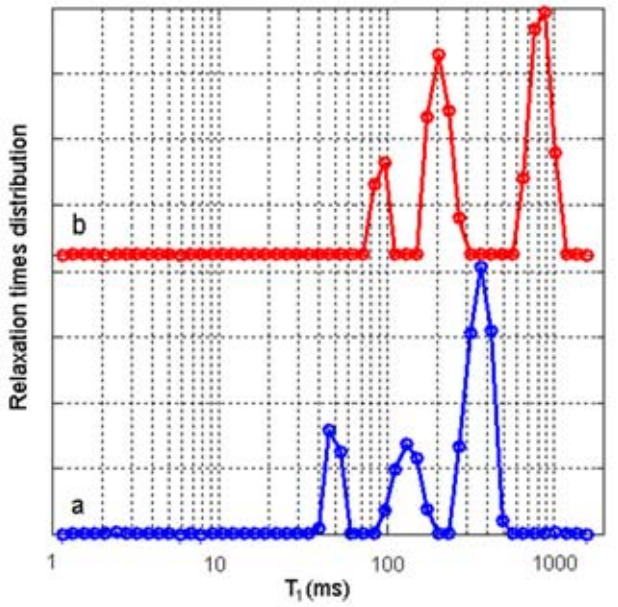

Figure 3. The relaxation times distribution T_1 in $NaNO_2$ of UNI inhibitor: a - the control sample, b - the sample after contact with iron.

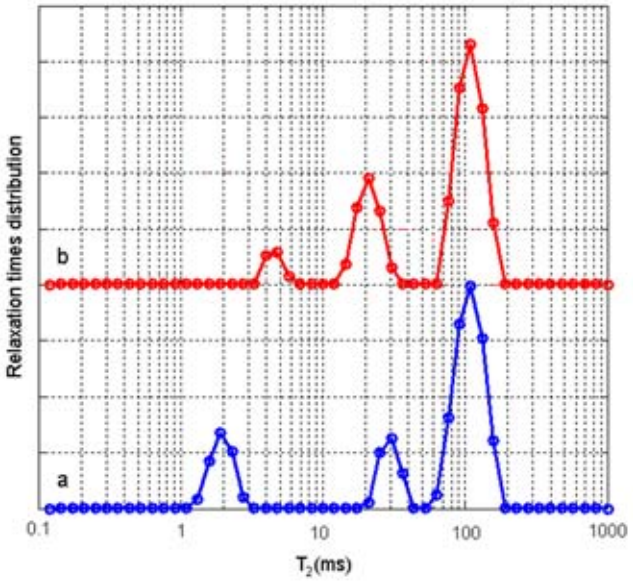

Figure 4. The relaxation times distribution T_2 in $NaNO_2$ of UNI inhibitor: a - the control sample, b - the sample after contact with iron.

The relaxation times distribution of spin-lattice in the UNI inhibitor on nuclei of nitrogen sodium nitrite at frequency $\nu_- = 3.603$ MHz at the temperature T = 297 K after contact with the iron for about 1.5 months and in the control sample are shown in Fig. 5.

Spin-lattice relaxation in the rotating frame ($T_{1\rho}$) is the mechanism through which the excited magnetization vector is decays under the influence of the spin-locking RF irradiation. $T_{1\rho}$ - filtration is used to separate signals from a mixture of amorphous and crystalline material in NMR methods.

As seen from the figure, the time distributions $T_{1\rho}$ are unimodal, and $T_{1\rho}$ value in the inhibitor contacting with the iron decreases 3-4 times compared to the control sample.

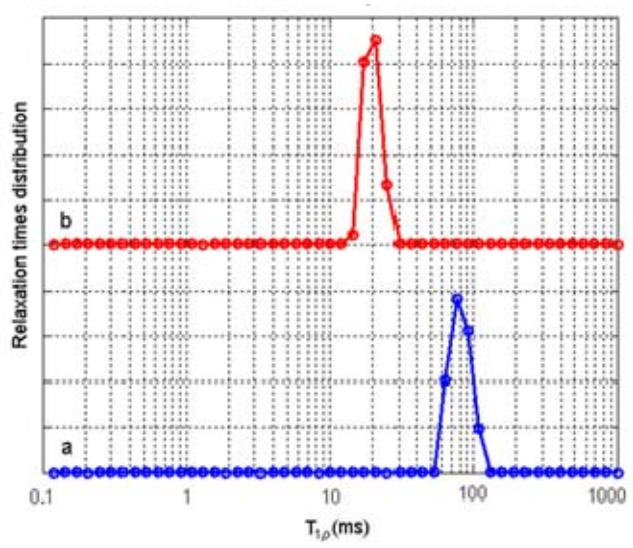

Figure 5. The relaxation times distribution $T_{1\rho}$ in $NaNO_2$ of UNI inhibitor: a - the control sample, b - the sample after contact with iron.

4 CONCLUSION

Thus, unlike traditional approaches, when studied surface state corrode in the presence of inhibitor, we examine the changes occurring inhibitor with itself after its contact with the protected surface. For the first time for this purpose we used the NQR relaxometry method and the Laplace transform inversion method for the relaxation times distribution of the nuclear magnetization.

The results of experimental studies of spin-spin and spin-lattice relaxation time distribution in crystallite powder of sodium nitrite and urotropine, which mixture is used as a corrosion inhibitor of ferrous metals. It was found that these distributions are very sensitive to the state of the layer surface of the investigated inhibitor crystallites and material of their environment. It is shown (the UNI inhibitor was the example) that the proposed method can be successfully used to study the inhibitory properties of drugs used to prevent corrosion in different conditions.

The results obtained in this paper can be applied to the study of corrosion inhibitors, in order to find the most effective means of protecting of the cooling systems and of water ballast tanks of sea water on ships and in the floating docks, of various metal constructions in the water, in ports, during storage and transportation of the metal products, etc.

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