Oxide films state analysis by IR spectroscopy based on the simple oscillator approximation

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Abstract. Stabilization of structure-phase state in a wide temperature range is one of the most important problems of improving properties of oxide compounds. As such, the search of new effective methods for obtaining metal oxides with desired physic-chemical, electro-physical and thermal properties and their control is important and relevant. The aim of this work is identification features state of the oxide films of some metals Be, Al, Fe, Cu, Zr on the metal surface of the polycrystalline samples by infrared spectroscopy. To identify the resonance emission bands the algorithm of IR-spectra processing was developed and realized on the basis of table processor EXCEL-2010, which allow revealing characteristic resonance bands successfully and identification of inorganic chemical compounds. In the frame of simple oscillator model, resonance frequencies of normal vibrations of water and some inorganic compounds: metal oxides – Be, Al, Fe, Cu, Zr were calculated and characteristic frequencies for different states (aggregate, deformation, phase) were specified. By means of IR-spectroscopy fundamental possibility of revealing oxides films on metal substrate features state is shown, that allow development and optimization of the technology for production of the oxide films with desired properties.

1. Introduction
The presence of non-destructive control methods of the state of structural materials, for example, which are used as cladding materials for the fuel elements of VVER-reactors, is important to improve technological processes. One of the most important properties of structural materials is the corrosion resistance that decreases at the violation of the continuity and structure of protective oxide films. To investigate the properties of oxide films after corrosion tests, infrared (IR) spectroscopy, which is a non-destructive control method, can be applied. The aim of the work is to study the features of the state of zirconium alloys oxide films on a metal substrate by IR spectroscopy.

2. Experimental technique
Fragments of Zr-1% Nb tubes with a diameter of 9.1 mm were used as samples for the investigation. The oxidation was carried out in a water-steam environment for four groups of samples under the following conditions: No. 1 (T = 500 °C, t = 30 s); No. 2 (T = 500 °C, t = 300 s); No. 3 (T = 400 °C, t = 600 s); No. 4 (T = 350 °C, t = 1112 h).

The structure of oxide films on a metal substrate was studied by scanning ion microscopy (SIM) using the scanning ion microscope Helios 650 Nanolab. A beam of Ga+ ions was used as a probe beam under the following conditions: the ion energy was 30 keV, the ion beam current was 1÷10 nA, the
beam cross-section was 10–30 nm, and the residual gas pressure in the working chamber was below 10⁻⁸ Pa.

The emission spectra of oxide films were measured using the IR spectrometer Nicolet 6700. Figure 1 shows the scheme of measuring the reflected flux of the "oxide-metal" system, where \( I_o \) is the primary incident flux, \( I(z=0) \) is the reflected flux from the oxide surface at the angle \( \alpha \), \( I(z_t) \) is a part of the reflected flux at the angle \( \alpha_1 \) that passed through the oxide layer with a thickness \( z_t \) and a refractive index \( n_1 \).

![Figure 1. Scheme of forming the reflected flux from a uniform film on a metal surface.](image)

The relationship between the energy of incident, reflected and transmitted electromagnetic waves is described by the following equation

\[
R + T + \chi = 1,
\]

where \( R \) is the reflection coefficient that is characterized by the ratio of the reflected flux to the incident flux \( F(R)/F_o \), \( \chi \) is the radiation absorption coefficient – \( F(\chi)/F_o \), and \( T \) is the transmission coefficient – \( F(T)/F_o \).

On the assumption that the oxide is transparent, the absorption process can be neglected (\( \chi \approx 0 \)) and then the refractive index can be defined as

\[
n = \frac{1}{1 - R^{0.5}}.
\]

In the field of frequencies of infrared radiation, optical properties are mainly determined by conduction electrons and the bond type of molecular compounds. The resonance frequency of non-deformed molecules can be estimated within the framework of the harmonic oscillator model from the expression:

\[
\nu = \left(\frac{1}{2\pi}\right) f^{0.5} \left(M_1^{-1} + M_2^{-1}\right)^{0.5},
\]

where \( f \) is the rigidity coefficient of the interatomic bond of the molecule, for example, for diatomic molecules with atomic masses \( M_1 \) and \( M_2 \),

\[
f = cv^2 \left(M_1^{-1} + M_2^{-1}\right)^{1/2} \approx 5.863 \times 10^{-2}.
\]

To conveniently process and present IR spectra, the algorithm is implemented on the basis of the table processor of Microsoft Excel 2010. When working with this program, the main peaks of absorption and reflection were revealed. This program is developed for wavelengths in the range from 1.0 to 25.0 μm with a 0.1 μm step. The developed algorithm allows identifying and recognizing the affiliation of the emission peak to an inorganic compound or a group of compounds. The resonance reflection peaks of inorganic compounds in the wavelength range from 1 to 25 μm are extracted and systematized from the literature data that contain more than 2100 types of compounds and cover more than 10000 characteristic resonance lines.

Figure 2 shows the typical emission spectra of the samples after oxidation. The most intensive lines are observed in the spectrum of water (H₂O) for the wavelength ranges of 2.5–3.5, 5.3–7.2 and 13.4–
17.8 μm, and in the spectrum of a hydroxyl group (–OH) for the wavelength ranges of 2.0–3.3 and 3.8–4.5 μm.

![Figure 2](image1.png)

**Figure 2.** Initial IR spectrum of a sample of group No. 1 after oxidation at 500 °C for: a) 30 s and b) 300 s.

3. Results and discussion

The IR spectra obtained were processed using the software package OMNIC-2000 and the developed algorithm based on the table processor of Microsoft Excel-2010, which made it possible to identify the position of the most intensive peaks, a part of which is presented in table 1.

**Table 1.** Emission peaks in the IR range of the samples after oxidation.

| Wave- | Location of emission peaks for various groups | No. 1 | No. 2 | No. 3 | No. 4 |
|-------|-------------------------------------------|------|------|------|------|
| length, μm | T=500 °C, t=30 s | Experiment | Calculation | Experiment | Calculation | Experiment | Calculation |
| 2     | 2.71 | 2.7±0.03 | 2.65 | 2.7±0.03 | 2.74 | 2.70±0.03 | 2.71 | 2.70±0.03 |
|      | 2.78 | 2.7±0.03 | -   | -   | -   | -   | 2.79 | 2.70±0.03 |
|      | 2.81 | 2.88±0.03 | -   | -   | -   | -   | - | - |
|      | -   | -   | 2.98 | 2.94±0.04 | 2.97 | 2.94±0.04 | 2.98 | 2.94±0.04 |
|      | -   | -   | -   | -   | 3.21 | 3.25±0.03 | - | - |
| 3     | -   | -   | 3.95 | -   | -   | -   | 3.39 | - |
|      | -   | -   | -   | 3.96 | -   | 3.96 | - | - |
| 4     | 4.75 | -   | -   | -   | -   | -   | 4.51 | - |
|      | 4.98 | -   | -   | -   | -   | -   | - | - |
| 5     | 5.04** | -   | -   | -   | 5.10** | -   | 5.08** | - |
|      | 5.15** | -   | -   | -   | -   | -   | - | - |
|      | -   | -   | -   | - | 6.13* | 6.13±0.06 | - | - |
| 6     | 6.23 | 6.26±0.06 | 6.73** | 6.5±0.6 | - | - | - | - |
|      | -   | -   | -   | - | - | - | - | - |
| 7     | 7.19 | -   | -   | -   | -   | - | - | - |
|      | 7.23 | -   | 7.23 | -   | - | - | - | - |
| 10    | -   | -   | -   | 9.85 | 10.5±0.9 | - | - | - |
| 14    | 14.22 | 14.9±1.4 | -   | - | - | - | - | - |

* vibrations of a deformed H2O molecule
** vibrations of a deformed ZrO2 molecule
It follows from the analysis of the position of extracted emission peaks (by an experiment) and comparison with the calculated values (using the harmonic oscillator model) that the appearance of peaks is mainly due to the stretching vibrations of water molecules and zirconium oxide except for vibrations in the wavelength area of 5 and 6 μm (5.04, 5.15, 5.19 and 6.73 μm) that are usually due to incipient internal mechanical stresses.

Table 1 also shows a shift of the peaks of normal vibrations of water that is caused by the distortion of bonds and the formation of new hydrogen bonds influencing the force constant of the valence bonds and angles of the molecule.

The shift of the peaks of normal vibrations of zirconium oxides ZrO, ZrO₂-x, and ZrO₂ to the high-frequency area usually takes place because of the presence of internal mechanical stresses in the film resulting from the presence of phase transformations with various crystal lattices. If the emission peaks shift to the low-frequency area, it is due to a decrease in the force constant f owing to the loosening of the oxide film structure (the presence of defects in the form of pores and cracks).

4. Conclusion
As a result of the study on the emission spectra of oxide films on a metal surface of zirconium samples after autoclave tests of the samples with the following oxidation regimes: No. 1 (500 °C, 30 s), No. 2 (500 °C, 300 s), No. 3 (400 °C, 600 s), No. 4 (350 °C, 1112 h), it has been found the following:

- The number of emission peaks typical of ZrO and ZrO₂ compounds decreases with increasing the temperature of tests;
- The number of peaks of the oxide film with an oxygen deficiency (ZrOₓ) increases with the oxidation time, which, apparently, is due to an increase in the thickness of the protective oxide film and an increase in the oxygen deficiency along its thickness;
- The number of emission peaks of –OH and H₂O compounds decreases with an increase in the time and the temperature of tests.

An algorithm has been developed for processing the spectra to identify the resonance emission peaks. The algorithm has been implemented on the basis of the table processor of Microsoft Excel-2010.

References
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