Measurement of internal friction of Zr–1%Nb alloy after oxidation and nitriding

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Abstract. This paper presents results of research of the Zr–1% Nb alloy using internal friction on sheet samples after oxidation due to leakage of air into the measurement facility, as well as after nitriding in an atmosphere of technical nitrogen. The measured temperature dependences of internal friction have been separated into partial maxima with the calculation of the effective activation energy according to the Wert-Marx formula. The purpose of the work is to detect the maxima of the internal friction of interstitial impurities in the alloy. It has been established that the oxygen maximum in successive measurements has activation energy 225, 222, 204 kJ/mol, and the nitrogen maximum has 234–236 kJ/mol. After lengthy high-temperature measurements, a carbon maximum appeared with activation energy 165 kJ/mol. For the grain-boundary maximum activation energy from 197 to 203 kJ/mol was obtained for different samples, while the maximum height monotonously decreased with oxidation. These results for the Zr–1% Nb alloy were obtained for the first time and can be useful in corrosion tests of zirconium alloys.

1. Introduction
The internal friction method using Snoek relaxation is widely used to study the behavior of interstitial impurities in bcc metals and alloys. In pure hcp metals, Snoek relaxation is not observed due to the lattice symmetry. However, if there is a sufficient amount of substitutional impurities in the alloy, asymmetric distortion of the lattice can occur, and when an alternating load is applied, under certain conditions it is possible to observe the Snoek relaxation of interstitial atoms near substitutional atoms [1]. From the literature on internal friction in zirconium, the position of the grain boundary maximum (its activation energy is ~ 241, 288, 222 kJ/mol in various studies), the oxygen maximum in zirconium, and in zirconium alloys with a high oxygen content (activation energy 184 and ~ 192–202, as well as 219–207 kJ/mol are known, respectively) and a nitrogen maximum (activation energy ~ 270 and 241 kJ/mol) [2]. The diffusion parameters of interstitial impurities in alpha-zirconium are also known [3], reliable results of which are shown in Table 1.

Table 1. Activation energies of diffusion of interstitial impurities in zirconium and the calculated position of relaxation maxima (Tm) for an oscillation frequency of 2 Hz.

| Impurity | H, kJ/mol | D0, m² / s | Tm, °C |
|----------|-----------|------------|--------|
| C        | 152       | 2·10⁻⁷     | 350    |
| O        | 204.4     | 3.58·10⁻⁴  | 553    |
| N        | 231.8; 231.0 | 10.2·10⁻⁵; 1.9·10⁻⁵ | 660    |
Thus, a purpose of this work is to detect relaxation maxima of the internal friction of interstitial impurities in the Zr–1% Nb alloy.

2. Materials and Experimental Methods

Measurement of amplitude-independent internal friction by the method of damped oscillations with a frequency of about 2-2.3 Hz was carried out on a MIFI-9 low-frequency relaxometer with a direct bending pendulum in a vacuum of about 0.013 Pa, using the measuring and processing programs described in [4]. The obtained temperature dependences of internal friction were divided into partial relaxation maxima with the calculation of the effective activation energy according to the Wert-Marx formula [5]. The experiment was carried out on samples with a width of 7 mm, a working length of 20-22 mm, a thickness of 0.3 mm, made of a sheet of alloy Zr-1%Nb in the delivery state. All graphs are presented in coordinates of $Q^{-1}$ versus temperature in °C.

3. Results and Discussion

3.1. Measurements after oxidation

A series of measurements of internal friction was performed on a single sample. Figure 1 and 2 shows the temperature dependence of internal friction (TDIF) of the sample in the initial state and its separation into partial maxima.

![Figure 1. TDIF of the initial sample (No.6).](image1)

![Figure 2. Separation into partial maxima. The grain boundary maximum: Tm = 547 °C, H = 202.7 kJ/mol, Qmax$^{-1}$ = 0.0114.](image2)

The results of repeated measurement of sample No.6 (experiments 711 and 712) in terms of separating the curve into partial maxima are shown in Figure 3 and 4.

| № | T, °C | H, kJ/mol | $Q_{max}^{-1}$ |
|---|------|---------|-------------|
| 1 | 547  | 202.4   | 0.00965     |
| 2 | 635  | 224.8   | 0.00794     |

![Figure 3. Separation in partial maxima of 711.](image3)

![Figure 4. Separation in partial maxima of 712.](image4)
A comparative analysis of the data in Figures 1, 2, and Figures 3, 4 shows that after sufficiently long heating to 700 °C in the previous experiment, in experiments 711 and 712 a maximum appeared, that is close to oxygen in activation energy (see above). The explanation is simple - the sample was oxidized in a bad vacuum during the measurement process. In these two measurements, the position of the maxima and their parameters remained practically unchanged, as did the ratio of the heights of the oxygen maximum to the grain boundary maximum (0.823), with a general small decrease in the height of both maxima.

In the following two measurements, under similar conditions (exp 714 and 715), two more peaks appeared – a low-temperature maximum and a maximum located to the right of the oxygen one. Figure 5 shows the results of experiment 715:

| № | Tmax, °C | H, kJ/mol | Qmax\(^{-1}\) |
|---|----------|-----------|---------------|
| 1 | 407      | 166.3     | 0.00227       |
| 2 | 518      | 194.5     | 0.00501       |
| 3 | 562      | 205.8     | 0.00435       |
| 4 | 636      | 224.6     | 0.00741       |

**Figure 5.** 5th measurement of the sample No.6 in experiment 715 and separation into partial maxima.

Our interpretation of the possible nature of the maxima in experiment 715 is as follows. Maximum No.1, with activation energy 165.4 kJ / mol - in all probability, carbon, because it appeared after repeated high-temperature measurements with steam-oil diffusion pump; it has been observed before. Maximum No. 2 – grain-boundary maximum, with a small decrease of activation energy. Maximum No.3 is oxygen, the activation energy 204.4 kJ/mol is less than in the first experiments, but it coincides well with the literature data on diffusion. And the maximum number 4 is nitrogen; the reason for the appearance is the same as that of oxygen - poor dynamic vacuum in the chamber.

3.2. Measurements of nitrided samples

For nitriding, the samples were placed in a quartz ampoule, the system was pumped out with a foreline pump, washed three times with nitrogen of technical purity, and after cutting off the pump, the furnace was put into nitriding mode. Three samples from one batch were simultaneously nitrided - the first nitriding of 600 °C - 0.5 h, then the second nitriding of the 2 remaining samples - another 600 °C - 0.5 h. Figure 6 shows the TDIF of nitrided samples:
Further, Figures 7 and 8 show the division into partial maxima of the nitrided samples.

**Figure 6.** TDIF source and nitrided samples: 740 – initial sample; 748 – sample No. 5, nitrided at 600 °C – 1 h; 749 – remeasurement of the same sample No. 5.

Further, Figures 7 and 8 show the division into partial maxima of the nitrided samples.

**Figure 7.** Division into partial maxima in experiments 740 and 747: 740 – the original sample of this batch; 747 – sample No. 4, nitrided at 600 °C – 0.5 h.

In these results maximum № 1 is grain-boundary in both experiments; maximum № 2 in 747 is nitrogen.

**Table:**

| №  | T, °C | H, kJ/mol | $Q_{max}$' |
|----|------|-----------|-------------|
| 1  | 527  | 196.9     | 0.01627     |

| №  | T, °C | H, kJ/mol | $Q_{max}$' |
|----|------|-----------|-------------|
| 1  | 542  | 199.9     | 0.01929     |
| 2  | 680  | 235.0     | 0.01854     |

**Figure 8.** Division into partial maxima in the following two experiments. In experiments 747 and 748, which differ in nitriding time is observed only the grain-boundary (No.1) and nitrogen (No.2) maxima, the parameters of which practically coincide in these experiments. But after re-measuring the sample from experiment 748 (exp 749), an intermediate maximum appeared (No.2 in Figure 8), with an activation energy of 221.8 kJ/mol close to oxygen; its appearance can be explained by oxidation during measurements. The nature of the 4th maximum is unknown.
After additional nitriding, both maxima decreased, but the nitrogen maximum relative to the grain boundary increased, which is logical. A decrease in the height of the grain boundary maximum was also observed in a series of experiments with oxidation in air.

4. Conclusions
It was established that during oxidation in repeated measurements an oxygen maximum appeared, the activation energy decreases in successive experiments: 225, 222, 204 kJ/mol. In repeated measurements of nitried samples, the oxygen maximum has activation energy 222 kJ/mol. The nitrogen maximum during nitriding has activation energy 234–236 kJ/mol, and the oxygen maximum that appears in these measurements is 225 kJ/mol. After repeated measurements, the carbon maximum appeared with activation energy 165 kJ/mol. The height of the grain boundary maximum in sequential measurements decreases monotonically with an insignificant temperature shift, depending on the measurement conditions, with activation energy from 197 to 203 kJ/mol in different samples.

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