Effect of interstitial impurities on internal friction measurements in niobium

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Abstract

Measurements of internal friction as a function of temperature were carried out in samples of niobium containing different amounts of interstitial solutes (oxygen and nitrogen) and one sample of niobium containing initially only nitrogen as interstitial solute. The experimental spectra of internal friction as a function of temperature were obtained with a torsion pendulum of the inverted Kê-type and resolved, using the method of successive subtraction, into a series of constituent Debye peaks corresponding to different interactions. For each relaxation process it was possible to obtain the height ($Q^{-1}_{max}$) and temperature ($T_p$) of the peak, the activation energy ($E$) and the relaxation time ($t_0$).

The height, shape and temperature of these peaks depend on the concentration of interstitial elements. The observed peaks were associated with matrix-interstitial (Nb–O, Nb–N) and interstitial–interstitial (O–N) interaction processes.

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1. Introduction

Metals containing solute atoms dissolved interstitially often show anelastic behaviour due to a process known as stress-induced ordering. One manifestation of this anelastic behaviour is the internal friction, which was originally observed by Snoek [1] in Fe containing carbon and nitrogen as interstitial solutes. The anelasticity has its cause in the stress-induced migration of interstitial atoms in octahedral positions of bcc lattices. Several techniques can be used to measure the internal friction [2–5], and the torsion pendulum is the one most suited to the study of metal-interstitial solute interactions (such as carbon, nitrogen, or oxygen). At low interstitial-solute concentrations, the relaxation strength of internal friction at a given temperature is a function of the nature, positions and concentration of the interstitial atoms.

In the present work, the internal friction was measured as a function of temperature in samples of niobium containing different amounts of interstitial solutes, such as oxygen and nitrogen.

2. Experimental

Niobium samples were obtained by electro-beam zone melting and were supplied in the form of swaged rods of 3 mm diameter, and were referred to Nb20, Nb22 and Nb416. The Nb416 was obtained as described in reference [6]. Samples 60 mm long, which had been chemically polished to 1.2 mm thickness in a mixture of nitric and fluoric acids, were used for the internal friction measurements.

These values were obtained in the temperature range between 300 and 650 K, using a torsion pendulum of the inverted Kê-type [7] which was set to give an oscillation frequency in the hertz bandwidth, applying a heating rate of 1 K/min, at a pressure, which was kept near $10^{-5}$ mbar. A laser beam was deflected by a mirror on the pendulum bar, and data on the decay of the oscillations was collected automatically by two phototransistor connected to a computer. The internal friction was found from the decay in amplitude.

The internal friction curves as a function of temperature would be decomposed into elemental Debye peaks [8] using...
the method of successive subtraction (in the present work, Peak Fitting Module of Origin was used), and the anelastic relaxation processes could be identified comparing our data with literature [9–12].

3. Results and discussion

The experimental spectra of internal friction as a function of temperature were obtained for the Nb20, Nb22 and Nb416 samples. The chemical analysis of the interstitial impurities in the metals in the as-received condition was 0.016 at.% of oxygen and 0.015 at.% of nitrogen for the Nb20 and Nb22 and 0.007 at.% of nitrogen for the Nb416.

The resolution of the internal friction spectra as functions of temperature into their constituent Debye peaks was criticized by Weller et al. [13]. They contested the existence of pairs and triplets of oxygen atoms in interstitial solid solution in bcc metals to explain the observed asymmetric broadening of anelastic relaxation peak, and that in the case of high oxygen contents, oxygen atoms would also occupy interstitial tetrahedral positions, this double occupancy would then cause the shifting and broadening of the peak, justifying the existence of a single anelastic relation process.

The curves of internal friction as a function of temperature obtained in the present work for Nb20 and Nb416, however, are asymmetric. The correction proposed was tested for these values, but the asymmetry continued to be evident. This corroborates the existence of more than one process of interaction.

Fig. 1 shows the experimental spectrum for Nb22 that was resolved into three constituent peaks of Debye corresponding to the interactions Nb–O, O–N and Nb–N; this results was obtained during the first run. These data were obtained with an oscillation frequency of about 2.8 Hz (at room temperature). Other measurements were carried out at this sample using oscillation frequency of 1.4 and 2.9 Hz.

Fig. 2 shows the data for the Nb20 sample after several runs, this spectrum was resolved into four constituent peaks of Debye corresponding to the interactions Nb–O, Nb–O–O, Nb–O–O–O and Nb–N. These data were obtained with an oscillation frequency about 2.6 Hz (at room temperature).

Fig. 3 shows the internal friction as a function of temperature for the Nb20 sample, after annealing at 1170 K for 2 h in helium flow. This experimental relaxation spectrum was resolved into four constituent peaks, however with the highest relaxation strength which is attributed to the greater amount of interstitial elements in solid solution. These data were obtained with an oscillation frequency of about 2.1 Hz (at room temperature).

Fig. 4 shows the experimental spectrum for Nb416 that was resolved into four constituent peaks of Debye corresponding to the interactions Nb–O, O–N, Nb–N and Nb–N. These data were obtained with an oscillation frequency about 2.8 Hz (at room temperature).
Table 1

<table>
<thead>
<tr>
<th>Samples</th>
<th>Q&lt;sub&gt;1&lt;/sub&gt; × 10&lt;sup&gt;13&lt;/sup&gt;</th>
<th>Interactions</th>
<th>T&lt;sub&gt;p&lt;/sub&gt; (K)</th>
<th>E (eV)</th>
<th>t&lt;sub&gt;0&lt;/sub&gt; (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb&lt;sub&gt;22&lt;/sub&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>first run</td>
<td>5.54</td>
<td>Nb–O</td>
<td>428</td>
<td>1.15</td>
<td>1.03 × 10&lt;sup&gt;-14&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>1.73</td>
<td>O–N</td>
<td>507</td>
<td>1.35</td>
<td>1.38 × 10&lt;sup&gt;-14&lt;/sup&gt;</td>
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<tr>
<td></td>
<td>2.64</td>
<td>Nb–N</td>
<td>580</td>
<td>1.52</td>
<td>2.24 × 10&lt;sup&gt;-14&lt;/sup&gt;</td>
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<tr>
<td></td>
<td>5.53</td>
<td>Nb–O–O–O</td>
<td>444</td>
<td>1.21</td>
<td>4.29 × 10&lt;sup&gt;-14&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>2.95</td>
<td>Nb–O–O–O–O</td>
<td>473</td>
<td>1.27</td>
<td>6.78 × 10&lt;sup&gt;-14&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>2.82</td>
<td>Nb–N</td>
<td>570</td>
<td>1.52</td>
<td>8.41 × 10&lt;sup&gt;-14&lt;/sup&gt;</td>
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<tr>
<td>Nb&lt;sub&gt;20&lt;/sub&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>after four runs</td>
<td>16.40</td>
<td>Nb–O</td>
<td>429</td>
<td>1.15</td>
<td>6.59 × 10&lt;sup&gt;-14&lt;/sup&gt;</td>
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<tr>
<td></td>
<td>10.26</td>
<td>Nb–O–O–O</td>
<td>443</td>
<td>1.21</td>
<td>3.64 × 10&lt;sup&gt;-14&lt;/sup&gt;</td>
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<tr>
<td></td>
<td>3.64</td>
<td>Nb–O–O–O–O</td>
<td>474</td>
<td>1.27</td>
<td>6.87 × 10&lt;sup&gt;-14&lt;/sup&gt;</td>
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<tr>
<td></td>
<td>4.26</td>
<td>Nb–N</td>
<td>562</td>
<td>1.52</td>
<td>9.02 × 10&lt;sup&gt;-14&lt;/sup&gt;</td>
</tr>
<tr>
<td>after annealing</td>
<td>14.48</td>
<td>Nb–O</td>
<td>426</td>
<td>1.15</td>
<td>7.17 × 10&lt;sup&gt;-14&lt;/sup&gt;</td>
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<td></td>
<td>1.22</td>
<td>O–N</td>
<td>530</td>
<td>1.35</td>
<td>2.37 × 10&lt;sup&gt;-15&lt;/sup&gt;</td>
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<td></td>
<td>1.43</td>
<td>Nb–N</td>
<td>561</td>
<td>1.52</td>
<td>6.35 × 10&lt;sup&gt;-14&lt;/sup&gt;</td>
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<tr>
<td></td>
<td>1.56</td>
<td>Nb–N–N–N</td>
<td>576</td>
<td>1.58</td>
<td>4.20 × 10&lt;sup&gt;-12&lt;/sup&gt;</td>
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<tr>
<td>Nb&lt;sub&gt;416&lt;/sub&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>after three runs</td>
<td>1.48</td>
<td>Nb–O</td>
<td>426</td>
<td>1.15</td>
<td>7.17 × 10&lt;sup&gt;-14&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>1.22</td>
<td>O–N</td>
<td>530</td>
<td>1.35</td>
<td>2.37 × 10&lt;sup&gt;-15&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

The interstitial elements in solid solution of metals with bcc lattice are responsible for the Snoek peaks in the relaxation spectrum of internal friction, due to the stress-induced ordering. The height, shape and temperature of these peaks depend on the concentration of interstitial elements. The identification of the three constituent peaks Nb–O, Nb–O–O and Nb–O–O–O due to matrix–interstitial interactions was based on the results Ahmad and Szkopiak [9]. Assuming that the peaks are true Debye peaks, one can compute the activation energies (E) for the processes, measuring the width at half of the peak height. It was not possible to deduce the activation energies from their shift in temperature with change of frequency because the pendulum was set in the hertz bandwidth (1 Hz ≤ f ≤ 10 Hz). Considering that the peaks obey Arrhenius type equation, \( t = t_0 \exp(E/RT) \), where R is the gas constant and T the peak temperature, it is possible to calculate the relaxation time (t<sub>0</sub>). Table 1 shows the parameters of mechanical relaxation for each kind of interaction.

Analyzing these results, it is possible to estimate the amounts of interstitial elements based in the work by Ahmad and Szkopiak [9]. The estimated values are: 0.02 at.% of oxygen and 0.02 at.% of nitrogen for Nb<sub>22</sub> sample; 0.8 at.% of oxygen and 0.018 at.% of nitrogen for Nb<sub>20</sub> sample (after four runs); 1.04 at.% of oxygen and 0.03 at.% of nitrogen for Nb<sub>20</sub> sample (after annealing) and 0.008 at.% of oxygen and 0.03 at.% of nitrogen for Nb<sub>416</sub> sample.

The values estimated for Nb<sub>22</sub> sample were very close to the obtained by chemical analysis of the interstitial impurities in this metal in the as-received condition. The increase of the interstitial elements in the samples Nb<sub>22</sub> and Nb<sub>416</sub> can be associated with the leak of pressure that was about 10<sup>-3</sup> mbar.

### 4. Conclusions

The mechanical relaxation spectra for Nb samples containing different amounts of interstitial elements were obtained as a function of temperature with a torsion pendulum at oscillation frequency in the hertz bandwidth. The values found in the Nb<sub>22</sub> sample were very close to the chemical analysis of the interstitial impurities in the metal as-received condition.

The internal friction spectra for the Nb<sub>20</sub> sample containing different amounts of oxygen and nitrogen were obtained as a function of temperature and were resolved into four interactions processes: Nb–O, Nb–O–O, Nb–O–O–O and Nb–N characterizing the mechanical multiple relaxation in the niobium containing interstitial elements in solid solution.

The internal friction spectrum for Nb<sub>416</sub> sample containing oxygen and nitrogen were obtained as a function of temperature and was resolved into four intersections processes: Nb–O, O–N, Nb–N and Nb–N–N. This result presented the interstitial–interstitial and matrix–interstitial interaction processes.
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