Anelastic relaxation processes due oxygen in Nb–3.1 at.% Ti alloys

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Abstract
In the last 50 years several studies have been made to understand the relaxation mechanisms of the heavy interstitial atoms present in transition metals and their alloys. Internal friction measurements have been carried out in a Nb–Ti alloy containing 3.1 at.% of Ti produced by the Materials Department of Chemical Engineering Faculty of Lorena (Brazil), with several quantities of oxygen in solid solution using a torsion pendulum. These measurements have been performed by a torsion pendulum in the temperature range from 300 to 700 K with an oscillation frequency between 0.5 and 10 Hz. The experimental results show complex internal friction spectra that have been resolved, into a series of Debye peaks corresponding to different interactions. For each relaxation process it was possible to obtain the height and temperature of the peak, the activation energy and the relaxation time of the process.

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1. Introduction
In bcc metals, such as niobium and niobium alloys, interstitial solute atoms cause local strain distortion of tetragonal symmetry. Thus, an interstitial atom in this lattice forms an elastic dipole that can lie along one of the three cubic axes. When an external stress is applied, differences in the free energy for different dipole orientations occur and these interstitial atoms are redistributed among the different sites, causing energy loss, i.e. internal friction. Each species of interstitial atoms gives rise to a maximum in the internal friction spectra, which may be observed at a different temperature, depending on measuring frequency (thermally activated process). This maximum is called Snoek effect [1].

In diluted interstitials alloys (c < 0.01 at.%), the Snoek peaks may be described as a single Debye peak [2]. In concentrated alloys, the peaks are broadened, obviously owing to interactions between the interstitial atoms. If more than one species of interstitial atoms is present, the analysis of internal friction spectra becomes rather complicated. The broadening was interpreted by assuming configurations of clusters of interstitial atoms, which should cause additional discrete loss maxima at higher temperatures than the Snoek maximum [3–5]. Weller et al. [6–8] questioned the clustering model by introducing a continuous distribution of relaxation times which should correspond a long-range interaction models.

The presence of substitutional solutes in bcc metals containing interstitial impurities modifies the stress-induced ordering of the interstitial atoms due, in general, to the formation of substitutional-interstitial complexes [9]. The purpose of this work was to investigate the influence of titanium on niobium containing oxygen in solid solution and the consequential effect on the mechanical properties of the alloy.

2. Experimental part
The tested samples were polycrystals foils of the Nb–Ti alloy, with 3.1 at. % of titanium (Nb–3.1 at.% Ti), containing 0.87 at.% of oxygen in solid solution. The oxygen content was estimated by a TC-136 equipment (Leco Co.) using the technique of sample melting and inert gas carrier. The Nb–Ti...
alloy was produced at Faculdade de Engenharia Química (FAENQUIL) in Lorena (Brazil), by electron-beam zone melting. Metallic impurities were determined in a 3410-JCP inductively coupled plasma spectrophotometer (ARL) and the maximum content of these impurities are presented in the Table 1. Samples were prepared from 8.0 mm diameter swaged rods. The rods were cold worked to a final thickness of 0.5 mm. The samples were cut of foil with 40 mm × 5 mm × 0.5 mm.

Measurements of internal friction and frequency were carried out as a function of temperature by means of an inverted torsion pendulum of K*e type [10] between 300 and 700 K at a heating rate of 1.0 K/min in a vacuum of 5 × 10⁻⁵ mBar. The data were acquired by an automatic system which measured the angular velocity of the pendulum around the equilibrium configuration.

3. Results and discussion

A typical dependence of internal friction and oscillating frequency on temperature is shown in Fig. 1. The spectrum appears to consist of several interaction processes between the metallic matrix and interstitials elements.

Internal friction caused by stress induced ordering of interstitial atoms may be described by a Debye equation [2]:

\[ Q^{-1}(\omega T) = \frac{4\pi f}{1 + \omega^2 T^2} \]

(1)

where \( \omega \) is the relaxation strength, \( \omega = 2\pi f \) and \( f \) is the oscillating frequency.

For the relaxation time \( \tau \) that controls the thermally activated redistribution of the defects, we can use the Arrhenius equation:

\[ \tau(T) = \tau_0 \exp\left(\frac{H}{k_B T}\right) \]

(2)

where \( H \) is the activation enthalpy, \( k_B \) is the Boltzmann’s constant, and \( \tau_0 \) is the pre-exponential factor.

By combining Eqs. (1) and (2) and taking into account the frequency correction (the frequency changes with the temperature because of the temperature-dependent elastic modulus is proportional to \( f(T) \)), the internal friction can be written as [6]:

\[ Q^{-1}(T) = Q_{eq} \frac{T_m}{T} \cosh^{-1}\left[ \frac{H}{k_B (\frac{1}{T} - \frac{1}{T_m})} + \ln\left(\frac{f(T)}{f_m}\right) \right] \]

(3)

The three parameters which characterize a Debye maximum are: the peak height \( Q_{eq}^{-1} \), the temperature of peak \( T_m \) and the activation enthalpy of the process \( H \); they can be determined by applying appropriate methods of numerical analysis in order to fit the experimental data (in the present work, we used the PeakFitting Module of Microcal® Origin®). The other parameter \( f_m \), is the frequency at \( T_m \).

When more than one relaxation process is present, a more complicated behavior of the anelastic spectra is expected and defects interactions may broaden the peaks with a distribution of relaxation times. Thus, the anelastic spectrum is a superposition of several Debye peaks and the internal friction can be written as:

\[ Q^{-1}(T) = \sum_{i=1}^{n} Q_{eq_i}^{-1} \frac{T_m}{T} \cosh^{-1}\left[ \frac{H_i}{k_B (\frac{1}{T} - \frac{1}{T_m})} + \ln\left(\frac{f(T)}{f_m}\right) \right] \]

(4)

In order to investigate if the anelastic relaxation peak observed in the Fig. 1 is thermally activated, we measured the internal friction at three different frequencies: 0.4, 0.9 and 2.6 Hz. Fig. 2 shows the internal friction for the sample of Nb-3.1 at.% Ti containing 0.87 at.% of oxygen, without the background, for frequencies of 0.4, 0.9 and 2.6 Hz. We can observe that the relaxation peak is thermally activated and shifts to high temperature zone with the increase of oscillation frequency. The internal friction background was estimated by interpolation between the measured internal friction levels at both sides of the maximum in a distance sufficiently long from it, using the same computer software. A linear function was used for background interpolation.

Using a non-linear regression method based in the successive subtraction process, we analyzed the \( Q^{-1} \) spectrum and have decomposed it into three processes (Figs. 3-5). The first process, at lower temperature, is attributed to stress-induced ordering of free oxygen atoms among tetrahedral sites of metallic matrix; it is the Nb-O Snoek peak.
Fig. 2. Internal friction as a function of frequency and temperature for a Nb–3.1 at.% Ti sample containing 0.87 wt.% of oxygen.

Fig. 3. Component Debye peaks of the anelastic relaxation spectrum measured with frequency of 0.4 Hz, for a Nb–3.1 at.% Ti alloy and their sum.

Fig. 4. Component Debye peaks of the anelastic relaxation spectrum measured with frequency of 0.9 Hz, for a Nb–3.1 at.% Ti alloy and their sum.

Fig. 5. Component Debye peaks of the anelastic relaxation spectrum measured with frequency of 2.6 Hz, for a Nb–3.1 at.% Ti alloy and their sum.

The second process, which is dominant, is located at intermediate temperature. Because the substitutional Ti, in the Nb–Ti alloy is a strong trapping centre for oxygen atoms, we propose that this main process be due the stress-induced ordering of oxygen atoms around titanium atoms of metallic matrix, here labeled Ti–O process. The third relaxation at high temperature is ascribed to nitrogen (Nb–N Snoek peak), which represents the second interstitial impurity content of the alloy. The activation enthalpy for the three processes proposed was fixed, based in values determined earlier by internal friction experiments, i.e. 1.15, 1.23 and 1.57 eV, respectively. Figs. 3–5 present the decomposition mentioned above, where the full line represent the sum of three Debye peaks (dot lines), that represent the three relaxation process proposed. The relaxation parameters, $H$ and $T_m$, for the three process are presented in the Table 2.

The fact that that the peak temperatures and frequency of the processes at lower and middle temperatures do not fit the Arrhenius plots of Nb–O relaxation and of the Ti–O relaxation can be explained considering that, at high concentration, the substitutional Ti markedly perturbs the periodic potential of the interstitial sites so affecting the relaxation parameters of the processes.

Table 2
Relaxation parameters for the relaxation process proposed in this work

<table>
<thead>
<tr>
<th>Process</th>
<th>$f$ (Hz)</th>
<th>$T_m$ (K)</th>
<th>$H$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb–O</td>
<td>0.4</td>
<td>388</td>
<td>1.15</td>
</tr>
<tr>
<td></td>
<td>0.9</td>
<td>397</td>
<td>1.15</td>
</tr>
<tr>
<td></td>
<td>2.6</td>
<td>401</td>
<td>1.15</td>
</tr>
<tr>
<td>Ti–O</td>
<td>0.4</td>
<td>406</td>
<td>1.23</td>
</tr>
<tr>
<td></td>
<td>0.9</td>
<td>418</td>
<td>1.23</td>
</tr>
<tr>
<td></td>
<td>2.6</td>
<td>427</td>
<td>1.23</td>
</tr>
<tr>
<td>Nb–N</td>
<td>0.4</td>
<td>515</td>
<td>1.57</td>
</tr>
<tr>
<td></td>
<td>0.9</td>
<td>528</td>
<td>1.57</td>
</tr>
<tr>
<td></td>
<td>2.6</td>
<td>542</td>
<td>1.57</td>
</tr>
</tbody>
</table>
4. Conclusions

We made internal friction measurements in the Nb–3.1 at.% Ti alloys, containing 0.87 at.% of oxygen in solid solution. The obtained relaxation spectra were analyzed in terms of the their constituents peaks. We identified peaks that were attributed to the stress-induced ordering of oxygen atoms around niobium atoms of the metallic matrix (Nb–O process); stress-induced ordering of oxygen atoms around titanium atoms of the metallic matrix (Ti–O process) and stress-induced ordering of nitrogen atoms around niobium atoms of the metallic matrix (Nb–N process).

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References