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Anelastic relaxation due to O–H pairs in Nb–Zr alloys

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Abstract

In the last 30 years several studies have been made to understand the relaxation mechanisms of the hydrogen atoms present in transition metals and their alloys. In this work, we observed the stress-induced ordering of hydrogen atoms around the interstitial oxygen atoms near the niobium matrix atoms. We studied this relaxation process by measuring the attenuation of longitudinal ultrasonic waves. These measurements were made in Nb–1.0%Zr polycrystalline alloys at 10 and 30 MHz, pure and doped with 0.7 and 4.2 at.% hydrogen. The results revealed a thermally activated relaxation structure around 202 K and 235 K for 10 MHz and 30 MHz respectively. This relaxation structure increases with increasing hydrogen concentration.

1. Introduction

For the last 30 years, internal friction measurements have been utilized for anelastic relaxation studies in transition metals and their alloys [1–3]. When impurity atoms are introduced in a b.c.c. metallic matrix, they produce anelastic behaviour known as stress-induced ordering [4–6]. This behaviour can be easily detected by internal friction measurements. The internal friction measurements provide a correlation between the metallurgical effects due the presence of hydrogen atoms and the physical mechanisms that cause these effects [7–13]. Recently, other researchers studied transition metals with hydrogen but in the presence of oxygen. In these publications evidence is given of the O–H pair [14–18]. In this work, we studied the relaxation process due to the O–H pair by ultrasonic attenuation measurements in Nb–1.0%Zr alloys with oxygen, pure and doped with hydrogen.

2. Experimental details

The polycrystalline Nb–1.0%Zr alloys used in our experiments were produced by CEMAR of the FAENQUIL at Lorena (Brazil). Table 1 shows the analysis of the impurities present in the as-received sample. The internal friction was obtained by ultrasonic attenuation measurements using the echo–pulse technique with automatic register of the attenuation [19–21]. The samples used were small cylinders with 8.0 mm length and 8.4 mm diameter. The measurements were performed by longitudinal ultrasonic waves with frequencies of 10 and 30 MHz produced by quartz transducers. The attenuation measurements were performed in three different conditions: cold worked; annealed in a high vacuum of 10^{-5} Torr for 26 h at 1173 K; charged with 0.7 and 4.2 at.% hydrogen, subsequent to vacuum annealing.

TABLE 1. Analysis of the impurities present in the as-received Nb–1.0%Zr polycrystalline sample

Element	H	O	N	C
Concentration (at.%)	0.001	0.040	0.011	0.005

3. Results and discussion

Figure 1 shows the dependence of internal friction on temperature for the sample charged with 0.7 and 4.2 at.% hydrogen, measured with frequencies of 10 and 30 MHz. In this case we can observe the presence of a thermally activated relaxation structure near 200 K and 240 K for 10 MHz and 30 MHz respectively. The size of this relaxation structure increases linearly with increasing hydrogen concentration.

Figure 2 shows the internal friction as a function of the inverse of the temperature for the hydrogen-charged samples with the background subtracted. These experimental data were analysed by two different methods: the first is a computer method known as "successive subtraction method", developed by Grandini [22], and the second is based in the procedure developed by

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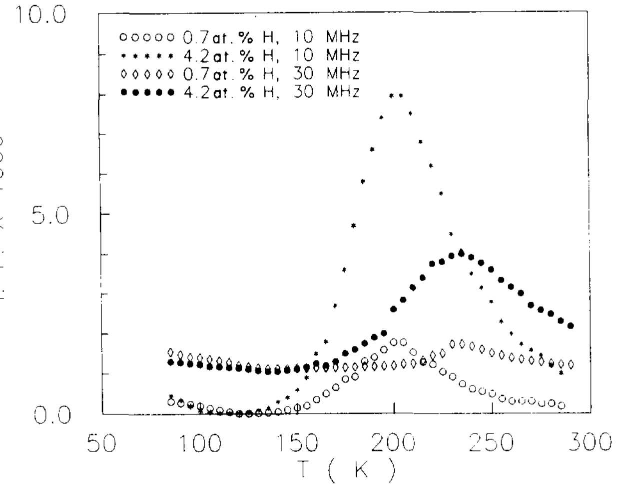

Fig. 1. Internal friction spectra of the samples charged with 0.7 and 4.2 at.% hydrogen, in the presence of oxygen, measured with frequencies of 10 and 30 MHz.

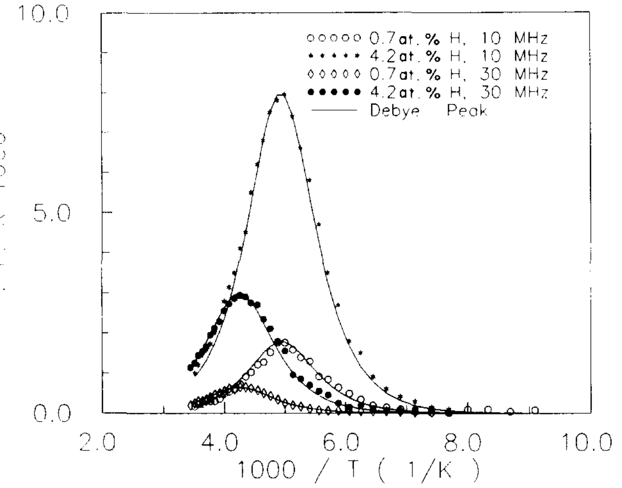

Fig. 2. Internal friction spectra of the samples charged with 0.7 and 4.2 at.% hydrogen, in the presence of oxygen, measured with frequencies of 10 and 30 MHz, and analysed by a Debye peak.

Weller *et al.* [23, 24]. These two procedures are based on the supposition that the relaxation structure is due to a relaxation process composed of a single relaxation time characterized by a single Debye peak. In this case the internal friction can be written as [5]

$$Q^{-1}=Q_{\mathrm{m}}^{-1}\ \mathrm{sech}[E/k(1/T_{\mathrm{m}}-1/T)]$$

where Q_{m}^{-1} is the peak height, T_{m} is the peak temperature and E is the activation energy.

In the first procedure we can put the initial parameter characteristics of a Debye peak in the above equation and after a least-squares regression analysis obtain the adjustable parameters of the process. The result of this analysis is shown in Fig. 2. We can observe in this figure that there exists an excellent agreement between the theoretical curve and the experimental points. This theoretical curve is a Debye peak and confirms our supposition that a single relaxation process is present in this case. The relaxation parameters are shown in Table 2.

The second procedure consists in the analysis of the relaxation structures in terms of the Arrhenius equation. If the relaxation structure is composed of a single relaxation time the logarithmic curve of relaxation time as a function of the inverse of temperature must be a straight line. The curves are shown in Fig. 3 for the hydrogen-charged samples measured with frequencies of 10 and 30 MHz. We observe in this figure that the experimental points suggest a linear behaviour which is confirmed by linear regression (full line). The relaxation parameters for this analysis are shown in Table 2.

The measurements made by Grandini [25] for the Nb–1.0%Zr alloy without oxygen and doped with the same quantity of hydrogen did not reveal any relaxation structure in the temperature range examined here. Thus the relaxation structure obtained by us is due to the stress-induced ordering of the hydrogen atoms around the oxygen atoms. In this relaxation process the heavy interstitial atoms, in our case oxygen, were frozen in octahedral sites of the b.c.c. metallic matrix and the hydrogen atoms jump between equivalent tetrahedral sites. The heavy interstitial captures the hydrogen atom, giving the origin of the relaxation process.

The relaxation process due to the stress-induced ordering of hydrogen atoms around zirconium atoms (Zr–H process) occurs, theoretically, in our frequency range, at lower temperatures than those used by us. The Zr–O–H relaxation process did not occur because we did not observe the Zr–O relaxation process, owing to the low concentration of oxygen in the alloy [26, 27].

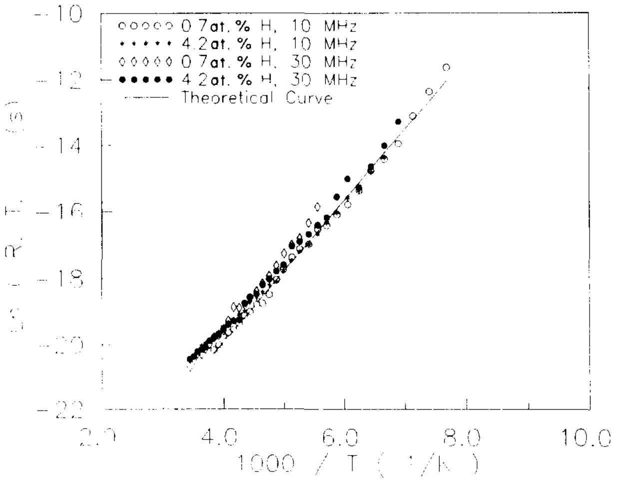

Fig. 3. Analysis of the internal friction spectra using the relaxation time procedure.

TABLE 2. Relaxation parameters for the sample measured with frequencies of 10 and 30 MHz

T (K)	Charge (at.% H)	f (MHz)	E (eV)	τ_0 ($\times 10^{-12}$ s)	Method
202	0.7	10	0.172	0.44	Relaxation time
202	0.7	10	0.182	0.52	Successive subtraction
202.5	4.2	10	0.158	2.01	Relaxation time
202.5	4.2	10	0.171	1.98	Successive subtraction
235	0.7	30	0.186	0.57	Relaxation time
235	0.7	30	0.173	0.62	Successive subtraction
235	4.2	30	0.173	1.08	Relaxation time
235	4.2	30	0.171	1.14	Successive subtraction

Reference should be made to a paper by Cannelli *et al.* [28] on similar measurements of Nb–Zr alloys. These researchers worked in a different frequency range and hence different temperatures were found. Their study confirms that the relaxation structure observed in Nb–Zr alloy is due to Zr–H pairs and not the Nb–O–H complex as confirmed by our study. We do not cast doubt on the work of Cannelli *et al.* although we stand by our hypothesis. We would like to leave this difference as an open question that might be resolved by further work by Cannelli *et al.* in the frequency range studied by us or by re-examination by us of Cannelli *et al.*'s work.

4. Conclusions

Ultrasonic attenuation measurements were made in Nb–1.0%Zr polycrystalline alloys at frequencies of 10 and 30 MHz, in pure samples and in samples charged with 0.7 and 4.2 at.% hydrogen, in the presence of residual fusion oxygen.

In the hydrogen-charged samples, we found a thermally activated relaxation structure. The size of this structure increases linearly with the hydrogen concentration and it was attributed to a relaxation process due to stress-induced ordering of hydrogen atoms around the oxygen atoms present in the sample. This relaxation process occurred at 202 K and was fitted by a single Debye peak with an activation energy of 0.171 eV and jump frequency of 1.2×10^{12} s^{-1}, for the frequency of 10 MHz. For the frequency of 30 MHz, this process occurred at 235 K with an activation energy of 0.176 eV and a jump frequency of 0.8×10^{12} s^{-1}.

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