

DETECTION OF OXYGEN CONTENT IN A BETA-ZIRCONIUM BASED ALLOY BY INTERNAL FRICTION

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RESUME

Le frottement intérieur peut être une méthode alternative et non destructive pour contrôler la quantité de gaz dans les métaux par le moyen du pic de relaxation de Snoek dans les métaux b.c.c.

Dans notre travail, des études préliminaires sont présentées dans un alliage β -Zr-8 %pd Nb - 1 %pd Al (bcc) avec un contenu d'impuretés de base de 570 ppm en poids d'Oxygène, 67 ppm de Nitrogène et 29 ppm d'Hydrogène. Des échantillons dopés avec 173 et 210 ppm d'O additionnels, et 345 ppm de N additionnels ont été mesurés.

Pendant les premières montées, de la température ambiante jusqu'à 450°C, les spectres de frottement intérieur se caractérisent par les effets suivants:

a) Un pic P1 situé à 325°C (25 Hz) pour l'échantillon avec le contenu gazeux de base. La température du pic est sensible au contenu d'O: elle descend de 120°C pour 210 ppm additionnels. A l'envers, elle n'est que légèrement affectée par le N: elle augmente de 10°C pour 345 ppm additionnels.

b) Un pic P2 à 360°C (22 à 27 Hz), avec une hauteur croissante avec le contenu d'O. L'énergie d'activation d'environ 1.75eV est de l'ordre de grandeur de la diffusion de l'O dans la phase β des alliages de Zr. En conséquence, et par d'autres caractéristiques, on conclut que ce pic est un pic de Snoek.

c) Un pic P3 à 400°C (20 à 27 Hz), qui présente un comportement similaire à un pic des joints de grains. Les paramètres ne dépendent pas du contenu d'O.

On arrive à la conclusion suivante: le pic P1 peut être potentiellement meilleur que le pic P2 pour tester l'O après traitements thermo-mécaniques pendant la route d'élaboration de ces alliages.

ABSTRACT:

Internal Friction could be an alternative and non-destructive method for checking the gas content in metals by using the Snoek relaxation peak occurring in bcc metals. In this work, preliminary internal friction measurements are presented in a β -Zr-8 wt% Nb-1 wt% Al alloy (bcc) containing a basic impurity level of 570 wt ppm Oxygen, 67 ppm Nitrogen and 29 ppm Hydrogen. Samples with additional 173 and 210 ppm O, and 345 ppm additional N are also measured. During the first heatings from room temperature to 450°C, the internal friction spectra are described by the following effects:

a) A peak P1 placed at 325°C (25 Hz) for samples with a basic gas impurity content. The peak temperature is shown to be sensitive to the O content, since for additional 210 ppm it shifts 120°C downwards. Conversely, an additional 345 ppm N affects the peak temperature slightly by shifting it upwards by 10°C.

b) A peak P2 located around 360°C (22 to 27 Hz), with its maximum increasing with the O content. Its activation energy (about 1.75eV) is of the order of the one for O diffusion in beta Zr based alloys. From these and other characteristics we assume that this is a Snoek peak.

c) A peak P3 placed at 400°C (20 to 27 Hz) presenting a similar behaviour as a grain boundary peak. The P3 parameters do not change with the O content.

Potentially the P1 peak could be used better than P2 for controlling the picking up of O after thermo-mechanical processes during the fabrication of this type of alloys.

INTRODUCTION

The properties of metals and alloys are severely affected by the presence of gaseous elements in their composition, such as hydrogen, oxygen and nitrogen (1)

In zirconium alloys, the content of interstitial solutes above a certain level (which ranges up to 100 wt ppm for H and 1000 ppm for O and N) is detrimental for their mechanical properties (2). This is due not only to direct hardening mechanisms conducting to loss of ductility, like solution or precipitation hardening, but also to indirect effects related to changes in the stability of phases. In fact, O and N, for instance, are strong stabilizers of the α phase (3) and small variations in their contents produce significant changes in the microstructures obtained after the same thermomechanical treatment. Hence, for zirconium alloys the control of impurity content is critical with relation to fabrication routes and final product properties if uniform production is desired.

A traditional way of analyzing gases in metals is by the method of vacuum melting (4) which involves gaseous chromatography or mass spectrometry. In the latter case the limits of detection run from fractions of wt ppm to 1000 ppm for H, 2000 ppm for N and 4000 ppm for O, and the reproducibility of measurements is about 3 to 10% (5). This would be enough for the purpose named. But even when this method has proved to be useful in routine and investigation, there are some negative aspects such as:

- a) The method does not discriminate whether the gas is occluded, in solid solution or as a non metallic phase. The result is a global index.
- b) It requires frequent tests with standard samples to correct the results for possible interactions of gases with the walls of the equipment and with deposits of evaporated metal.
- c) It takes a relatively long time to set up the equipment (in some cases even a whole day for outgassing) and there are also some significant consumable goods such as the metal for the bath (in the case of Zr, Platinum is commonly used), graphite crucibles, etc..

On the other hand, the possibility of applying the internal friction (IF) technique to determine interstitial impurity content was established by Snoek (6) in the year 1939. In that case the height of the peak in α -Fe resulted proportional to the content of interstitial carbon within the bcc lattice. Since then, in many cases it has been possible to detect gases in solid solution in several metallic structures (7,8), in particular α zirconium (hcp) doped with O (9,10).

In pure bcc metals, precise measurements of Snoek peaks are shown by Weller (11) in coincidence with Falanga et al. (12) and Delobelle et al. (13) whenever the O content is not higher than 100 wt ppm. Otherwise, "modified Snoek peaks" appear involving more than one point defect.

Therefore, the aim of the present work is to study the possible application of this technique to check gas contents in zirconium based alloys in order to use it as a quick and non-destructive test along several stages of alloy development or production. Preliminary results are presented corresponding to Zr-8wt% Nb-1wt% Al. In this alloy it is possible to retain the high temperature β phase (bcc) by quenching (14). In this phase, the occurrence of Snoek peaks could be expected, related to interstitial solutes like H, O and N. The presence of these impurities in more or less quantity in zirconium alloys is practically unavoidable, depending on the purity of the starting materials and the fabrication history.

The results presented correspond to quenched samples measured in a torsion pendulum at frequencies between 20 to 27 Hz in the temperature range (20-450) $^{\circ}$ C.

EXPERIMENTAL

A small ingot of about 40 grams and approximate dimensions 35 \times 20 \times 10 mm, of the nominal composition mentioned above is obtained from nuclear grade zirconium sponge, niobium granules of 2N8 purity and pieces of aluminum rod of 4N purity. The necessary meltings are carried out in a refrigerated copper crucible by means of an electric arc furnace with a tungsten electrode under argon atmosphere (15).

The material thus obtained is then hot rolled at 700 $^{\circ}$ C in the α plus β phase field. Its initial thickness of about 10 mm is reduced to 2.7 mm by successive

passes of 0.5 reduction each. Subsequently the plate obtained is annealed for 20 minutes at 900°C in air to homogenize the β phase and immediately quenched in water. In this condition the microstructure presents an average grain size of 0.2 mm.

The plate is then machined over both surfaces in order to remove the oxide crust and to further strip the metallic layer contaminated by diffusion of gases, mainly O from the oxide. The machining has to be performed gradually in order not to introduce excessive martensite on the surface by deformation (16). Finally, a metallographic polishing, consisting in grinding up to paper Nr. 600 followed by a chemical attack in a solution of 50:45:5 parts water, nitric and hydrofluoric acids respectively, is used to eliminate the deformed material.

The resulting plate of 1.5 mm thickness is then spark-cut in strips of approximate dimensions of $1 \times 4.5 \times 65$ mm to serve as IF probes. All the remaining faces of the probes are given the same metallographic polishing.

A piece of this material is sent to be gas analyzed by the method of vacuum melting and gaseous chromatography. This gives us the basic level of gaseous impurity content as indicated in Table I. One of the probes is left as representative of this basic level and the remaining ones are doped with additional quantities of O and N.

TABLE I
GAS CONTENT OF DIFFERENT PROBES

Probe Nr.	Oxygen		Nitrogen		Hydrogen	
	Basic Added wt ppm		Basic Added wt ppm		Basic Added wt ppm	
1	570	--	67	345	29	-
2	570	--	67	--	29	--
3	570	173	67	--	29	--
4	570	210	67	--	29	--

The doping method consists in annealing the samples at 1050°C inside quartz capsules under a gas pressure given by the moles of the gas intended to be absorbed by the metal. Due to the low partial pressures of O and N in equilibrium with zirconium at that temperature, it can be assumed that the whole gas is absorbed (1). The annealing time (not less than 4 hours for O and 12 for N) is calculated to be sufficient for homogenization by diffusion. In these cases the samples are also immediately quenched after the annealings by breaking the capsules in water, and a final metallographic polishing given to their surface. In all cases the retention of β phase by quenching is verified by optical microscopy.

The IF measurements are carried out in an inverted torsion pendulum electronically automatized by the method of keeping a constant oscillation amplitude (17). Depending on the samples, the frequency ranges between 20 to 27 Hz. The analog output is corrected for the variation of frequency during the measurement (18). Continuous recordings of both a signal proportional to the IF (which is calibrated by free decay) and another signal proportional to the last three digits of the period are simultaneously obtained as a function of temperature. The heating and cooling runs are made at a speed of 65 degrees/hour under argon atmosphere.

RESULTS

The first measurements carried out in undoped material show the necessity of using the smallest amplitude attainable by the equipment in order to minimize the effect of the background, which would otherwise mask any possible peak. Hence, the deformation amplitude is kept constant at $e = 1.45 \times 10^{-5}$ in all measurements.

In figure 1 the IF as a function of temperature is shown for different samples during the first heating run. The preliminary results presented here will be restricted only to the first heating because of two reasons:

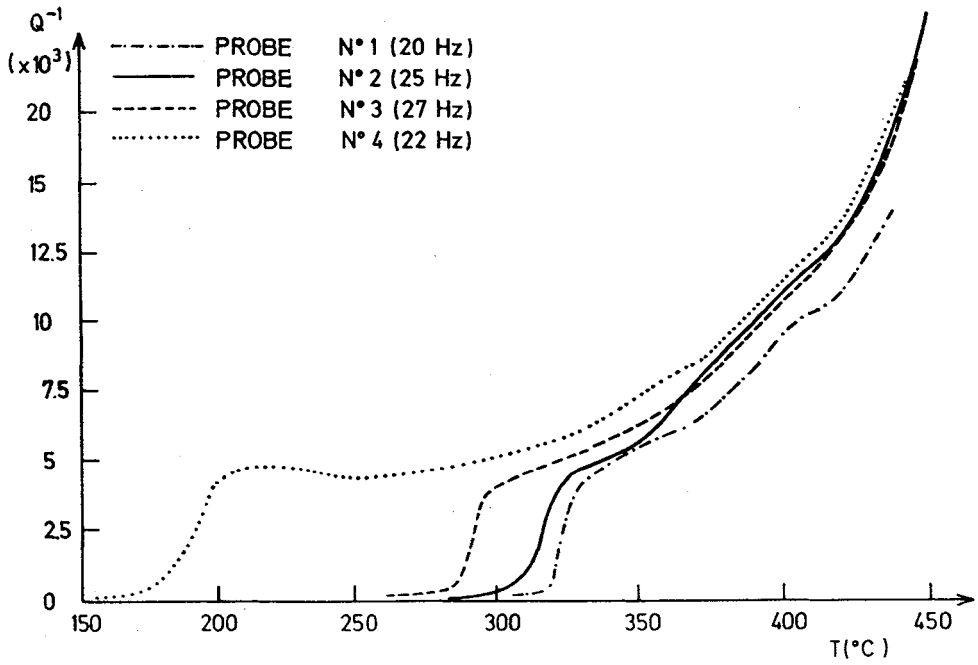


Figure 1.- Internal friction spectra during the first heating run.

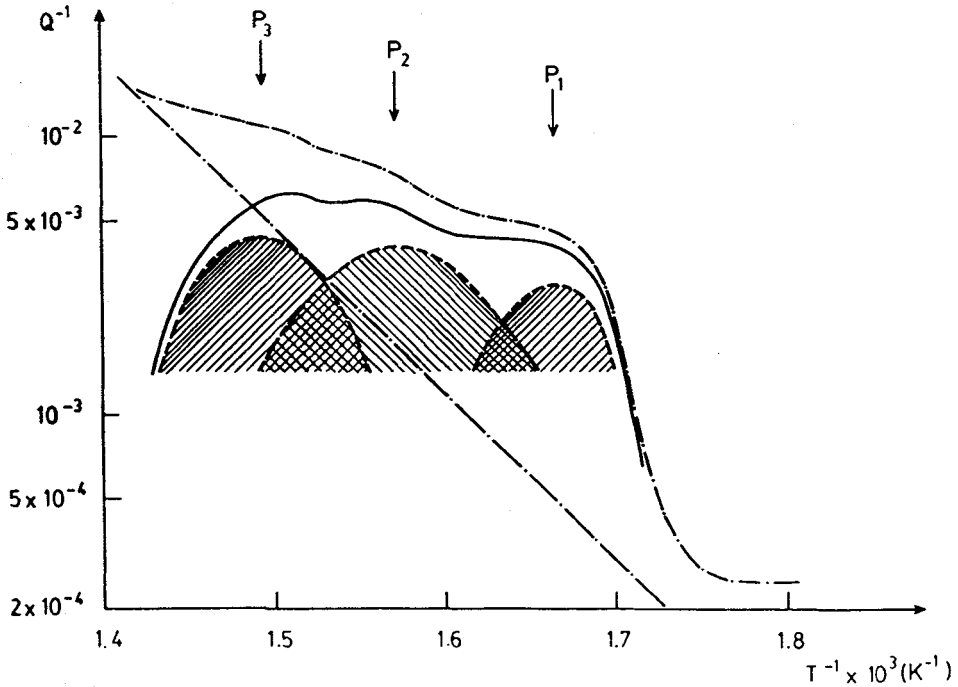


Figure 2: Logarithm of the internal friction as a function of the inverse of the absolute temperature.

1) If the technique is intended to be useful as a quick test, from a practical point of view it is important that the information be drawn as easily as possible.

2) It is observed that upon further cooling and re-heating, significant changes in the spectrum take place, possibly related to ageing effects.

Referring to figure 1, it can be observed that the sample with a basic impurity content (probe Nr. 2) presents a low background of IF, $Q(b) = 2.6 \times 10^{-4}$, up to 310° C. A first peak P1 shows up over the background with its maximum localized at 325° C. The sample doped with 345 ppm of additional N (probe Nr. 1) has a similar behaviour, but the peak is shifted about 10° C towards the higher temperatures. Finally, the samples doped with 173 ppm and 210 ppm of additional O (probes Nrs. 3 and 4) show the presence of the same peak P1 but significantly shifted towards the lower temperatures for about 30° C and 120° C respectively.

In all cases the background is low until the appearance of the first peak, after which a significant increase is observed.

By subtracting the background with an activation enthalpy $H(b) = 1.15\text{eV}$ in a $\ln(1/Q)$ versus $1/T$ plot, fig.2, apart from peak P1 another peak P2 can be distinguished, located at a higher temperature, about 360° C. The apparent activation enthalpies of these, estimated by their width, are $H(P1) = 2.8\text{eV}$ and $H(P2) = 1.75\text{eV}$. The location of P2 in temperature does not seem to be affected by the additional interstitial contents.

A third peak P3 apparently exists at about 400° C, not affected by the O content but appearing quite distinctly in the N-doped probe.

DISCUSSION

For P1, the results show clearly that the impurities do not affect the height of the peak, as would be expected from a Snoek-type relaxation. However, they do change significantly the peak location in temperature. The estimated activation enthalpy of P1 is consistent with an interpretation in terms of a phase transition rather than a Snoek relaxation.

In fact, taking into account that:

- 1) Precipitates of the hexagonal ω phase are formed athermally within the β phase while quenching (15), these quenched ω precipitates, ω_q , being coherent with the matrix, and
- 2) Upon heating, diffusion takes place and the ω_q phase suffers a transition by which the aged omega precipitates ω_a become of incoherent nature with little change in the c/a ratio (19).

Consequently, it is possible that P1 is related to the $\omega_q - \omega_a$ transition. The increase of the background level after P1 would be consistent with the loss of coherency of the precipitates according to Mondino and Schoek's theory (20).

Within this framework, the shifting of the peak with different interstitial contents would indicate that their presence induces a modification in the TTT diagram of the transition, since the heating speed is the same in all cases.

With respect to P2, it may be a relaxation peak of the Snoek type related to the O content. This assessment is supported by the fact that the estimated activation enthalpy compares well with the 1,78eV for the diffusion of O in β zirconium (21). Further support is given by the observation of an increase in the height of P2 with additional O.

Peak P3, which height appears distinctly lower in the N doped probe, could be related to the fact that this material requires a longer annealing time than the rest to allow for homogenization. Consequently the grains have more time to increase their size. This could support the interpretation of P3 in terms of a grain boundary relaxation peak, but with the present preliminary data it cannot be assured.

CONCLUSION

The internal friction spectrum of the β quenched Zr-8wt%Nb-1wt%Al upon the first heating run presents three peaks.

The first peak, P1, located at 325° C for undoped material, is clearly

distinguishable from the initial low background. After this peak, the background suffers a significant increase and tends to blur the following peaks. The location of P1 in temperature, but not its height, is very sensitive to the content of O, and to a smaller degree, to N. Due to its characteristics, the P1 peak is possibly related to the ageing of the ω_q phase precipitates present in the β matrix after quenching. This result suggests the use of transmission electron microscopy to verify the correlation between P1 and the ω phase.

With respect to the other two peaks, P2 and P3, at temperatures of 360 and 400°C respectively, the present results do not allow to draw a conclusive interpretation, further measurements and study being necessary.

The final conclusion is that, due to the sensitivity of P1 to the O content, it would be useful to apply the IF technique as a quick method to determine the O content in this alloy during the different processes that run from melting to final product, specially, considering that O is the gaseous impurity from air that most easily and in greatest quantity is incorporated to zirconium base alloys under various treatments.

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