Journal of Alloys and Compounds, 211/212 (1994) 50–53
JALCOM 100

Internal friction in pure iron nitrogenated by different methods

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Abstract

A method for the determination of nitrogen in solid solution using internal friction in ion-implanted and diffusion-doped pure α-Fe is presented. It also allows the indirect determination of some combined nitrogen (Fe nitride concentration). The method consists in measuring the Snoek relaxation during isotherms at low frequencies in a subresonant forced pendulum. Chemical analysis by a vacuum fusion technique is necessary to check the proportionality factor between the height of the internal friction peak and the interstitial nitrogen content. It is assumed that the polycrystalline samples are not textured and that the nitrogen is completely dissolved by annealing in an inert atmosphere. This kind of evaluation could be useful for characterizing b.c.c. metals in relation to certain applications where mechanical properties could be altered by the free nitrogen content.

1. Introduction

The Snoek effect [1, 2] in b.c.c. metals provides a standard tool to determine the interstitial solute contents of elements such as carbon and nitrogen. This is because the interstitial solute content C_i is directly related to the height $Q_{\max}{}^{-1}$ of the Snoek internal friction peak by a factor which depends on the solute nature. As an example, for nitrogen the relation is

$$C_N\ (\text{wt.\%}) = 1.3 Q_{\max}{}^{-1} \qquad (1)$$

This method assumes a Debye behaviour for the dependence of internal friction on frequency and an Arrhenius law for the dependence of the relaxation time on temperature.

2. Experimental details

The device utilized in the ion implantation processes was a plasma gun operated in the detonation mode [3]. In this system the ion beam is accelerated during the dense plasma focus formation as the result of a fast and high energy focalized discharge.

The electric energy stored in a capacitor bank is discharged, through a transmission line, into a coaxial electrode system immersed in a pure gas (nitrogen in our case) at 300 mTorr pressure. In an optimized system the breakdown is produced as a current sheath in one of the ends of the gun. Meanwhile, the electric discharge continues, and the current sheath moves through the interelectrode space ionizing and incorporating the gas which it finds along its way, accelerated by the Lorentz force. When the current sheath reaches the other (open) end, it is deformed, collapsing in front of the central electrode, generating a highly densified plasma column 1 mm in diameter and 6 mm in length, through which, if the system is optimized, will circulate the maximum of the current discharge, which in our case is about 100 kA.

The high current circulating through the small plasma column generates the conditions for the development of Rayleigh–Taylor instabilities, with the acceleration of ions (of the same species as the filling gas) forward and electrons backward.

The ion beams accelerated in such a small region have a conical geometry with a solid angle of 40°. The acceleration time is about 300 ns and the energy spectrum of the ions follows the spectral law [4]

$$dN/dE \propto E^{-3.4} \qquad (2)$$

where N is the number of ions with energy E, with the condition 20 keV $< E <$ 500 keV. The total number of ions emitted per discharge is 1×10^{15}.

For implantation purposes, the samples are located downstream and the total flux can be reached by the accumulation of a predetermined number of single

SSDI 0925-8388(93)00100-Q

beams. The system can be operated in a repetitive mode with frequencies higher than once every second.

Taking into account the continuous energy spectrum of the beams, and the fact that the penetration of ions depends on their kinetic energy (range), the implanted layers have an almost constant concentration profile from the surface down to a depth which for stainless steel is 300 nm or more [3].

The interaction of nitrogen ions with iron also generates vacancies; it can be estimated, for 50 keV nitrogen ions (a weighted average of energy for the continuous energy spectrum of the ions), that there are about 320 vacancies per ion. A strongly perturbed surface layer of thickness comparable with that of the nitrogen concentration profile can be expected.

Two cylindrical samples (1 mm in diameter and 15 mm in length) were taken from pure iron (99.99%) wires. They were nitrogen implanted with different nitrogen doses by means of the pulsed ion implanter described before, with a total accumulated flux of 6.5×10^{17} N atoms cm^{-2}.

The sites implanted were focused on eight points of the samples as shown in Fig. 1 with the ion beam cross section ($\sim$2.5 cm^2) centred at these points. In this manner, a complete implantation on the wire surface is expected.

The samples were measured in this "recently implanted condition", and then they were annealed at 590 °C for 1 week. They were slowly cooled inside the furnace while it was turned off, in order to homogenize the N in the bulk, to precipitate N into iron nitride, and also to precipitate C (present as impurity, less than 70 ppm by weight) into cementite (Fe_3C). In this situation, the samples can be considered as a binary system Fe–N for this study.

The internal friction measurements were made in a subresonant forced pendulum [5], during isotherms at temperatures near the Snoek peak. The amplitude of the oscillation was maintained constant at about 4×10^{-5}. A previous evaluation of amplitude dependence revealed no influence, as was expected from the Snoek model.

The principle of measurement is based on the time-dependent stress–strain relationship observed in linear isotropic anelastic solids. That is, a stress σ which varies sinusoidally in time with a circular frequency $\omega=2\pi f$ is imposed on the system, and a strain ϵ with a phase angle ϕ is obtained. The behaviour of the system is described by the complex elastic modulus $G^*(\omega)$:

$$G^*(\omega)=\sigma/\epsilon=|G(\omega)|\exp[-\mathrm{i}\phi(\omega)] \tag{3}$$

The internal friction (relative energy dissipation) is the tangent of that angle, *i.e.*

$$Q^{-1}=\tan[\phi(\omega)] \tag{4}$$

and the absolute elastic modulus G is given by

$$|G(\omega)|=\sigma_0/\epsilon_0 \tag{5}$$

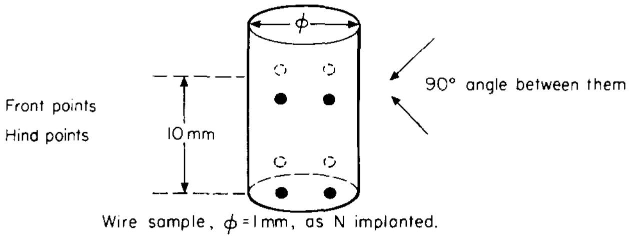

Fig. 1. Positions of implanted sites in the wire.

3. Results

In Fig. 2 the internal friction and the torsion elastic modulus in the recently implanted condition for sample 2 are shown.

Figures 3(a) and 3(b) show the results of the same type of measurement for the "implanted-and-treated condition", for samples 1 and 2 respectively.

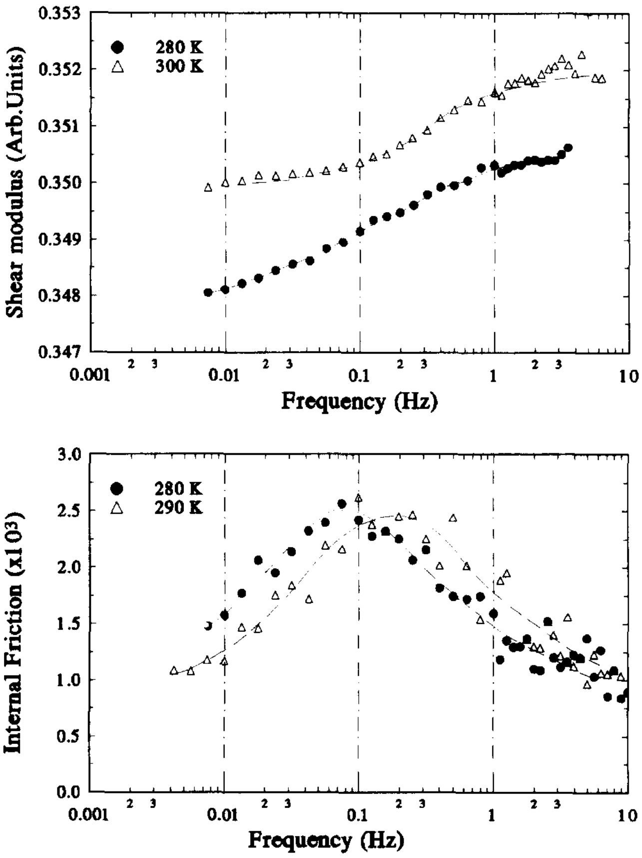

Fig. 2. Internal friction and torsion elastic modulus (in arbitrary units) as a function of frequency measured during isotherms, for sample 2, in the recently implanted condition.

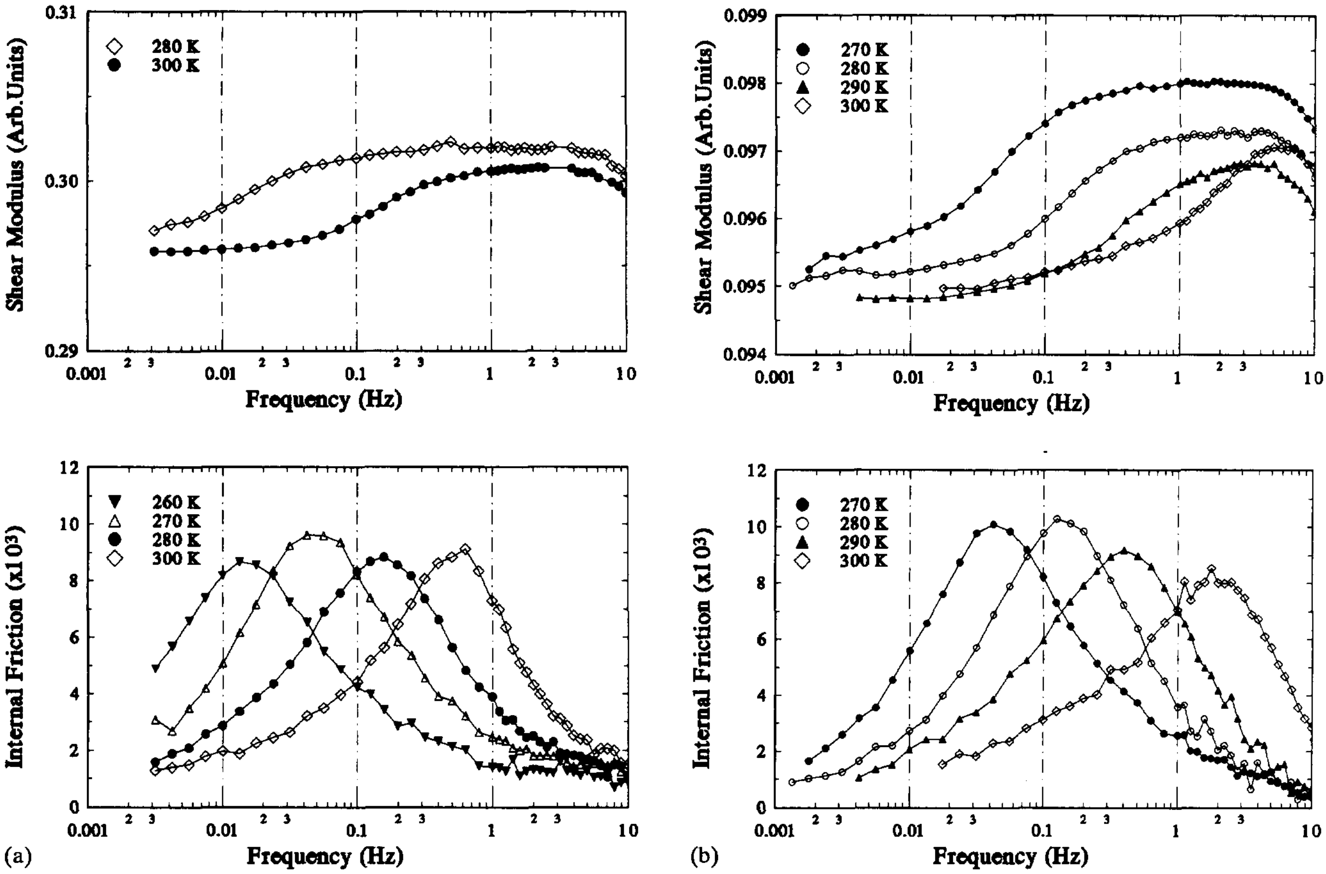

Fig. 3. The same plots as in Fig. 2 but in the implanted-and-treated condition, (a) for sample 2 and (b) for sample 1.

The chemical analysis for total N determination in the samples was made by the vacuum fusion technique, destroying the samples used in the internal friction measurements. The results are as follows:

sample 1, $C_N = 212$ ppm (by weight)

sample 2, $C_N = 140$ ppm (by weight) (6)

4. Discussion

The analysis of experimental data was made by assuming that the internal friction peak is due to the Snoek effect [1, 2], *i.e.* the interstitial N atom reordering induced by the applied stress in the α-Fe matrix (b.c.c.). The isothermal measurements were fitted, confirming the Debye peak shape and other characteristics.

The activation energy calculated from these results is as follows:

sample 1, (0.80 ± 0.04) eV

sample 2, (0.63 ± 0.15) eV

This is in agreement with the reported data, around 0.80 eV in refs. 1 and 2.

After these considerations, it is possible to determine the free N content (as interstitials in solid solution (SS)) from the height of internal friction peaks as proposed by eqn. (1). The results are as follows: (1) in the recently implanted state,

sample 2, C_N (in SS) = 30 ppm (by weight) (7)

(2) in the implanted-and-treated state,

sample 1, C_N (in SS) = 124 ppm (by weight)

sample 2, C_N (in SS) = 102 ppm (by weight) (8)

This represents 60% and 73% respectively of the total N content indicated in eqns. (6). This is due to the presence of the iron nitride phase.

This shows that the amount of iron nitride phase present in both samples, as well as that of free N, depends on the implanting conditions.

Figure 4 is a plot of the percentage of the interstitial N content with respect to the total N content *vs.* the total N content, assuming that for zero total concentration N is present only in interstitial SS. The last point is added from other results [6] for pure iron doped by a volume diffusion method (annealing for 4 h at 590 °C in ammonia gas at 0.8 atm, and solubilized for 1 week at 590 °C in Ar atmosphere).

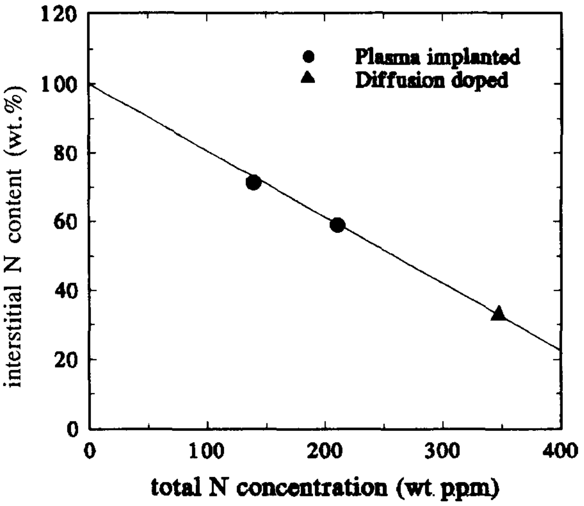

Fig. 4. Percentage of interstitial N content (from internal friction) with respect to the total N content *vs.* total N content (from chemical analysis).

This plot (Fig. 4) allows the interstitial N in a nitrogen diffusion-doped or plasma-implanted sample to be determined if a chemical analysis is provided.

5. Conclusions

It is shown that internal friction could be a useful tool to study the effects of N plasma implantation, especially for determining N in SS even in very small concentrations.

The iron nitride content can be estimated subtracting this free N content from the total N given by the chemical analysis.

In the implanted condition the N is concentrated near the surface, predominantly in the combined state. This is in agreement with the temperature profiles during plasma implantation calculated in ref. 7, as it is possible that N is concentrated in phases other than the b.c.c. phases (γ, δ and nitrides), and in less than a 0.5 μm depth from the surface.

For a quick use of this method, a chemical analysis would be enough if a previous study provided that an "interstitial N content" *vs.* "total N content" plot (like Fig. 4) for the system could be made.

More studies have to be made for higher N contents (more than 1000 ppm by weight), as a new peak due to N–N relaxation could appear.

The free N determination by internal friction is valid independently of the method used to introduce it: pulsed-ion implantation or volume diffusion doped.

Acknowledgments

This work was partially supported by the Comisión Nacional de Energía Atómica and the Consejo Nacional de Investigationes Científicas y Técnicas and partially granted under IAEA Research Contract RC/6477/R1/RB and ICTP TWAS Research Grant MP 90-090.

References

1 A.S. Nowick and B.S. Berry, *Anelastic Relaxation in Crystalline Solids*, Academic Press, New York, 1972.
2 J.D. Fast, *Interaction of Metal and Gases*, Vol. 2, Academic Press, New York, 1971.
3 J. Feugeas, E. Llonch, C.O. de Gonzalez and G. Galambos, *J. Appl. Phys.*, *64* (5) (1988) 2648.
4 W. Stygar, G. Gerdin and F. Venneri, *Nucl. Fus.*, *22* (9) (1982) 1161.
5 G. D'Anna and W. Benoit, *Rev. Sci. Instrum.*, *61* (1990) 3821.
6 A. Vertanessian and A. Ghilarducci, *Int. Congr. on Metallurgy and Mater. Technol., São Paulo, Brazil, October 9–14, 1994.*
7 J. Feugeas, G. Sanchez and G. Grigioni, *SLAFS 7-CIACSA 1, Bariloche, November 15–20, 1992*, Paper C24.