

Internal friction peaks in cold-worked and hydrogen-charged nickel

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Internal friction measurements are made on deformed and hydrogenated Ni at frequencies of 2 Hz, 800 Hz, and 30 kHz over the temperature range between 4.2 and 373 K. Two kinds of relaxation peaks P_d and P_{dH} accompanied by clear ΔM effects are commonly observed. P_d peak is generated at low temperature only by plastic deformation in uncharged Ni. Electrolytic charging with hydrogen suppresses this peak but instead induces P_{dH} peak at a temperature well above P_d peak. On aging (outgassing) at temperatures between room temperature and 473 K, P_d further diminishes temporarily, but recovers to the original height thereafter; conversely, P_{dH} first grows to a maximum height and then decays. These aging characteristics are related with nonuniform distributions of hydrogen in the samples. A good proportionality exists between the maximum height of P_{dH} and the height of P_d before H charging. In fully annealed samples where P_d is absent, P_{dH} is not generated evidently by H charging. From these results, it is concluded that P_d peak is ascribable to the dislocation relaxation peak of the Bordoni type, while P_{dH} peak to the cold-work peak which involves the interaction between hydrogen atoms and dislocations.

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I. INTRODUCTION

It has been shown by a number of investigations that hydrogen dissolved in metals causes various kinds of internal friction peaks at low temperatures.¹ For example, it gives rise to (1) Snoek-type relaxation peaks which originate from the stress-induced reorientation of hydrogen pairs or of hydrogen trapped in the vicinity of other impurity atoms, (2) precipitation peaks which are related to the precipitation of hydrides during cooling or heating runs of the measurements, (3) cold-work peaks which are caused by the interaction between hydrogen atoms and dislocations in deformed metals. These phenomena have been extensively investigated in such metals (V, Nb, Ta, Ti, Zr, and Pd) that absorb a large quantity of hydrogen stably at room temperature. In contrast, such investigations are rather limited in Fe,²⁻⁴ Ni,^{5,6} and Cu.⁷

Gibala² studied the effects of H concentration, aging and deformation on a Snoek-type peak and the cold-work peak of Fe cathodically charged with hydrogen, and estimated the binding energy between an H atom and a dislocation from the behaviors of the relaxation times and the relaxation strengths of both peaks. The energy (0.27 eV) was in reasonable agreement with those obtained from a thermodynamic analysis of the anomalous diffusion of hydrogen in steels.⁸ Less work is now available on Ni which is known, like Fe, to dissolve hardly any amount of hydrogen stably at room temperature. However, studies on the plastic deformation of Ni hydrogenated by means of cathodic charging⁹ or quenching from high temperatures in H₂ atmosphere¹⁰ have revealed that hydrogen can segregate to dislocations and strongly influence their motion. The segregation has been demonstrated by the presence of a sharp yield point and the occurrence of the Portevin-Le Chatelier phenomena (serrated yielding) at appropriate temperatures. More direct evidence of the hydrogen-dislocation interaction may therefore be derived from measurements of the internal friction.

Several researches¹¹⁻¹⁵ were reported which dealt with the effects of plastic deformation and subsequent annealing on the internal friction of pure Ni especially at high frequencies (15–30 kHz). According to these works, a clear relaxation peak can be observed at low temperature, which may have its origin in the intrinsic motion of dislocations under alternating stress. However, the nature of this peak, specifically the effect of impurities, does not seem to have been made clear enough by these investigations.

The present work aims firstly to elucidate the behavior of this low-temperature peak in hydrogen-free samples particularly at low frequencies, secondly to investigate the effect of hydrogen addition and subsequent aging upon this peak, and thirdly to search for additional peaks which may be induced by hydrogen dissolved in Ni. Measurements are made over a wide frequency range not only to determine the relaxation parameters as accurately as possible but also to examine the effect of the specimen size on the aging characteristics of these peaks by changing it significantly. It will be shown that hydrogen strongly suppresses the dislocation relaxation peak but instead induces an extra peak (the hydrogen cold-work peak) at a temperature well above the dislocation peak. These effects will be discussed in terms of the hydrogen-dislocation interaction in Ni.

II. EXPERIMENTAL PROCEDURE

The internal friction at low frequency was measured using an inverted torsion pendulum over the temperature range between liquid He temperature and 373 K at a frequency of about 2 Hz. The strain amplitude at the surface of a specimen was usually kept to 1×10^{-5} . Measurements were made at 5-degree intervals with a constant heating rate of 1 K/min. When necessary, an axial dc magnetic field was applied by a solenoid immersed in the liquid N₂ bath. However, because the low-frequency internal friction in deformed Ni was found to be little affected by the magnetic

field, the measurements were usually carried out without it. Measurements at higher frequencies were made employing transverse and longitudinal vibrations at about 800 Hz and 30 kHz, respectively, in the temperature range above liquid N₂ temperature. In the latter measurement, a magnetic field of 39 kA/m (500 Oe) was applied to minimize the ferromagnetic damping which was found to dominate the internal friction particularly in the kHz range in Ni.¹⁶

Samples used for the torsion pendulum were wires (1-mm diameter and 50 mm long) which had been prepared from 99.99% Ni rods (Johnson-Matthey Chemicals) or from 99.95% Ni rods through cold-drawing and annealing for 3 h at 1173 K in vacuum. The grain size was approximately 100 μm. They were deformed in appropriate amounts by tension at room temperature and subjected to the measurements 24 h after the deformation. No clear difference in the internal friction spectra was found between the two kinds of samples of different purity. For the measurements with transverse and longitudinal modes, samples in the forms of rectangular plates (1 mm thick and 80 mm long) and cylindrical rods (4.5-mm diameter and 81.8 mm long) were used, respectively. They were prepared by rolling or swaging from ingots which had been produced by melting 99.95% Ni pellets in alumina crucibles in vacuum. These samples were chemically polished and annealed as mentioned above. The main impurities contained were Co < 0.03 wt.%; Fe, Cu, Si < 0.005 wt.%.

Hydrogen charging was performed by an electrolytic method in which each specimen was immersed as a cathode in an aqueous solution of 1N H₂SO₄ kept at 323 K, and a regulated current density of 50–100 mA/cm² was supplied through a Pt anode for 1–20 h. The hydrogen contents of the specimens subjected to charging were not analyzed. According to the work of Saga and Miyata,¹⁷ the hydrogen concentration (H/Ni) in thin Ni plates, 20 μm thick, subjected to cathodic charging under similar conditions ranges between 0.1 and 0.5. However, because the diameter or the thickness of the specimens used in the present damping measurements

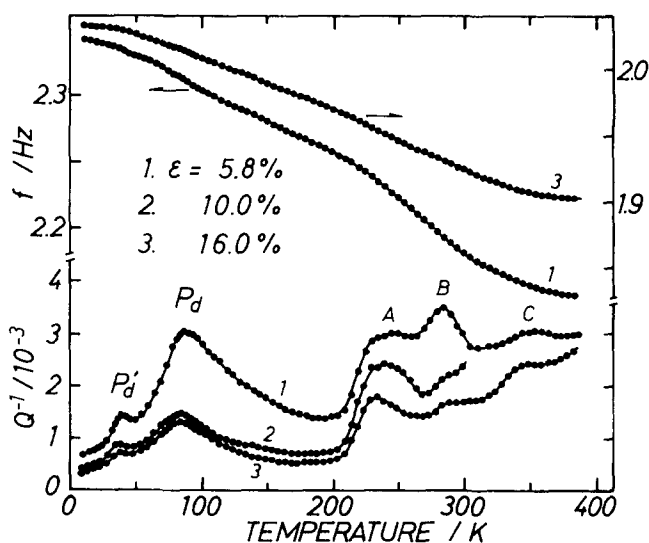


FIG. 1. Internal friction and oscillation frequencies of Ni samples elongated to 5.8, 10.0, and 16.0% measured in the torsional vibration.

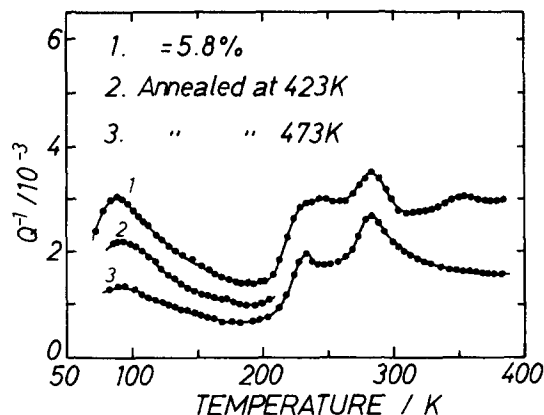


FIG. 2. Annealing behavior of the internal friction of Ni strained by 5.8%.

greatly exceeds this size, and because the diffusivity of hydrogen in Ni is relatively low at this charging temperature,¹⁸ it generally follows that hydrogen is no longer distributed uniformly over the cross sections of the specimens but is concentrated in the surface layers after the charging treatments. This point will be discussed in detail in Sec. IV.

III. RESULTS

A. Internal friction peaks in uncharged Ni

Figure 1 shows internal friction spectra (Q^{-1}) of Ni samples elongated to $\epsilon = 5.8, 10.0,$ and 16.0% together with their oscillation frequencies (f). We can observe a prominent peak (labelled P_d) centered at 85 K and a small subsidiary one (P'_d) at 38 K accompanied by respective modulus defects (ΔM effect). In addition, other structures $A, B,$ and C can be seen between 200 and 373 K, some of which may be equivalent to the damping peaks observed in a prior study.¹⁹ The abnormally large modulus drop seen in this temperature range is associated with the ferromagnetism of Ni (ΔE effect).²⁰

Figure 2 displays the effect of annealing ($\frac{1}{2}$ h at 423 and 473 K) on the internal friction in the 5.8% strained sample. P_d peak along with its background damping decreases monotonically during annealing, while the structures A and B near 240 and 280 K, respectively, which are not well characterized yet, undergo less changes. The structure C near 350 K, which could be the relaxation peak due to self-interstitials,¹⁹ completely anneals out at 473 K. Since the present work primarily concerns with the behaviors of P_d and P'_d peaks, no further investigation has been made on the other peaks in pure Ni.

In Fig. 3 are plotted the heights of P_d peak (Q_m^{-1}) corrected for the background damping against prestrain and annealing temperature. One notices that P_d attains a maximum strength at about 5% prestrain and reaches a plateau level at above 10%. It progressively recovers during isochronal annealing ($\Delta t = \frac{1}{2}$ h) after 5.8% prestrain and disappears on recrystallization at above 773 K.

From the strain-amplitude dependence of the internal friction in deformed samples, both P_d and P'_d peaks were found to undergo little changes when the amplitude increased from 1×10^{-5} to 4×10^{-5} though the background level increased significantly. It was additionally found that

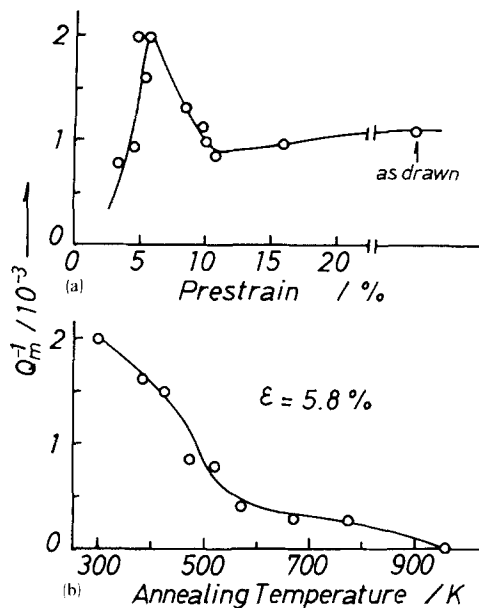


FIG. 3. Heights of P_d peak plotted against (a) prestrain and (b) annealing temperature. $f \approx 2$ Hz.

an external magnetic field of 8 kA/m (100 Oe) greatly modified f above 200 K owing to the ΔE effect involved, but it scarcely influenced Q^{-1} in cold-worked samples.

The internal friction and resonant frequencies of 4.0, 10.9, and 17.5% elongated samples measured in the longitudinal mode of vibration under a magnetic field of 39 kA/m close to saturation are shown in Fig. 4, where a single broad peak accompanied by a clear modulus defect can be seen at a temperature around 135 K. This peak corresponds to peak Y first observed by Sommer and Beshers at 30 kHz in deformed Ni,¹¹ and is considered to be the counterpart of P_d peak observed at low frequencies. The effects of deformation and annealing on this peak were very similar to those observed above in the low-frequency measurements.

B. Effect of hydrogen charging

Hydrogen addition causes drastic changes of the spectra of Q^{-1} and f of deformed Ni.^{5,6} Figure 5 displays data for

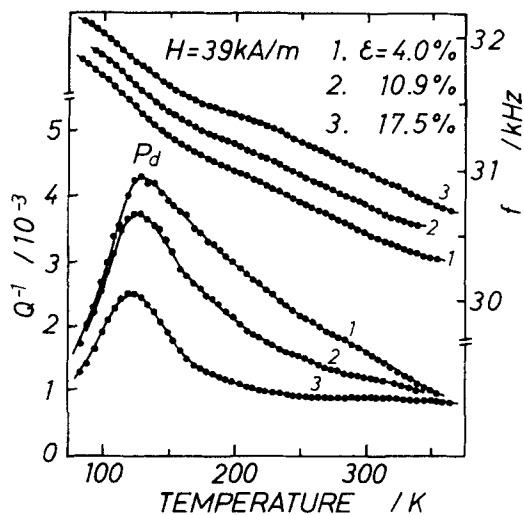


FIG. 4. Internal friction and resonant frequencies of Ni samples elongated to 4.0, 10.9, and 17.5% measured in the longitudinal vibration.

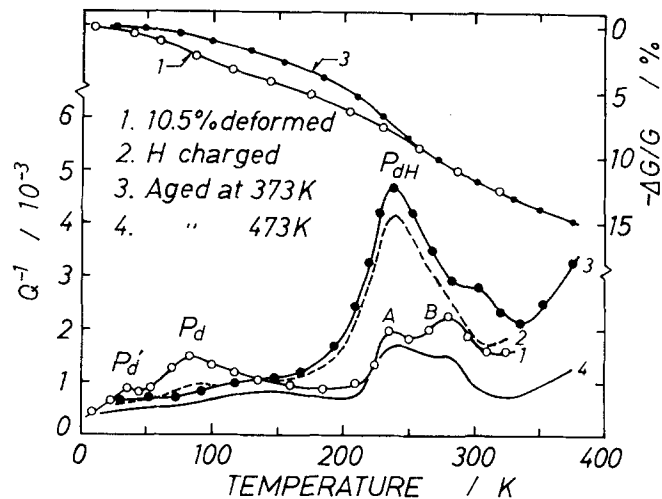


FIG. 5. Effects of hydrogen charging ($50 \text{ mA/cm}^2 \times 1 \text{ h}$) and subsequent aging upon the internal friction and modulus change in Ni elongated to 10.5%. $f \approx 2$ Hz.

a specimen strained 10.5% and charged with hydrogen ($50 \text{ mA/cm}^2 \times 1 \text{ h}$) measured in the torsional vibration at $f \approx 2$ Hz. It is obvious from this figure that H charging effectively suppresses P_d and P'_d peaks and the respective ΔM effects, but instead induces a great maximum (P_{dH}) at about 240 K accompanied by a clear ΔM effect. This new damping maximum is supposed to be an additional peak superimposed on smaller pre-existing peaks (A and B) in the uncharged state. Subsequent aging at 373 K for 1 h somewhat increases P_{dH} peak, but further aging at elevated temperatures suppresses it and reproduces a profile similar to the one observed before H charging after aging for 1 h at 473 K, except that a broad hump is still remaining at around 150 K. However, P_d peak is not yet reproduced in this stage; note that the aging temperatures are not high enough to eliminate it in uncharged samples. Another important feature to note is that the modulus defect associated with P_{dH} peak nearly cancels the sum of those of P_d and P'_d peaks before the hydrogenation. Similar features of the internal friction and modulus change have been observed between a low-temperature peak and a hydrogen-induced peak in deformed Fe by Takita and Sakamoto,³ and by Moser *et al.*⁴

The behaviors of P_d , P'_d , and P_{dH} peaks during isothermal aging at 373 K observed at $f \approx 2$ Hz are shown in Fig. 6. A specimen deformed by 4.0% was subjected to a heavy H charging ($50 \text{ mA/cm}^2 \times 10 \text{ h}$), which led P_d and P'_d to be entirely suppressed and P_{dH} to be enhanced to its maximum height of saturation. Upon aging, P_{dH} monotonically decayed shifting toward lower temperature and vanished after 148 h, where P_d and P'_d were clearly reproduced. As shown later, these charging and aging characteristics are closely related with the hydrogen diffusion into and desorption out of the Ni samples.

Figure 7 shows data taken employing the transverse vibration at $f \approx 800$ Hz. After 8.8% prestrain one can observe a broad maximum at about 120 K, which no doubt corresponds to P_d peak mentioned above. Hydrogen charging ($50 \text{ mA/cm}^2 \times 1 \text{ h}$) depresses this peak and produces another distinct one P_{dH} at 300 K. The aging features of both

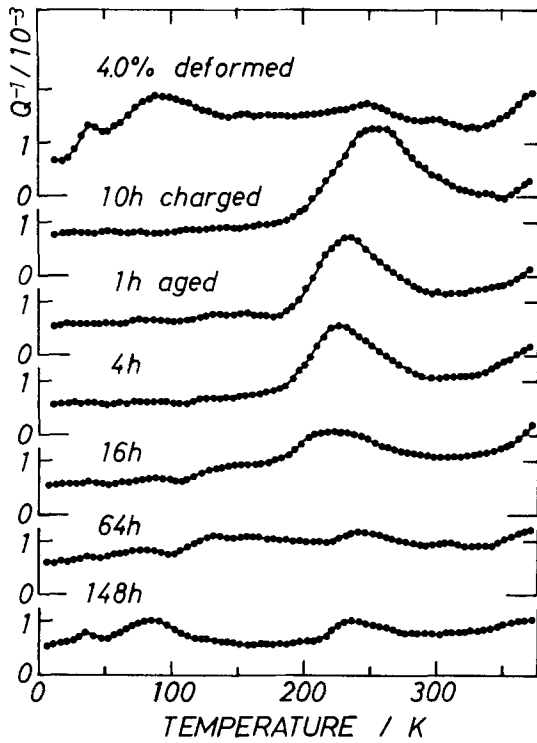


Fig. 6. Evolution of the internal friction during isothermal aging at 373 K in a Ni sample elongated by 4.0% and charged with hydrogen ($50 \text{ mA/cm}^2 \times 10 \text{ h}$), measured in the torsional vibration at $f \approx 2 \text{ Hz}$.

peaks are similar to the low-frequency data presented above.

Figures 8 (a) and 8(b) display similar data obtained using the longitudinal vibration at $f \approx 30 \text{ kHz}$ for a sample elongated by 3.2%. Electrolytic charging ($100 \text{ mA/cm}^2 \times 10$ to 20 h) lowers P_d peak but generates, as expected, a broad maximum P_{dH} at around 330 K which grows and tends to shift upward with increasing charging time. As shown in Fig. 8(b), P_d continues decreasing during subsequent isochronal aging until it is entirely lost after aging at 423 K, while P_{dH} first grows remarkably and then decays with appreciable downward shifts of the peak temperature. Aging at 473 K for 1 h

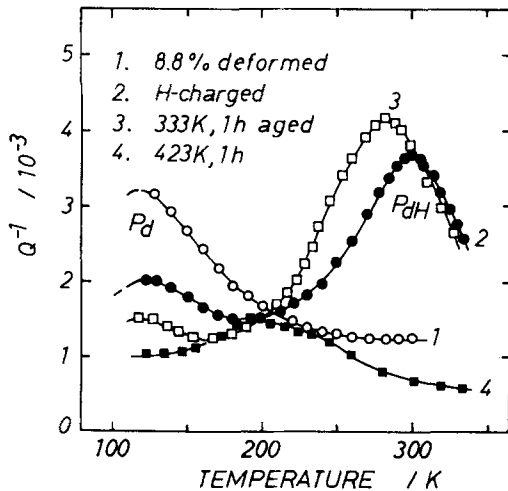


Fig. 7. Internal friction spectra of Ni deformed by 8.8% in tension, hydrogen charged ($50 \text{ mA/cm}^2 \times 1 \text{ h}$) and then aged. Measurements are made using the transverse vibration at $f \approx 800 \text{ Hz}$.

markedly reduces the strength of P_{dH} , but the complete elimination of it is not yet achieved. No indication of the recovery of P_d peak is obtained in this aging stage.

In Fig. 9 (a) is shown the evolution of the two internal friction peaks during isothermal aging at 373 K measured in the longitudinal vibration for a sample deformed by 10.9%. The sample is annealed for 1 h at 423 K before H charging ($100 \text{ mA/cm}^2 \times 10 \text{ h}$). This preannealing treatment reduces the strength of P_d peak, but is useful to stabilize it thermally during subsequent aging. It is evident from this figure that P_d peak initially decreases with aging time until it becomes hardly noticeable after 64 h. However, it begins to increase once more and recovers to the original strength with prolonged aging up to 1053 h. Conversely, P_{dH} peak first increases to attain a maximum strength after 16–64 h, then decays and disappears completely after 1053 h, where the original internal friction spectrum before H charging is precisely reproduced. These variations of the internal friction are properly followed by changes in the resonant frequency, as shown in Fig. 9(b); note that the modulus defect associated with P_d is suppressed and the one associated with P_{dH} is

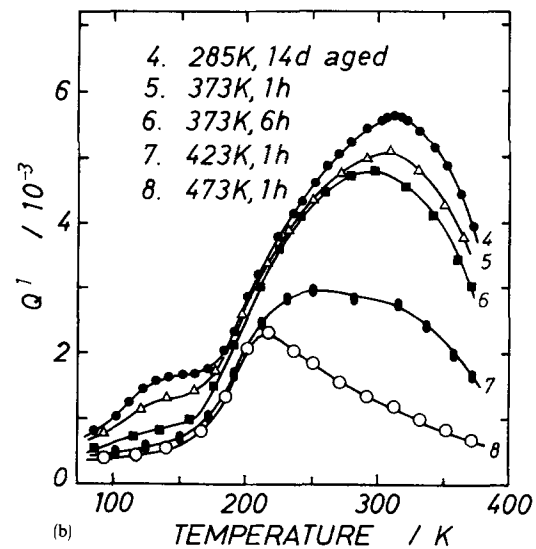
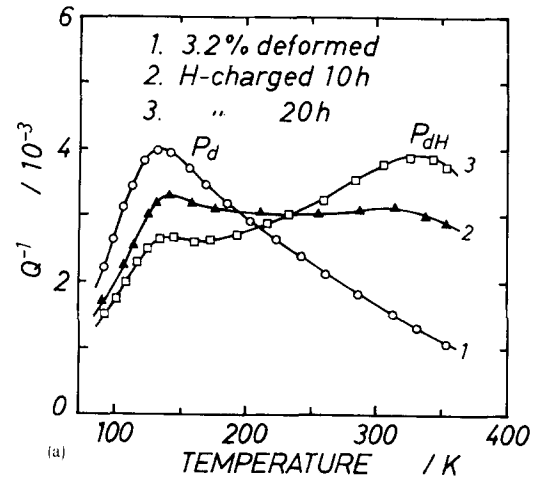


FIG. 8. Behavior of the internal friction in 3.2% deformed Ni after (a) hydrogen charging ($100 \text{ mA/cm}^2 \times 10$ and 20 h) and (b) subsequent aging. Measurements are made using the longitudinal vibration at $f \approx 30 \text{ kHz}$.

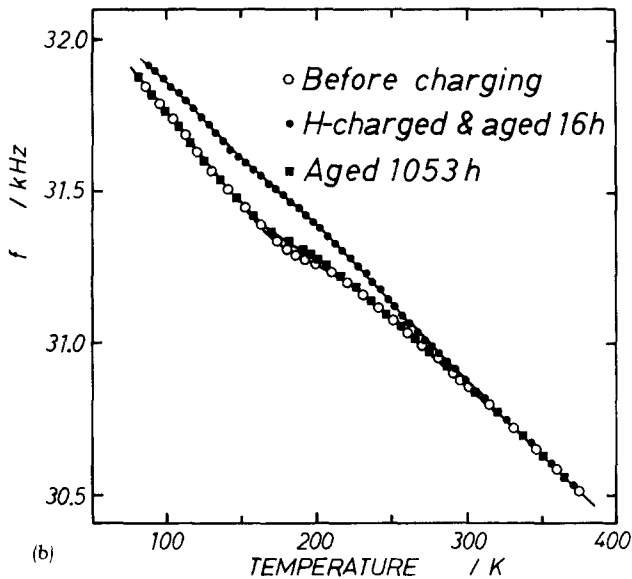
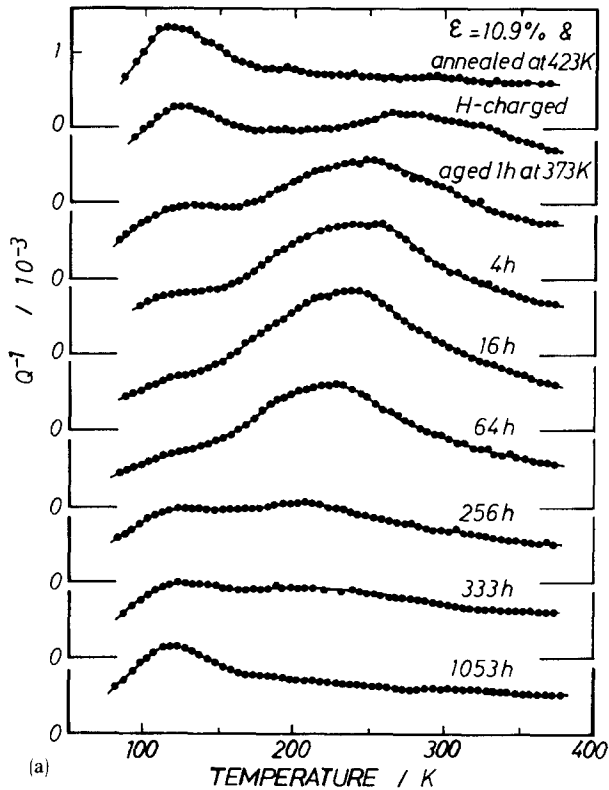


FIG. 9. (a) Internal friction spectra during isothermal aging at 373 K of a Ni sample elongated by 10.9%, preannealed at 423 K for 1 h and charged with hydrogen ($100 \text{ mA/cm}^2 \times 10 \text{ h}$); (b) the corresponding changes in the resonant frequency.

enhanced by H charging + aging for 16 h, but a complete recovery of the resonant frequency occurs after aging for 1053 h. These aging characteristics of the internal friction and elastic modulus are consistent with those observed at a low frequency (Fig. 6). The difference in the aging times necessary to achieve the complete recovery between the two measurements can be attributed to the difference in the specimen diameters employed.

The strength of P_{dH} peak seems to be correlated with that of P_d peak before H charging as shown in Fig. 10, where

the maximum height of P_{dH} observed during isothermal aging is plotted against the height of P_d for several samples tested using the longitudinal vibration. The amount of H charging is fixed to $100 \text{ mA/cm}^2 \times 10 \text{ h}$. In this condition, P_{dH} grows the highest and appears around 250 K after aging for 16 h at 373 K. It is noteworthy that a good proportionality exists between the two quantities.

Figure 11 shows the effect of hydrogen on the internal friction in an as-annealed specimen. The internal friction displays a small but broad damping maximum around 200 K. This maximum represents a ferromagnetic damping peak caused by the microeddy current loss in Ni,¹⁶ remaining even in a magnetic field of 39 kA/m. It can be seen that the hydrogen addition causes only a minor change in Q^{-1} above 300 K; no clear evidence of the development of P_{dH} peak has been given after hydrogen charging ($100 \text{ mA/cm}^2 \times 10$ to 30 h) and subsequent aging (16 h at 373 K). This result indicates that the presence of both deformation and hydrogen is required to develop P_{dH} peak. The ferromagnetic damping peak seems to be modified a little by the hydrogen addition.

IV. DISCUSSION

A. Summary and analysis of the results

It follows from the preceding results that P_d and P_{dH} peaks, commonly observable over the wide frequency range investigated, are caused by some relaxation mechanisms which are mutually closely related. The fact that plastic deformation is required to produce both P_d and P_{dH} peaks suggests that dislocations play dominant roles in causing the two peaks. Before discussing the nature of these peaks, we summarize some damping parameters associated with them below.

Figure 12 displays an Arrhenius diagram where $\ln f$ is plotted against the inverse peak temperature T_m^{-1} for P_d and P_{dH} peaks. The peak temperature of P_{dH} shifts upwards with increasing amount of H charging and downwards with the progress of aging irrespective of the oscillation frequencies, so that T_m is tentatively defined here at the peak temperature in a lightly charged state; i.e., $50 \text{ mA/cm}^2 \times 1 \text{ h}$ for the torsional and transverse vibrations, and $100 \text{ mA/cm}^2 \times 10 \text{ h}$ for the longitudinal vibration. As shown in the figure,

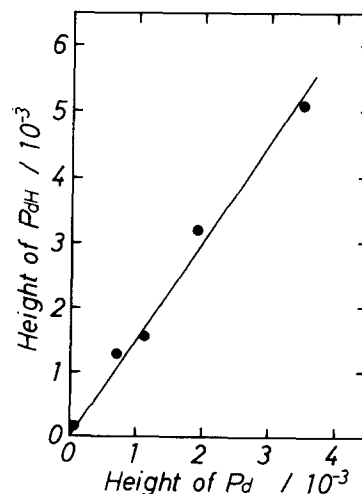


FIG. 10. Maximum height of P_{dH} peak produced by hydrogen charging ($100 \text{ mA/cm}^2 \times 10 \text{ h}$) plus subsequent aging, plotted against the height of P_d peak before the H charging. Measurements are made in the longitudinal vibration for Ni samples deformed in appropriate amounts by tension.

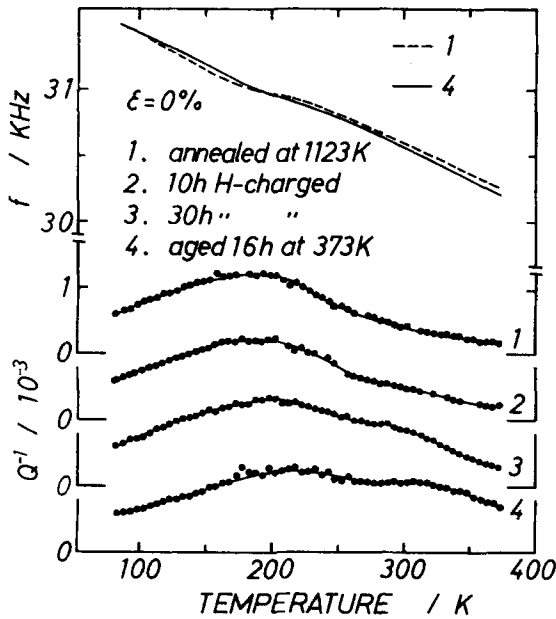


FIG. 11. Internal friction spectra of a fully annealed Ni sample after hydrogen charging and subsequent aging.

straight lines can be drawn through the points of both peaks, from which their activation parameters can be determined by making use of the relationships

$$f = 1/2\pi\tau = f_0 \exp(-H/k_B T_m), \quad (1)$$

where τ is a relaxation time and k_B is Boltzmann's constant. Table I summarizes values of f_0 and H thus obtained, together with typical values of $r = (\Delta M/M)/2Q_m^{-1}$ and

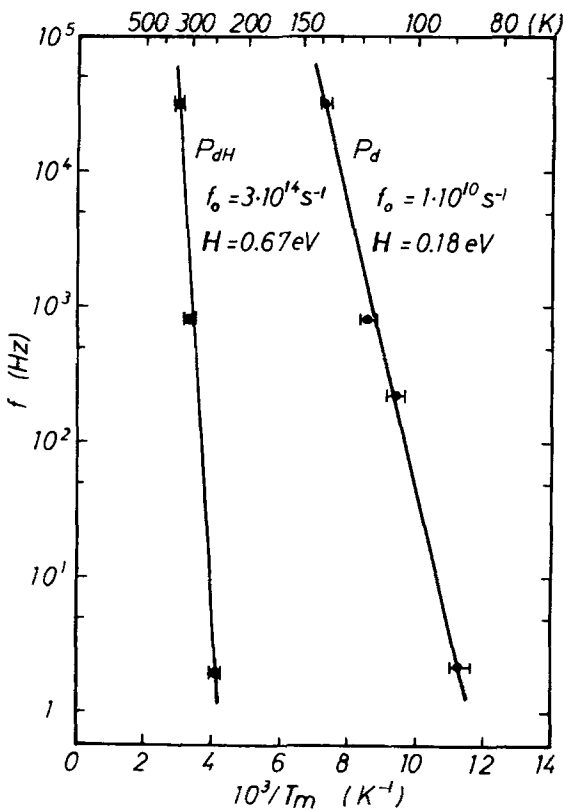


FIG. 12. $\ln f$ plotted against T_m^{-1} for P_d and P_{dH} peaks.

TABLE I. Typical values of the vibrational frequencies f , the peak temperatures T_m , the parameters $r = (\Delta M/M)/2Q_m^{-1}$ and $w = \Delta(T^{-1})/\Delta_0(T^{-1})$, the frequency factors f_0 , and the activation enthalpies H for P'_d , P_d , and P_{dH} peaks.

Peaks	f (Hz)	T_m (K)	r	w	f_0 (Hz)	H (eV)
P'_d	2.3	38	2.9	2.5	$(1 \times 10^7)^a$	$(0.051 \pm 0.003)^a$
	2.3	85	2.9	6.0		
P_d	800	120	1×10^{10}	0.18 ± 0.02
	31 000	135	2.8	4.5		
	2.0	240	2.3	3.2		
P_{dH}	800	300	1.8	3.6	3×10^{14}	0.67 ± 0.08
	31 000	333	3.1	6.4		

^a Obtained by means of combining the present data with those of Ref. 14.

$w = \Delta(T^{-1})/\Delta_0(T^{-1})$ for P'_d , P_d , and P_{dH} peaks. Here, r means the ratio of a modulus defect to a corresponding relaxation strength, and w is the ratio of a measured peak width in the reciprocal temperature scale T^{-1} to the corresponding width of a single Debye peak given by $\Delta_0(T^{-1}) = 2.635k_B/H$. The magnitudes of r and w for P_d and P_{dH} peaks are much larger than unity valid for a single relaxation peak, indicative of widely distributed relaxation times involved. This fact is not inconsistent with the foregoing anticipation that dislocations are involved in the relaxation mechanisms of these peaks. Values of f_0 and H of P'_d peak are tentatively evaluated by combining our data at 2 Hz with those of P'_d of deformed Ni measured in the kHz range.¹⁴

B. The effect of hydrogen on P_d peak

The activation parameters of this peak obtained in this work are in close agreement with those reported for P'_d by Besson and Boch,¹⁴ who have assigned it to the Bordoni peak in Ni. The behavior of P_d peak following cold working and annealing (Fig. 3), along with its insensitivity to strain amplitude and external magnetic field,¹⁶ seems to be in favor of the above assignment. The relaxation parameters of P_d have magnitudes typical of the Bordoni peaks in other fcc metals.^{21,22} The small subsidiary component P'_d could be corresponding to the Niblett-Wilks peak observable in certain fcc metals.²¹

The effect of hydrogen addition on P_d peak (Figs. 5-9) can be accounted for in terms of pinning of dislocation lines by hydrogen atoms. Though the solubility of hydrogen in Ni is very small at ambient temperature, H atoms introduced at the surface of a specimen by cathodic charging diffuse into the lattice and may segregate in the vicinity of dislocations and pin them down.^{9,10} Now, let us consider the distribution of the hydrogen concentration, c , within a cylindrical rod of radius a . When the concentration at the surface is kept constant during charging, i.e., $c = c_0$ at $r = a$, it follows from Fick's law that²³

$$\frac{c}{c_0} = 1 - 2 \sum_{n=1}^{\infty} \frac{\exp(-k_0 x_n^2) J_0[(r/a)x_n]}{x_n J_1(x_n)}, \quad (2)$$

with $k_0 = D_0 t_0/a^2$, where $J_0(x)$ and $J_1(x)$ are the Bessel functions of zeroth and first order, respectively, and x_n 's are the

roots of $J_0(x) = 0$. Subsequent aging may cause hydrogen to be desorbed out of the surface and alter its distribution into the form (see the Appendix)

$$\frac{c}{c_0} = 2 \sum_{n=1}^{\infty} \frac{J_0[(r/a)x_n]}{x_n J_1(x_n)} \exp(-kx_n^2) [1 - \exp(-k_0 x_n^2)], \quad (3)$$

with $k = Dt/a^2$. In the above expressions, D_0 and D denote the diffusion coefficients of hydrogen during the charging time t_0 and the aging time t , respectively. The diffusion coefficient of H in Ni is best written, for $T < T_c (= 618 \text{ K})$, as¹⁸

$$D (\text{cm}^2/\text{s}) = 4.8 \times 10^{-3} \exp(-0.408 \text{ eV}/k_B T). \quad (4)$$

As an example we take, assuming the longitudinal vibration, $a = 0.225 \text{ cm}$, $D_0 = 2.1 \times 10^{-9} \text{ cm}^2/\text{s}$ at 323 K, and $t_0 = 10 \text{ h}$ to obtain $k_0 = 0.001$. On the other hand, taking $D = 1.5 \times 10^{-8} \text{ cm}^2/\text{s}$ at 373 K and $t = 1, 4, 16, 64, 256$, and 1024 h, we get $k = 0.001, 0.004, 0.017, 0.068, 0.272$, and 1.085, respectively. Figure 13 shows calculated curves of c/c_0 against r/a at t_0 and t given above, which indicates that hydrogen is concentrated within the surface layer of a thickness $\sim a/10$ in an as-charged state (curve 1). Most of it is removed (outgassed) via the following short-time aging, but there still remains a minor quantity of hydrogen diffusing deeper into the rod (curves 2–4) and becoming distributed over the entire cross section for longer aging times (curves 5–7).

The inhomogeneity of the hydrogen distribution and its variation with aging time inside the rod calculated above may properly explain the progressive decay of P_d peak during isothermal aging shown in Fig. 9(a). If one assumes a value $c_0 \approx 0.1$ in H/Ni,¹⁷ the concentration for $t = 64 \text{ h}$ aver-

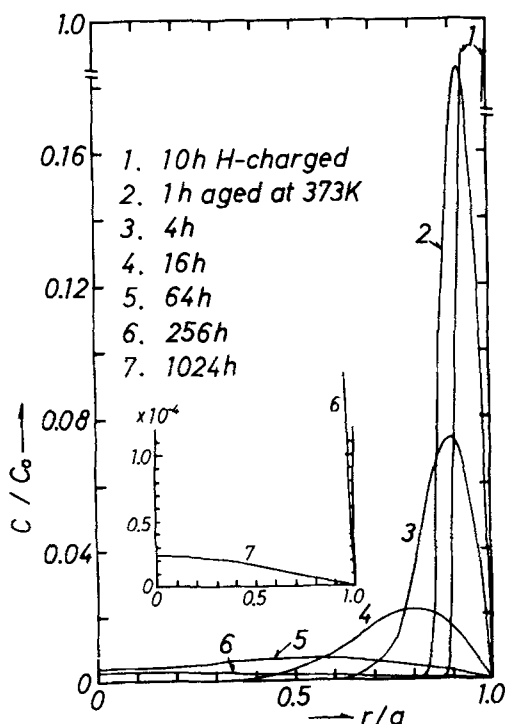


FIG. 13. Hydrogen distributions within a cylindrical Ni rod of radius a , calculated using Eqs. (2) and (3) with charging and aging times indicated.

aged over the cross section becomes $\bar{c} \approx 5 \times 10^{-4}$. This concentration appears to be high enough for hydrogen atoms to pin down almost all dislocations causing P_d peak and thereby suppress it completely, if an appropriate binding energy is assumed between a H atom and a dislocation. This suppressed P_d peak appears again when the hydrogen concentration is more reduced via further outgassing for $t \gtrsim 256 \text{ h}$, where the concentration may have been reduced to the level $\bar{c} \lesssim 1 \times 10^{-4}$. A complete recovery of this peak is achieved for $t = 1053 \text{ h}$, where \bar{c} becomes as low as $\sim 10^{-6}$. In the case of the torsional vibration ($a = 0.05 \text{ cm}$) shown in Fig. 6, an entire recovery of P_d peak has been achieved for $t = 148 \text{ h}$ at 373 K, for which we have $k = 3.197$ and $\bar{c} < 10^{-6}$.

C. Interpretation of P_{dH} peak

There is probably little possibility that P_{dH} peak represents a Snoek-type relaxation peak of dissolved hydrogen atoms or their complexes, because it does not occur in fully annealed samples even if sufficient amounts of hydrogen are introduced into the samples, which seems to be unlikely for Snoek-type peaks of H atoms. In contrast, a relaxation mechanism of the cold-work peak (CWP)²⁴ which involves the interaction between interstitial impurity atoms and dislocations appears to be favorable to explain some aspects of the nature of this peak properly. Specifically, it is useful to account for the close correlation observed between P_d and P_{dH} peaks. Based on this interpretation, the initial increase of the P_{dH} peak height upon aging in lightly charged samples can be explained as follows: the deeper the added hydrogen diffuses into the samples, the more dislocations interact with the hydrogen and participate in producing P_{dH} at the expense of P_d ; the subsequent decay should be due to the desorption of the hydrogen. On the other hand, in heavily charged samples, P_{dH} peak undergoes a saturation and hence no longer exhibits a peak growth on subsequent aging. These aging characteristics are consistent, at least qualitatively, with the calculated hydrogen distributions within the samples. A more quantitative analysis of the aging feature of P_{dH} peak is necessary and is now in progress.

Hydrogen CWP's in fcc metals and alloys have hitherto been studied in Pd,^{25,26} and in austenitic stainless steels.²⁷ In Pd, hydrogen is absorbed in a great deal precipitating hydrides at room temperature. In this system both the CWP in the metal phase and a Snoek (or Zener)-type peak in the hydrides have been found to coexist. The Bordoni peak is suppressed by hydrogen addition, in agreement with our present investigation on Ni. Combette *et al.*⁵ observed a damping peak at 230 K at a frequency of 0.5 Hz in Ni hydrogenated in H_2 gas atmosphere and deformed at 77 K. They suggested that it might be due to the reorientation of hydrogen pairs bound in the vicinity of dislocations. Though the nature of this peak has not been made clear enough, it would probably originate from the same relaxation process as does P_{dH} peak observed in this work.

V. SUMMARY AND CONCLUSION

The main results and conclusions are summarized as follows.

(1) In cold-worked pure Ni an internal friction peak P_d accompanied by a small subsidiary component P'_d is observed at 85 K at a frequency of 2 Hz with an optimum prestrain in tension of about 5%. It decreases on annealing at elevated temperatures and disappears on recrystallization. The relaxation parameters of this peak determined in the frequency range between 2 Hz and 30 kHz are $f_0 = 1 \times 10^{10} \text{ s}^{-1}$, $H = 0.18 \pm 0.02 \text{ eV}$.

(2) P_d peak is entirely suppressed by hydrogen charging followed by isochronal or isothermal aging at temperatures between room temperature and 473 K. Complete outgassing of hydrogen during prolonged aging reproduces this peak.

(3) Another peak P_{dH} is produced at 240 K at 2 Hz in Ni subjected to hydrogen charging after deformation at the expense of P_d . It grows with charging time shifting toward higher temperature. This peak does not occur in fully annealed and H charged Ni. The relaxation parameters of P_{dH} peak are $f_0 = 3 \times 10^{14} \text{ s}^{-1}$, $H = 0.67 \pm 0.08 \text{ eV}$.

(4) During aging after the hydrogen addition, P_{dH} first grows to attain a maximum strength, then decays and disappears when the hydrogen is completely outgassed. The peak temperature decreases significantly with the progress of ageing.

(5) A close correlation exists between P_d and P_{dH} peaks. Namely, the maximum height of P_{dH} during aging is proportional to the height of P_d before H charging, and the decrease in the modulus defect associated with P_d is precisely cancelled by the increase in that of P_{dH} and vice versa.

(6) P_d peak is ascribable to the Bordoni relaxation peak, while P_{dH} peak to the hydrogen cold-work peak in Ni. Hydrogen atoms effectively interact with dislocations suppressing P_d by pinning them at low temperatures and generating P_{dH} by some cooperative effect at elevated temperatures.

(7) The evolutions of P_d and P_{dH} peaks during aging described above can be properly accounted for in terms of nonuniform hydrogen distributions which vary with charging and aging times in Ni samples, as shown by a phenomenological calculation based on Fick's diffusion equation.

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APPENDIX

Equation (3) is derived as follows. When the initial and boundary conditions are given by

$$c = 0, r = a, t \geq 0$$

$$c = f(r), 0 \leq r < a, t = 0,$$

the solution of Fick's diffusion equation is written as²³

$$c = 2 \sum_{n=1}^{\infty} \exp(-kx_n^2) \frac{J_0[(r/a)x_n]}{J_1^2(x_n)} \int_0^1 \frac{r}{a} f(r) J_0\left(\frac{r}{a} x_n\right) d \frac{r}{a} \quad (\text{A1})$$

Substituting for $f(r)$ the expression given by Eq. (2), i.e.,

$$f(r) = c_0 \left(1 - 2 \sum_{m=1}^{\infty} \frac{\exp(-k_0 x_m^2) J_0[(r/a)x_m]}{x_m J_1(x_m)} \right)$$

and utilizing the formulae of Bessel functions

$$\int_0^1 \frac{r}{a} J_0\left(\frac{r}{a} x_m\right) J_0\left(\frac{r}{a} x_n\right) d \frac{r}{a} = \begin{cases} \frac{1}{2} [J_1(x_n)]^2 & (m = n) \\ 0 & (m \neq n) \end{cases}$$

and

$$\int_0^1 \frac{r}{a} J_0\left(\frac{r}{a} x_n\right) d \frac{r}{a} = \frac{J_1(x_n)}{x_n},$$

one can obtain from Eq. (A1)

$$\frac{c}{c_0} = 2 \sum_{n=1}^{\infty} \frac{J_0[(r/a)x_n]}{x_n J_1(x_n)} \exp(-kx_n^2) [1 - \exp(-k_0 x_n^2)].$$

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