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A STUDY OF DISLOCATION IMPURITY INTERACTIONS IN NIOBIUM BY INTERNAL FRICTION MEASUREMENTS *

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ABSTRACT

The effects of the impurity-dislocation interactions on the low temperature internal friction peaks have been investigated in cold-worked polycrystalline niobium samples. The α-peak has been shown to occur as a result of the hydrogen-dislocation interaction and the δ-peak seems to correspond to a Bordoni type relaxation. The decrease in the height of the α-peak and its temperature on annealing, is due to the pinning of dislocations by the impurities like oxygen, nitrogen and carbon. The interaction of these impurities with the dislocations is elastic in nature and is shown to arise as a result of the size effects as compared with the interaction between hydrogen and dislocations which is due to electrostatic effects. The enhancement of the peak height and peak temperature on hydrogen charging is explained on the basis of the dragging of hydrogen atmospheres by the moving dislocations and consequent phase lag between them. Activation energy "H" obtained from the relation between peak height and peak temperature is assumed to be the sum of the activation energy "W" for dislocation motion and the impurity-dislocation binding energy H_b. The decrease in activation energy "H" on hydrogen charging is attributed to the lowering of energy barrier to the dislocation motion, as a result of proton-dislocation interaction. The inability of hydrogen to pin dislocations at α-peak temperatures is explained as due to the high mobility of hydrogen.

I. INTRODUCTION

Of all the relaxation peaks observed in cold-worked materials, the one that has attracted the most attention is that originally observed by Bordoni [1] in fcc metals and now called the "Bordoni peak". It has been interpreted in terms of the fundamental properties of dislocations and subsequently researches have been made to seek such relaxations in crystal structures other than fcc metals. Several anelastic relaxation effects have been observed below room temperature in cold-worked bcc metals and reviewed by Chambers [2]. Although initially there has been great difficulty in identifying which of these peaks corresponds to the "Bordoni peak" of the fcc metals, it is now well established [3] that there are some similarities between the α-peak in bcc metals and the "Bordoni peak". Similarly, there has been much controversy regarding the origin of the α-peak. Brunner [4] identified the α-peak with the hydrogen cold-work peak (CWP), whereas Bordoni et al. [5] have identified it with a Bordoni type of relaxation. Later, Mazzolai and Nuovo [6] carried out investigations on hydrogen charged Ta and Nb and showed that both plastic deformation and presence of interstitial hydrogen are essential for the occurrence of the α-peak. They concluded that α-peak is the hydrogen CWP. They suggested that the impurity atmosphere dragging model of Schoeck [7] is best suited to explain most of the charcteristics of the hydrogen CWP. However, this model fails to explain the most important observation, namely the increase in the relaxation strength Q_{α}^{-1} with C_d the concentration of the hydrogen impurity. Chang and Wert, [8] from their studies on the effect of hydrogen and other interstitials on the low temperature relaxation of deformed vanadium, distinguished three types of peaks:

(a) The α-peak occurring in cold-worked specimens.

(b) The type I hydrogen CWP which is produced in hydrogen charged specimens which show the α-peak.

(c) The type II hydrogen CWP produced in hydrogen charged specimens where the α-peak is suppressed.

The type II hydrogen CWP they termed as hydride precipitation peak.

From the studies on the effects of impurities like oxygen and nitrogen, strain aging and deformation on the α-peak, they concluded that both α-peak in bcc metals and "Bordoni-peak" arise from the same mechanism. They applied Penguin and Birnbaum's theory [9] of thermomechanical unpinning of dislocations to explain the α-peak and Schoeck's theory [7] to explain the type I and type II hydrogen CW peaks. Yet, in another paper, Buck, Thomson and Wert [10] have

suggested that the enhancement of the α-peak by hydrogen in niobium is caused by the formation of punched-out dislocation loops around the hydride precipitate. In this interpretation, the hydrogen acts indirectly through an increase of the dislocation density and hence the kink density. On the other hand, Seeger and Sestak [11] suggested that the shift of the α-peak temperature to higher temperatures with increasing hydrogen content as well as the excessive width of the peak as due to strong kink-kink interactions and effects of internal stresses when the local dislocation densities are high. They believe that the α-peak arises as a result of the motion of kinks in < 111 > screw dislocations and the δ-peak as due to double-kink formation in non-screw (71° —) dislocations.

Although insufficient attention was paid to possible effects of hydrogen in the earlier works, the later studies and our recent studies on hydrogen charged niobium have conclusively proved that hydrogen plays a prominent role in the occurrence and enhancement of the α-peak. The results of Verdini and Vienneau,[12] Mazzolai and Nuovo [6] and our recent studies make us believe that the δ-peak which is observed at much lower temperatures (around 25°K) actually corresponds to the "Bordoni-peak". However, further experimental studies have to be carried out on δ-peak to confirm these arguments. In this paper we restrict ourselves to the hydrogen CW peak.

II.   SUMMARY OF THE RESULTS

The results of the recent studies on dislocation relaxations at low temperatures on cold-worked and hydrogen-charged polycrystalline niobium, carried out at the Istituto di Fisica of the University of Trieste by our group, can be summarized as follows:

(1) The as received and vacuum annealed samples (at temperatures ~ 850°C) showed no relaxation peaks.

(2) Subsequent cold-work of the samples produced both α - and δ-peaks with not very large maxima.

(3) Annealing the samples at temperatures slightly higher than room temperature decreases both peak height and peak temperature.

(4) Charging the specimens with hydrogen which initially show no α-peak after deformation, introduces a peak (hydrogen CWP), and charging the specimens which initially show a peak (α-peak) with hydrogen, enhances both peak height and peak temperature.

(5) Annealing the hydrogen-charged specimens at temperatures slightly higher than room temperature decreases both peak height and peak temperature.

(6) Although recharging the specimens with hydrogen increases the peak height and peak temperature, the increase is much smaller as compared with the first charging.

(7) Cold-working the specimens recharged with hydrogen substantially increases the peak height and temperature.

(8) The activation energy "H" for the relaxation process, calculated from the relation between peak height and peak temperature before hydrogen charging, is nearly three times the activation energy "W" calculated from the frequency-peak temperature relationship.

(9) The activation energies "W" and "H" are found to be almost equal after charging with hydrogen.

(10) The change in activation energy "W" due to hydrogen charging is very small as compared with the change in "H".

Some of the characteristics of the hydrogen CWP in a niobium specimen are shown in Fig. 1.

We presume that the existing theories based on either intrinsic lattice mechanism or vibrating string models of dislocations are inadequate to explain the experimental results outlined above and there exists a need for the development of a proper dislocation model which will satisfactorily explain the essential characteristics of the hydrogen CWP in bcc metals and the relaxations associated with dislocation-impurity interactions in general.

III.   DISLOCATION MODELS

Since it is now well established that the α-peak in bcc metals is the hydrogen CWP, any dislocation model proposed for this peak has to take into consideration the impurity-dislocation interactions. Several theories have been put forward to explain the relaxations associated with deformed and aged bcc metals containing interstitial impurities. The first proposal is that due to Köster et al.[13] who assumed that it was sufficient to consider a structure consisting of a dislocation line pinned along its core by a row of interstitial atoms. It was argued that application of a shear stress at low temperatures would not cause the dislocation to move because the interstitial atoms bound to it are immobile, while at high temperatures (i.e. well above the peak temperature)

the dislocation and bound impurities move together in phase with the stress and again cause no damping. In the temperature range of the peak, the damping is associated with the lag of impurity atoms as they are dragged to neighbouring sites, by analogy to the reorientation process involved in the Snock relaxation.

Schoeck,[7] on the other hand, suggested a different mechanism for the source of anelastic strain. Whereas Köster et al.[13] assumed the strain to arise from the reorientation of bound interstitial atoms and neglected the strain produced by the motion of the dislocation line, Schoeck [7] has taken the opposite view point, namely that the anelastic strain is due only to the motion of dislocation segments which bow out (until stopped by line tension) at a rate controlled by the migration rate of the bound solute atoms. The damping is given by

$$Q^{-1} = \frac{\gamma \Lambda l_o^2 \pi}{4} \int_0^\infty \frac{\omega \tau \bar{\rho}(z) z^3}{1 + \omega^2 \tau^2 z^4} \, dz \, ,$$

(1)

where Λ is the dislocation density (total length per unit volume); γ is a geometrical factor shown by Schoeck [7] to be about 0.1; l_0 is the average free dislocation length; z is given by the individual values, l/l_0, for each free length l . If there are $\rho(l)dl$ free dislocation units of lengths between l and $l + dl$, then the normalized distribution function is given by

$$\bar{\rho}(z) = \frac{l_o^2 \rho(z l_o)}{\Lambda} .$$

(2)

The maximum value of the integral, and thus of the damping, arises at values of $\omega\tau$ which depend upon the choice of $\rho(z)$. If the lengths of unpinned dislocation line are uniformly equal to l_0 , then the integral has a maximum value of 0.5 for $\omega\tau$ equal to unity. On the other hand, for a Poisson distribution, the integral has a maximum value of 2.2 when $\omega\tau$ is equal to 7×10^{-2}. The relaxation time τ is given by

$$\tau = \frac{9 \pi R^2 k T C_\alpha l_o^2}{16 \sqrt{3} \, G \, b^5 D} ,$$

(3)

where C_d is the atom fraction of impurity atoms in the dislocation atmosphere, G is the shear modulus, b the Burgers vector of the dislocation, and R the

radius around the dislocation in which interstitial atoms are assumed to take part in this damping process. R is assumed to be of the order of b. K and T have their usual meaning, and D is the diffusion coefficient of the interstitial impurity atoms. It is to be noted that τ depends strongly on both C_d and ℓ_0. Schoeck's model also offers an explanation for the magnitude of the relaxation activation energy which appears implicitly in Eq. (3), through the diffusion coefficient D. In the unstrained lattice, there are three distinguishable sets of sites of equal energy but different orientation (x, y and z) that may be occupied by an interstitial atom. However, the large distortions near the core of a dislocation produce an appreciable shifting and splitting of these levels with a preferential occupancy of low-energy sites. Successive neighbouring sites of different orientation will then have alternately favourable and unfavourable interactions with the dislocation stress field. Accordingly, an interstitial atom in a favourable site on the dislocation will have an activation energy H which is larger than the Snoek activation energy H_d by an amount of approximately its binding energy H_b to the dislocation. Thus Schoeck and Modino [14] propose that

$$H = H_d + H_b .$$

$$(4)$$

IV. RELAXATION STRENGTH

The experimental results outlined in Sec. II, and also of earlier workers, indicated that the variation in the relaxation strength of the CW peak due to the presence of interstitials like oxygen, nitrogen and carbon is different as compared with the presence of hydrogen. The as received niobium specimens generally contain oxygen, nitrogen, carbon and hydrogen as impurities. The activation energy for the migration E_m of the pinning impurities obtained by the method of Mazzolai and Nuovo [15] indicated that these impurities in the samples can be carbon, oxygen or nitrogen. The results show that the height of the CWP and its temperature, decrease on annealing at temperatures slightly higher than the room temperature. The amount of decrease depends on the temperature of annealing and time. This suggests that during the process of annealing, the impurities present in the sample migrate towards the fresh dislocations that are introduced during CW and pin or immobilize them. This pinning process can be visualized as follows. Cottrell [16] has shown that in an elastic continuum the interaction potential between a unit edge dislocation

and a point defect is given by

$$U = - A \sin \theta / |\bar{r}| \quad , \tag{5}$$

where $|\bar{r}|$ is the magnitude of the radius vector from the dislocation line to the defect, θ is the angle between $\bar{r}$ and the Burgers vector of the dislocation, and A is a parameter called the impurity-dislocation interaction constant and is given as

$$A = \frac{4}{3} \left(\frac{1+n}{1-n} \right) M b \eta \rho^3 \quad , \tag{6}$$

where "b" is the Burgers vector, M is Young's modulus, n is Poisson's ratio, ρ is the normal radius of an atomic site and $(1 + \eta)\rho$ is the radius of a site with an impurity atom. Eq. (5) is only valid in the region of purely elastic interaction of the impurity and the dislocation. The elastic force exerted by the dislocation on the defect is $-\nabla U$. This force may be attractive on repulsive depending on the size of the defect and on its location with respect to the dislocation. If the concentration of the point defects far from the dislocation is C_0/cm^3, then for small C_0 the concentration near the dislocation is given by

$$C_d = C_0 e^{-U/KT} \quad , \tag{7}$$

once the pinning results from this elastic interaction, the pinned dislocations, do not contribute to the internal friction. During pinning process, it is reasonable to assume that Λ the dislocation density remains constant. However, ℓ_0, the mean dislocation length between pinning points decreases. According to the Schoeck model, the relaxation strength is determined mainly by $\Lambda \ell_0^2$ and the decrease in ℓ_0 due to pinning of dislocations by interstitial impurities like carbon, oxygen and nitrogen results in the decrease of peak height and peak temperature. In all the theories so far developed to explain internal friction, whether they are based on intrinsic lattice mechanism or on string model of a dislocation, the relaxation strength is directly proportional to the loop length ℓ_0. Whereas in the theory of Seeger et al.[17] it is proportional to ℓ_0^3, in the Koehler-Granato-Lücke (KGL) theory[18] it is proportional to ℓ_0^4. Further, the Brailsford theory,[19] which is based on an entirely different approach, namely the abrupt kink model of a dislocation, also

predicts a dependence of ℓ_0^2 . Thus, although the extent of dependence varies from one theory to the other, all the theories predict a strong dependence on ℓ_0 . Thus, on the basis of the above models, we can account for the annealing characteristics of the CW peaks in the presence of interstitial impurities like carbon, oxygen and nitrogen, which act as pinning points.

The same reasoning cannot be extended to the hydrogen charged specimens. On charging the specimens with hydrogen, both peak height and peak temperature increase and this peak has been termed as hydrogen CWP. If hydrogen also pins dislocations just like carbon, oxygen and nitrogen, we should again expect a decrease in peak height and peak temperature. On the contrary, the results show the opposite effect, namely, the increase in peak height and peak temperature indicating that the hydrogen is not pinning the dislocations and that the interaction between hydrogen and dislocations is different as compared with other interstitials. Let us consider what happens as a result of the introduction of hydrogen. As suggested by Buck et al.[10] the dislocation density may increase as a result of punched-out dislocation loops around hydride precipitates or, as suggested by Seeger and Sestak,[11] there may be strong kink-kink interactions, when the local dislocation densities are high. In our experiments and in the experiments of Mazzolai and Nuovo[6] for tantalum the concentration of hydrogen charged into the specimens is very small and the measurements taken while cooling and heating showed no precipitate formation. Thus these theories which suggest an increase in dislocation density on hydrogen charging cannot be extended to our results which involve dilute concentrations. Let us consider, therefore, the other view-point which was proposed as early as 1954 by Rogers[20] and, later, Adair and Hook[21] observed complicated effects when hydrogen was dissolved in iron. They freed dislocations from carbon and nitrogen by introducing hydrogen and found that a yield point appeared if the specimen was tested below – 120°C. On the other hand, Cracknell and Petch[22] observed that the yield point normally present in annealed steel at room temperature is suppressed by the addition of hydrogen. They suggested that hydrogen may be bound more tightly than carbon or nitrogen to dislocations and that the introduction of hydrogen at room temperature displaces carbon and nitrogen from dislocations and remains mobile until the temperature is lowered.

In order to explain the observed yield drop and an associated increase in yield and flow stress, Lawley et al.[23] suggested a model of dragging of hydrogen atmospheres along with the moving dislocations. Further, from their experimental results they concluded that for group VA and VIA metals there is a strong electrical interaction between hydrogen and dislocations in addition to

the small long-range elastic interaction. When the interaction between impurity and dislocations is electrical in nature, then in the formula (7) $U \gg KT$ and the concentration of the impurity at the dislocation will be much higher than that given by Eq. (7). From estimates of the interaction between a charged ion and the electrical field (dipole) associated with the dilational elastic field around an edge dislocation, Cottrell[24] has shown that in most cases this interaction energy should be small compared with the elastic component. However, in the case of ionic bonding, these interactions will be stronger. Labowitz[25] studied the nature of transition metal hydrides and concluded that these are definite chemical compounds, deviation from stoichiometry being due to either vacancies or hydrogen interstitials. The atomic bonds in these compounds are largely ionic and the tendency to form hydrides decreases towards the right of the periodic table. Metals above group V do not in general form hydrides. So when the metal-hydrogen interaction is ionic in character as with group VA metals, this is reflected in a strong electrical interaction between solute atoms and dislocations, even though the hydrogen concentration may be well below the level required for precipitate or hydride formation as in our case.

Even though there is a large concentration of hydrogen around the dislocations due to this electrical interaction, hydrogen is unable to pin the dislocations. As suggested by Cracknell and Petch[22] and Lawley et al.,[23] hydrogen may be relatively more mobile at the ambient temperatures to cause effective pinning. On the other hand, at low temperatures around $25°K$ where the δ-peak is observed, the hydrogen is less mobile and so it may effectively pin the dislocations causing a reduction in the relaxation strength of the δ-peak. On application of shear stress at ambient temperatures, the dislocations move and drag the hydrogen atmospheres along with them. Since the activation energy for the diffusion of hydrogen being different as compared with one of dislocation motion, there will be a lag between the impurity atoms and dislocations which results in the observed dissipation of elastic energy.

V.   ACTIVATION ENERGY

For a simple relaxation process, thermally activated, the relaxation time "τ" depends on temperature according to the Arrhenius equation

$$\tau = \tau_0 \exp(W/KT) \quad ,$$

where "W" is the activation energy, K is the Boltzmann constant independent of temperature. When measured at a frequency "f" or angular frequency $\omega = 2\pi f$, the internal friction Q^{-1} arising from this process is a function of the product $\omega\tau$ and has a maximum value when $\omega\tau = 1$ or when $2\pi f\tau = 1$ or $\tau = \dfrac{1}{2\pi f}$. Therefore, Q^{-1} has a maximum value at a temperature T_m when,

$$\frac{1}{2\pi f} = \tau_0 \exp\left(W/K T_m\right),$$

$$\text{or} \quad f = f_0 \exp\left(-W/K T_m\right),$$

(8)

where $f_0 = \dfrac{1}{2\pi\tau_0}$ is called "attempt frequency".

Considering two different frequencies f_1 and f_2 with the corresponding values of T_m, namely $T_{m,1}$ and $T_{m,2}$, we obtain

$$W = K \frac{\ln f_2/f_1}{(T_{m,1})^{-1} - (T_{m,2})^{-1}} .$$

(9)

From Schoeck's theory [7] the maximum value of damping Q_m^{-1} depends primarily upon Λ and ℓ_0^2. So, from Eq. (1) we obtain

$$Q_m^{-1} \propto \Lambda \ell_0^2 ,$$

(10)

and from Eq. (2), the relaxation time τ is proportional to

$$\tau(T_m) \propto T_m C_d \ell_0^2/D(T_m) ,$$

(11)

where

$$D = D_0 \exp(-\{H_b + H_d\}/KT_m) .$$

(12)

Here H_b is the impurity-dislocation binding energy and H_d is the activation energy for the diffusion of impurity in a perfect crystal. Combining Eqs. (10), (11) and (12) we obtain:

$$T_m Q_m^{-1} \propto \frac{\Lambda \tau(T_m) D_0}{C_d} \exp\left(-\{H_b + H_d\}/KT_m\right).$$

(13)

It is possible to change the maximum value of the dissipation coefficient Q_m^{-1} by annealing treatments. In this case is is reasonable to assume Λ, the dislocation density, and C_d, the concentration of impurity along the dislocations, to remain constant during the annealing process. Therefore, we obtain from Eq. (13),

$$T_m Q_m^{-1} \exp(H/KT_m) = const, \qquad (14)$$

where $H = H_b + H_d$. From Brailsford's theory [19] an expression similar to Eq. (14) can be obtained for the annealing process.

Before charging the specimens with hydrogen, the activation energy "W" calculated from Eq. (9) is 0.28 ± 0.02 eV and, from the annealing studies at different temperatures, Eq. (14) gives a value of 0.74 ± 0.03 eV for H, which is more than W by 0.46 eV. According to Schoeck's theory, these two activation energies should be equal. Further, H is given by the sum of impurity-dislocation binding energy H_b and diffusion energy of impurities H_d. The impurities are oxygen, nitrogen or carbon because H_d as obtained during the annealing process by the method of Mazzolai and Nuovo [15] is 1.37 ± 0.04 eV. "H" therefore cannot be the sum of $H_b + H_d$ for the pinning impurities. Instead let us assume that H represents the sum of $W + H_b$, W being the activation energy for the dislocation motion in the hydrogen atmosphere. The impurity-dislocation binding energy calculated from the difference of H and W is $\simeq 0.46$ eV. Ino and Sugeto [26] have shown the impurity-dislocation binding energy in iron containing nitrogen or carbon to be 0.5 eV, whereas Petarra and Beshers [27] have obtained a value of 0.47 eV. Our value of 0.46 eV for H_b in niobium agrees quite well with their values.

After introduction of a larger amount of hydrogen the activation energy drops from 0.74 eV to 0.28 eV, the decrease being again 0.46 eV whereas the change in W is small. This decrease from 0.74 eV to 0.28 eV may be due to the lowering of energy barrier to the dislocation motion. Hydrogen perhaps shields the dislocations from impurity centres like carbon, oxygen and nitrogen. The values of W after hydrogen charging is 0.22 ± 0.02 eV as compared with 0.28 ± 0.02 eV for H. The hydrogen-dislocation binding energy calculated as a difference of H and W is about 0.06 eV. Mazzolai and Nuovo [6] have obtained 0.13 eV for the hydrogen-dislocation binding energy in tantalum and 0.07 eV for niobium. These results show that we are justified in assuming "H" to be equal to $W + H_d$. Further studies, however, are necessary to confirm these arguments and to check the validity of Eq. (14) derived from Schoeck's theory which implies that $W = H$.

VI.   ANNEALING CHARACTERISTICS OF THE HYDROGEN CWP

Let us now consider the annealing characteristics of the hydrogen cold-work peak, ie. the peak produced after cold-working and hydrogen charging. Annealing the samples at temperatures slightly higher than room temperature, say, "T_a" decreases again both peak height and peak temperature.   To determine the nature of the pinning impurities responsible for this decrease, their activation energy for migration has been estimated by the method discussed by Friedel [28] and Mazzolai and Nuovo [15].

If the impurities interact with the dislocations, the migration of impurities towards the dislocations takes place by means of a diffusion process controlled essentially by the interaction energy between impurities and dislocations. The interaction energy can be written as

$$U_i \left(\rho, \phi \right) = U \left(\frac{b}{\rho} \right)^n f \left(\phi \right) ,$$
(15)

where ρ is the distance between the impurity and the dislocation, U is the binding energy when $\rho \simeq b$, and the function $f(\phi)$ takes care of angular dependence of the interaction around the dislocation.   Finally, it is n = 1 for the size effects which arise as a result of the difference in size of the impurity atom and the atom of the matrix, and n = 2 for the effects due to a difference in elastic constants.   As a result of the presence of a uniform concentration C_0 of impurity atoms at a distance R from the dislocation, the dislocation will be subjected to a force

$$F = - \text{grad } U_i ,$$
(16)

which draws them towards the dislocations.   Thus they will move with a drift velocity,

$$V = - \frac{D}{k T_\alpha} F ,$$
(17)

where

$$D = D_0 \exp \left[- E_m / k T_\alpha \right]$$

is the coefficient of diffusion of the impurities at the annealing temperature T_a, E_m being the activation energy for migration.

Taking the interaction energy to be of the form given by Eq. (15) and neglecting its angular variation to a first approximation, the force on the dislocation is

$$F \simeq \frac{n \, U \, b^{n}}{\rho^{n+1}} \qquad \qquad ..(18)$$

at a distance ρ from the dislocation. After a time t, all the impurities at a distance less than or equal to $\rho = -\int_0^t v \, dt$ have been drawn towards the dislocation. Hence,

$$\rho_0 = \left[\frac{n(n+2) \, D \, U \, b^{n} \, t}{k \, T_\omega} \right]^{1/n+2} . \qquad \qquad (19)$$

The concentration $C-C_0$ of impurity atoms having arrived on the dislocation will be given by

$$C(t) - C(0) = \pi \rho_b^2 \, b \, \frac{C_0}{b^3}$$

$$\doteq \frac{\pi C_0}{b^2} \left[\frac{n(n+2) \, D \, U \, b^{n} \, t}{k \, T_\alpha} \right]^{2/n+2}$$

or

$$C(t) \doteq C_0 \left[1 + \beta \, t^{2/n+2} \right] . \qquad \qquad (20)$$

As a result of segregation of impurities along the dislocation, the average loop length ℓ_0 of the dislocations changes with time and is given as

$$\frac{1}{\ell_0(t)} = \frac{1}{\ell_0(0)} + \frac{C(t) - C_0}{b}$$

or

$$\frac{1}{\ell_0(t)} = \frac{1}{\ell_0(0)} \left(1 + \frac{C(0)}{C^* + C(0)} \beta \, t^{\frac{2}{n+2}} \right) ,$$

where

$$\ell_0(0) = \frac{b}{C^* + C(0)} \qquad \qquad (21)$$

and $C^* + C(0)$ is the concentration of impurities present initially along the dislocation before segregation.

According to Brailsford's model, the maximum Q_M^{-1} of the coefficient of dissipation depends upon the loop length $\ell_0(t)$ as

$$Q_M^{-1}(t) \propto \frac{\Lambda \ell_0^2(t)}{K T_m}, \qquad (22)$$

where T_M is the peak-temperature, Λ is the dislocation density per unit volume. Combining Eqs. (21) and (22) we obtain:

$$Y(t) - 1 = \left[\frac{Q_M^{-1}(o) T_m(o)}{Q_M^{-1}(t) T_m(t)} \right]^{1/2} - 1 = \frac{C_o}{C^* + C(o)} \beta t^{\frac{2}{n+2}}. \qquad (23)$$

Eq. (23) can be written in the form

$$Y(t) - 1 = A \left[\frac{t \exp\left(-E_m / K T_a \right)}{T_a} \right]^{\frac{2}{n+2}},$$

where

$$A = \frac{\pi}{b^2} \frac{C(o)}{C^* + C(o)} \left[\frac{n(n+2) b^n U D_o}{K} \right]^{\frac{2}{n+2}}.$$

The study of the annealing kinetics of the Q_M^{-1} as a function of time t_a at an annealing temperature T_a, shows that $Y - 1 = const$, which gives a relation between t_a and T_a as

$$\frac{t_a}{T_a} \exp\left[-E_m / K T_a \right] = Const. \qquad (24)$$

The plot between $\ln(t_a T_a^{-1})$ vs $\frac{1}{T_a}$ is a straight line, the slope of which

will give E_m, the activation energy for the migration of pinning impurities. From this method, an activation energy $E_m = 1.31 \pm 0.05$ eV has been obtained

for our niobium samples which is close to the activation energy for migration of carbon interstitials in niobium as given by Wert [29]. Further, the parameter Y varies linearly as $t_a^{2/3}$, suggesting that $n = 1$ and that the interaction

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between these impurities and dislocations is elastic in nature and arises as a result of the difference in size of the impurity and host lattice atoms. These studies therefore reveal that even after hydrogen charging, the decrease in peak height is due to the pinning of dislocations by impurities like carbon, oxygen and nitrogen and this perhaps may be the reason for the small increase observed in peak height on recharging with hydrogen as compared with the first charging (Fig. 1, curves 3 and 4). As shown in curve 5, Fig.1, further deformation is necessary to obtain large dissipation of elastic energy.

VII.   CONCLUSIONS

(1) The absence of relaxation peaks (α and δ peaks) in the as-received and vacuum annealed samples and their occurrence on subsequent cold-work suggests that they are associated with dislocations.

(2) The decrease in the height of α—peak and its temperature on annealing the samples at temperatures slightly higher than room temperature and the study of its kinetics suggest that pinning of dislocations is due to impurities like oxygen, nitrogen and carbon present in the samples, possibly carbon.

(3) The requirement of cold-work and the presence of hydrogen to get large dissipation suggests that the α-peak is the hydrogen cold-work peak.

(4) The increase in peak height and peak temperature on hydrogen charging is attributed to the dragging of hydrogen atmospheres by moving dislocations with consequent phase lag between them.

(5) The activation energy H is different from W , when the hydrogen atmosphere is dilute. They become almost equal when the hydrogen concentration is high enough to cause saturation.

(6) The decrease of the activation energy "H" on hydrogen charging is due to the lowering of energy barriers to the dislocation motion by interaction with protons.

(7) The inability of hydrogen to pin the dislocations is attributed to its high mobility at hydrogen CWP temperatures.

(8) The essential characteristics of the hydrogen cold-work peak are explained by considering primarily the electrical interaction of hydrogen with dislocations as compared with the long-range elastic interaction associated with impurities like oxygen, nitrogen or carbon.

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FIGURE CAPTION

Fig. 1   The variation of energy dissipation and peak temperature of the hydrogen CWP in polycrystalline niobium NbH6 on annealing, charging and deformation measured at a frequency of 60 KHz.

0-0-0   After annealing at 850°C in high vacuum and subsequent 2.5% deformation.

●-●-●   After electrolytic charging with hydrogen at 160 mA for 10 mts.

▲-▲-▲   After 1 hr anneal at 100°C.

□-□-□   Recharging with hydrogen at 160 mA for 10 mts.

■-■-■   After a 2.5% deformation and anneal at room temperature for a week.

Fig.1