Low-Temperature Internal Friction in Quenched Niobium

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Internal friction measurements (at 1 cycle/sec) have been carried out over the temperature range from 100 to 280° K on niobium specimens quenched to room temperature from 2350° C. Internal friction curves immediately after quenching exhibited irregular peaks which were practically removed by a 20 h anneal at room temperature. On subsequent isochronal annealing three well-defined peaks occurred at about 185°, 200°, and 220° K. The relaxation strength of the peaks increased with increasing annealing temperature up to about 140° C, remained practically constant between 140° and 220° C, and subsequently gradually decreased to negligibly low values at about 380° C.

The variation of the damping spectrum, as a result of quenching and subsequent room temperature and isochronal annealing, indicates the presence of an excess of quenched-in vacancies in the material. Most of the vacancies are probably trapped at dislocations, at interstitial impurities or in clusters.

The 185, 200 and 220° K relaxation peaks developed by post-quench annealing have been identified as β-peaks observed in cold-worked BCC transition metals. The relaxation mechanisms causing these peaks have been shown to be vacancy clusters, which may also involve interstitial impurities.

1. Introduction

If the damping of mechanical vibration at constant frequency is measured, as a function of temperature, internal friction (relaxation) peaks are observed. Those whose origin is known are normally attributed to the thermal activation of lattice defects over potential energy barriers in the crystal†. In particular, two groups of low-temperature peaks are observed in cold-worked fcc metals. One group (the Bordoni peaks) has been explained in terms of thermally-activated motion of dislocation kinks [1], and the other (the Hasiguti peaks) in terms of dislocation/point defect interactions [2]. Two groups of low-temperature (about 100 and 200° K at 1 cycle/sec) peaks have also been observed in cold-worked bcc metals. It is generally agreed that the lower-temperature peaks (α-peaks) are caused by relaxation mechanisms involving dislocations only [3-6]. The higher-temperature peaks (β-peaks), on the other hand, have been attributed to relaxation mechanisms involving dislocations and/or point defects. Chambers [3, 4] proposed that they were due to the thermally-activated motion of dislocations, as in the case of the Bordoni peaks in fcc metals. De Batist suggested that, because the β-peaks show some similarity to the Hasiguti peaks in fcc metals, they may be due to dislocation/point defect relaxations [7]. The present authors, on the other hand, from a study of both cold-worked [6-8] and irradiated [5] niobium, concluded that a more likely hypothesis would be the stress-induced ordering of some kind of point defect complex not associated with dislocations.

It was thought that a suitable investigation, to help to solve the problem of which of these relaxation mechanisms is actually causing the β-peaks, would be the study of low-temperature internal friction in quenched niobium. By quenching, it was hoped that an excess of point defects would be introduced while maintaining

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†Peaks due to other processes are found at higher temperatures

a low density of dislocations.

Until recently, there has been doubt about the possibility of quenching-in point defects in bcc metals, particularly in view of Gregory's [9] theoretical estimation of the quenching rates necessary to produce a measurable excess of vacancies in bcc metals. However, since then, Schultz [10] has claimed to have detected enhanced resistivity due to quenched-in vacancies in tungsten, and Meakin *et al* [11] believe they have produced direct evidence, using electron microscopy, of the aggregation of quenched-in vacancies in molybdenum.

2. Material and Experimental Procedure

The material used in this work was the same niobium of commercial purity as that used in earlier investigations [5, 6, 8]. The as-received wire (0.75 mm diameter) was annealed, by direct resistance heating, for 5 min at 2350° C in vacuum at a pressure of between 10^{-5} and 10^{-4} torr. At the end of the annealing treatment, specimens were quenched to room temperature by simultaneously switching off the heating current and allowing helium gas to enter the vacuum-furnace chamber. To prevent the specimen from being plastically deformed on contraction during quenching, a tensioning device, incorporated in the furnace to take up expansion during heating, was also simultaneously screwed down to a pre-set position. The quenching rate was estimated to be about 5000° C per second.

Chemical analysis of the quenched specimens is given in table I. Oxygen and nitrogen contents were determined using the micro-vacuum fusion technique, whilst the analysis of metallic impurities has been given by the suppliers of the material.

TABLE I Chemical analysis of quenched niobium.

Element	Atomic ppm
Oxygen	210
Nitrogen	120
Carbon	<150
Hydrogen	<150
Tantalum	510
Titanium	5400
Zirconium	3000
Iron	570
Silicon	910

Internal friction measurements were carried out in a Kê [12] type freely-oscillating torsion pendulum, operating at a frequency of about 1 cycle/sec. The length of the specimen constituting the torsion pendulum was 15 cm. The inertia bar of the pendulum exerted a stress of 0.1 kg/mm^2 on the wire specimen, producing a tensile strain of 10^{-5}. The pendulum assembly was suspended in an evacuated tube surrounded by a liquid nitrogen cooling-bath. Internal friction measurements were taken on heating from 100 to 290° K at a steady rate of about 0.75° C per min. The temperature gradient along the specimen was less than 2° C.

Internal friction of quenched specimens was found to be strain-amplitude-independent up to a shear strain of 10^{-4}. A maximum shear strain of 5×10^{-5} was, therefore, used for the experiments of the present study.

3. Results

3.1. Quenching Effect

A typical internal friction curve of an as-quenched specimen is shown in fig. 1. The curve was obtained at a frequency of oscillation of about one cycle per second over the temperature range from 100 to 280° K. The total time required to mount the specimen in the internal friction apparatus, and to cool it to 100° K was about 7 min. Without removing the specimen from the apparatus, internal friction was re-measured, over the same temperature range, following resting at room temperature for 20 h. The resultant curve, together with an internal friction curve of an annealed specimen [5, 6], is also included in fig. 1.

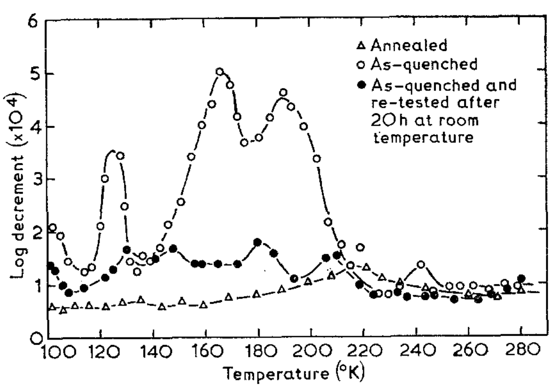

Figure 1 Internal friction curves of quenched-and-annealed niobium.

The main features of the internal friction curves of the as-quenched specimen are: (i) the presence of peaks over a temperature range from

120 to 220° K, (ii) their virtual disappearance after 20 h at room temperature, and (iii) slightly increased background damping, as measured at 260° K.

3.2. Effect of Annealing

Following the pattern of previous work on irradiated [5] and cold-worked [6] niobium, the quenched-and-room-temperature-tested specimens were isochronally annealed up to 300° C, using 2 h pulses. Internal friction curves obtained after annealing at 120 and 140° C are given in fig. 2. From the curves it is apparent that annealing at temperatures higher than the ambient temperature gives rise to three well-defined peaks at about 185, 200, and 220° K, which were stable at room temperature.

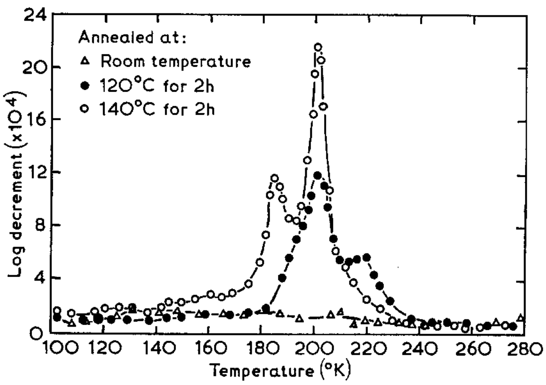

Figure 2 Effect of annealing on the internal friction of a quenched specimen.

TABLE II Activation energies of stable peaks in quenched niobium calculated using the "half-width" formula (equation 1).

Peak Temp. (°K)	Activation energy (eV)
185	0.96
200	1.03
220	1.15

The activation energies, Q, of these peaks were determined using the "half-width" formula

$$Q = 5.26/W_{\frac{1}{2}} \quad (1)$$

where $W_{\frac{1}{2}}$ is the width (in reciprocal ° K) of the relaxation peak at half its height. The resulting values of the energies, representing a lower limit, are given in table II.

From the Arrhenius relation,

$$f = f_0 \exp(-Q/RT) \quad (2)$$

where f is the frequency of oscillation, and R and T have their usual meaning, the attempt frequency, f_0, of the relaxation process causing the β-peaks was determined to be about 10^{27} cycle/sec for each peak.

The peaks varied in height with increasing annealing temperature in a rather complex fashion. The variation of their heights, and of the background damping, with annealing temperature is shown in figs. 3 and 4. The temperature at which the peaks occurred showed good reproducibility from specimen to specimen, but the heights of the peaks did not follow exactly the pattern shown in figs. 3 and 4. In each case, however, the overall relaxation strength (area under the curve of logarithmic decrement against temperature) increased on annealing over the temperature range from 60 to 140° C, remained practically constant between 140 and 220° C, and decayed to a negligible value from 220 to 380° C.

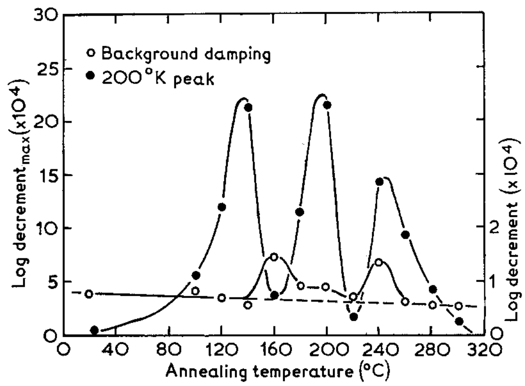

Figure 3 Isochronal annealing curves of background damping and the 200° K stable (β) peak in quenched niobium.

The background damping, as measured at 260° K, decreases with increasing annealing temperature up to about 140° C. At higher temperatures it goes through maxima at 160 and 240° C, and then decreases to a lower value than that of the annealed material (table III). The variation of the background damping with annealing temperature showed good reproducibility from specimen to specimen.

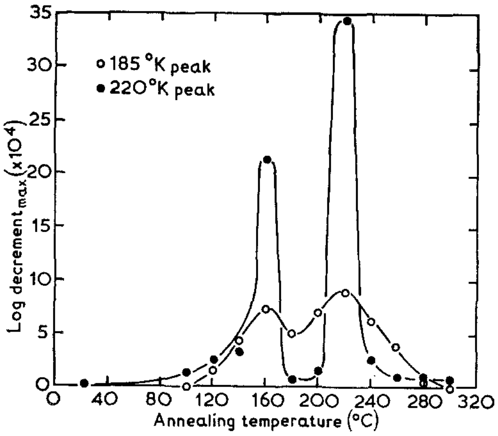

Figure 4 Isochronal annealing curves of the 185 and 220° K stable (β) peaks in quenched niobium.

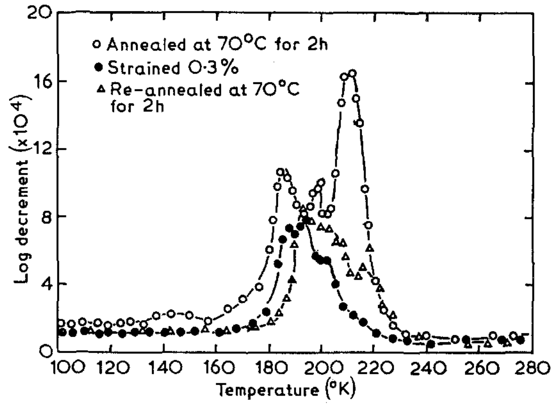

Figure 5 Effect of 0.3% strain and re-annealing at 70° C on the internal friction of a quenched specimen annealed at 70° C for 2 h.

TABLE III Comparison of background damping as measured at 260° K.

Condition	Log. decr. $\times 10^4$
Annealed	0.8
Quenched	0.9
Quenched + 20° C anneal	0.7
Quenched + 300° C anneal	0.5

3.3. Effect of 0.3% Strain

Again, following the pattern of previous work [5, 6], a quenched-and-annealed (for 2 h at 70° C) specimen was strained in tension to 0.3% elongation, and allowed to rest at room temperature for 20 h before internal friction was re-measured. The internal friction curve of the specimen before straining exhibited all three peaks normally observed (fig. 5). As a result of the room temperature straining-and-annealing treatment, the 200 and 220° K peaks were practically completely removed, and the 185° K peak was reduced by about 50% (fig. 5). The specimen was then re-annealed for 2 h at 70° C and internal friction measured again. The effect of the re-annealing treatment was to increase the 200 and 220° K peaks, and to remove the 185° K peak (fig. 5).

4. Discussion

4.1. Stable Relaxation Peaks

By "stable" relaxation peaks are meant those peaks which are developed as a result of isochronal annealing at temperatures above the ambient temperature (fig. 2). The peaks, which are observed in the as-quenched specimens and anneal out at room temperature (fig. 1), are, in contrast, referred to as "unstable" peaks. The present study, however, is concerned with the stable peaks only and, therefore, the unstable peaks will not be discussed in detail.

The stable peaks occur in the temperature region from 160 to 240° K, which is the β-peak region in cold-worked niobium [6]. Furthermore, the temperatures at which the individual peaks occur correspond very well for quenched, cold-worked and irradiated specimens, as shown in table IV. Other similarities between the stable peaks in quenched specimens and the β-peaks in cold-worked materials are the facts that (i) they are absent after quenching or cold-work and room temperature annealing, (ii) they are only developed on annealing at higher than ambient temperature, (iii) they commence to decay at practically the same temperature (table V), and (iv) they are affected in a similar way by a 0.3% strain, and subsequent re-annealing at 70° C (fig. 5). Finally, the activation energy (table III) of the stable peak occurring at 200° K (fig. 2) is the same as the value 1.02 eV (calculated

TABLE IV Comparison of peak temperatures of the stable peaks in quenched niobium with those of the β-peaks in cold-worked and irradiated niobium (frequency 1 cycle/sec).

Type of damage	Peak temperature (°K)			Reference
Quenching	185	200	220	This work
Cold-work	190	200	220	6
Irradiation	196	208	213, 230	5

TABLE V Comparison of growth and decay temperature regions of β-peaks in cold-worked, quenched and irradiated niobium.

Type of damage	Growth region (°C)	Decay region (°C)	Reference
Cold-work	20-120	240-350	6
Quench	60-220	220-320	This work
Irradiation	< 60-200	220-380	5

using equation 1) for the main β-peak occurring at 200° K in cold-worked niobium (table IV). It is, therefore, reasonable to assume that the stable peaks in quenched niobium are of the same origin as the β-peaks observed in cold-worked [3, 6, 7] and irradiated [5] bcc metals.

4.2. Evidence of Quenched-in Vacancies

The presence of quenched-in vacancies in quenched niobium can be inferred from the annealing-out at room temperature of the unstable peaks observed immediately after quenching (fig. 1). If these peaks were due to relaxation mechanisms involving dislocations only and there were no excess vacancies, they should remain stable up to temperatures high enough for the migration of interstitial impurities (about 100° C [13]), or for dislocation re-arrangement (about 200° C [14]). Therefore, either the peaks or their decay must be attributable to the presence of a non-equilibrium concentration of vacancies in the lattice. Consider also the slight lowering of background damping (table III) brought about by room temperature annealing. The background damping, being proportional to the average loop length of dislocations, can be reduced by increasing the number of pinning points on a dislocation line. The additional pinning points formed at room temperatures are most likely to consist of vacancies, as, in the present material, interstitial impurities cannot migrate at this temperature [13].

Further evidence for the possibility of quenching-in vacancies into niobium is provided by the comparison of the overall relaxation strength of the β-peak complex in quenched and cold-worked materials [6]. Cold-work introduces relatively high dislocation densities into the material, but the overall relaxation strength of the β-peak complex is relatively low (9 area units)*. The overall relaxation strength of the β-peak complex in quenched specimens, on the other hand, is relatively high (24 area units). If the quenching treatment did not produce an excess of vacancies, one would then be forced to attribute the β-peaks to relaxation mechanisms involving dislocations. This is unreasonable in view of the relative dislocation densities and the fact that the relaxation strength of the β-peaks was found not to increase with increasing degree of cold-work [6], and thus dislocation density.

In view of the calculations carried out by Gregory [9], the equilibrium concentrations of excess vacancies in the free lattice is expected to be very small at room temperature. Most of the excess of quenched-in vacancies are, therefore, probably trapped at dislocations, as suggested in a previous paragraph, at interstitial impurities, or in clusters. Interstitial impurities are believed to act as sinks for vacancies [15]. Further work, is however, necessary, preferably on zone-refined niobium containing controlled amounts of impurity, to determine the concentration of quenched-in vacancies and to identify the key element in the interaction process.

4.3. Relaxation Mechanisms of β-Peaks

It was previously shown that the β-peaks, and their variation during isochronal annealing, in irradiated [5] and cold-worked [6] niobium could best be accounted for in terms of point-defect complexes. It was suggested that these complexes consisted of vacancies and/or interstitials paired in some way with interstitial impurities. The fact that the relaxation strength of the β-peaks in quenched specimens is more than double that in the cold-worked material is further and more conclusive evidence that the β-peaks are due to point-defect relaxations not involving dislocations.

Comparison of the development of the β-peaks in cold-worked [6], irradiated [5] and quenched material shows that the overall relaxation strength of the β-peak complex in quenched and irradiated samples grows on isochronal annealing up to about the same temperature, which is about 100° C higher than that required in cold-worked specimens (table V). This is to be expected if the β-peaks are caused by point-defect-complex relaxations. Cold-work produces a much greater density of sinks at dislocations than either quenching or irradiation. After cold-work, therefore, as compared to after

*Area units represent the area under the curve of logarithmic decrement against temperature quenching or irradiation, the overall average distance between an intrinsic defect and trapping and clustering sites will be much shorter. Thus, saturation of trapping and clustering should occur at a lower temperature in cold-worked material.

In terms of the point-defect-complex relaxations, it is also to be expected that the temperature at which the β-peaks commence to anneal out should be the same for quenched, irradiated and cold-worked specimens. This is so because dislocations will have no effect on the binding energy of point-defect clusters in the free lattice. As shown in table IV, the annealing out temperatures are the same.

4.4. Activation Energy

The activation energies, of the β-peaks as determined from the half-width of the peaks, in quenched (table II) and cold-worked [6] niobium are close to the value of 1 eV. From frequency shift, on the other hand, the activation energies in cold-worked [6] and irradiated [5] niobium were found to be about 0.6 eV. Other workers have reported a value of 0.46 eV, which was obtained from frequency shift of the β-peaks in cold-worked niobium [3, 16]. Calculation of activation energy of the β-peak from frequency shift, using the present results at 1 cycle/sec and those of Chambers and Schultz [4] at 7.8 cycle/sec, 9 kcycle/sec and 15 kcycle/sec, yields values ranging from 0.45 to 0.6 eV, which are in agreement with the values of 0.46 eV and 0.6 eV quoted above. Activation energies, as determined by the frequency shift are, therefore, lower by a factor of 2 than those obtained from the half-width of the peak.

Assuming that the activation energy of the relaxation process causing the β-peak is 1 eV, it would imply that there must be a large curvature in the Arrhenius plot of $\ln f$ against $1/RT_p$, where T_p is the peak temperature, in order to account for the low value (0.5 to 0.6 eV) of the activation energy obtained from the frequency shift of the peak. However, it has been shown that large curvatures in the Arrhenius plot are not to be expected [17]. If, on the other hand, the lower value (0.5 eV) is taken to be correct, it follows that the experimental β-peaks are about half the width of a single Debye peak. Peaks have been reported that are narrower than theoretical Debye peaks estimated from the usual assumed value of τ_0 of about 10^{-14} sec. These peaks are, normally, found to be unstable and unreproducible [3, 7].

In the present and previous [6] work, the group of β-peaks occurring over the temperature range from 180 to 230° K after quenching or cold-work, has shown good reproducibility. However, the individual peaks have been found to increase and decrease with the variation of annealing temperature in an irregular fashion, indicating a certain degree of instability. The irregular variation of the peak heights is associated with slight changes in peak temperature. Further work, to establish the shape of the β-peaks in bcc metals and to determine their properties, is needed before any definite conclusions can be drawn from their parameters.

5. Summary and Conclusions

Niobium quenched to room temperature from 2350° C and annealed at temperatures in the range from 70 to 220° C exhibits relaxation peaks at 185, 200, and 220° K. These peaks have been identified as β-peaks observed in bcc transition metals after cold-work or irradiation. The relaxation mechanisms causing these peaks have been confirmed to be due to vacancy clusters [5, 6], associated in some way with interstitial impurities.

It has been shown that an excess of vacancies can be introduced into niobium by quenching from just below its melting point. Most of the quenched-in vacancies, however, are probably trapped at dislocations, at interstitial impurities or in clusters.

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