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Grain-Size Dependence of Snoek Peaks in Niobium

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The effect of grain size on the oxygen and nitrogen Snoek peaks in niobium has been studied. It has been observed that the conversion factor K given by $C = K\delta_{\max}$, where C is the concentration of oxygen or nitrogen and $\delta_{\max}$ the height of the corresponding Snoek peak, is concentration independent up to about 0.06 and 0.04 wt % oxygen and nitrogen respectively.

The variation of K with grain size (d) obeys the relationship $K = K_0 + k_K d^{-\frac{1}{2}}$, where K_0 represents the value of K for an "aggregate of crystals without boundaries" and k_K the grain size dependence of K.

1. Introduction

Body-centred cubic (bcc) transition metals exhibit appreciable solid solubility for oxygen, nitrogen and carbon, forming interstitial solid solutions. As a consequence of the lattice geometry the interstitial solute atoms act as elastic dipoles, giving rise to anelastic effects and constitute a group of extrinsic point defects [1]. The presence of interstitial solutes in bcc transition metals is detectable by the internal friction technique through the well-documented Snoek relaxation peaks [2-5]. These peaks occur at characteristic temperatures for a given frequency of oscillation. The magnitude of the Snoek peak, caused by the stress-induced migration of a given interstitial atom, is proportional to the concentration of that interstitial solute [2, 5, 6]. Frequently this relationship is given by

$$C = K\delta_{\max} \qquad (1)$$

where C is the interstitial concentration, $\delta_{\max}$ the logarithmic decrement at the height of the Snoek peak and K a proportionality constant generally referred to as the *Conversion Factor*. The conversion factor (K) is obtained experimentally by measuring $\delta_{\max}$ by internal friction and determining the interstitial solute content of the material by analysis.

Experimental and theoretical determinations of K for carbon and nitrogen in single crystals of alpha-iron give reasonable agreement and confirm equation 1 [6, 7]. Experiments of polycrystalline alpha-iron specimens, however, reveal a large variation in K with differing grain sizes [8-18]. The explanations put forward to account for the variation of K with grain size in iron are: (a) the interstitial atoms situated near grain boundaries are immobilised by the stress fields of the boundaries and do not take part in the Snoek stress-induced ordering [8]. (b) An appreciable fraction of interstitial solute atoms diffuses to the grain boundaries during cooling from the solution treatment or recrystallisation temperature [16, 17]. (c) The variation is attributed to changes in texture with grain size [18].

The solid solubility of carbon and nitrogen in alpha-iron is comparatively low and may result in precipitation of the interstitials from free solid solution during internal friction measurements. The existence of wide immobilisation or depletion zones near the grain boundaries is, therefore, expected. The dependence of K on texture has not yet been conclusively established as the *sole* factor accounting for the variation of K with grain size in polycrystalline materials. The grain-size dependence of the conversion factor for carbon and nitrogen in alpha-iron is, therefore, not yet accounted for unambiguously.

The object of the present study is to investigate the effect of grain size on the Snoek peaks in an interstitial solid solution well within the limits of solid solubility. Niobium satisfies this requirement, as it dissolves comparatively large quantities of oxygen [19, 20] and nitrogen [21] and the resultant interstitial solid solutions are stable during internal friction measurements even after vacuum-quenching from annealing temperatures [22, 23].

TABLE I Analysis of electron-beam refined niobium.

Element	Wt ppm
Oxygen (a)	150–250
(b)	450–550
Nitrogen (a)	40– 60
(b)	120–140
Carbon	10
Hydrogen	< 5
Tantalum	800
Zirconium	Trace
Iron	50
Titanium	100
Silicon	100

2. Material and Experimental Procedure

The material used was Murex electron-beam-refined niobium wire 1.25 mm in diameter in the as-drawn condition. The chemical analysis, as supplied by the manufacturers, is given in table I.

In order to permit an unambiguous determination of the effect of grain-size on the Snoek peaks, specimens of as wide a range of grain sizes as possible are required. This, in turn, requires widely differing mechanical/thermal treatments. A criticism has been made that such widely differing treatments could also produce other microstructural differences affecting the properties of the polycrystalline specimens [24, 25]. In the present work, therefore, an attempt was made to standardise, as far as possible, the various heat-treatment procedures used. All specimens were cold-swaged from 1.25 mm diameter to the thickness required for either straight or strain-annealing treatments. Wires about 40 cm long and 0.76 mm diameter were annealed by direct resistance-heating in a dynamic vacuum of 10^{-6} to 10^{-5} torr at temperatures ranging from 900 to 1550°C. The concentration of oxygen and nitrogen of each specimen was kept constant as far as possible, sometimes by re-charging.

Specimens for the grain-size measurement were hand-polished and etched with a 1:1 mixture of concentrated hydrofluoric and nitric acids. The grain size of each specimen was determined by the linear intercept method. Each grain-size measurement represents an average of ten to twenty readings.

Internal friction measurements were carried out in a Kê-type torsion pendulum apparatus [26] in which specimens in the form of a wire (0.76 mm diameter and 25 cms long) constitute the suspension of a freely-oscillating pendulum, operating at a frequency of about 1 Hz. Measurements were taken on heating at a rate of about 1°C per min.

Oxygen and nitrogen contents were determined on the internal friction specimens by the micro-vacuum fusion technique.

3. Results

In the first part of the study internal friction measurements were carried out on polycrystalline specimens of fine and coarse grain sizes, containing approximately the same amount of oxygen and nitrogen. In fig. 1 are plotted the experimental internal friction spectra (at 1 Hz) of two sets of niobium-0.033 wt% oxygen-0.015 wt% nitrogen specimens having average grain sizes of 0.061 and 0.62 mm respectively. It is apparent from fig. 1 that there is a substantial difference in the heights of the Snoek peaks of

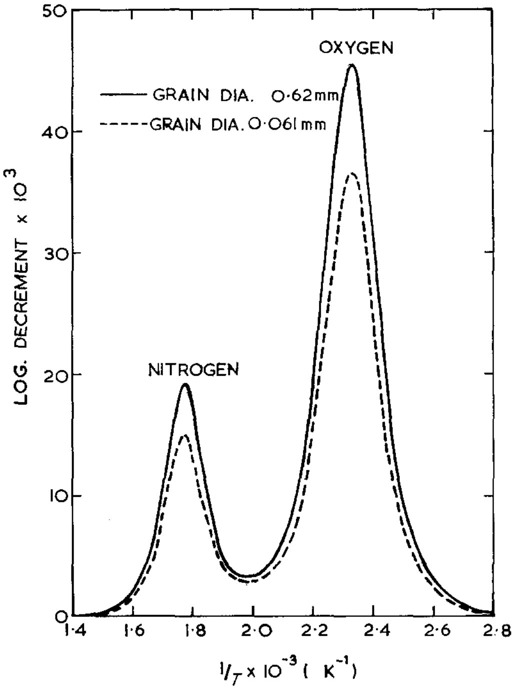

Figure 1 Effect of grain size on the internal friction curve (at 1 Hz) of niobium-0.033 wt% oxygen-0.015 wt% nitrogen alloy.

the two specimens, whilst there is no significant change in their shape.

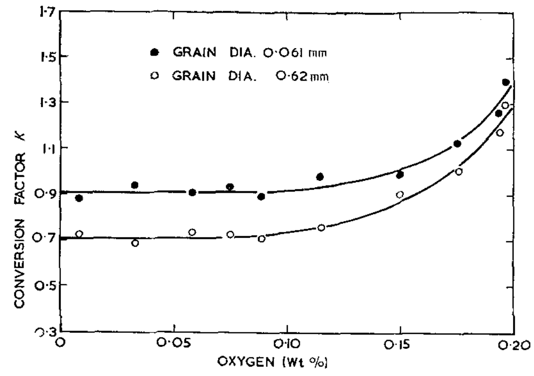

Figure 2 Effect of grain size and concentration of oxygen on the conversion factor (*K*).

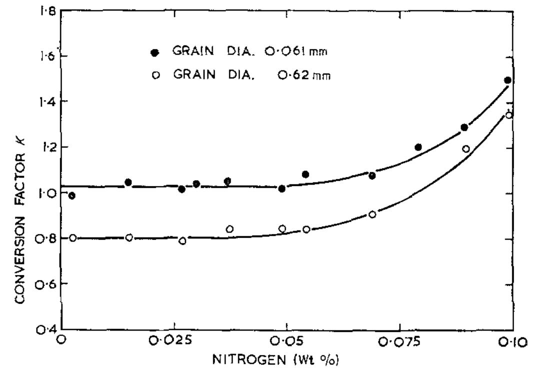

Figure 3 Effect of grain size and concentration of nitrogen on the conversion factor (*K*).

3.1 Effect of Interstitial Content

Having established the effect of grain size on the heights of the oxygen and nitrogen Snoek peaks (fig. 1), and hence *K* of equation 1, the next step was to determine the effect of interstitial content on *K*. Two batches of specimens of 0.62 and 0.061 mm average grain diameter were prepared, one having a constant nitrogen and the other a constant oxygen content, while the concentrations of oxygen and nitrogen varied up to 0.2 and 0.1 wt%, respectively. The values of *K* for oxygen and nitrogen obtained from these specimens are plotted in figs. 2 and 3 against the concentration of oxygen and nitrogen, respectively. It is apparent from these figures that *K* for oxygen and for nitrogen is, within the experimental scatter, independent of concentration up to about 0.06 wt% oxygen and 0.04 wt% nitrogen, respectively, for both grain sizes. These results indicate that variations in the concentration of oxygen and nitrogen over the range of up to 0.06 and 0.04 wt%, respectively, can safely be used for the study of the effect of grain size on *K*.

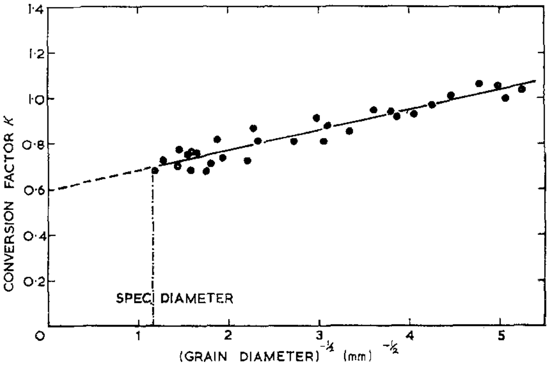

Figure 4 Variation of the oxygen conversion factor (*K*) with grain size for niobium-0.033 wt% oxygen-0.015 wt% nitrogen alloy.

3.2 Effect of Grain Size

The grain-size dependence of *K* for oxygen and nitrogen was studied on niobium specimens containing about 0.033 and 0.015 wt % oxygen and nitrogen, respectively, for average grain sizes ranging from 0.035 to 0.75 mm. The values of *K* obtained are plotted against the reciprocal square root of the average grain diameter (*d*) in figs. 4 and 5 for oxygen and nitrogen, respectively. From the figures it is apparent that in both cases,

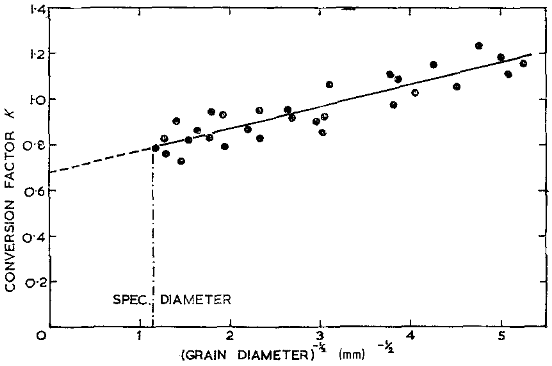

Figure 5 Variation of the nitrogen conversion factor (*K*) with grain size for niobium-0.033 wt% oxygen-0.015 wt% nitrogen alloy.

K shows a linear relationship with $d^{-\frac{1}{2}}$ of the form

$$K = K_0 + k_K d^{-\frac{1}{2}} \qquad (2)$$

where K_0 is the intercept of the straight line representing the value of K for a "grain-boundary free aggregate of crystals" of niobium, and k_K the slope of the straight line representing the grain-size dependence of K. The relationship of equation 2 is of the form of the Hall-Petch ($d^{-\frac{1}{2}}$) relationship for the variation of mechanical properties with grain size [27]. In table II are given the values of K_0 and k_K for both oxygen and nitrogen, as determined by linear least squares analysis of the results of figs. 4 and 5.

TABLE II Grain-size dependence parameters of the conversion factor K (equation 2).

Interstitial solute	K_0 (wt%)	k_K (wt% mm$^{\frac{1}{2}}$)
Oxygen	0.59 ± 0.03	0.089 ± 0.009
Nitrogen	0.68 ± 0.05	0.095 ± 0.015

The results of figs. 4 and 5, when plotted against the reciprocal of the average grain diameter did *not* fall as a straight line (which is proportional to the total grain-boundary area).

3.3 Effect of Annealing Treatments

During the present study it was noted that specimens, annealed for short times (less than 30 min) at temperatures in the lower part of the temperature range used (900 to 1550°C), yielded lower values of K for a given grain size, whereas specimens, annealed for long times (greater than 120 min) at temperatures in the upper part of the temperature range used, yielded higher values of K for a given grain size, than specimens strain-annealed or "straight" annealed for 60 min. On further study of this effect it was confirmed that in this case K for a given grain size was affected by annealing time. The results for oxygen and nitrogen are plotted against the average grain diameter (d) in figs. 6 and 7 respectively. In the figures, values of K for short-time-anneal specimens are shown as full circles (●) and those for long-time-anneal specimens are shown as open circles (○). For comparison the results of figs. 4 and 5 are included and shown as crosses (×).

In the case of the short-time-anneal specimens, K increased with increasing grain diameter fairly steeply until it merged with the curve obeying the relationship of equation 2 at a grain diameter of about 0.14 mm. This variation in K was obtained either by annealing at increasing temperatures for a constant short-time, or at constant temperature for increasing time. K for the long-time-anneal specimens, on the other hand, commenced to deviate from the curve at a grain diameter of about 0.4 mm. The upward deviation of K was also obtained either by annealing at increasing temperatures for a constant long-time, or at constant temperature for increasing time.

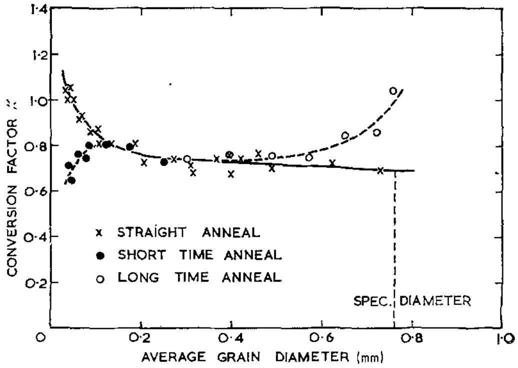

Figure 6 Effect of annealing treatments on the variation of the oxygen conversion factor (K) with grain size.

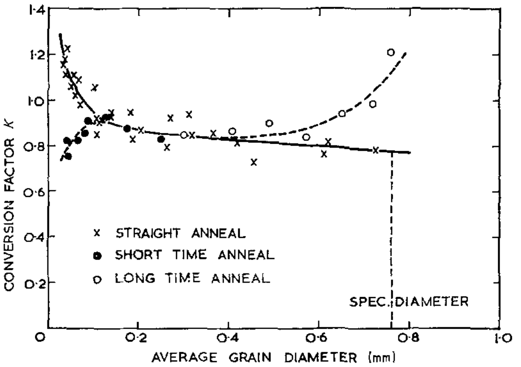

Figure 7 Effect of annealing treatments on the variation of the nitrogen conversion factor (K) with grain size.

4. Discussion

4.1 Variation of K with Solute Concentration

The conversion factor (K) (equation 1) for oxygen and nitrogen in niobium increases with increasing concentrations of these solutes (figs. 2 and 3), because of the appearance of additional relaxation peaks [22, 23]. These peaks are due to stress-induced migration of the interstitial atoms associated in pairs and triplets of like atoms

[22, 23] and pairs of unlike atoms [23, 28, 29] resulting in lower Snoek peaks and hence higher *K*. The onset of concentration-dependence of *K* corresponds to concentrations of oxygen (~ 0.06 wt %) and nitrogen (~ 0.04 wt %) at which the height of the peak due to triplets of like atoms is significant [23]. The observed higher rate of increase of *K* in the coarse-grained material (figs. 2 and 3) as compared with the fine-grain material is probably due to higher solute content within the coarser grains [8, 30], hence a higher peak due to triplets for a given total solute concentration. Furthermore, at solute concentrations approaching saturation the solute atoms may tend to form clusters of higher order than triplets [31] which do not appear to take part in the relaxation process [23]. Consequently, higher-order clustering would have a more significant effect on the height of the Snoek peak [2] and hence on *K*.

4.2 Variation of *K* with Grain Size

The observed variation of *K* with grain size (figs. 4 and 5) appears unlikely to be affected by changes in concentration during the heat-treatment of the material. The alloys studied contained amounts of oxygen and nitrogen well within the range in which *K* is concentration-independent (figs. 2 and 3). The variation should, therefore, be attributed to the structural changes in the material caused by the heat-treatments to produce the given average grain size. Since solute atoms tend to segregate to grain boundaries [32], the solute concentration within the grains decreases with decreasing grain size (increasing grain boundary area). Interstitial solute atoms segregated to grain boundaries do not take part in the relaxation process [2] as they are trapped within the distorted structure at grain boundaries. The conversion factor (*K*) is thus expected to increase with decreasing grain diameter, as reported by many workers [9-17] and confirmed by the present study.

Besides this comparatively straightforward explanation for the grain-size dependence of *K* [16, 17] it has been suggested that interstitial solute atoms are immobilised by the grain-boundary stress fields near the boundary [9]. If this is considered as the sole reason for grain-size dependence of *K*, the solute atoms present at the interfaces of grains are not accounted for. Such interpretation appears difficult to accept unless it can be shown that the amount of solute atoms at the interface of grains is negligible as compared with the amount immobilised by the grain-boundary stress fields.

An interesting feature of the present results is the difference in *K* for grains smaller than 0.14 mm (figs. 6 and 7). The explanation of this difference in *K*, in terms of texture [18], would require markedly different textures at the same small grain sizes, which would change to an equivalent texture at a grain diameter of about 0.14 mm. This is unlikely, since all specimens, prior to annealing, were cold-swaged according to exactly the same programme. The only variable was the duration of the annealing treatment. In terms of solute segregation to grain boundaries this difference in *K* indicates that after short-time annealing at comparatively low temperatures the recrystallised structure of niobium remains in a non-equilibrium state with respect to the distribution of interstitial solute atoms. Since, for a given grain size, *K* is lower in the short-time anneal specimens (probably a non-equilibrium state) than in the material annealed for longer time (equilibrium state), the former material contains more interstitial solute in free solution.

4.3 Variation of *K* with Texture

In single crystals *K* is minimum (Snoek peak height maximum), when the stress is applied in the $\langle 100 \rangle$ direction, and infinitely large (Snoek peak height essentially zero), when the stress is applied in the $\langle 111 \rangle$ direction. *K* varies between these two extreme values when the stress is applied in directions between $\langle 100 \rangle$ and $\langle 111 \rangle$ [6, 7, 33, 34]. Swartz has, therefore, suggested that the variation of *K* for carbon and nitrogen in alpha-iron is actually caused by variations in texture [18]. In the present work no definite texture, as measured by the rotating-crystal method on the internal friction wire specimens, was observed with the exception of specimens treated for long times at high temperatures. These specimens showed higher *K* values, for a given grain size, than those treated for shorter times. This is illustrated in figs. 6 and 7 for grain diameters greater than 0.4 mm. The observed increase in *K* is, therefore, attributed to the presence of texture.

4.4. Relaxation Strength

The relaxation strength (Δ) of the Snoek relaxation peak is equal to $(2/\pi)\delta_{\max}$ [5] at the maximu of the peak, and per unit concentration of interstitial solute is given by

TABLE III Comparison of relaxation strength (Δ) of the present study with those previously reported for niobium and alpha-iron.

Alloy	Δ per at. % solute at			R $(10^{17}$ cal/mol-dyn-cm$^2)^{-1}$	Reference
	Peak temperature	0.1 T_m*	0.1 T_m for iron		
Nb-O	0.26	0.41	0.62	1.4	This work
Nb-N	0.20	0.42	0.62	1.1	,,
Nb-O	0.09	0.14	0.21	0.49	3
Nb-N	0.10	0.20	0.30	0.52	,,
Fe-C	0.40	0.57	0.57	2.2	36
Fe-N	0.43	0.66	0.66	2.7	,,

*T_m is the melting point of the metals in K.

$$\Delta = 2/(\pi K) \qquad (3)$$

where K is the conversion factor (equation 1). The relaxation strength is dependent on temperature (T) through the relation [7]

$$\Delta = A/(T - \alpha T_c) \qquad (4)$$

where A, α and T_c are constants for a given system. The second term in the denominator is not known for most of the systems exhibiting the Snoek relaxation, but it is believed to be small and is frequently neglected [35]. The value of Δ, therefore, varies with temperature through the factor $1/T$. In table III are compared the present values of Δ at the Snoek peak temperature, the values of Δ corrected to 0.1 T_m of the metal and at 0.1 T_m for iron, with those reported by Powers and Doyle for niobium [3] and those referred to by Beshers for alpha-iron [35]. The present Δ for oxygen and nitrogen in niobium were obtained by substituting values of K_0 (table II) for K in equation 3.

The interesting features of the results in table III are that (a) in the case of present results the relaxation strength, per at. % solute concentration, is the same for both oxygen and nitrogen at a common temperature, and, (b) the relaxation strengths, per at. % solute, of the niobium systems of the present study are practically the same as those for the alpha-iron systems at the same temperature. The latter observation is in agreement with the suggestion of Beshers that the proper procedure is to compare relaxation strengths at the same absolute temperature [35]. Furthermore, Beshers used the ratio

$$R = \Delta/(Q\,E_{100}) \qquad (5)$$

where Δ is the relaxation strength at 0.1 T_m for iron, Q the activation energy for interstitial diffusion derived from anelastic data and E_{100} the Young's modulus, as a criterion to determine whether the octahedral or tetrahedral site should be preferred. High values of R should indicate the preference for octahedral site occupation and low values for tetahedral site occupation. According to this criterion (table III) carbon and nitrogen in alpha iron should occupy the octahedral sites whereas oxygen and nitrogen in niobium the tetrahedral sites [35]. The R values obtained from the present results are smaller than those for iron by only a factor of about 2 as compared with the factor of about 5 originally reported by Beshers [35] (table III), and therefore do not lend unambiguous support to the R criterion for the type of interstitial occupancy. On this basis there would appear to be little reason to doubt the general belief that oxygen and nitrogen in niobium should occupy the octahedral sites [2, 6, 36].

5. Conclusions

1. The conversion factor $K (= C/\delta_{max})$ correlating the height of the Snoek peak (δ_{max}) with the concentration of the corresponding interstitial solute (C) in niobium is grain-size dependent.
2. The grain-size dependence of K shows a linear relationship with the inverse square root of the average grain diameter ($d^{-\frac{1}{2}}$) of the form of the Hall-Petch equation.
3. For a given grain size K is concentration independent up to about 0.06 wt% and 0.04 wt% oxygen and nitrogen, respectively.
4. The grain-size dependence of K is believed to be primarily due to segregation of interstitial solute atoms to grain boundaries.
5. For a given grain size K can also be affected by the annealing treatments.

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