Internal Friction in the Interstitial Solid Solutions of C and O in Tantalum*

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A strongly temperature-dependent type of internal friction is observed in tantalum specimens containing a small amount of carbon or oxygen. Internal friction peaks occur, respectively, around 150° C and 170° C for carbon and oxygen when the frequency of vibration is about one cycle per second. The activation energies associated with these relaxations are found to be 25,000 calories per mole for carbon and 29,000 calories per mole for oxygen. These observations are consistent with the viewpoint that the relaxations observed are associated with the anelasticity caused by the stress-induced preferential distribution of C or O among the various interstitial positions which have tetragonal symmetry in body-centered cubic tantalum. Such a picture has been proposed by Snoek in

I. INTRODUCTION

STRONGLY temperature-dependent type of internal friction has been observed in iron for many years. An internal friction peak occurs around room temperature when the frequency of vibration is of the order of one cycle per second. Recently, Snoek1 proposed that this internal friction is due to the anelasticity associated with the stress-induced preferential distribution of carbon or nitrogen atoms in primary solid solution of alpha-iron. Let us consider the octahedral interstitial positions in the lattice of alpha-iron which has a body-centered cubic structure. If carbon or nitrogen atoms go into these positions, tetragonal deformation will be introduced in the lattice with the tetragonal axis along one of the three $\langle 100 \rangle$ directions. When a tensile stress is applied along one of these axes, there will be a greater probability that a solute atom be in an interstitial position with tetragonal axis along this axis. The establishment of this preferential distribution of solute atoms causes a relaxation phenomenon and will manifest itself as internal friction and related effects.

It can be seen that no anelastic effects are to be expected when the tensile stress is applied along a $\langle 111 \rangle$ direction, for then all interstitial interpreting the relaxation phenomena observed in alphairon (body-centered cubic) containing small amounts of carbon or nitrogen. The observations in tantalum might thus indicate that such relaxations are characteristic of all interstitial solid solutions of body-centered cubic metals. It has been further found that the carbon relaxation peak can be interpreted in terms of a relaxation process having a single relaxation time with a unique activation energy while the oxygen peak can not. This suggests that the interstitial atoms responsible for the observed relaxation peaks in tantalum are situated at the octahedral positions in the case of carbon and at both octahedral and tetrahedral positions in the case of oxygen.

positions are equivalent. This high anisotropy of the anelasticity in single crystals of alpha-iron has been confirmed by Dijkstra,² who showed that the relaxation strength along a $\langle 111 \rangle$ direction is only about 5 percent of that along a $\langle 100 \rangle$ direction.

If the above picture is correct, this type of strongly temperature-dependent anelastic effects observed in alpha-iron should also occur in the primary solid solution of other body-centered cubic metals containing interstitial solute atoms. On the other hand, accepting this picture of stress-induced preferential distribution of solute atoms, information can be derived from measurements of anelastic effects as to the properties of the interstitial solid solutions in other bodycentered cubic metals.

As far as the author is aware, there is no experimental information in the literature about the interstitial solid solutions of tantalum which has a body-centered cubic structure. The purpose of the present paper is to describe some internal friction measurements from which the conclusion can be drawn that carbon and oxygen do form interstitial solutions with tantalum. This observation is the first evidence that oxygen forms interstitial solid solution with a metal. A discussion is made of the location of C and O in the octahedral or tetrahedral position in the tantalum lattice.

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¹ J. L. Snoek, Physica 8, 711 (1941).

² L. J. Dijkstra, Philips Research Reports 2, 357 (1947).



FIG. 1. Variation of internal friction with temperature in tantalum specimens (containing 0.013 percent of carbon) annealed in vacuum at various temperatures. Frequency of vibration is about one cycle per second.

II. INTERNAL FRICTION IN TANTALUM CONTAINING CARBON

The tantalum used in the measurements was 99.9 percent pure and was received in annealed form in wires having a diameter of 0.03 inch. It was fine-grained and had a rather uniform grain size. A wire of about one foot long was cut from the spool and straightened by stretching. It was mounted in the furnace for torsional measurements. A description of the torsional apparatus has been given before.³ The natural frequency of the vibrating system, including the specimen and the auxiliary inertia member, was about 1.2 cycles per second and the total longitudinal load on the wire was about 28 g. As the Young's modulus of tantalum is 2.7×10^7 pounds per square inch, this load corresponds to a longitudinal elastic strain of the order of magnitude of 10^{-6} . This is smaller than the average shearing strain, which is about 10^{-5} , applied to the wire during the dynamic torsional measurements. Under these conditions it has been found



FIG. 2. Internal friction curves for tantalum specimen (containing 0.013 percent of carbon) with two frequencies of vibration having a ratio of 3.81.

that the internal friction in the specimen is independent of the stress amplitude.

All the internal friction measurements were taken in an atmosphere of argon having a purity of 99.8 percent. The temperature of the specimen was controlled and measured with a relative accuracy of 1°C with a Tag Celectray indicating temperature controller.

The variation of internal friction with temperature in this tantalum wire is shown in Fig. 1. The internal friction curve does not change by annealing in vacuum at various temperatures. This indicates that the internal friction peaks observed have nothing to do with cold-working. With a frequency of about one cycle per second, the first internal friction peak or the lower temperature peak occurs at a temperature of about 150°C and the second peak or the higher temperature peak occurs at about 350°C. Let us first confine ourselves to the lower temperature peak. The physical origin of the higher temperature peak will be discussed in a later paper.

The heat of activation associated with the lower temperature peak was determined by taking measurements at two different frequencies. The internal friction curves corresponding to these two frequencies are shown in Fig. 2. The lower frequency used was about 0.3 cycles per second. It is shown in Fig. 3 that these two curves can be superposed on each other by a horizontal shift of the 1/T scale through 0.105×10^{-3} . As the two frequencies of vibration have a constant ratio of 3.81 over the whole temperature range concerned, this gives a heat



FIG. 3. Determination of heat of activation associated with the lower temperature peak shown in Fig. 1 by a horizontal shift of the two internal friction curves shown in Fig. 2. The two curves were superposed on each other by a relative shift of the 1000/T scale through 0.105. This gives a heat of activation of 25,000 calories per mole. The triangles indicate the calculated points assuming a single relaxation time and a unique heat of activation.

³ T. S. Kê, Phys. Rev. 71, 533 (1947).

of activation of 25,000 calories per mole following similar calculations made before.⁴

In relaxation processes having a single relaxation time, τ , the internal friction Q^{-1} associated with this relaxation is given, if the relaxation is small, by the following well-known relation:

$$Q^{-1} = \Delta_M(\tau \omega/1 + \tau^2 \omega^2), \qquad (1)$$

where Δ_M is the total relaxation strength and ω is the angular frequency of vibration. It can be shown that the internal friction will reach its maximum value when

$$=1,$$
 (2)

and Eq. (1) becomes

$$Q^{-1} = 2Q_{\max}^{-1}(\tau \omega/1 + \tau^2 \omega^2).$$
 (3)

The temperature dependence of the relaxation time can be represented by the expression

$$\tau = \tau_0 e^{H/RT},\tag{4}$$

where H is the heat of activation, R the gas constant, and τ_0 a coefficient which can be determined from Eqs. (2) and (4) and the known value of H. As H has been found to be 25,000 calories per mole and the frequency of vibration is 1.24 c.p.s. at the optimum temperature 148°C (421°K), we have

$$\tau_0 = 1.6 \times 10^{-14} \text{ sec.} \tag{5}$$

The theoretical internal friction at various temperatures for a relaxation process having a single relaxation time can thus be calculated according to Eq. (3). In our present case these calculated points are indicated by the triangles in Fig. 3. They lie fairly close to the observed curve. This shows that the observed relaxation phenomenon (the lower temperature peak) has a single relaxation time.

In order to confirm this conclusion, the internal friction curve shown in Fig. 3 was plotted in Fig. 4 with the logarithm of Q^{-1} against 1/T. The two straight-line asymptotes shown have slopes of equal magnitude but of opposite sign, and the heat of activation H determined from both slopes is 25,000 calories per mole, which is identical with the value previously obtained by a different method. These two straight lines intersect at a point where the internal friction is 0.04, which is twice as much as the maximum



FIG. 4. Internal friction in tantalum specimen containing 0.013 percent of carbon with log Q^{-1} plotted against 1/T. The straight-line asymptotes have slopes of equal magnitude but of opposite sign. The heat of activation calculated from these slopes is 25,000 calories per mole.

internal friction. All these results are in conformity with Eq. (1), indicating a single relaxation time.

The existence of a single relaxation time suggests that the observed relaxation phenomenon is associated with a diffusion process having a definite and unique diffusion distance.

Chemical analysis of the carbon content in the tantalum specimen by combustion method showed 0.013 ± 0.003 percent of carbon by weight.** This specimen was enriched in carbon



FIG. 5. Internal friction curve for tantalum specimen enriched with carbon compared with the curve for the original specimen containing 0.013 percent of carbon. The symmetrical increase of the original curve indicates that the internal friction peak concerned is due to carbon.

** Thanks are due Mr. R. E. Fryxell and Dr. N. H. Nachtrieb of this Institute for making this analysis.

⁴ T. S. Kê, Phys. Rev. 72, 41 (1947).

by painting on its surface a thin layer of colloidal graphite in alcohol. This coated specimen was annealed at 1200°C in vacuum for 48 hours and furnace cooled.*** After such a treatment the graphite layer disappeared, and chemical analysis showed that the carbon content in the specimen was raised to 0.062 ± 0.003 percent by weight. The internal friction curve of the enriched specimen is shown in Fig. 5 with that of the original specimen included for comparison. It is seen that the internal friction peak increases symmetrically with respect to the original peak when the internal friction is plotted against 1/T. This leads to the belief that the observed internal friction peak is connected with the presence of carbon. As we have demonstrated above that the relaxation process has a single relaxation time, this means that the observed internal friction peak (lower temperature peak in Fig. 1) is due to carbon alone.

In the case of alpha-iron, the carbon peak occurs around 35°C when the frequency of vibration is about one cycle per second. As the melting point of tantalum is higher than that of iron, the relaxation peak for carbon would be expected to occur at a higher temperature in tantalum than in alpha-iron. This was found to be the case as the carbon peak in tantalum occurs around 150°C. Thus, with reference to the previous work on alpha-iron, it is reasonable to infer that the observed internal friction peak is due to the stress-induced preferential distribution of C among the various interstitial positions in body-centered cubic tantalum. A corrobora-



FIG. 6. Effect of oxygen in tantalum upon the internal friction peak observed in tantalum specimen containing 0.013 percent of carbon. The original internal friction curve was raised and shifted toward higher temperatures because of the addition of oxygen.

*** Thanks are due Mr. Harold H. Hirsch of this Institute for help in treating the specimen.

tion of this inference by stress relaxation measurements will be described in a later paper.

The higher temperature internal friction peak shown in Fig. 1 was found not to change with the amount of carbon in tantalum. Accordingly, it is not connected with the presence of carbon.

It should be mentioned that the internal friction peak for the specimen enriched with carbon (Fig. 5) is not stable, and all the measurements should be made as rapidly as possible. Thus it has been found that when the temperature of the specimen is raised, the internal friction increases with annealing time at a given temperature. This indicates that segregation of carbon from the solid solution has taken place when the specimen was furnace cooled from 1200°C to room temperature during the treatment. As the temperature of the specimen is raised during the measurement, some carbon will redissolve, resulting in the increase of internal friction, until the saturation value is reached. It is evident, then, that the carbon content in the specimen as determined by chemical analysis (0.062 percent) is more than the saturation value at 150°C. Taking the lower curve in Fig. 5 as standard (containing 0.013 percent of carbon), estimation can be made from the relative height of the two peaks that the solubility of carbon in tantalum at 150°C is approximately 0.02 percent assuming that the internal friction is linear with the carbon concentration in the specimen concerned.

III. INTERNAL FRICTION IN TANTALUM CONTAINING OXYGEN

The effect of oxygen in tantalum upon the internal friction peak described in the last section is shown in Fig. 6. Curve a shows the internal friction observed in the original tantalum specimen containing 0.013 percent of carbon. This specimen was annealed in an atmosphere of oxygen at 500°C for five hours. Such a treatment resulted in the formation of a thin oxide layer on the surface of the specimen. The internal friction peak (curve b) for this specimen was raised and shifted toward higher temperatures relative to the original curve. This indicates that some oxygen atoms have diffused into the specimen during the annealing to form interstitial solid solution with tantalum. According to this viewpoint, the new internal friction peak



FIG. 7. Internal friction curves for original tantalum specimen (dotted curves) and for the oxygen-enriched specimen (solid curves). Both were determined with two frequencies of vibration.

is a combination of the original carbon peak and an additional oxygen peak with its maximum at a higher temperature. This viewpoint is strengthened by the finding that the raise and shift toward higher temperatures of the internal friction peak are much more marked (curve c) after the oxide-coated specimen was again annealed in vacuum at 1200°C and furnace cooled. After such a treatment, the oxide layer originally formed on the surface of the specimen disappeared. As the weight of specimen remains unchanged before and after the treatment at 1200°C, the surface layer must have been diffused into the specimen. The increase in weight of the specimen compared with the original specimen was about 0.06 percent. If all this oxygen goes into solution, then the oxygen content in solution will be about 0.06 percent by weight. From Fig. 6, the internal friction curve for this specimen reaches a maximum value of about 0.1, which is higher than any internal friction peak so far reported in the literature. This internal friction peak has been found to be very stable, indicating that the oxygen content in solution can be further increased. The solubility of oxygen in tantalum is thus greater than 0.06 percent at 170°C.

The higher temperature peak (Figs. 1 and 6) has been found to be independent of the oxygen content in tantalum.

The question may arise that some nitrogen may have been introduced into the tantalum specimen during the annealing in oxygen. However, later experiments show that nitrogen does not give a relaxation peak anywhere close to this lower temperature peak. It may be mentioned here that the higher temperature peak shown in Figs. 1 and 6 has been found to be connected with the presence of nitrogen in tantalum.

Let us assume that curve c in Fig. 6 is a combination of a carbon peak and an oxygen peak. We should be able, then, to resolve this curve into its components. In Fig. 7 the dotted curves indicate the carbon peak determined at two frequencies of vibration. The solid curves



FIG. 8. Internal friction curves resulting from oxygen in tantalum obtained by subtracting the dotted curves from the corresponding solid curves shown in Fig. 7.



FIG. 9. Variation of natural frequencies of vibration with temperature for the oxygen-enriched tantalum specimen. The two curves correspond to the two solid internal friction curves shown in Fig. 7.

are the composite curves determined at two frequencies of vibration identical to those used for the dotted curves. By subtracting the dotted curves from the corresponding solid curves, we get the contribution attributable to oxygen alone. This is shown in Fig. 8. We can see that the internal friction peak occurs at a temperature of about 20°C higher in the case of oxygen than in carbon.

Figure 9 gives the temperature variation of the natural frequencies of vibration corresponding to the two solid internal friction curves shown in Fig. 7. The frequency decreases with a rise of temperature, and the variation is con-



FIG. 10. Determination of heat of activation associated with the oxygen peak by a horizontal shift of the two internal friction curves shown in Fig. 8. The two curves were superposed on each other by a relative shift of the 1000/T scale through 0.0875. Taking the frequency ratio to be 3.59, this gives a heat of activation of 29,000 calories per mole. The triangles indicate the calculated points assuming a single relaxation time and a unique heat of activation.



FIG. 11. Examples illustrating the octahedral and tetrahedral interstitial positions in a body-centered cubic lattice. The closest atoms to these positions were indicated by dashed and dotted lines.

siderable over the temperature range concerned. This is because the relaxation concerned is rather large. In spite of the variation of frequency with temperature, it has been found that the ratio of the two frequencies at any given temperature changes very slightly with temperature and that the average ratio of the two frequencies is 3.59. As the contribution of oxygen to the solid curves shown in Fig. 7 is by far greater than that of carbon, we can take this frequency ratio of 3.59 in the evaluation of the heat of activation associated with the oxygen relaxation from the two curves shown in Fig. 8. The horizontal shift in 1/T scale to bring these two curves to superpose on each other was found to be 0.0875×10^{-3} (Fig. 10), and this gives a heat of activation of about 29,000 calories per mole which is higher than the value for carbon.

It can be seen from Fig. 10 that the internal friction in the oxygen peak reaches its maximum value at 172°C (445°K) and the frequency of vibration at this temperature is 1.11 c.p.s. according to the upper curve of Fig. 9. Using the heat of activation of 29,000 calories per mole, we find that

$\tau_0 = 1.0 \times 10^{-15}$ sec.

Following similar procedures as made in the case of carbon, the theoretical curve for a single relaxation time was calculated and is shown by the dotted curve in Fig. 10. It is much narrower than the observed curve. This indicates that the observed oxygen peak cannot be interpreted in terms of a single relaxation time with a unique activation energy. A discussion of this point will be given in the next section.

IV. DISCUSSION

The condition for stress-induced preferential distribution of interstitial solute atoms is that an unsymmetrical distortion be introduced in the lattice when the solute atoms go into the interstitial positions. In a body-centered cubic lattice there are two kinds of interstitial positions for the solute atoms. One kind is octahedral, situated at the center of the faces or the middle of the edges of an elementary cell. A typical example of such positions is shown in Fig. 11, which has the coordinates $(\frac{1}{2}, \frac{1}{2}, 0)$. The other kind is tetrahedral, situated at the center of a tetrahedron constituted by two corner and two center atoms. It can be seen that in both kinds of interstitial positions there are three types of positions each having tetragonal axis along one of the principal axes. Therefore, as far as the mechanism of the stress-induced preferential distribution of the solute atoms is concerned, all the arguments are valid for both kinds of interstitial positions, octahedral or tetrahedral. However, the unsymmetrical distortion introduced in the lattice is much greater in cases where a solute atom goes into an octahedral position. Consequently the internal friction peak should also be greater.

In the case of carbon in alpha-iron reference can be made to the case of martensite, for which it has been shown that the carbon atoms occupy the octahedral positions.5 This may indicate that it is easier to push away the two nearest atoms around an octahedral position to make room for the carbon atom than to push away all the four atoms around a tetrahedral position, although the octahedral position is smaller than the tetrahedral position as far as the two nearest neighbors are concerned. As the metallic radius of tantalum is larger than that of iron, we can assume that carbon atoms can also go into the octahedral positions in tantalum. Now we have demonstrated above that the observed carbon peak around 150°C has a single relaxation time with a unique heat of activation. This indicates that this peak can be associated with only the stress-induced preferential distribution among the various types of interstitial positions of one single kind: octahedral or tetrahedral. If the observed 150°C peak is associated with the carbons in the tetrahedral positions, then there should be another relaxation peak of larger magnitude associated with the carbon atoms in the octahedral positions. As no other conspicuous relaxation peak the presence of carbon in tantalum was observed within the wide temperature range from -75° C to 550° C, we may assume that the observed peak is associated with the carbon atoms in octahedral positions.

The situation in the case of oxygen is different because the relaxation curve observed cannot be interpreted in terms of a single relaxation time with a unique activation energy. This may indicate that the relaxation process does not consist of a single relaxation time or that there is more than one activation energy involved in the relaxation process. The observed relaxation time and activation energy are thus only the mean values. This leads us to assume that oxygen, probably with metallic bond, can go into both the octahedral and tetrahedral positions, as the metallic radius of oxygen is about 12 percent smaller than that of carbon.⁶

It can be seen from Fig. 11 that each octahedral position is surrounded by four tetrahedral positions. When a solute atom at the octahedral position $(\frac{1}{2}, \frac{1}{2}, 0)$ having a tetragonal axis along z axis diffuses into the octahedral position $(\frac{1}{2}, 0, 0)$ having a tetragonal axis along x axis. it must pass through the tetragonal position $(\frac{1}{2}, \frac{1}{4}, 0)$. If, in non-quantum-mechanical language, the tetrahedral position cannot accommodate the solute atom, then the solute atom can only accomplish its journey by one single jump with a unique value of activation energy. A single relaxation time is thus involved in the process. This may correspond to the case of the carbon relaxation. However, if the tetrahedral position can also accommodate the oxygen as we assumed above, then the stress-induced diffusion among the octahedral positions may be accomplished by two intermediate steps having different heats of activation. Accordingly, the relaxation process involved is much complicated with a broadened relaxation curve.

⁵ N. J. Petch, J. Iron and Steel Inst. **147**, 221 (1943); H. Lipson and A. M. B. Parker, *Ibid.* **149**, 123 (1944).

⁶ Linus Pauling, J. Am. Chem. Soc. 69, 542 (1947).