

Internal Friction and Precipitation from the Solid Solution of N in Tantalum*

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The internal friction or acoustic absorption peak (*versus* temperature) around 350°C previously observed in tantalum with a frequency of vibration of about one cycle per second was further analyzed. It is shown that this peak has its origin in the stress-induced interstitial diffusion of N in tantalum similar to the cases of C and O in tantalum reported before. The precipitation of N from the solid solution with tantalum was followed by internal friction measurements.

IT has been reported previously that three internal friction or acoustic absorption peaks (*versus* temperature) were observed in tantalum containing small amounts of minor constituents as impurities.¹ With a frequency of vibration of about one cycle per second, these peaks occur at about 150°C, 170°C, and 350°C, respectively. The first two peaks are believed to be caused, respectively, by the stress-induced diffusion of C and of O among the various interstices in tantalum lattice in which the interstices have tetragonal symmetry. This viewpoint was later substantiated by experiments on the temperature-dependence of the relaxation strength associated with these peaks.² The physical origin of the third peak at 350°C, however, remained obscure.

It has been found that this 350°C peak does not change by annealing cold-worked metal in vacuum at various temperatures (600°C, 980°C, 1200°C). This indicates that it has nothing to do with cold-working. Furthermore, it does not change

with the amount of carbon or oxygen in tantalum. Accordingly, it is not connected with the presence of carbon or oxygen.

The tantalum specimens used in the following study are similar to those used before. It is 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.

Figure 1 shows that the peak concerned was considerably raised when the amount of nitrogen in the specimen was increased by annealing successively at 980°C and 1200°C in an atmosphere of nitrogen. This peak must, therefore, be connected in some way with the presence of nitrogen in tantalum as we have shown that annealing alone did not change this peak. The small peak observed before the "loading" of nitrogen is presumably due to the presence of some trace of nitrogen in the original specimen.

Further experiments have shown that this peak is a manifestation of a relaxation phenomenon. The sudden drop of the shear modulus (in arbitrary units) in the nitrogen-loaded specimen is shown in Fig. 2, and the stress relaxation at very small constant strain is shown in Fig. 3.

It is but natural to think that this peak is caused by the stress-induced diffusion of N in

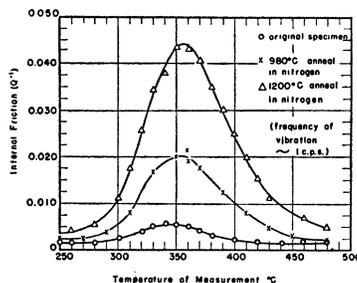


FIG. 1. Effect of nitrogen content in tantalum upon the 350°C internal friction peak. The peak is raised when the amount of nitrogen in the specimen was increased by annealing successively at 980°C and 1200°C in nitrogen.

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¹ T. S. Kê, *Phys. Rev.* **74**, 9 (1948).

² T. S. Kê, *Phys. Rev.* **74**, 16 (1948).

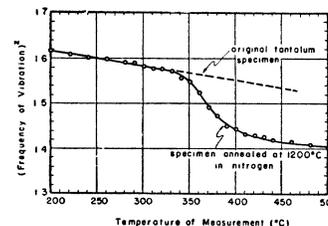


FIG. 2. Variation of "rigidity" (in arbitrary units) with temperature in tantalum specimen loaded with nitrogen.

tantalum similar to the case of C and O in tantalum. But it is puzzling that the nitrogen peak should occur at a temperature 200°C higher than those of carbon and oxygen. We know that the peaks of carbon and oxygen are only about 20°C apart. Another possible interpretation is that this peak may have its origin in the viscous behavior of the interphase boundaries between tantalum nitride and the tantalum matrix, similar to the viscous behavior of the grain boundaries in metals.^{3,4} A decisive test on these two possibilities is to ascertain whether the nitrogen responsible for the observed internal friction peak is in solid solution or is in the form of tantalum nitride.

The heat of activation associated with the absorption peak was determined by using the conventional procedure of determining the internal friction curve with two frequencies of vibration (see Fig. 4). This gives a value of about 44,000 calories per mole, which is much larger than the corresponding values for C and O in tantalum which are, respectively, 25,000 and 29,000 calories per mole. It is also much higher than the corresponding value of 20,000 calories per mole for N in alpha-iron.⁴ By calculating the theoretical internal friction curve as was done in the case of oxygen,¹ it is shown in Fig. 4 that the observed peak cannot be interpreted in terms of a single relaxation time with a unique heat of activation.

An important clue to this problem was the observation that the internal friction in a tantalum specimen freshly "loaded" with nitrogen decreases with tempering at a given temperature. Figure 5 shows the value of the internal friction (Q^{-1}) at the optimum temperature, 350°C, plotted as a function of tempering time at this temperature. A specimen previously loaded with nitrogen by annealing at 1200°C in an atmosphere of nitrogen was quenched in vacuum from 900°C to room temperature, and internal friction measurements were made at 350°C after quenching (curve A). The internal friction reaches a somewhat stable value after about twenty hours. Metallographic examination shows that the specimen after quenching has a clear appearance

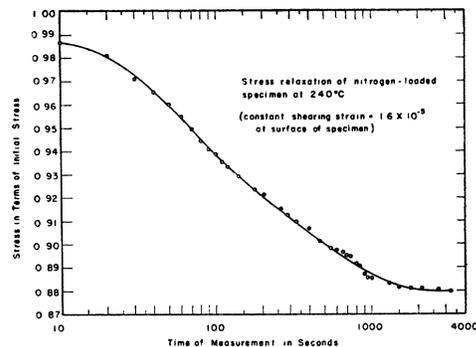


FIG. 3. Stress relaxation under constant strain of nitrogen-loaded specimen at 240°C.

similar to the original specimen before being "loaded" with nitrogen, while the same specimen tempered at 350°C for twenty hours shows needle-like precipitates. When this tempered specimen was again annealed in vacuum at 600°C and then quenched, the initial value of the internal friction is lower than is the case when the quenching was made from 900°C (curve B). The initial rate of precipitation for the specimen quenched from 600°C is also slower. The final stable value is, according to Fig. 5, about the same in both cases. Metallographic examination on this specimen shows also needle-like precipitates but these are larger in size.

These observations can be easily understood if we assume that the internal friction observed is caused by the nitrogen in solid solution in tantalum rather than caused by nitrogen precipitated

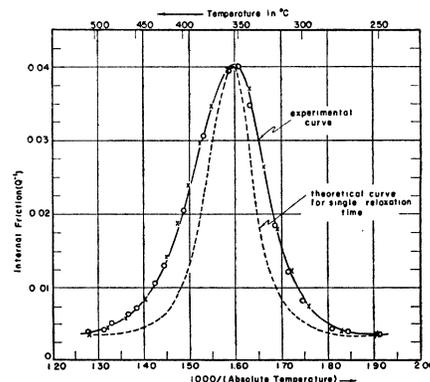


FIG. 4. Determination of heat of activation associated with the nitrogen peak by a relative horizontal shift of two internal friction curves measured with two different frequencies of vibration. (X, lower frequency; O, higher frequency.) The dotted curve was calculated assuming a single relaxation time and a unique heat of activation.

³T. S. Kê, Phys. Rev. **71**, 533 (1947); **72**, 41 (1947); J. App. Phys. **19**, 285 (1948).

⁴T. S. Kê, *Metals Technology* (Tech. Pub. 2370, June, 1948).

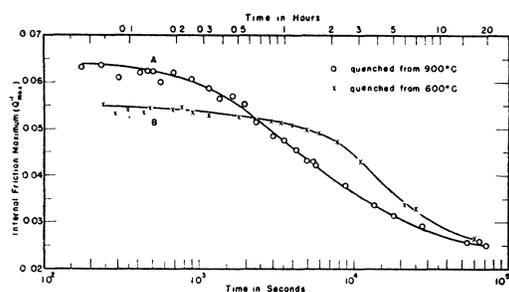


FIG. 5. Variation of internal friction maximum with time in nitrogen-loaded specimens quenched from different temperatures. The curves indicate the precipitation of nitrogen from solid solutions.

as nitride. Evidently a supersaturated solution of N in tantalum is formed by quenching from a higher temperature. The nitrogen then precipitates out from the solution when tempered at a lower temperature. The initial rate of precipitation increases with the degree of supersaturation which, in turn, increases with the temperature from which the quenching was made. The final stable value of internal friction is presumably a measure of the solubility of N in tantalum at the tempering temperature. The internal friction observed cannot be due to nitrogen in precipitated form since then the internal friction should be raised instead of being reduced while precipitation proceeds.

The precipitation of N from the solid solution with tantalum as indicated by internal friction measurements is similar to that observed by Dijkstra⁵ in the cases of C and N from the solid solutions with alpha-iron. It may be worth while to point out that such a procedure furnishes a powerful tool for the study of the behavior of

⁵L. J. Dijkstra, Phillips Research Rep. 2, 357 (1947); also later works by Dijkstra, communicated to A.I.M.E.

nucleation and precipitation from metallic solid solutions. The value of internal friction is a sensitive indicator of the instantaneous concentration of solute atoms in solid solution which is difficult to determine by other methods.

The concept of stress-induced interstitial diffusion of N in tantalum implies that the diffusion distance covered in the relaxation process associated with the diffusion should be of the order of magnitude of, and somewhat smaller than, one atomic diameter of tantalum. An estimation of this diffusion distance from internal friction data by a procedure previously described⁴ gives a value which is close to the atomic diameter of tantalum.

The fact that the observed internal friction peak cannot be interpreted by a single relaxation time with a unique heat of activation (see Fig. 4) may mean that the nitrogen atoms are situated at both the octahedral and the tetrahedral interstitial positions in the tantalum lattice similar to the case of oxygen.¹

It is difficult to see, however, why the heat of activation associated with the nitrogen peak is so much higher than the corresponding cases of C and O resulting in the nitrogen peak occurring at a much higher temperature. A higher heat of activation implies a larger distortion introduced in the lattice by the presence of the solute atoms.

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