

Stress Relaxation by Interstitial Atomic Diffusion in Tantalum*

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In a preceding article, it was shown that the internal friction peaks observed in tantalum containing small amounts of C and O are caused by the stress-induced preferential distributions of C or O among the interstices in tantalum. In order to further elucidate this viewpoint, the relaxation strength associated with these relaxations has been determined by rigidity and stress relaxation measurements in torsion covering a wide range of temperature. When the reciprocal of relaxation strength is plotted against absolute temperature, the graph is a straight line passing through the origin. This linear relationship agrees with that predicted by theory assuming a model of stress-induced preferential distribution. The finding that the extrapolated line passes through absolute zero temperature shows that the interaction between solute atoms is negligibly small. This implies that the critical temperature for self-induced preferential distribution of solute atoms is close to absolute zero.

I. INTRODUCTION

IN a preceding article¹ it was shown that the internal friction peaks observed in tantalum containing small amounts of C and O are consistent with the viewpoint that C and O form an interstitial solid solution in tantalum, and hence lead to local distortions having tetragonal symmetry just in the same manner as C and N lead to local distortions having tetragonal symmetry when dissolved in alpha-iron,² which likewise has a body-centered cubic structure. When a tensile stress is applied to the specimen along a given direction, this tetragonal deformation will lead to a preferential distribution of the C or O among the various interstices having tetragonal axes along different directions. The establishment of such a stress-induced preferential equilibrium distribution of C and O requires some time. Consequently, strain lags behind the stress and gives rise to internal friction and related effects.

In the theoretical analysis of relaxation phenomena, it is often convenient to describe the magnitude of the relaxation in terms of a quantity known as the relaxation strength. It is defined by

$$\Delta_M = (M_U - M_R) / M_R, \quad (1)$$

where M_U and M_R are, respectively, the unrelaxed and relaxed elastic moduli. When the

relaxation arises from a stress-induced preferential distribution of solute atoms, it may be shown that the temperature dependence of the relaxation strength is given by³

$$\Delta_M = T_0 / (T - \alpha T_0). \quad (2)$$

In this relation, T is the absolute temperature; α is a numerical coefficient taking account of the interaction between solute atoms—it corresponds to the Weiss factor in the theory of ferromagnetism; and T_0 is a temperature-independent term which increases with the concentration of the solute atoms and the tetragonal distortion introduced in the lattice due to the presence of the solute atom.

Equation (2) is inapplicable at temperatures below αT_0 . However, before this temperature is reached from above, there is a critical temperature below which there will be a spontaneous ordering of the solute atoms under zero stress. At this temperature the interaction between the solute atoms reduces the energy of one of them if it goes to an interstices having a tetragonal axis parallel to the preponderant ones of the others. This is analogous to the Curie temperature below which the magnetic moments of the atoms, or, rather, the spins of the electrons in a ferromagnetic domain are orientated in such a way as to point all along the same direction at zero magnetic field. The critical temperature T_c

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

² J. L. Snoek, *Physica* **8**, 711 (1941).

³ C. Zener, *Elasticity and Anelasticity of Metals* (The University of Chicago Press, Chicago, 1948) p. 113. A somewhat different approach was given by D. Polder, *Philips Research Reports* **1**, 5 (1945).

for such a self-induced preferential distribution of interstitial solute atoms in body-centered cubic lattices has been computed by Zener to be

$$T_c = 1.05\alpha T_0, \quad (3)$$

and he pointed out that the persistence of the tetragonal structure of freshly quenched martensite at room temperature can be interpreted only as due to such a self-induced preferential distribution of carbon atoms in iron.⁴ Assuming α to be of the order of magnitude of unity, the critical temperature for such a spontaneous ordering was raised, according to Zener, to above the room temperature as the carbon content in iron reaches 0.14 percent by weight.

Before the concept of preferential distribution of solute atoms in alpha-iron was proposed by Snoek, early work of Richter⁵ on the elastic after-effect of carbonyl iron had shown that the relaxation observed had a temperature coefficient of 0.003 at room temperature, a temperature coefficient which is consistent with Eq. (2). However, his conditions of measurement were such that an estimate of the interaction constant α could not be obtained.

The purpose of this paper is to subject the theoretical Eq. (2) to an experimental test, and in particular, to obtain an estimate of the interaction parameter α . It is very difficult to test Eq. (2) over a wide temperature range by working with the C-Fe system. The solubility of C in iron is extremely small and segregation will take place even at room temperature when a fair amount of carbon was "loaded" in iron in solid solution. On the contrary, the interstitial solid solutions of C and O in tantalum are appropriate for such a study as, according to the observations described in the preceding article, the solubility of C and O in tantalum is fairly high and no perceptible segregation takes place up to a fairly high temperature.

II. RELAXATION STRENGTH BY RIGIDITY MEASUREMENTS

The relaxation strength was determined by rigidity (Section II) and stress relaxation measurements (Section III) in torsion. As we have demonstrated that the superposition principle is

⁴ C. Zener, *Trans. A.I.M.E.* **167**, 550 (1946).

⁵ G. Richter, *Ann. d. Physik* **32**, 683 (1938).

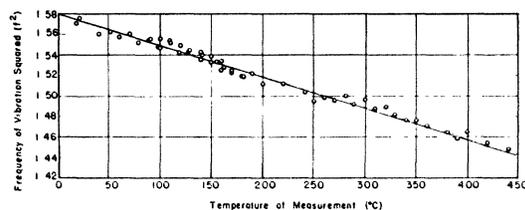


FIG. 1. Variation of "rigidity" with temperature in high purity tantalum.

valid in the relaxation processes concerned,¹ Eq. (2) holds for torsional stress as well as for tensile stress.

The variation of rigidity with temperature of high purity tantalum** was determined by measuring the frequency of the free torsional vibration of a wire specimen at various temperatures with an apparatus which has been described before.⁶ The observations are shown in Fig. 1. The rigidity was plotted in arbitrary units. It is seen that the rigidity decreases linearly with temperature up to 450°C, the highest temperature of measurement. This is in conformity with the finding of a number of workers that if no relaxation processes occur, the normal variation of the elastic coefficients with temperature is linear over a wide range of temperature.⁷

In the following study of the relaxation phenomena caused by the presence of C and O in

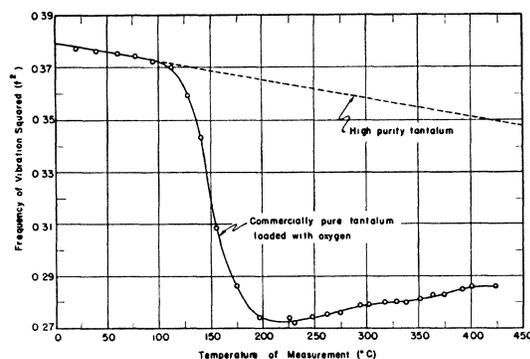


FIG. 2. Variation of "rigidity" with temperature in tantalum containing C and O.

** Thanks are due to Fansteel Metallurgical Corporation for supplying the high purity tantalum.

⁶ T. S. Kê, *Phys. Rev.* **71**, 533 (1947).

⁷ F. Rose, *Phys. Rev.* **49**, 50 (1936); M. A. Durand, *Phys. Rev.* **50**, 449 (1936); S. L. Quinby and S. Siegel, *Phys. Rev.* **54**, 293 (1936); S. Birch and D. Bancroft, *J. Chem. Phys.* **8**, 642 (1940); S. Siegel and R. Cummerrow, *J. Chem. Phys.* **8**, 847 (1940); T. S. Kê, see reference 6.

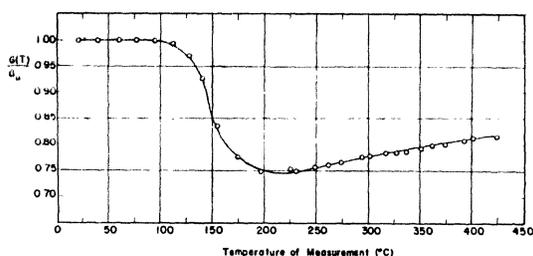


FIG. 3. Rigidity relaxation in tantalum containing C and O.

tantalum, the tantalum specimen used was of commercial purity. It contained 0.013 percent carbon by weight. This specimen was loaded with oxygen by a special diffusion procedure as described in the preceding article. Microscopic examination of the specimen after this treatment showed that no perceptible oxide was precipitated along the grain boundaries and inside the grains. The oxygen content in the specimen is about 0.06 percent by weight, assuming all the oxygen goes into solid solution in tantalum.

The temperature variation of rigidity of the tantalum specimen described above is shown in Fig. 2. The rigidity curve is a straight line up to a temperature around 100°C above which a sudden drop occurs. The internal friction also begins to rise around this temperature. According to the analysis made in the preceding paper, this sudden drop in rigidity is caused by the stress-induced preferential distribution of C and O among the various interstices in tantalum. The dotted line shown in Fig. 2 gives the rigidity

TABLE I. Temperature dependence of relaxation strength from rigidity measurements.

(°C)	T (°K)	f_R^2	f_U^2	G_R/G_U	ΔG	$1/\Delta G$
225	498	0.274	0.364	0.753	0.32 ₈	3.0 ₅
230	503	0.272	0.362	0.749	0.33 ₈	2.9 ₈
248	521	0.274	0.362	0.757	0.32 ₂	3.1 ₁
262	535	0.275	0.361	0.762	0.31 ₃	3.2 ₀
274	547	0.276	0.360	0.766	0.30 ₆	3.2 ₈
293	566	0.279	0.359	0.777	0.28 ₇	3.4 ₉
302	575	0.279	0.358	0.799	0.28 ₄	3.5 ₂
317	590	0.280	0.357	0.784	0.27 ₆	3.6 ₂
327	600	0.280	0.357	0.785	0.27 ₄	3.6 ₅
337	610	0.280	0.356	0.787	0.27 ₁	3.6 ₈
351	624	0.281	0.355	0.792	0.26 ₃	3.8 ₀
363	636	0.283	0.354	0.799	0.25 ₁	3.9 ₈
374	647	0.283	0.353	0.801	0.24 ₈	4.0 ₃
392	665	0.285	0.352	0.809	0.23 ₅	4.2 ₅
401	674	0.286	0.352	0.813	0.22 ₉	4.3 ₆
423	696	0.286	0.350	0.817	0.22 ₄	4.4 ₆

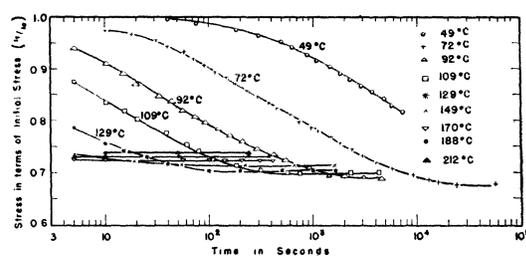


FIG. 4. Stress relaxation at constant strain at various temperatures in tantalum containing C and O.

curve for high purity tantalum. It was converted from Fig. 1.

The ratio $G(T)/G_U$ was determined from Fig. 2 and utilized the relationship

$$G(T)/G_U = (f_T/f_U)^2, \quad (4)$$

where f_T and $G(T)$ are, respectively, the observed frequency and rigidity at a given temperature T ; f_U and G_U are, respectively the unrelaxed frequency and rigidity at the same temperature obtained from the dotted line. This ratio is plotted as a function of temperature in Fig. 3, which shows that the relaxation is essentially complete at a temperature around 225°C. Accordingly, the value of $G(T)/G_U$ at 225°C is equal to G_R/G_U at that temperature. At still higher temperatures, the ratio G_R/G_U increases with a rise of temperature. As the relaxation has been complete at these temperatures, this increase tells us the temperature dependence of the ratio G_R/G_U . The values of G_R/G_U and ΔG , the relaxation strength in torsion, at various temperatures are summarized in Table I. It is seen that the relaxation strength decreases with an increase of temperature in agreement with the theoretical relationship given by Eq. (2).

TABLE II. Temperature dependence of relaxation strength from stress relaxation measurements.

(°C)	T (°K)	$S_R/S_0 = G_R/G_U$	ΔG	$1/\Delta G$
72	345	0.675	0.48 ₁	2.0 ₈
92	365	0.690	0.45 ₀	2.2 ₂
109	382	0.699	0.43 ₉	2.2 ₈
129	402	0.707	0.41 ₃	2.4 ₂
149	422	0.715	0.39 ₈	2.5 ₁
170	443	0.726	0.37 ₉	2.6 ₄
188	461	0.736	0.35 ₃	2.7 ₉
212	485	0.750	0.33 ₃	3.0 ₀

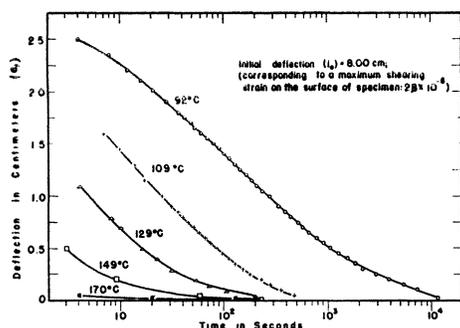


FIG. 5. Some typical examples of the recovery curves at various temperatures in tantalum containing C and O, initial deflection (D_0) = 8.00 cm.

III. RELAXATION STRENGTH FROM STRESS RELAXATION MEASUREMENTS

By the rigidity measurements described above, we can only determine the relaxation strength at temperatures at which the relaxation has been essentially completed in a half-cycle of the period of vibration. Thus, for the case described above in which the period of vibration is about one second, we could only determine the relaxation strength for temperatures above 225°C. To extend the measurement below this temperature, it is most appropriate to measure the stress relaxation at constant strain with the so-called torsional stress relaxometer developed in this laboratory.⁶ This stress relaxometer utilizes the principle of a moving coil galvanometer with the test specimen as the suspension fiber. The current passing through the galvanometer is a measure of the torque, S , acting on the wire; and the deflection, D , of the galvanometer is a measure of the shear strain. The specimen was twisted through a given amount, D_0 , by passing a suitable amount of current, i_0 , through the moving coil. In order to maintain the twist to the constant amount D_0 , the current was continu-

ously reduced and its value, i_t , recorded as a function of time. We have then

$$i_t/i_0 = S_t/S_0. \quad (5)$$

In the measurements at different temperatures, it is desirable to twist the specimen through the same angle. As the rigidity of the wire decreases with a rise of temperature, the initial current i_0 required to twist the specimen through D_0 also decreases with a rise of temperature. When the temperature of measurement is low, the relaxation is slow and the initial current, i_0 , can be easily determined by visual observation. At higher temperatures, however, it is difficult to locate the instantaneous deflection as creep starts immediately after the wire was twisted. Thus at those temperatures, we determine the corresponding value of i_0 from the static rigidity curve for high purity tantalum. This curve has an identical slope with the dynamic rigidity curve shown in Fig. 1.

The stress relaxation curves at various temperatures are shown in Fig. 4, in which the ratio i_t/i_0 , which is equal to S_t/S_0 , is plotted against the logarithm of time. The constant twist, D_0 , maintained at all temperatures was 8 cm on a scale three meters away from the specimen. This corresponds to a maximum shear strain of 2.8×10^{-5} on the surface of the specimen. These curves flattened out after a certain length of time depending on the temperature at which the measurement was taken. The flat portion of each curve gives the relaxed value of S_t/S_0 , which is S_R/S_0 . Table II summarizes the values of S_R/S_0 at different temperatures. The relaxation strength Δ_G can be calculated from S_R/S_0 as we have the relationship

$$S_R/S_0 = G_R/G_U. \quad (6)$$

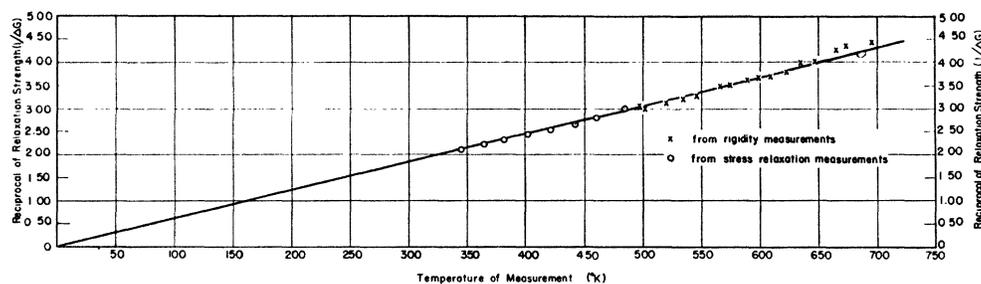


FIG. 6. Temperature dependence of the relaxation strength in tantalum containing C and O.

In these measurements, the temperature was controlled and measured with a Tag Celestray indicating temperature controller to a relative accuracy of 1°C. In measuring the current, we used a microammeter shunted with a suitable resistance. This set-up gives a relative accuracy of within one percent. We are, therefore, justified to include three significant figures in the calculated values of S_R/S_0 . On the other hand, we have only two significant figures for the relaxation strength, as subtraction was involved in its calculation.

After the stress relaxation had been completed at each temperature, the stress was suddenly relieved and the residual deflection observed as a function of time. Some typical examples of the recovery curves so obtained are given in Fig. 5, showing that the relaxation phenomena concerned are recoverable under the experimental conditions.

IV. TEMPERATURE DEPENDENCE OF RELAXATION STRENGTH AND CONCLUSIONS

To compare the experimentally observed temperature dependence of relaxation strength with the theoretical relation

$$\Delta_G = T_0/(T - \alpha T_0),$$

it is convenient to plot the reciprocal of relaxation strength against the absolute temperature. The values of $1/\Delta_G$ in torsion, which are included in the last column of Tables I and II, are plotted in Fig. 6 against the absolute temperature. These include the results from both rigidity and stress relaxation measurements. It is seen that the experimental points lie closely along a straight line passing through the origin. The fact that Fig. 6 gives a straight line supports the viewpoint that the relaxation phenomena observed in tantalum containing a small amount of C and O are caused by the stress-induced preferential distribution of solute atoms as described in the preceding paper.

Comparing the relationship

$$1/\Delta_G = T/T_0 - \alpha \quad (7)$$

with Fig. 6 shows that the interaction coefficient α must be negligibly small. This indicates that the interaction between solute atoms is negligibly small as far as the process of stress-induced preferential distribution is concerned and that the critical temperature for self-induced spontaneous ordering of the solute atoms is close to absolute zero according to Eq. (3).

The tantalum specimen used for the study of the relaxation processes described above contains 0.013 percent of carbon and about 0.06 percent of oxygen by weight. The relaxation observed is, according to the analysis made in the preceding article, principally due to oxygen. As T_0 in Eq. (2) increases linearly with the concentration of solute atoms,³ the question may arise that a higher concentration of oxygen might give rise to an observable critical temperature if the coefficient α is not exactly zero. Actually, the atomic concentration of O in the tantalum specimen is 0.68 percent which is already higher than the atomic concentration of C in iron (0.65 atomic percent corresponding to 0.14 percent by weight) necessary for the formation of tetragonal martensite above room temperature. On the other hand, the experimental accuracy involved in the determination of the straight line relationship shown in Fig. 6 leads us to believe that this line, if not passing exactly through the origin, can only give a very small value of α ; and therefore, according to Eq. (3), T_c must be close to absolute zero even if T_0 is very much increased by raising the concentration of the solute atoms.

We believe, thus, no spontaneous ordering can occur in the interstitial solid solutions of C and O in tantalum. If we generalize this conclusion to the case of the interstitial solid solution of carbon in iron, we can say that the formation of martensite is not likely to be due to the self-induced preferential distribution of carbon atoms in iron as was proposed by Zener.

In conclusion, the author wishes to express his appreciation to Dr. C. Zener for stimulating discussions.