Observations of the Oxidation of Pure and Sputtered Tantalum Via Dilatometry

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13. ABSTRACT ***(Maximum 200 Words)***
The oxidation of pure and sputtered tantalum foils was observed via dilatometry and weight gain measurements. Specimens were tested in both helium and laboratory air at isothermal temperatures ranging from 300 °C to 850 °C. Based on weight gain measurements of pure tantalum, it is apparent that oxygen saturation occurred. The activation energy for both the pure and sputtered tantalum was consistent with the activation energy for absorption rather than interstitial or grain boundary diffusion. This investigation is the precursor to subsequent dilatometry investigations on the effects on hydrogen in tantalum at elevated temperatures.

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ABSTRACT:

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KEYWORDS

Tantalum, sputtered tantalum, oxidation, refractory metals, coatings, elevated temperature testing, dilatometry, dilation, activation energy, diffusion, absorption, wear and erosion

BACKGROUND

These investigations were conducted in order to observe how oxygen interacts with tantalum (Ta). Subsequent tests will be conducted with a hydrogen (H)/helium (He) mixture to investigate the interaction of H with Ta.

Sputtered Ta is a primary candidate for combating the aggressive effects of wear and erosion in gun tubes fired with high energy propellants. It is advantageous to use Ta rather than the current chromium (Cr) plating because: 1) Ta has a much higher melting point than Cr (3000 °C vs. 1875 °C), 2) Ta has a modulus of elasticity less than gun steel (effective stress transfer to the gun steel substrate), 3) Ta can be deposited in using a "green" process (sputtering), 4) Ta has performed exceptionally well in previous firing tests using molten salt deposited Ta coatings [1-4].

In firing environments, the bore protective coating will be subject to high temperatures, thermal shock, wear, damage from firing byproducts (e.g. H, C), and exposure to air (i.e. O). Ta is known to be susceptible to H and O embrittlement [5, 6]; the former greatly depends on the integrity of the surface oxide present.

Sputtered Ta thin films have been used in the microelectronics industry for over 25 years; α Ta has been used for interconnectors and β Ta has been used for resistors [7]. This research on sputtered Ta thin films has been instructive in optimizing sputtering parameters and in understanding the mechanical behavior of such coatings. Cabral et al. [8] describe stress generation in sputtered β Ta during thermal cycling in a helium environment. High residual compressive stresses of several GPa were generated after only a few hours of thermal cycling at 400 °C. These high compressive stresses are attributed to O absorption and can lead to peeling and buckling of the coating.

EXPERIMENTAL PROCEDURE

Both 99.99% commercially pure Ta and sputtered α Ta (Battelle SPU-01) were used for the dilatometry tests. Table I shows the interstitial impurity levels and the ultimate tensile strength of both types of material tested [9]. The test specimens used for the dilatometry tests were 25.4 mm long (± 0.127 mm), 12.7 mm wide (± 2.54 mm), and 0.127 mm thick (± 0.0127 mm). The pure Ta specimen had a surface area of approximately 6.55 cm^2 and weighted approximately 680 mg.

Tests were conducted in both a He shielding gas and in laboratory air. Isothermal hold temperatures from 300 °C to 850 °C were investigated. Isothermal hold times were three hours. Some pure Ta specimens were weighted before and after each isothermal test in order to relate weight gain to amount of interstitial O present.

Labview™ data acquisition software was used to collect the linear voltage displacement transducer (LVDT) and thermocouple output from the dilatometer. Data was collected each minute during the test. This data was then imported into a spreadsheet for data analysis. Figures 1& 2 show the front panel and "virtual instrument" display used for these tests.

RESULTS/DISCUSSION

The LVDT data obtained was converted from millivolts (mV) to total strain by multiplying by $3e^{-5}$ (a calibration constant obtained using a platinum test standard). This strain includes both the strain due to the temperature increase (ε_T) and the strain due to oxidation (ε_{ox}). A thermal expansion coefficient (α) of $6.6e^{-6}$ °C^{-1} [10] was used in order to isolate the length change due to oxidation:

$$\varepsilon_{total,\,LVDT} = \varepsilon_T + \varepsilon_{ox} \quad (1)$$

and

$$\varepsilon_T = \alpha \Delta T \quad (2)$$

A typical plot of length change versus temperature can be seen in Figure 3. Figure 4 shows the percent oxidation strain on the pure Ta specimens tested in both He and laboratory air. Note that the strain is nearly identical for both environments over the given temperature range. This suggests that in both environments, O was saturated on the surface (high surface coverage).

Figure 5 shows the oxidation strain versus temperature for the Battelle sputtered Ta specimens. Note again, that similarity between both sets of data, suggesting saturation of O on the surface.

All tests conducted on both pure and sputtered Ta specimens in laboratory air failed prematurely by fracture in the dilatometer due to oxidation. This can be seen in Figures 6-8. In these tests the specimen was isothermally held for three hours then ramped up to the next isothermal temperature. This continued until the specimen broke. Figure 6 shows the results for pure Ta. Note that the strain dramatically increased above approximately 550 °C. The specimen broke at approximately 640 °C after reaching a maximum strain of 1.65%. Compare this to Figures 7 & 8, the temperature and strain data for the sputtered Ta in helium and lab air, respectively. The strain appears to dramatically increased above approximately 450 °C; moreover, the strain at failure in both He and lab air was approximately 0.6%, well below that of the pure Ta. The reason for the much lower strain at failure is probably due to the higher brittleness of the sputtered Ta from interstitial impurities.

Weight Gain

Table 2 shows the weight gain by pure Ta at different isothermal hold temperatures. The weight gain can be directly related to the amount of interstitial O present in the sample assuming that no surface oxide has formed and that the solubility limit has not been reached.

Solubility Limit for Oxygen in Tantalum

The solubility limit for O in Ta has been measured by a number of researchers. Garg et al. [11] have taken this data an have constructed a least-squares fit:

$$\log C_s = 1.25 - 1036/T \quad (3)$$

where C_s is the O solubility in atomic percent and T is the temperature [°K]. This equation is valid over the temperature range of 600 °C – 1550 °C. Figures 9 & 10 show the solubility limit of O in Ta in both atomic percent and wppm over the test temperatures of interest in this study. Note that one atomic percent O in Ta corresponds to 0.0892 weight percent O or 892 wppm of O.

Figure 11 shows the weight gain measurements plotted versus temperature. On the same plot is the extrapolated solubility limit for O in Ta [mg]. Upon examination of Figure 11, it is apparent that the solubility limit was exceeded above approximately 500 °C; therefore, the weight gain measurements did not correlate with the amount of interstitial O present above this temperature. After the solubility limit was exceeded, Ta_2O_5 probably precipitated at grain boundaries [11].

Oxidation Kinetics

It is assumed that the length change reflects oxygen absorption rather than surface oxidation and that the dilation is proportional to the interstitial oxygen concentration. Concentration gradient effects are not expected to be a factor since thin specimens were used and subjected to oxidation on both faces: The tests run in He and in lab air were plotted together since the measured strains were consistent until visible oxidation occurred. After analyzing the data, there was evidence of an activated (Arrhenius) process as can be seen from Figures 12 & 13. The general form an Arrhenius relationship is:

$$r = A\exp(-Q/RT) \quad (4)$$

where r relates to the strain from oxidation, A is a pre-exponential constant, Q is the activation energy, R is the universal gas constant, and T is the absolute temperature. The activation energies were obtained from these figures. The measured activation energy for the pure Ta is approximately –12.5 kcal/mol while the activation energy for the Battelle Ta is approximately –16.8 kcal/mol. The activation energy for the pure Ta is very similar to that measured in the literature for absorption of oxygen on Ta over the temperature range of interest (-11.3 kcal/mol) [12, 13] rather than interstitial or grain boundary diffusion. The transport and absorption of the oxygen onto the surface that are the rate limiting steps [13]. The activation energy measured for the Battelle sputtered Ta specimen may be higher because one side of the specimen contained a coating of niobium, Nb (interlayer coating). The activation energy for oxygen absorption on Nb over the temperature range of interest is approx. –18.2 kcal/mol [13].

The excellent fit to the Arrhenius function was unexpected. It is possible that at these pressure and temperature ranges the Ta surface is saturated with oxygen so that the results are not dependent on oxygen partial pressure. Studies of surface oxidation of tantalum have shown that a fifty-fold increase in oxygen partial pressure at 400 °C produces only a 20% change in reaction rate [14].

SUMMARY/CONCLUSIONS:

- The oxidation behavior of both pure and sputtered tantalum was observed via dilatometry tests conducted in both lab air and helium gas at isothermal hold temperatures between 300 °C and 850 °C.

- Weight gain measurements were conducted on some pure tantalum specimens in order to correlate with interstitial oxygen concentration.
- For the pure tantalum, the rate of oxidation appeared to accelerate above approximately 550 °C. For the sputtered tantalum, the rate of oxidation appeared to accelerate above approximately 450 °C. For the tests in lab air, the pure tantalum specimen strained 1.65% before it broke; the sputtered tantalum specimen only strain 0.6% before failure occurred. The increased strength (and brittleness) of the sputtered coating is the reason for the lower strain to failure.
- From the weight gain measurements and Ta-O phase diagram, it is apparent that oxygen saturation of the tantalum occurred above approximately 500 °C.
- The activation energy for the pure tantalum was measured to be approximately –12.5 kcal/mol, and agreed very well with the literature. The activation energy for the sputtered tantalum was measured to be approximately –16.8 kcal/mol. This value is believed to be higher because of the presence of a niobium coating on one side of the sputtered tantalum specimen. These values are consistent with surface absorption of oxygen rather than interstitial or grain boundary diffusion.

This work will be followed with dilatometry tests in hydrogen environments to observe the interactions of hydrogen with tantalum.

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Table 1. Interstitial Impurity Levels and Ultimate Tensile Strength (UTS) of Pure and Battelle Sputtered Tantalum Specimens.

	H	C	N	O	UTS (MPa)
Pure Ta	<1	<5	16	38	290
Batelle Sputtered Ta	45	147	510	821	724

Table 2. Weight Gain of Tantalum Test Specimens after Exposure to 3 Hour Isothermal Hold Temperatures.

Weight Gain (mg)	Weight Gain (μg/cm^2)	Temperature (°C)
0.2	30.5	449
0.4	61.0	496
0.9	137.0	520
2.7	412.2	544
3.05	465.6	556

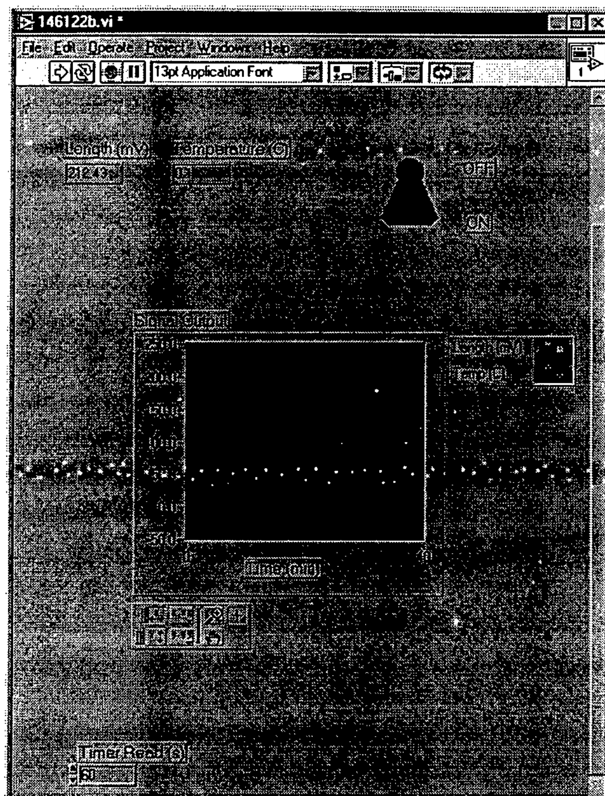

Figure 1. Labview™ Front Panel Display for Dilatometry Testing.

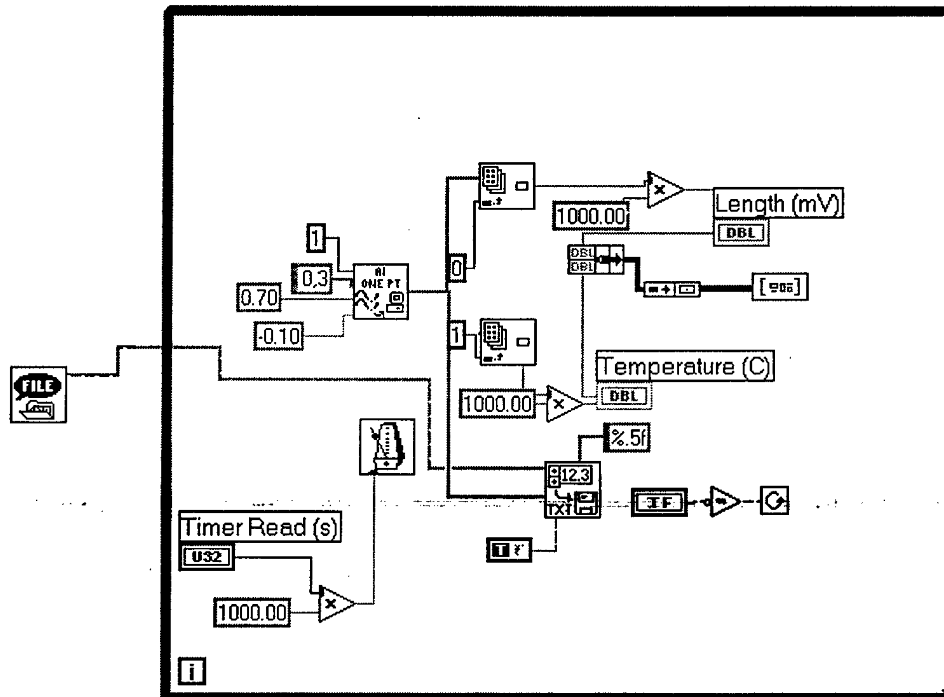

Figure 2. Labview™ Virtual Instrument Display For Dilatometry Testing.

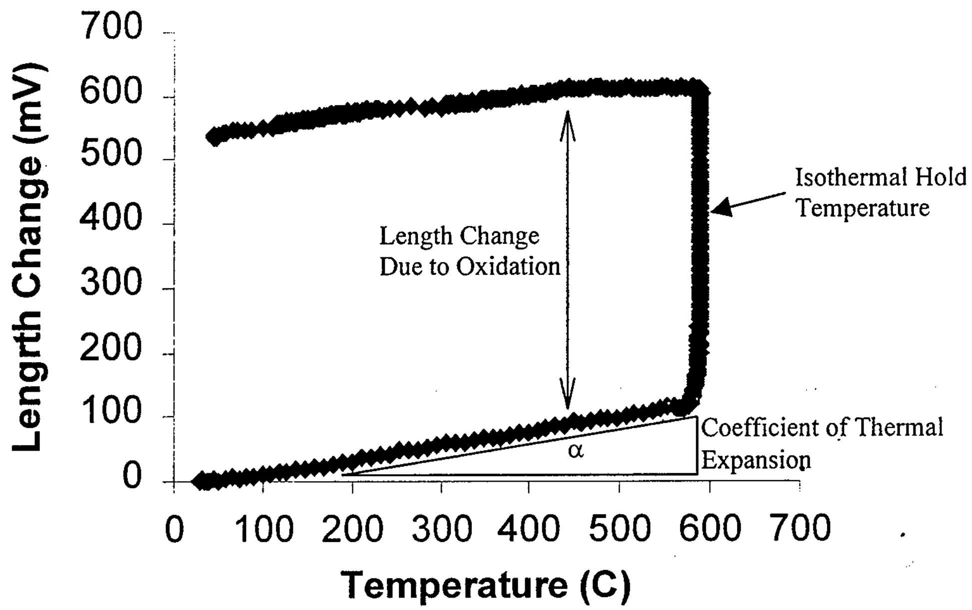

Figure 3. Typical Characteristics of a Dilatometer Plot.

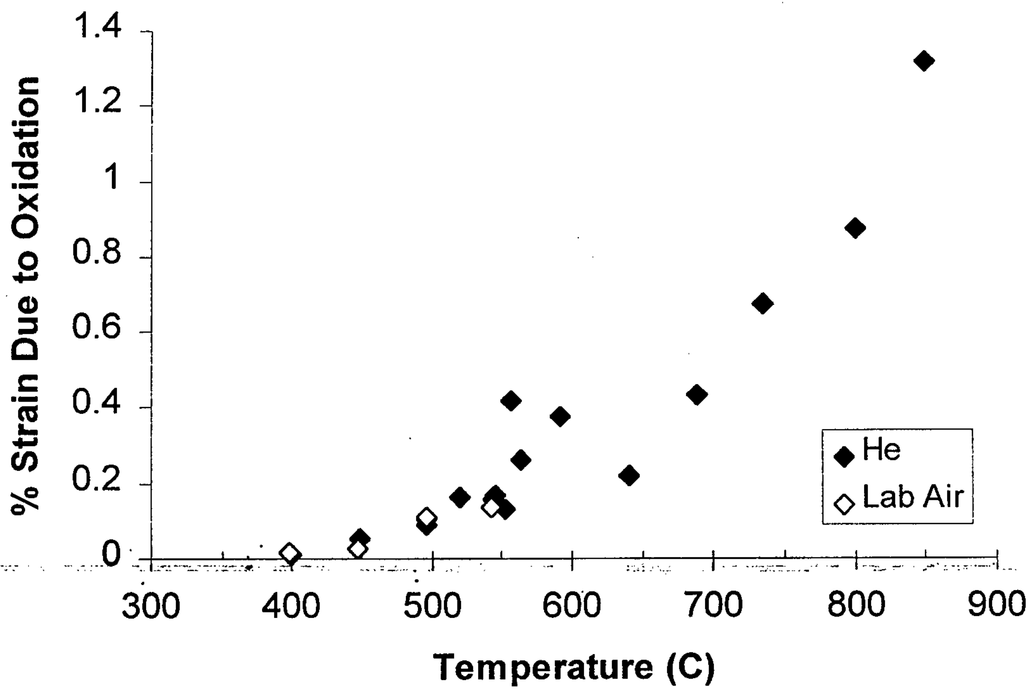

Figure 4. Oxidation Strain Versus Temperature for Pure Tantalum Foil.

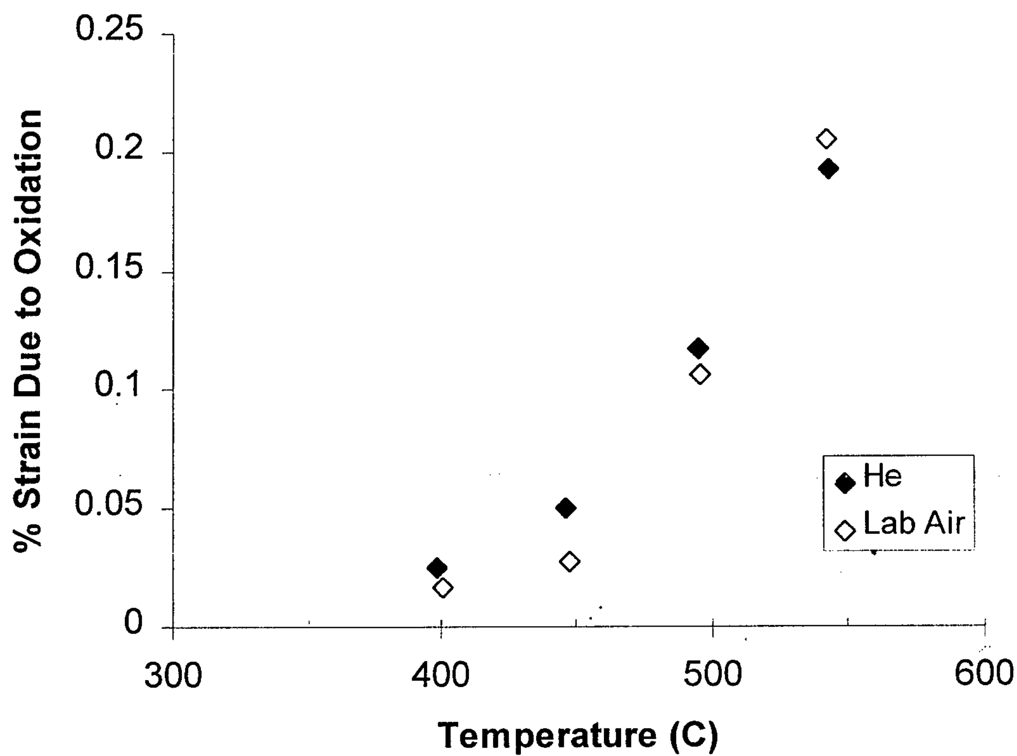

Figure 5. Oxidation Strain Versus Temperature for a Battelle Sputtered Ta Specimen.

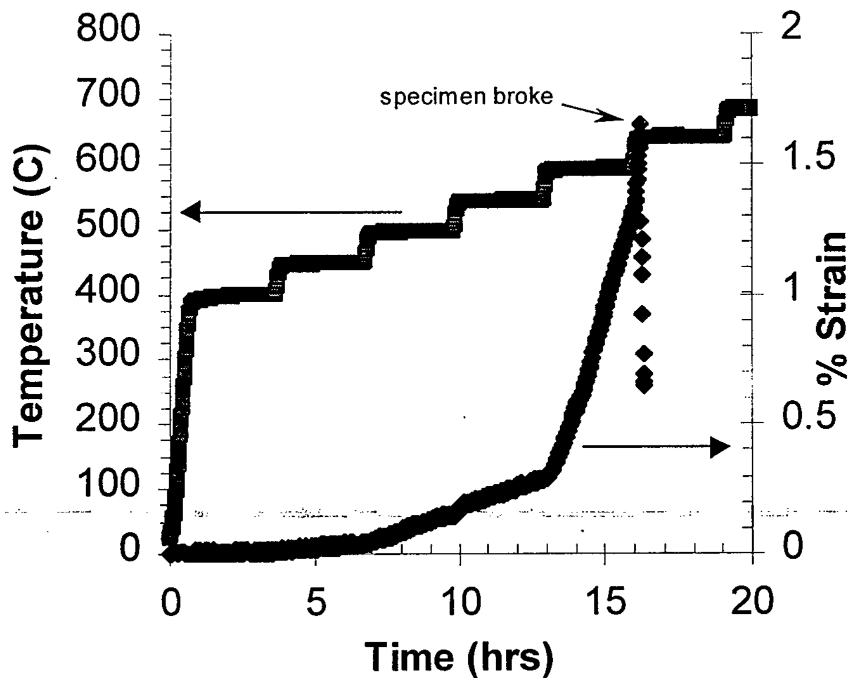

Figure 6. Temperature and % Oxidation Strain versus Time for a Pure Ta Specimen Tested in Laboratory Air.

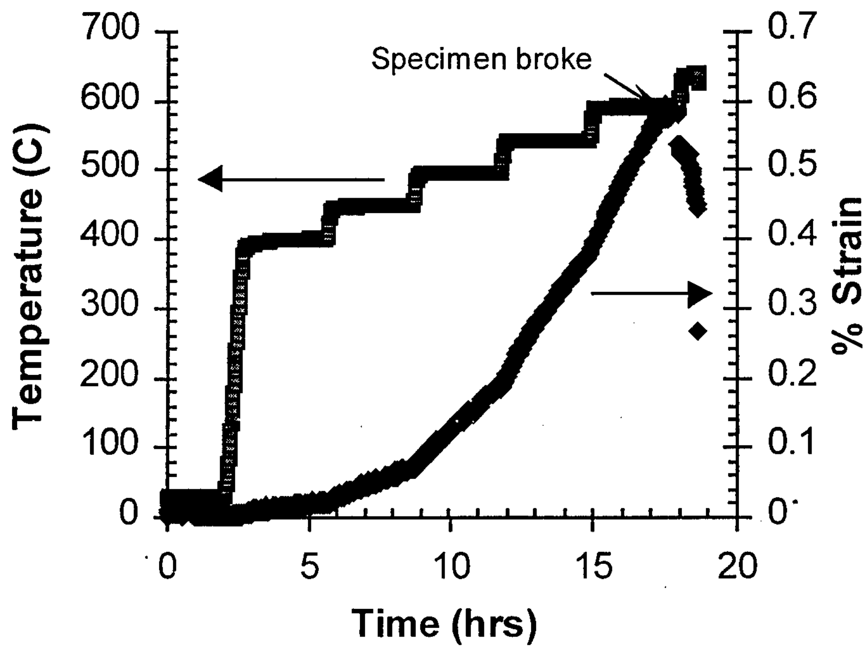

Figure 7. Temperature and Strain Versus Time for Battelle Sputtered Ta Tested in He.

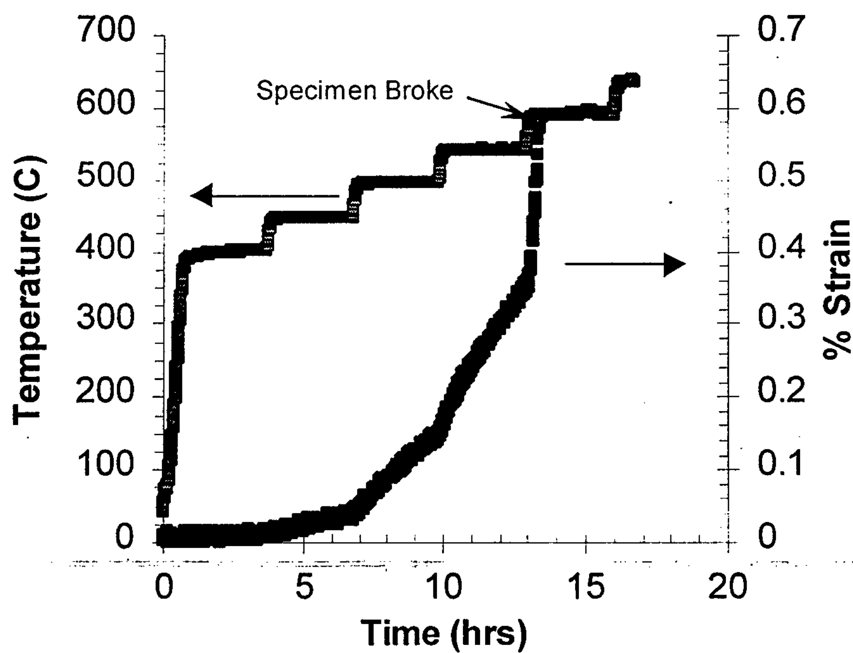

Figure 8. Temperature and Strain Versus Time for Battelle Sputtered Ta in Laboratory Air.

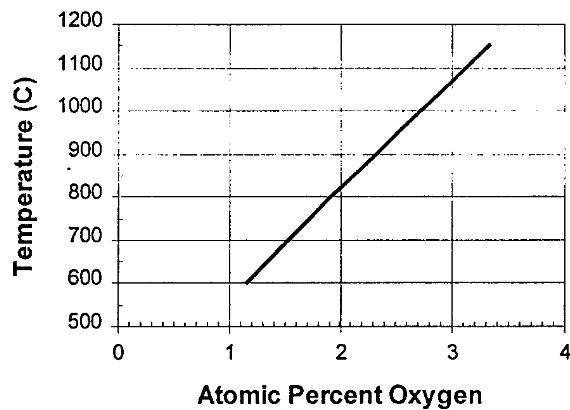

Figure 9. Solubility Limit for O in Ta (atomic %).

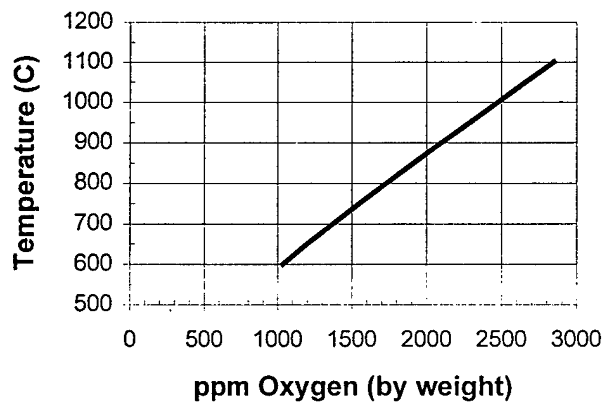

Figure 10. Solubility Limit for O in Ta (wppm)

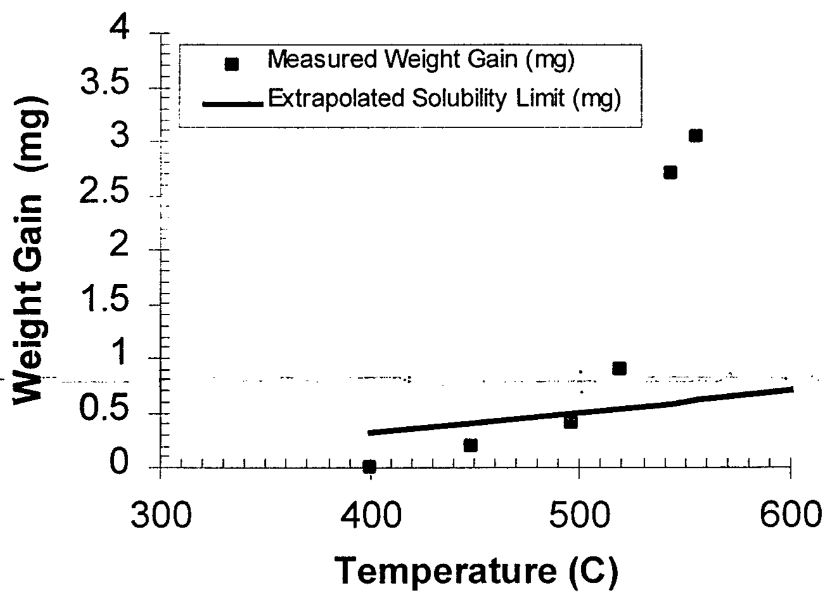

Figure 11. Measured Weight Gain and Extrapolated O Solubility Limit Versus Temperature.

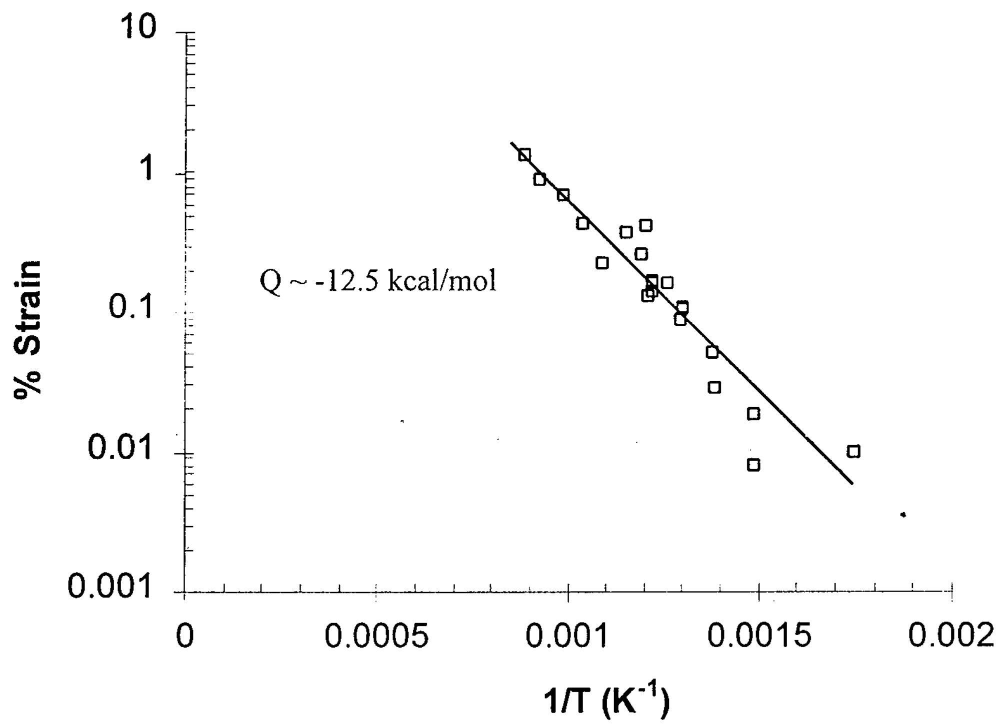

Figure 12. Activation Energy for Pure Tantalum.

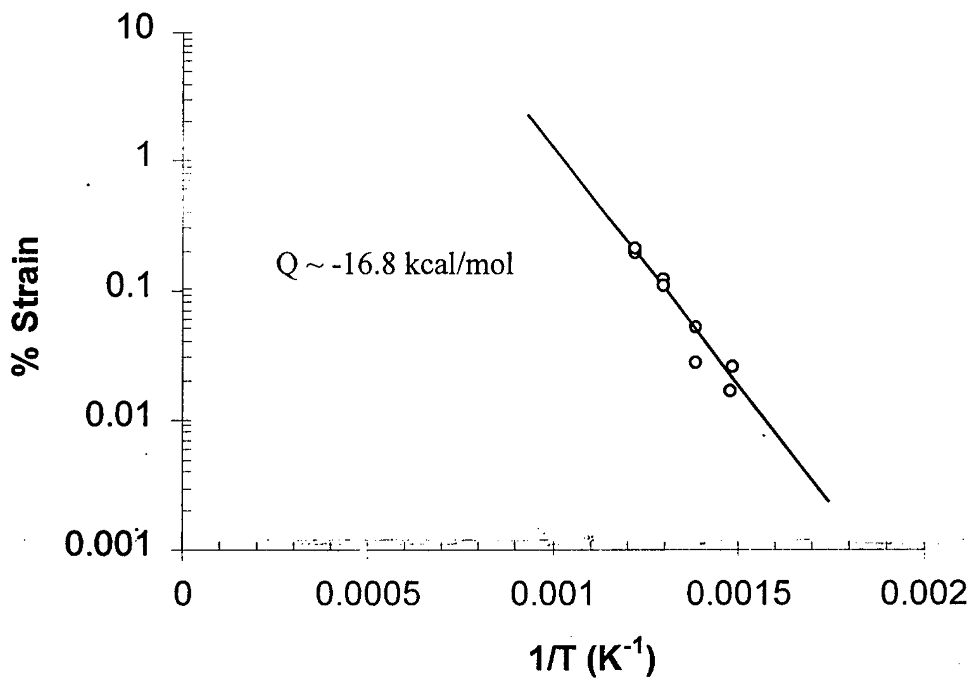

Figure 13. Activation Energy for Sputtered Ta.