

#### IV. PHYSICAL ELECTRONICS AND SURFACE PHYSICS\*

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#### A. QUASI-EQUILIBRIUM ANALYSIS OF THE REACTION OF ATOMIC AND MOLECULAR FLUORINE WITH TUNGSTEN

Rosner and Allendorf<sup>1</sup> have recently reported experimental data on the rate of attack of solid tungsten by gaseous atomic and molecular fluorine. Based on a comparison of these data with their interpretation of the quasi-equilibrium model of Batty and Stickney,<sup>2,3</sup> Rosner and Allendorf conclude that "the quasi-equilibrium model, combined with presently available thermochemical data, does not provide a self-consistent explanation of our observed Arrhenius behavior for the W(s)/F(g) reaction." The purpose of this report is to point out a limitation in their reasoning which, when corrected, invalidates their conclusion. Specifically, we shall show that the quasi-equilibrium model does provide a consistent, approximate explanation of Rosner and Allendorf's data for the reaction of F(g) and F<sub>2</sub>(g) with W(s).

In Appendix B of their paper, Rosner and Allendorf examine the predictions of the quasi-equilibrium model regarding the relative concentrations of the three most probable reaction products: WF<sub>6</sub>, WF, and F. They focus their attention on the temperature T ≈ 2000°K because their experimental data pass through a maximum at approximately that value. Using a straightforward analysis, they conclude that the quasi-equilibrium model fails to predict the observed maximum at T ≈ 2000°K. We agree with their analysis but we find their conclusion to be misleading because, although it is correct at 2000°K, a totally different conclusion is valid when the analysis is performed at a slightly lower temperature. Specifically, by employing Eqs. B-17 and B-18 of Rosner and Allendorf, we compute that the proportions of F and WF<sub>6</sub> will be comparable when T is between 1900°K and 2000°K. Furthermore, these equations predict that the dominant reaction product changes from WF<sub>6</sub> to F when T passes through the range 1900-2000°K, thereby producing the maximum observed in Rosner and Allendorf's data. (WF is negligible throughout the entire range of interest in this study.)

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To provide a more detailed comparison of the quasi-equilibrium predictions with the experimental data of Rosner and Allendorf, we have performed a complete analysis similar to that described elsewhere<sup>3</sup> for the  $O_2$ -W reaction. The results are shown in Fig. IV-1, which is a reproduction of Fig. 4 of Rosner and Allendorf<sup>1</sup> except for our

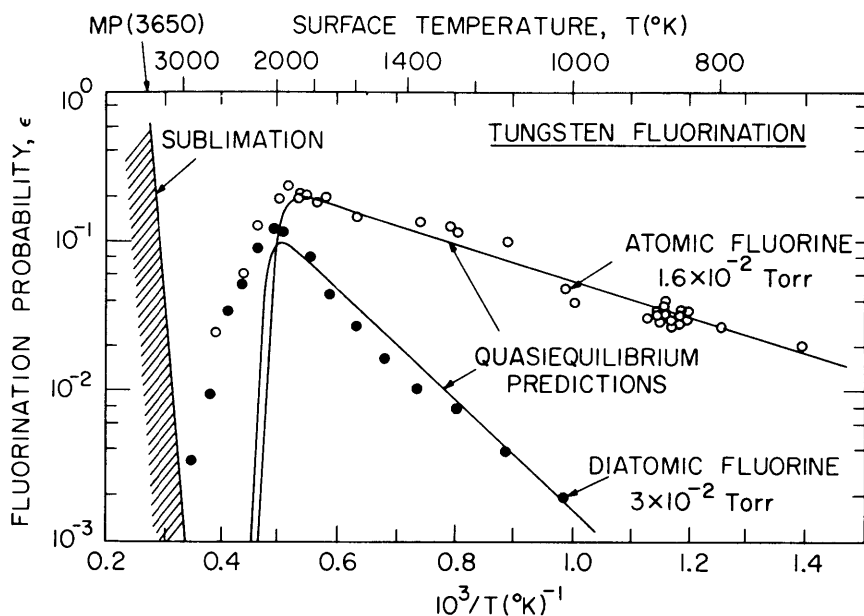


Fig. IV-1. Comparison of predictions of the quasi-equilibrium model with experimental data of Rosner and Allendorf,<sup>1</sup> where the fluorination probability  $\epsilon$ , is defined as the ratio of the rate of removal of W atoms from the specimen to the rate at which fluorine atoms or molecules impinge upon the specimen.

addition of the curves representing the quasi-equilibrium predictions. For simplicity, we have approximated their data for  $T < 1800^\circ\text{K}$  by straight lines, thereby causing the empirically determined equilibration probabilities<sup>2,3</sup> for F and  $F_2$  to be simple exponential functions of temperature.<sup>4</sup> Although the procedure by which the equilibration probabilities are determined<sup>2,3</sup> causes the predictions to agree closely with the experimental data in the region  $T < 1800^\circ\text{K}$ , the maxima appearing at  $\sim 2000^\circ\text{K}$  result primarily from the fact that the thermodynamic aspect of the quasi-equilibrium model causes the dominant reaction product to change from  $WF_6$  to F as T increases. The predictions provide a satisfactory semiquantitative explanation of the experimental data, but we are disappointed by the increasing discrepancy at the highest temperatures. We are unable to present a definite explanation of this discrepancy, but we suspect that it may

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be the result of (a) oxygen impurities,<sup>5</sup> (b) inaccuracies in determining the fluorine impingement rates,<sup>3</sup> and/or (c) slight errors in the thermochemical property data for  $WF_6$  at high temperatures.

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4. Although this simplifying assumption does not have a substantial effect on the general (qualitative) nature of the predictions, it does neglect the fact that Rosner and Allendorf's data exhibit definite structure,<sup>1</sup> such as the "bump" in the curve for atomic fluorine at  $T \approx 850^\circ K$ . We shall not attempt to consider the possible explanations of the structure.
5. In a recent mass-spectrometric investigation of the reaction of  $F_2$  with W, J. D. McKinley (National Bureau of Standards; unpublished results) has found that it is extremely difficult to reduce the partial pressure of  $O_2$  to a sufficiently low level that the  $F_2$ -W reaction is not influenced significantly by the formation of  $WOF_4$ .

#### B. CREEP-RUPTURE BEHAVIOR OF DOPED TUNGSTEN WIRE AT HIGH TEMPERATURE (1600-2925°C)

There is considerable evidence that the mechanical properties of tungsten are influenced markedly by the presence of extremely small quantities of impurities.<sup>1</sup> A practical example is the commercial product called doped tungsten, which is commonly used for the filaments in lamps and electron tubes because its resistance to sag at temperature is far greater than that of undoped (i. e., standard purity) tungsten.<sup>1</sup> The purpose of the work described in this report was to obtain creep-rupture data for doped tungsten wire at temperatures in the normal operating range of filaments. Such temperatures are above those for which data are available for doped tungsten.<sup>2</sup> A second aim was to attempt to relate these data to the results of recent investigations of the formation and growth of cavities in doped tungsten.<sup>3</sup>

Presented here are the results of short-duration creep tests of 5 mil ( $1.27 \times 10^{-2}$  cm) diameter doped tungsten wire (Sylvania NS 86). The tests were carried out in vacuum ( $p \lesssim 5 \times 10^{-7}$  Torr); loading was by deadweight; and extensions were recorded continuously using a displacement transducer (Hewlett Packard 7DCDT-050). The wires, 10 cm long, were heated resistively by a dc current. The wire temperature was determined from this current<sup>4</sup> and checked by optical pyrometer.

Experiments were conducted on as-received doped wire at a stress of  $8.28 \times 10^7 \text{ Nm}^{-2}$  ( $12,000 \text{ lb/in.}^{-2}$ ) for temperatures from  $1600^\circ C$  to  $2925^\circ C$  ( $0.51 T_m$  to  $0.88 T_m$ ) and

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also over a stress range of  $8.28 \times 10^7$  to  $1.38 \times 10^8 \text{ Nm}^{-2}$  (12,000 to 20,000 lb/in.<sup>-2</sup>) for a single temperature, 2500°C ( $0.76 T_m$ ). Results are presented in Figs. IV-2 through IV-4; for comparison, Figs. IV-2 and IV-3 include results we obtained for 5 mil ( $1.27 \times 10^{-2}$  cm) diameter undoped tungsten wire (Linde high purity).

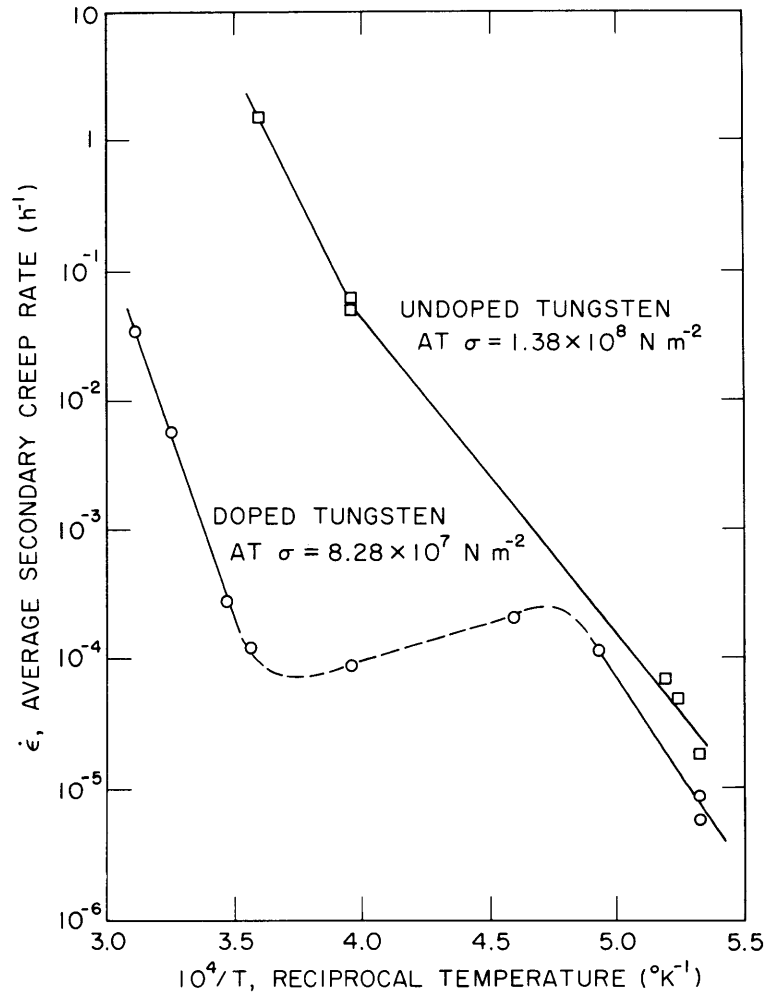


Fig. IV-2. Temperature dependence of the undoped tungsten wires [diameter = 5 mil ( $1.27 \times 10^{-2}$  cm)].

The creep rates for doped tungsten (Fig. IV-2) are extremely small, several orders of magnitude below those for undoped tungsten<sup>5</sup> at the same values of temperature and stress. (The data in Fig. IV-2 for doped and undoped wire should not be compared directly since they are for different stresses.) We encountered a number of difficulties in measuring the creep rate of doped tungsten. A truly constant rate for secondary creep, in the same sense of that for the pure metal, was not obtained for doped tungsten;

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therefore average values have been computed. At the highest values of temperature and stress, the time to rupture was so short that we suspect that our assessment of the average creep rate was less reliable than at lower temperature and stress; on the other hand, at the lowest values of temperature and stress, the creep rates are so small that extraneous effects influence the readings.

The results shown in Fig. IV-2 indicate that the creep behavior of doped tungsten wire falls into three regimes depending on temperature. At both the higher and lower values of temperature, creep appears to proceed with approximately the same value of activation energy ( $\sim 250 \text{ kcal mol}^{-1}$ ) while at intermediate temperatures there is a transition region that cannot be characterized by a single value of activation energy. Since this transition region coincides with that for recrystallization,<sup>1</sup> it appears that the transition is closely related to the changing size and character of the grain structure.<sup>6</sup>

The creep behavior of doped tungsten appears to be similar to that of precipitation-hardened alloys.<sup>7</sup> The extension-time curves we obtained in our tests are similar in shape and character to those reported by Ansell and Weertman<sup>8</sup> for dispersion-hardened aluminum alloy. Furthermore, our value of the activation energy for creep of doped tungsten is  $\sim 2 \frac{1}{2}$  times that for self-diffusion in tungsten, while Ansell and Weertman<sup>8</sup>

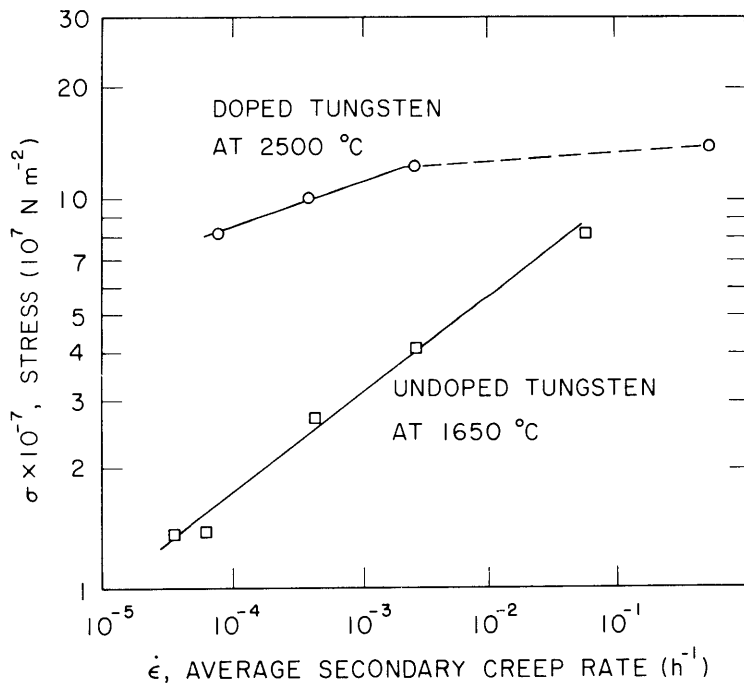


Fig. IV-3. Stress dependence of the creep rate of doped and undoped tungsten wires [diameter = 5 mil ( $1.27 \times 10^{-2}$  cm)].

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found that the activation energy for creep of dispersion-hardened aluminum alloy is  $\sim 5$  times that for self-diffusion, and Mukherjee and Martin<sup>9</sup> report that this ratio is  $\sim 1.6$  for a nitrided molybdenum alloy.

The data presented in Fig. IV-3 may be described satisfactorily by the expression

$$\dot{\epsilon} = c\sigma^n,$$

where  $\dot{\epsilon}$  is the secondary creep rate,  $c$  is a constant, and  $\sigma$  is the stress. These data indicate that  $n \approx 10$  for doped tungsten at  $2500^\circ\text{C}$ ; stresses below  $\sim 1.24 \times 10^8 \text{ Nm}^{-2}$ , and  $n \approx 4$  for undoped tungsten at  $1650^\circ\text{C}$ .

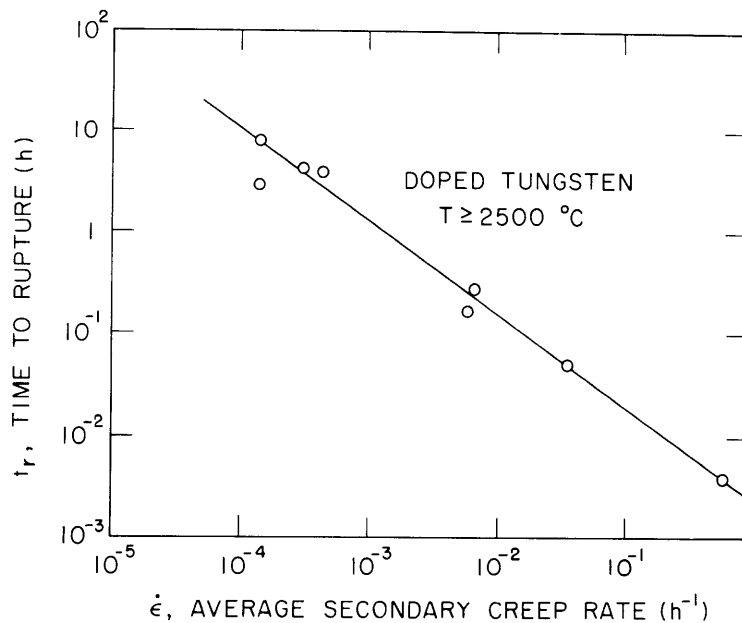


Fig. IV-4. Relationship between the time to rupture,  $t_r$ , and the creep rate,  $\dot{\epsilon}$ , for doped tungsten wire [diameter = 5 mil ( $1.27 \times 10^{-2}$  cm)].

The data in Fig. IV-4 may be represented quite accurately by the expression

$$t_r \dot{\epsilon} = C,$$

where  $t_r$  is the time to rupture and  $C$  is a constant. For  $t_r$  in h and  $\dot{\epsilon}$  in  $\text{h}^{-1}$  these data indicate that  $C \approx 3.6 \times 10^{-2} \text{ h}^{0.1}$ . Machlin<sup>10</sup> has shown that when failure occurs by void growth through vacancy condensation, the product of minimum creep rate and rupture time should be a constant. Undoped tungsten conforms to this fairly closely,<sup>11</sup> and our results indicate a similar pattern of behavior for doped tungsten. For undoped tungsten,<sup>11</sup> however, the value of the constant is some fifty times greater than that

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which we have obtained here. Based on the work of Holloman and Turnbull,<sup>12</sup> we suggest that this implies that the void (cavity) concentration and/or dislocation density at rupture is higher in doped tungsten than in undoped tungsten.

Recent work by Moon et al.<sup>3</sup> has shown that the dopants in commercial doped tungsten wire lead to the formation of cavities within the bulk. According to the model proposed by Coulomb,<sup>13</sup> cavities effectively hinder dislocation movement. Additionally, it is known that bubbles act like dispersed particles for hardening materials,<sup>14</sup> and both theory<sup>7</sup> and experiment<sup>15</sup> assign high values of activation energy to the movement of dislocations through embedded obstacles. It seems reasonable, therefore, to believe that the very low creep rates observed for doped tungsten wire result primarily from the effect of the cavities on inhibiting dislocation motion.

The creation of cavities in refractory metals is not restricted to dopant action but can be brought about also by neutron irradiation<sup>16</sup> and electron bombardment.<sup>17</sup> The effect on creep of the cavities created in these ways is similar to our observations for doped tungsten wire.<sup>18</sup>

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