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THE REACTION OF TUNGSTEN WITH SELENIUM VAPOUR

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SUMMARY

The kinetics of reaction of coupons of annealed tungsten with pure selenium vapour have been investigated by a thermogravimetric technique at temperatures between 400 and 550°C and at selenium pressures between 0 and 55 Torr. Hexagonal tungsten diselenide was the only reaction product detected under all experimental conditions. The actual selenization curves commenced gradually but accelerated with increasing reaction time. The apparent activation energy for tungsten selenization, as determined from the terminal parts of the reaction curves, was 26 ± 4 kcal/mole at 0.71 Torr selenium pressure; a similar value was obtained at 11.1 Torr. At 532°C, the terminal selenization rate increased rapidly with increasing selenium pressures in the range 0 to 10 Torr, but greater pressure increases produced relatively little additional acceleration of the selenization rate. These observations were interpreted as indicating rate control by a surface reaction, possibly the adsorption of selenium, occurring at either the W/Se or WSe_1/Se interfaces.

INTRODUCTION

Tungsten diselenide and tungsten disulphide have been suggested as general purpose solid lubricants[1]. Because the sulphide is rare in nature and the selenide is unknown in the natural state, these compounds must be synthesized for commercial use. Tungsten diselenide can be prepared either by the reaction of tungsten trioxide with hydrogen selenide gas at 900–1300°C[2] or, more simply, by direct combination of the elements[3,4]. For the latter preparatory technique, kinetic information would be desirable to select the conditions under which the diselenide forms rapidly and is the only reaction product. Also, kinetic information on the reaction of tungsten with selenium vapour could assist in the understanding of similar reactions with either sulphur vapour or oxygen gas, and could, consequently, assist in the development of corrosion-resistant tungsten alloys. During the processing of either high-purity selenium metal or selenium-bearing, semi-conducting compounds, high selenium vapour pressures can be generated. It would be desirable to have equipment constructed from metals or metal alloys that could withstand the attack by selenium vapour. The development of such alloys must be based on the knowledge of the rates and the rate-controlling processes involved during the selenization of many metals such as tungsten.

If the kinetics of reaction of a particular metal with oxygen, sulphur, or selenium are compared, a definite pattern emerges. The oxidation kinetics have generally been well studied and definite reaction mechanisms have been postulated; the sulphurization kinetics have received some study, but definite mechanisms have not yet emerged. The selenization kinetics have, by contrast, been studied in only a preliminary manner. This situation certainly exists for tungsten. The behaviour of tungsten in oxygen gas has been fairly well characterized[5]; initially, the low-temperature oxidation is controlled by oxygen-ion diffusion through the scale, followed by linear kinetics as the thicker scales become non-protective. The sulphurization behaviour of tungsten has been studied by several workers[6], but no detailed reaction mechanism has been given. No systematic studies have been reported in the literature for the selenization of tungsten.

In this study, the kinetics of reaction of annealed tungsten metal with pure selenium vapour were studied thermogravimetrically at temperatures between 400 and 550°C and at selenium pressures between 0 and 55 Torr. The results obtained have been discussed with reference to the corresponding oxide and sulphide systems.

EXPERIMENTAL

Materials

The tungsten sheet assayed 99.95 wt.% and conformed to the following specifications: molybdenum 200 ppm max., carbon, oxygen, silicon, nickel, iron, each 100 ppm. max. The sheet was cut into coupons about $2.3 \times 1.1 \times 0.04$ cm; the exact size of each specimen was measured by micrometer. A small hole was drilled at the top of each coupon for the attachment of a suspension hook. All cutting of the metal was done by electrical-discharge machining to prevent splitting of the tungsten. The machined surfaces of the coupons were polished with emery paper down to 4/0 grade; other surfaces were used in the as-rolled condition. The machined coupons were degreased consecutively in trichlorethylene, acetone and ethanol. All the coupons were annealed for one hour at 1600°C under a dynamic vacuum of 10^{-6} Torr. The coupons were prepared before annealing to minimize handling the annealed metal. The annealed tungsten had a hardness of 360 VHN (5 kg load) but was very brittle. Figure 1 shows the microstructure of the annealed tungsten. The structure is equiaxed, the grains are fairly-well developed and the rolling texture has been eliminated almost completely. The selenium assayed 99.99+% Se and, before each experiment, it was melted in the apparatus under a dynamic vacuum in an effort to remove adsorbed and dissolved gases.

Apparatus

The silica-spring thermogravimetric apparatus used in the experiments has been described previously[7]. It consisted of an all-glass apparatus, every part of which was heated above the condensation temperature of selenium. For the experiments with tungsten, a lightweight silica dish was attached to the spring

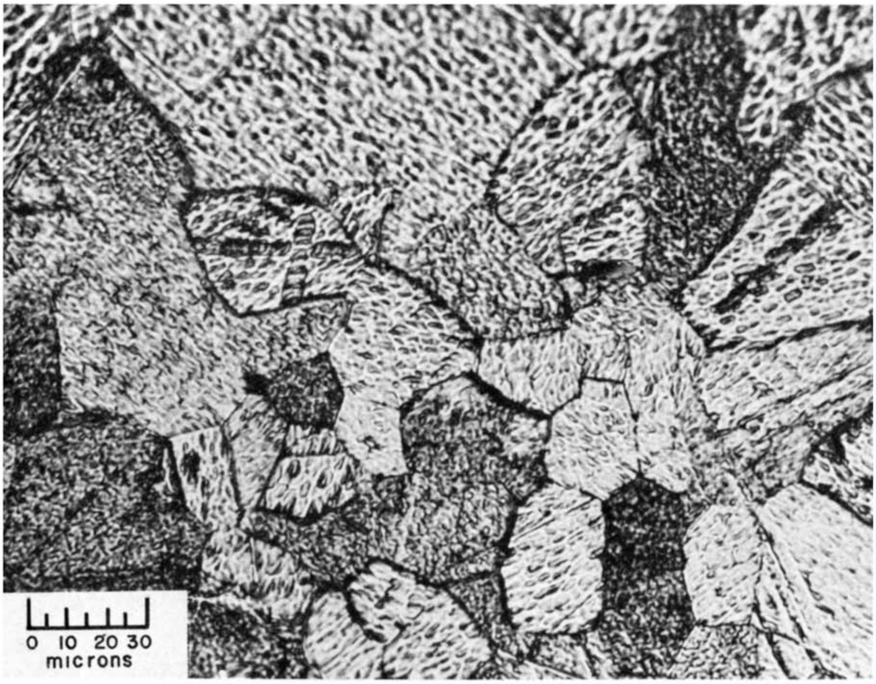


Fig. 1. Photomicrograph illustrating the structure of tungsten sheet annealed for 1 h at 1600°C (etched with potassium ferricyanide).

balance and allowed to hang under the metal coupon to catch spalled material. For small amounts of spalling, the dish caught all the material, but for heavy spalling some of the material overflowed the dish. A bulb, containing an excess of selenium, was maintained at the lowest temperature in the system. The temperature of this bulb determined the selenium pressure. The actual pressures were calculated from the data of Gattow and Schneider[8]. The selenium temperature, as determined by a calibrated chromel–alumel thermocouple placed against the bulb, was kept constant to within ±2°C for periods as long as two days. This temperature uncertainty corresponds to ±0.2 Torr in an applied pressure of 3.4 Torr. The vessel containing the tungsten coupon suspended from the silica-spring balance was heated in a hot-box, the temperature of which was controlled to ±2°C. The temperature of the tungsten strip was assumed to be the same as that of a thermocouple placed in a well adjacent to the metal.

Procedure

The silica-spring balance was calibrated at 25°C and the spring constant (approximately 0.5 g/cm extension) was adjusted to the reaction temperature by a previously described method[7]. The spring constants, as defined above, were about 4% larger at 500°C than the room-temperature values.

The experimental procedure was as follows: the various parts of the cell were assembled and then outgassed at a pressure of about 10 μm. The system was then sealed within the hot-box and the furnaces were heated to their respective reaction temperatures. When both temperatures were constant, the furnace was moved over the selenium cell which attained the operating temperature in about 5 min. Thus, for the purpose of calulation, zero time was taken as 5 min after placing the furnace over the selenium bulb. The progress of the reaction was followed by measuring the spring extension at various times by means of a cathetometer sighted through a window in the hot-box. At the end of the experiment, the furnaces were cooled differentially to condense the selenium vapour into the bulb. The reaction cell was then opened and the selenized tungsten coupon was removed for examination.

RESULTS AND DISCUSSION

The effect of temperature

Figures 2 and 3 show the type of selenization curve obtained at 0.71 Torr

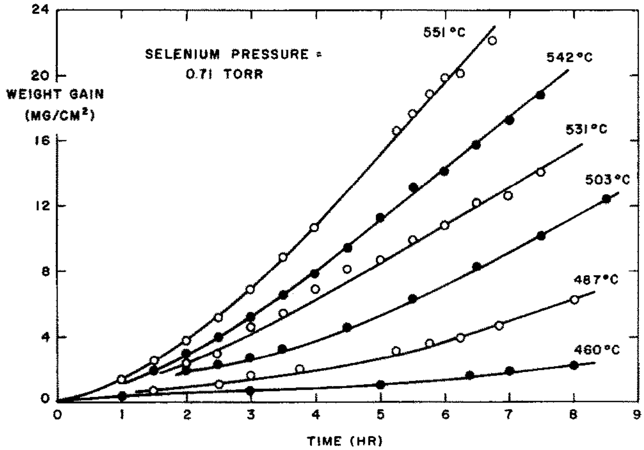


Fig. 2. Selenization curves of tungsten at temperatures above 460°C and at 0.71 Torr selenium pressure.

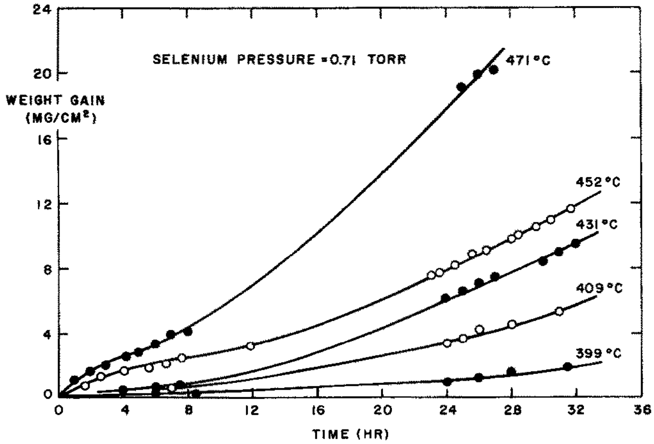


Fig. 3. Selenization curves of tungsten at temperatures below 471°C and at 0.71 Torr selenium pressure.

selenium pressure in the temperature interval 400–550°C. At all temperatures, the reaction curves begin slowly and then the slopes of these curves increase with increasing degree of reaction. There is some suggestion that the terminal slopes become linear, although this may simply represent a slower rate of increase than for the earlier parts of the reaction. For the curves obtained at 452 and 471°C (Fig. 3), there is some evidence of a reaction plateau after a few hours of corrosion, although still longer reaction times resulted in progressively more rapid rates. As was noted at the more elevated temperatures, all the reaction curves appear to become nearly linear after substantial reaction periods. The initial rates of the reaction curves for which the plateaux were observed (471 and 452°C) are not in good agreement with the results obtained at the other temperatures, and the reason for this is not known. As will be seen later, the initial reaction rates are not as reproducible as the terminal values and this might indicate that a varying and unknown mechanism is generally operative during the initial reaction stage. The shapes of the selenization curves are, in many ways, similar to those previously reported[6] for the sulphurization of tungsten. Tungsten and selenium vapour react quickly, even at fairly low temperatures and selenium pressures. At 500°C, for example, the limiting rate of attack is about 2 mg $Se/cm^2\ h^{-1}$; in this regard, the reaction of tungsten with selenium vapour is about two times by weight more severe than the reaction of sulphur vapour with this metal under similar conditions. On an atomic basis, the two reaction rates are essentially the same. Tungsten offers no substantial resistance to corrosion by either selenium or sulphur vapours.

One consequence of the accelerating kinetics is that the determination of an "activation energy" becomes a somewhat arbitrary proposition because there is no unique rate constant for a given set of experimental conditions. The rate constant of any particular reaction curve starts at a low value and increases progressively until, eventually, a nearly constant terminal value is reached. Two criteria have been used in this work to determine rate constants. For either method, the kinetic results were fitted to an equation of the form: $(\mathrm{wt./cm^2}) = a + bt + ct^2$ (where t = elapsed reaction time), and the slope at any time was evaluated as: slope $= b + 2ct$. In the first method, initial rate constants were determined from the slope at $t = 0$. Because the initial parts of some reaction curves were almost flat, this method often produced low and erratic reaction-rate constants. Also, when accelerating kinetics are encountered, the initial reaction rates do not always give a good indication of the total or long-term corrosion resistance of the metal in the active environment. Accordingly, a more practical rate constant was evaluated by taking the slopes of the terminal regions of each reaction curve. In practice, this was effected by calculating the slope at the time of the last experimental reading. This method suffers somewhat because the rates are being compared at varying degrees of reaction. As will be seen later, however, the scales formed on selenized tungsten are not protective and the use of the terminal values probably does not introduce a serious error into the calculations. The particular advantage of using the terminal rate contants is that these give a good indication of the long-time corrosion resistance of the metal.

Figure 4 shows an Arrhenius plot derived from both the initial and terminal rate constants; the experimental data were obtained at 0.71 Torr selenium pressure. The initial rate data lie below the values obtained from the terminal rates and are more erratic; in some instances there are substantial differences between the

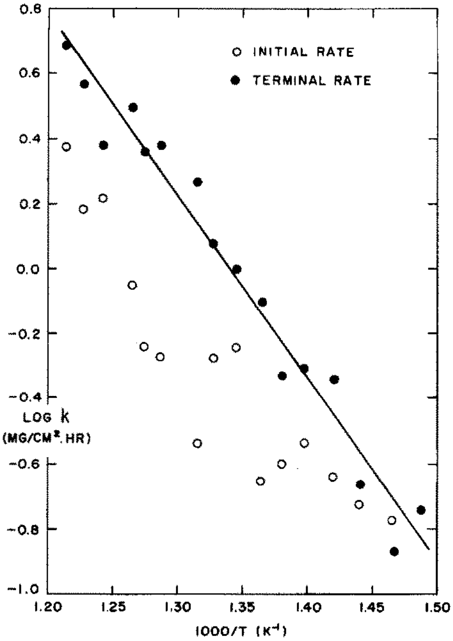


Fig. 4. Arrhenius plot for the selenization of tungsten between 399 and 551°C at 0.71 Torr selenium pressure, illustrating the difference between the initial and terminal selenization rates.

initial and terminal rates. At lower temperatures, the two rate constants are more nearly equal because the low-temperature corrosion curves approach a linear shape. The terminal rate constants, derived from the selenization curves, are more consistent and the data tend to lie smoothly on a straight line. The line drawn on Fig. 4 is the statistical fit to the terminal rate constants only; it is reasonably clear that the best fit to the initial rate data will yield a line of shallower but approximately similar slope. The equation of the indicated line for the terminal data is given by:

$$\log k(\mathrm{mg/cm^2 h^{-1}}) = 7.505 - 5603/T\,. \tag{1}$$

It is felt that this equation provides a reasonably accurate description of the long-time corrosion of tungsten by selenium vapour at 0.71 Torr. The activation energy calculated from this equation was:

$$\Delta H^* = 25.6 \pm 4.0(3\sigma)\ \text{kcal/mole}. \tag{2}$$

Although no published value appears to exist for the apparent activation energy for the reaction of tungsten and selenium vapour, the present value is of the same magnitude as the 28–35 kcal/mole apparent activation energy reported for the sulphurization of tungsten under a variety of reaction conditions[6].

Figure 5 shows the type of reaction curve obtained when tungsten was selenized at 11.1 Torr selenium pressure in the temperature range 473–543°C. The form of these curves is the same as that noted previously for tungsten selenization at 0.71 Torr in the same temperature interval (Fig. 2). The selenization rate is about five times faster at 11.1 Torr selenium pressure than at 0.71

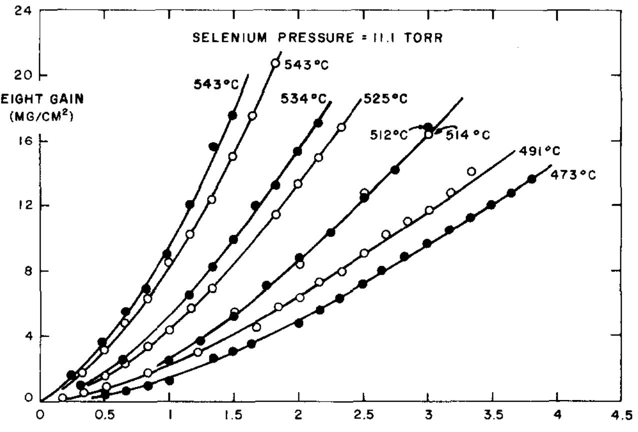


Fig. 5. Selenization curves of tungsten at 11.1 Torr selenium pressure.

Torr. An estimate of the reproducibility of the experimental results can be obtained by comparing the two selenization curves at 543°C and the two reaction curves at 512 and 514°C.

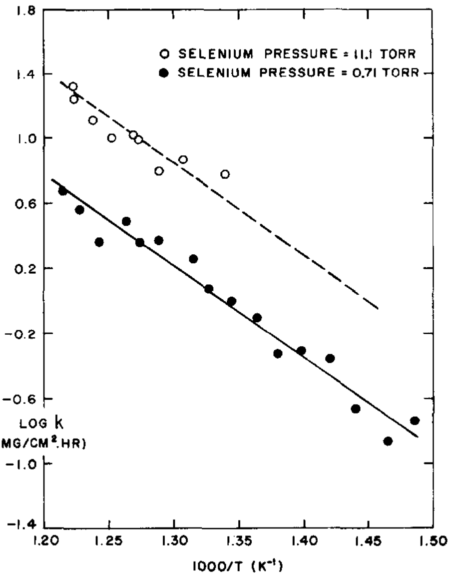
To obtain an estimate of the apparent activation energy for the corrosion of tungsten at this selenium pressure, the terminal rate constants of the individual selenization curves were deduced by the previously described procedure. These regression analysis data, together with the corresponding values obtained at 0.71 Torr selenium pressure, are displayed on the Arrhenius plot shown in Fig. 6. It is readily apparent that the selenization reaction is faster at the higher selenium pressure. Also, the temperature dependences at the two selenium pressures are nearly the same and correspond to an activation energy of about 26 kcal/mole. The dashed line drawn through the data at 11.1 Torr selenium pressure is not the least-squares fit to the actual data; it was simply drawn parallel to the corresponding line at 0.71 Torr. The actual best fit to the data at the higher pressure produced the equation:

$$\log k(\mathrm{mg/cm^2\,h^{-1}}) = 6.793 - 4539/T\,. \qquad (3)$$

This equation yielded an apparent activation energy of $21 \pm 9(3\sigma)$ kcal/mole. Although this value is not too different from the 26 kcal/mole activation energy obtained at the lower pressure, it is felt, nevertheless, that it is too low. The slightly low activation energy and the greater scatter of results arise because of the relatively narrow temperature range that could be investigated at the higher selenium pressure before condensation of elemental selenium occurred. It is for this reason that the two lines in Fig. 6 were drawn parallel.

The reaction product

Figure 7 shows a tungsten coupon that was exposed to 0.71 Torr selenium pressure for 27 h at 470.9°C. The selenized coupon and the attached silica dish are both evident in this photograph. This dish is full of loose powder that has spalled from the selenized coupon which is coated with a thin layer of the



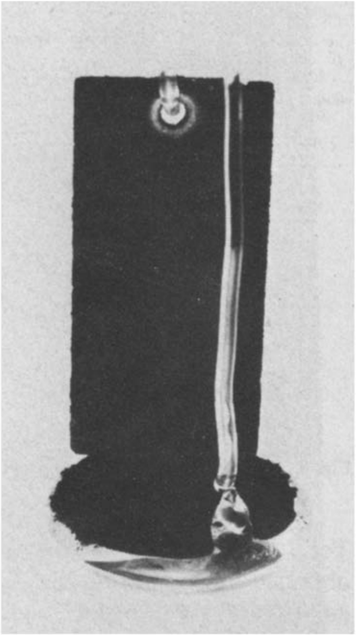


Fig. 6. Arrhenius plot using terminal rates for the selenization of tungsten at 0.71 and 11.1 Torr selenium pressures.

Fig. 7. Tungsten coupon selenized for 27 h at 470.9°C and 0.71 Torr selenium pressure, illustrating the pulverent type of reaction product. (× 2.3)

grey-black reaction product. Spalling occurred from all surfaces of the coupon. The residual material adhering to the sample was very pulverulent and could be removed simply by a light brushing. The product adjacent to the metal and the spalled material were both identified by X-ray diffraction analysis as being hexagonal WSe_2, similar in structure to WS_2 (tungstenite). Although the initial reaction product adhered to the metal coupon, spalling was observed early in the experiments. Thereafter, the reaction product tended to spall about as rapidly as it was formed. The attached silica dish caught virtually all the spalled material; the experiments were usually terminated before significant quantities of the loose powder overflowed the dish.

The appearance of the reaction product shown in Fig. 7 was typical of that obtained in the majority, but not in all, of the experiments. Figure 8 illustrates the type of product that was observed in a few instances. This particular specimen was reacted for 1 h at 532°C and 54.7 Torr selenium pressure. This type of reaction product appeared occasionally during the tests but did not appear to be associated with any particular condition of temperature and applied pressure. Close examination of the edges of this coupon reveals three distinct layers. The central, straight portion is the unreacted tungsten sheet, and the plates diverging to either side are reaction product. Although the scale appears quite solid, it is, in fact, very pulverulent and could be reduced to powder by light

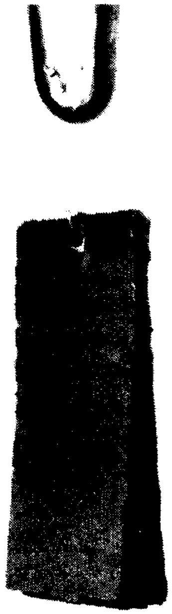


Fig. 8. Tungsten coupon selenized for 1 h at 532°C and 54.7 Torr selenium pressure, illustrating the compact type of reaction product. (× 2.2)

pressure or by rubbing with a needle. The structures shown in Figs. 7 and 8, or combinations of these forms, characterized all the reaction products observed in this study. The apparently compact scale was shown by X-ray diffraction analysis to consist only of hexagonal WSe_2 and, indeed, it appears that this is the only reaction product formed, even at the metal/scale interface. The pulverulent character of the scale precluded the microscopic and microprobe examination of polished cross-sections of this material. As a result, the exact homogeneity of the product is not known, although the X-ray patterns indicated stoichiometric WSe_2. It appears that tungsten and selenium vapour react directly according to the equation:

$$W_{\text{solid}} + Se_{2\ \text{vapour}} \rightarrow WSe_{2\ \text{solid, hexagonal}} \qquad (4)$$

This observation is consistent with reported data[3] on the thermal stability of tungsten selenides.

Effect of selenium pressure

Figure 9 shows the type of selenization curve obtained for different selenium pressures at 532°C. At this temperature, the vapour consists almost entirely of Se_2 molecules at all the pressures studied; also, the decomposition pressure of WSe_2 is negligible. The shapes of the reaction curves are similar to those reported earlier in this paper. Although the initial selenization rates are somewhat erratically dependent on the applied selenium pressure, the terminal rates increase systemetically with increasing pressure at a given temperature. The terminal rates increase rapidly

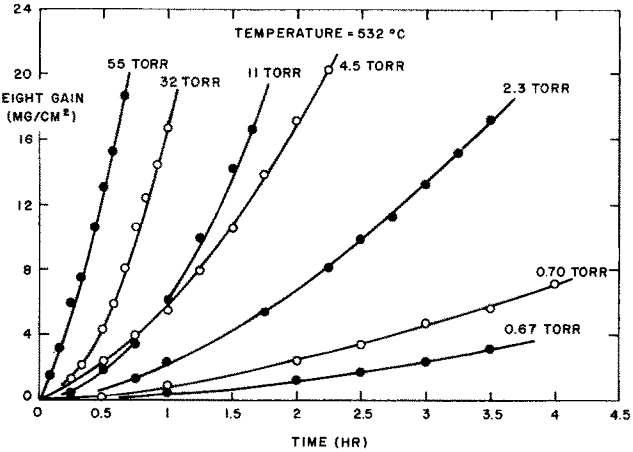


Fig. 9. Selenization curves of tungsten at various selenium pressures and 532°C.

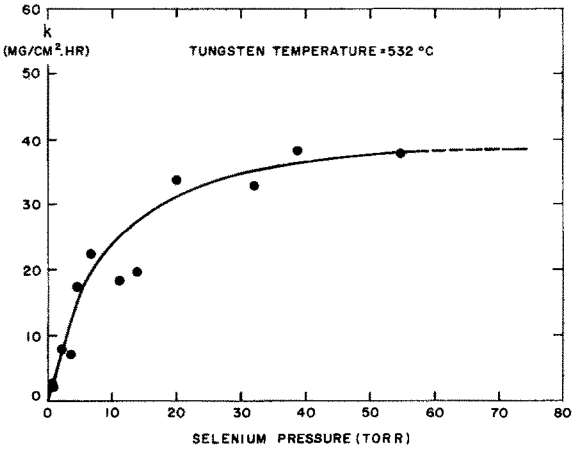


Fig. 10. The effect of selenium pressure on the rate of selenization of tungsten at 532°C.

for increasing selenium pressures below about 10 Torr; at higher pressures, the rates increase less rapidly. Even at the lowest pressures, tungsten is rapidly attacked by the selenium vapour. This behaviour is shown more clearly in Fig. 10 where the terminal rate constants are plotted against the applied selenium pressure. Initially, the rate increases rapidly with increasing selenium pressure, but thereafter the rate increase is less pronounced for additional pressure increases. In this regard, the selenization of tungsten closely follows the sulphurization of this metal. It should also be remembered that the terminal rate constants shown on this graph would approximate the bulk corrosion of this metal during long exposure in an active environment. Clearly, tungsten offers little corrosion resistance to selenium vapours present at any substantial pressure. Conversely, the reaction of selenium with tungsten is a convenient and rapid method of preparing WSe_2 for various uses. A commercial reaction could be accommodated in the presence of excess liquid selenium because selenium boils at 679°C; the excess selenium could subsequently be distilled away from the WSe_2 reaction product.

Possible reaction mechanisms

The similarity in the forms of the selenization curves obtained under various conditions suggests that the same reaction mechanism is operative over the whole temperature–pressure regime investigated in this study. The relatively high activation energy rules out rate control by selenium mass transfer. The rate of selenization increases with increasing degree of reaction and appears to approach a linear terminal rate. The increasing rates suggest an interfacially-controlled reaction occurring at a surface whose area increases with elapsed reaction time. This increasing surface could be the reaction product formed adjacent to the tungsten or the metal itself, if this became roughened during the experiments. A similar mechanism was postulated by Colson and Barret[9] to explain the increasing rates observed during the sulphurization of tungsten powders. Because non-linear kinetics were observed in this study, even at the lowest temperatures at which heat evolution was less than 0.1 cal/cm^2 h^{-1}, it was felt that auto-heating was not the principal cause of the accelerating kinetics. Separate experiments, in which a thermocouple was attached directly to the surface of the tungsten, have shown that the actual temperature rise of the metal during selenization was minor, even at the higher temperatures where the reaction was rapid. For example, auto-heating produced a temperature rise of less than 1°C when a metal coupon was reacted at 557°C and 16 Torr selenium pressure. This temperature difference was less than the normal thermal fluctuation of the apparatus. The WSe_2 reaction product is certainly not protective and, in fact, it spalls from the metal with great ease. This spalling is, in part, associated with the large molar volume of the selenide relative to that of the metal and, in part, with the relatively low temperatures which effectively preclude appreciable sintering or grain growth of the reaction product. The general form of the pressure dependence of the terminal reaction rates perhaps indicates that adsorption of selenium on the active surface plays an important role in the rate determining process. The relatively high activation energy would then indicate the strength of the bond between the surface atoms and the adsorbed selenium.

The reaction of tungsten with selenium vapour bears some similarity to the reaction with oxygen gas or, especially, with sulphur vapour. Table I lists some of the properties that have been determined for the corrosion of annealed tungsten by these vapours at temperatures near 500°C. Unannealed tungsten splits into lamellae[5,6] during the corrosion reaction and its attack, consequently, will not be discussed. Although the reaction of tungsten with either sulphur or selenium produces only the dichalcogenide, this metal reacts with oxygen to form tungsten trioxide. At higher corrosion temperatures, other oxides have been reported. Except for the parabolic sulphurization kinetics reported by Gerlach and Hamel[10], only linear or time-increasing kinetics have been observed for either the sulphurization or selenization reactions. By contrast, paralinear kinetics have been widely observed for tungsten oxidation. As the corroding agent for tungsten is varied from O_2 to S_2 to Se_2, the activation energy appears to fall steadily and the corrosion rate to increase greatly. The corrosion rate increases by about four orders of magnitude on passing from oxygen attack to attack by either sulphur or selenium vapour. This table illustrates that, although tungsten and oxygen are reasonably compatible at 500°C, this metal is quickly consumed by either sulphur or selenium vapour under these conditions.

TABLE I

COMPARISON OF THE KINETICS OF REACTION OF TUNGSTEN WITH OXYGEN, SULPHUR, AND SELENIUM NEAR 500°C

Reaction	*Kinetics*	*Activation energy (kcal/mole)*	*Pressure dependence*	*Approximate corrosion rate at 500°C*	*Refs.*
$W + \frac{3}{2}O_2 \rightarrow WO_3$	Paralinear, initially parabolic, indicative of oxygen-ion diffusion.	45–48	Almost independent of oxygen pressure at 500°C.	$< 10^{-3}$ mg/cm^2 h^{-1} at 76 Torr O_2 pressure.	5,11
$W + S_2 \rightarrow WS_2$	Linear Rates increasing with increasing reaction times Parabolic	28–35	Rate directly proportional to P_{S_2} for temperatures above a minimum value.	5 mg/cm^2 h^{-1} at 9.5 Torr sulphur pressure.	6,10
$W + Se_2 \rightarrow WSe_2$	Rates increasing with increasing reaction time, becoming linear.	26	Rate increases directly with the selenium pressure at lower pressures. At higher pressures, complex behaviour.	8 mg/cm^2 h^{-1} at 11.1 Torr selenium pressure.	This work

CONCLUSIONS

Annealed tungsten metal and selenium vapour react in a complex manner in the temperature interval 400–550°C and at selenium pressures up to 55 Torr. The selenization rates at a given temperature and pressure increase with increasing reaction time and appear to approach a nearly-constant terminal value. The apparent activation energy for the terminal or longer-term selenization of tungsten is about 26 kcal/mole; this value appears to be essentially constant over the pressure range investigated. The selenization rate increases rapidly with increasing selenium pressures at low applied pressures, but is relatively insensitive to further pressure increases. The reaction product is pulverulent and tends to spall from the metal during the experiments. The results suggest that the rate is controlled by some reaction, possibly the adsorption of selenium, on the surface of either the tungsten metal or the tungsten diselenide scale which was the only reaction product detected. The rate increases with elapsed reaction time, possibly because the surface area also increases, because of either the formation of loose WSe_2 particles or of the roughening of the tungsten metal substrate. Under the conditions investigated in this study, tungsten reacts quickly with selenium. This property renders tungsten unsuitable for containing selenium vapours but, by contrast, permits the rapid production of tungsten diselenide by direct combination of the elements at relatively low temperatures.

ACKNOWLEDGEMENTS

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X-ray diffraction analyses were done by P. Belanger and photographs were obtained by P. Carriere. All are members of the Extraction Metallurgy Division of the Mines Branch.

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