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Oxidation of Molybdenum Disilicide

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The oxidation kinetics of molybdenum disilicide over the temperature interval, 1328 to 1765° K, has been studied using a thermal conductivity method. The rates of oxidation were found to follow a parabolic relationship once a protective coating was formed. From the temperature dependence of the parabolic rate constants, an activation energy of 20 kcal/mole was obtained.

1. Introduction

Since the earlier work of Kieffer and Cerwenda [1], it has been recognised that the oxidation resistance of $MoSi_2$ is due to the formation of a protective silica layer. More recently the oxidation products of $MoSi_2$ have been discussed in great detail by Berkowitz-Mattuck and Dils [2] and Wirkus and Wilder [3] in terms of the Mo–Si phase relationships and the available thermodynamic data. However, the kinetics of oxidation after a protective coating is formed have not been well established. In the present study, rates of oxidising $MoSi_2$ in a helium-oxygen gas mixture were measured over the temperature interval, 1328 to 1765° K. The apparatus used to obtain the rate data is basically similar to that of Berkowitz-Mattuck [4] utilising a thermal conductivity method. This method continuously measures the amount of oxygen consumed, by comparing the oxygen concentration in a carrier gas stream before entering and after leaving the heated zone. The sample to be oxidised was brought to any desired temperature by means of high-frequency induction heating using a current concentrator. A quartz tube placed in between the current concentrator and the specimen was used by Berkowitz-Mattuck to achieve a closed system but in the present study a new furnace design was conceived [5] which eliminated the use of a quartz or any other kind of oxide tube. This is desirable since any metallic deposit on the inside surface of the ceramic tube, owing to sublimation of the sample, will cause heating by susception and may pose an upper temperature capability of the system.

2. Experimental

Single-phase molybdenum disilicide cylindrical specimens 1.2 cm in diameter by 1.5 cm were prepared by cold-pressing fine powders purchased from Stark Chemical Company, followed by sintering at 1500° C for 4 h under a helium atmosphere. The exact dimensions of each sample were measured using a calibrated micrometer in order to obtain oxidation rates for each experiment. A black-body cavity 0.15 cm diameter by 0.65 cm deep was drilled in the top of each sample, while three holes 0.08 cm diameter by 0.25 cm deep were drilled at the bottom for the purpose of support, using three alumina rods. The temperature of the specimen during each experiment was maintained constant within ± 5° C using a Leeds and Northrup feed-back control system, while the absolute temperature was measured by a calibrated optical pyrometer [5]. The total flow rate of the gas stream was kept close to 100 ml/min and the individual flow rates of oxygen and helium were determined using capillary-type flow-meters.

3. Experimental Results and Discussion

The experimental result of a typical run is presented in fig. 1 in terms of $\Delta m/A_0$ as a function of time. The term Δm is the mass of oxygen consumed and A_0 is the initial surface area of the sample. This figure shows that the rate of change of $\Delta m/A_0$ decreases with time, demonstrating that the rate of $MoSi_2$ oxidation is not linear. On the other hand, when $(\Delta m/A_0)^2$ is plotted as a function of time, as shown in fig. 2, a linear relationship is obtained. However, this

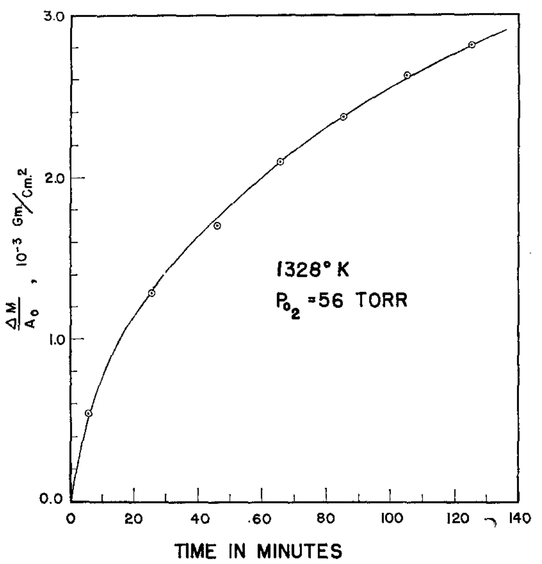

Figure 1 A plot of the mass of oxygen consumed in terms of the initial sample surface area at 1328° K as a function of time.

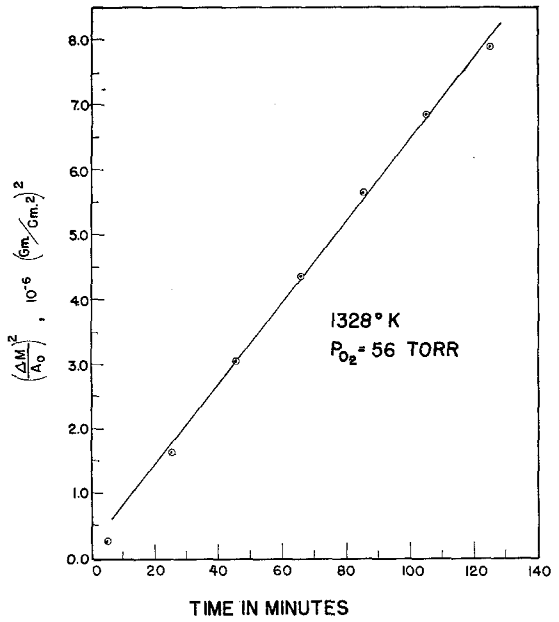

Figure 2 A parabolic plot for the oxidation of molybdenum disicilicide.

line does not pass through the origin of the graph because the initial rate deviates from the parabolic relationship.The analysis of the initial rate is difficult, partially owing to the complex nature of chemical reactions taking place between O_2 and $MoSi_2$, leading to the simultaneous formation of volatile MoO_3, SiO_2 and Mo_5Si_3. A second affecting factor is inherent in the experimental method. Before the start of each experiment, a helium-oxygen mixture with a known oxygen partial pressure was allowed to flow through the system until the thermal conductivity bridge was in balance. Then the sample was suddenly brought up to temperature by turning on the induction power supply. The time required to stabilise the sample temperature varied from 1 to 3 min. During this initial period, the amount of oxygen consumed could not yield any quantitative kinetic data.

TABLE I Summary of experimental results.

T °K	Time interval min	P_{O_2} torr	k_p $\frac{\text{gm}^2}{\text{cm}^4\text{-min}}$
1432	0-55	12	7.82×10^{-8}
1334	0-130	56	1.03×10^{-7}
1328	130-210	56	6.06×10^{-8}
1767	0-70	33	5.28×10^{-7}
	70-105	14	
1645	105-160	14	2.88×10^{-7}
1715	0-120	55	3.55×10^{-7}

The experimental results expressed in terms of the parabolic rate constants k_p for all the runs are summarised in table I as functions of both temperature and oxygen partial pressures. At 1767° K, the partial pressures of oxygen were varied from 33 torr during the first 70 min to 14 torr during the next 35 min. The effect of varying oxygen partial pressure on the rates of oxidation was not observed within the precision of the experimental method. Based on the values of k_p given in table I, an Arrhenius plot was made as shown in fig. 3. The straight line obtained by means of a least-square fit of the data yields an activation energy of 20 kcal/mole. From a study of the diffusion of gaseous oxygen through silica over the temperature interval, 1373 to 1773° K, Norton [6] obtained a value of 22 kcal/mole as the activation energy. This indicates that the final rate of $MoSi_2$ oxidation is probably controlled by the diffusion of oxygen through the silica layer. In the data of Berkowitz-Mattuck and Dils [2], the final rates were so low that it was not possible to determine whether the rates were linear or parabolic. However, the authors stated

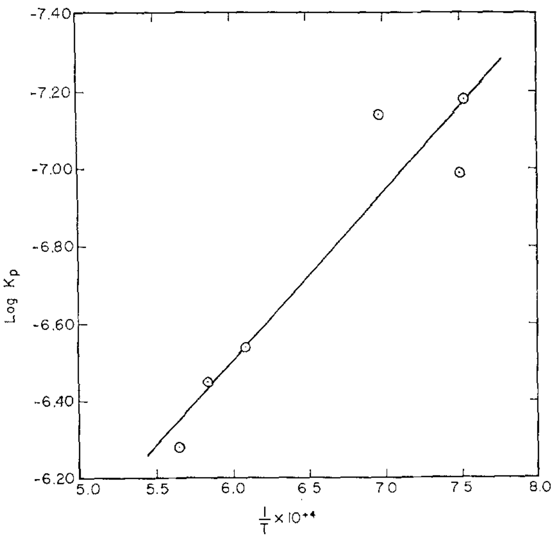

Figure 3 An Arrhenius plot for the oxidation of molybdenum disilicide.

that their data did suggest a value less than 20 kcal/mole as the activation energy.

More recently, Wirkus and Wilder [3] studied the air oxidation of pulverised $MoSi_2$ gravimetrically, over the temperature interval, 1437 to 1773° K, for periods of about 6 h. All the samples were pre-oxidised in air for 30 min to assure a layer of protective coating. Within the scatter of their results, they found the parabolic relationship fitted the data best. From the temperature dependence of the parabolic rate constants, a value of 81.3 kcal/mole was determined as the activation energy. This value is much higher than the 20 kcal/mole obtained in the present work. The reason for the large discrepancy is not entirely clear. One possible explanation may be that in the experiments of Wirkus and Wilder [3], Si_3N_4 is formed in addition to silica during the initial stage of pre-oxidation.

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