Hot corrosion of α-SiC ceramics by V_2O_5 melt

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The corrosion behaviour of α-SiC in V_2O_5 melt has been investigated at elevated temperatures. The corrosion products on the surface of the specimen are removed using HF. The morphologies are also examined. From the observations of bubble formation in the scale and the temperature dependence of the corrosion rate, a kinetic mechanism is proposed. Based on the consistency of the plotted data with the proposed equation and high values of surface reaction rate constant, a diffusion controlling process has been developed.

1. Introduction

Because of its low thermal expansion and high thermal conductivity silicon carbide (SiC) is an attractive material for gas turbine engines. Unfortunately, this material has been found disadvantageous because of its corrosive behaviour at elevated temperatures.

Many investigations have shown that SiC is corroded by molten salt [1–3]. Although the stable SiO_2 layer is formed to protect the SiC from further dissolution, the basic melt will accelerate the corrosion rate by dissolving the oxidized layer. McKee and Chatterji [4] concluded that the SiC was passive in neutral or acid salt melts under the normal conditions. However, the present experiments show that V_2O_5, as a low melting point (658° C) acid salt, is still able to corrode SiC. It is known that vanadium-rich oil is found in certain wells in South America. The ash of such oils may reach 65% V_2O_5 or higher, and the damage caused by the ash in engines is severe [5].

The purpose of this paper is to study the kinetic mechanism of the elevated temperature corrosion of sintered α-SiC in molten V_2O_5 acid salt.

2. Experiments

2.1. Materials

The material used was 4 g dense α-SiC ceramic with added 2 wt% AIN. The hot-pressed billets from Hitachi [6] were cut into 1 mm thick blocks 25 mm × 25 mm and have a freshly polished surface for each experiment. Reagent grade V_2O_5 (40 g) was used as the melting medium in the test. The cleaning solution was prepared by diluting 10% HF concentrate in deionized water.

2.2. Procedures

Silicon carbide and vanadium oxide were heated simultaneously at 700, 800, 900 and 1000° C respectively. Corrosion experiments were performed in a graphite crucible in which SiC specimen had been completely immersed in the V_2O_5 melt at the desired temperatures for up to 10 h. Oxide scales from each run of the corrosion tests were removed using a cleaning solution [3, 7]. Corrosion behaviour was studied by monitoring the specimen weight, which was measured in terms of weight change per unit area $\Delta W/A$ (cm^2). Meanwhile, an atomic absorption equipment (AA) was used to determine qualitatively the content of silicon, and scanning electron microscopy (SEM) was applied to examine the morphologies. Figure 1 is a flowsheet of the tests for each data point.

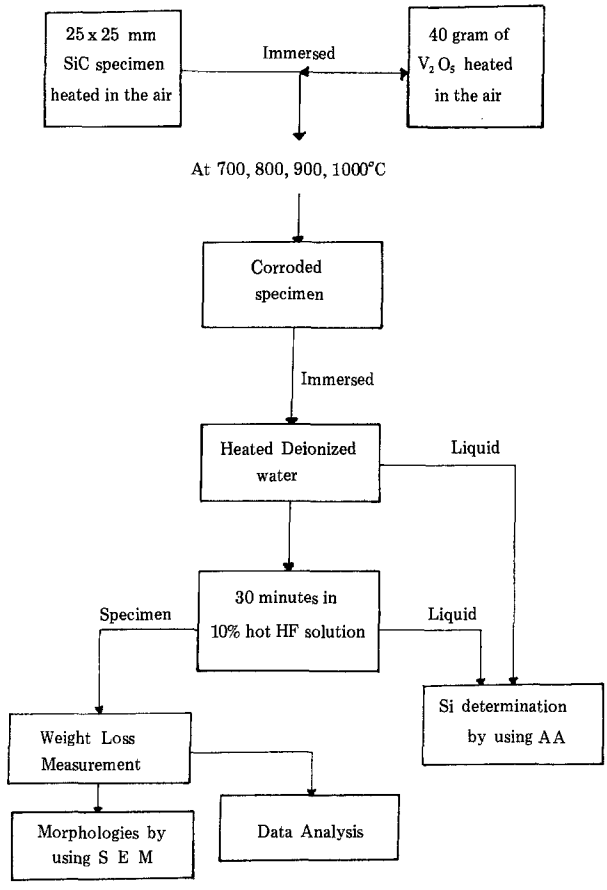

Figure 1 Schematic diagram of the experimental analysis for each data point.

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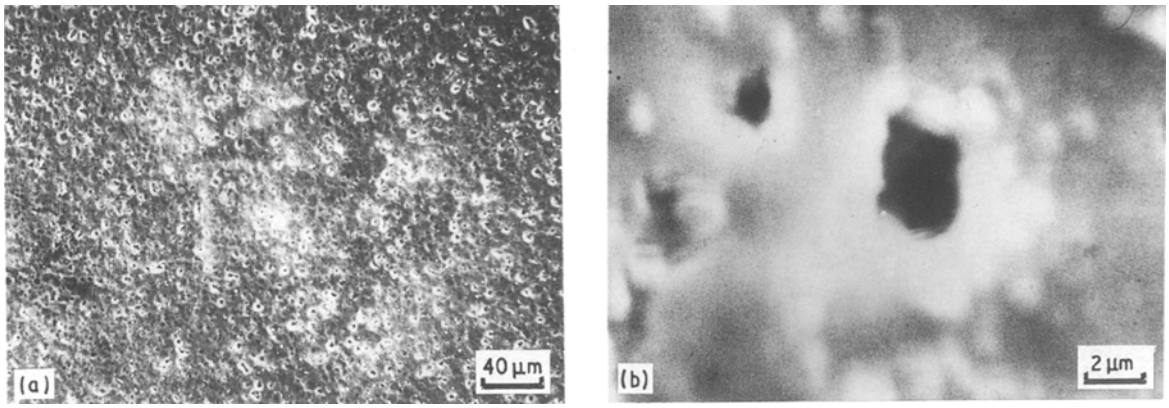

Figure 2 Morphology of the SiC surface after 10 h of V_2O_5 corrosion at 1000° C. The scale has been removed by HF dissolution. The surface shows a coarse network of pits (a), and pits averaging 2–3 μm in diameter.

3. Results and discussion

The SiC morphology after 10 h in V_2O_5 acid melt at 1000° C and after undergoing scale dissolution in HF solution is shown in Fig. 2. Figure 2a shows corrosion pits on the surface of the specimen. Figure 2b shows pits of on average 2–3 μm in diameter. Another morphology which shows less corrosion due to a shorter immersion time can be seen in Fig. 3, which illustrates a slight pitting attack and the start of bubble formation. The formation of bubbles in these figures clearly shows gas build-up at the solid–melt interface. Previous investigators [8–10] observed this phenomenon and attributed it to the evolution of CO at the SiC/SiO_2 interface during the generated oxidation and corrosion on the SiC substrate. The present investigation proposes that V_2O_5 is acting as a flux which carries a sufficient amount of oxygen from the heated air to enable the simple reaction:

$$SiC + 1.5O_2 \rightarrow SiO_2 + CO\ (g)$$

This process is supported by two reasons: first, SiC will not be attacked by HF solution; the scales removed by HF are only SiO_2. Secondly, the solubility between SiO_2 and the V_2O_5 melt is negligible [7]. The reaction may be considered as follows: the oxygen enters into the V_2O_5 flux, diffuses through the formed SiO_2 scale, reaches the interface of SiC/SiO_2, reacts with solid SiC, and then the gases formed diffuse out of the scale. However, the entire mechanism has not been fully developed.

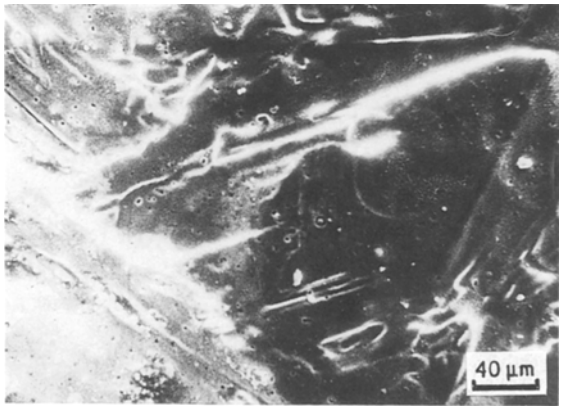

Figure 3 Slight pitting (bubbles start to form) on the surface of SiC after corrosion in the V_2O_5 melt for 2 h at 1000° C.

Here, we start with the weight loss measurement in which corrosion products are measured over each time interval. The results of these corrosion treatments at four different temperatures are presented in Fig. 4. It is seen from the figure that increasing the temperature increases the corrosion rate of silicon carbide. The reaction rate indicates it should have a complex temperature dependence. If D_0 is the diffusion coefficient of carbon monoxide and k_s is the rate constant at the solid surface, the rate can be written by

$$\frac{dW}{dt} = \frac{-CA}{b(W_0 - W)/D + k_s^{-1}} \qquad (1)$$

Further, Equation 1 may be integrated to give the

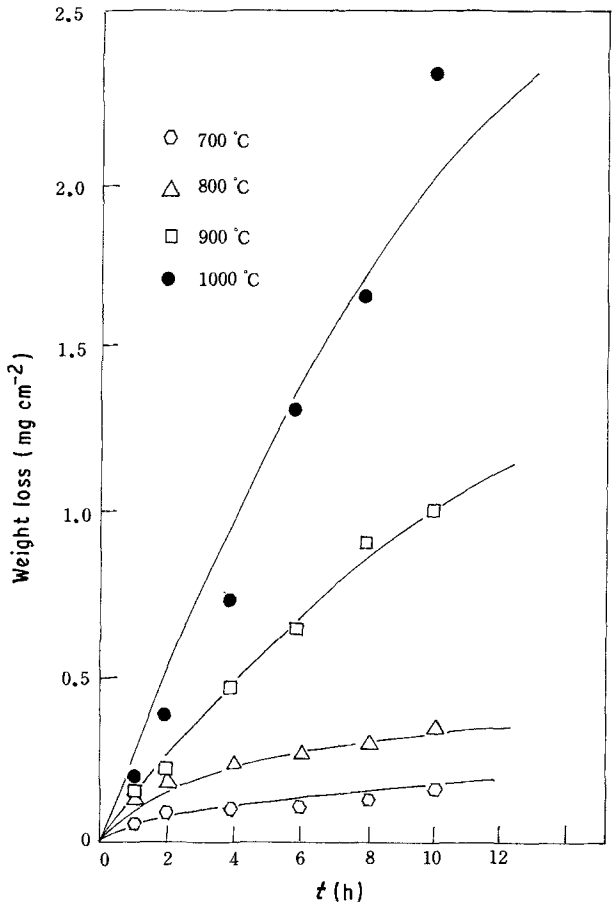

Figure 4 Weight loss of SiC in the V_2O_5 melt.

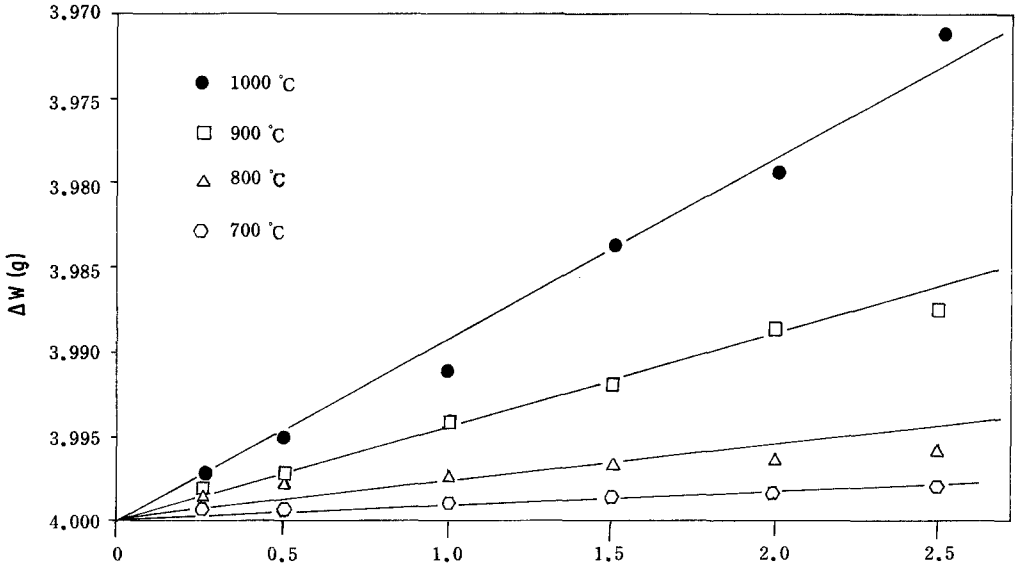

Figure 5 A data plot showing the correlation between the equations and linear kinetics.

expression:

$$t = \frac{b(\Delta W)^2}{2A_0CD} + \frac{\Delta W}{A_0Ck_s} \quad (2)$$

where A_0 and C are the initial reaction area and initial concentration in the bulk respectively, and b is a constant factor. If W is the remaining weight per unit area at any reacting time t, the quantity ΔW is then the difference between the initial weight of the unit area, W_0, and the value of W. It is known that both A_0 and C remain unchanged during the reaction.

Equation 2 represents the sum of the parabolic and linear rates and is similar to the earlier developed equation by Wagner and Grunnewald [11, 12]. The ΔW_0 term in the equation can be divided resulting in the following:

$$\frac{t}{\Delta W} = K_D\Delta W + K_s \quad (3)$$

If we let

$$K_D = \frac{b}{2A_0CD} \qquad K_s = \frac{1}{A_0Ck_s}$$

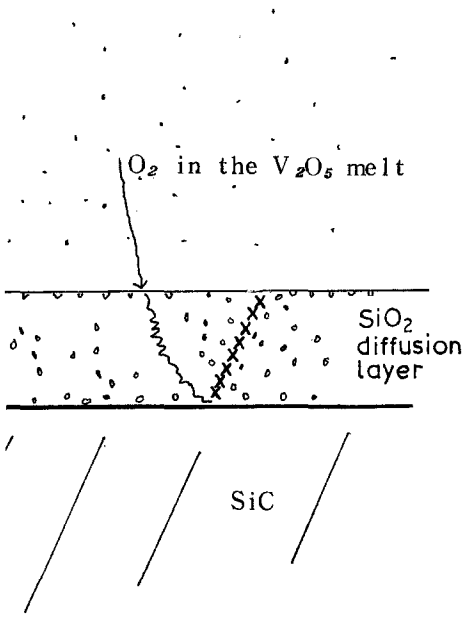

Figure 6 Schematic diagram of the hot corrosion mechanism. x represents the rate controlling step.

the equation predicts that $t/\Delta W$ plotted against ΔW should result in a straight line, the slope of which contains the rate constant due to the diffusion effect K_D. Figure 5 is plotted according to Equation 3 using the data from Fig. 4. The consistency of the linear relationship of the plotted data with the equation indicates that the above derivation is applicable to this study. It needs to be noted in Fig. 5 that the extrapolation of each straight line goes through the origin. This is because the diffusion coefficient D has a larger activation energy which is less sensitive to temperature change that the surface reaction constant k_s. Consequently at elevated temperatures k_s becomes much larger than D, so the reciprocal value K_s will be negligible. It is apparent from the equations that diffusion will be the rate controlling mechanism when hot corrosion behaviour occurs. These mathematical expressions correspond with the diagram shown in Fig. 6, and are able to explain the case of gas build-up in oxide scale on SiC. For instance, similar bubble formation has been observed by Mieskowski and colleagues [13], from which they also inferred that the rate of oxidation of SiC is controlled by the outward diffusion of CO. However, compared with other research, we would emphasize that here the severe corrosion of SiC in acidic V_2O_5 melt occurred at much lower temperatures (less than 1000° C). Therefore, a warning should be given regarding the use of oils containing V_2O_5 in engines which incorporate components made from SiC.

4. Conclusions

Silicon carbide is corroded in the hot acidic environment which is introduced by V_2O_5 flux. A mathematical kinetic expression is determined for the entire hot corrosion behaviour. The consistency of the plotted data with the deduced equations has shown the excellence of the proposed mechanism. The surface reaction constant k_s is large enough for the chemical reaction to be negligible in the controlling kinetics. The outward diffusion of gas build-up inside the scales appears to be the rate determining step. The corrosion rate is determined and the resulting bubble formation is

attributed to the evolution of CO from the interface of SiC/SiO_2. These observations suggest that careful protection of SiC engine components is required when using oils containing V_2O_5.

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