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Hydrogen-Silicon Carbide Interactions

Andrew J. Eckel
Sverdrup Technology, Inc.
NASA Lewis Research Center Group
Cleveland, Ohio

Nathan S. Jacobson
National Aeronautics and Space Administration
Lewis Research Center
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Ajay K. Misra and Donald L. Humphrey
Sverdrup Technology, Inc.
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Abstract

A study of the thermochemistry and kinetics of hydrogen environmental attack of silicon carbide was conducted for temperatures in the range from 1100°C to 1400°C. Thermodynamic maps based on the parameters of pressure and oxygen/moisture content were constructed. With increasing moisture levels, four distinct regions of attack were identified. Each region is defined by the thermodynamically stable solid phases. The theoretically stable solid phases of Region I are silicon carbide and silicon. Experimental evidence is provided to support this thermodynamic prediction. Silicon carbide is the single stable solid phase in Region II. Active attack of the silicon carbide in this region occurs by the formation of gases of SiO, CO, CH_4, SiH_4 and SiH. Analysis of the kinetics of reaction for Region II at 1300°C show the attack of the silicon carbide to be controlled by gas phase diffusion of H_2O to the sample. Silicon carbide and silica are the stable phases common to regions III and IV. These two regions are characterized by the passive oxidation of silicon carbide and formation of a protective silica layer.

Introduction

Silicon carbide (SiC) is a principal candidate material for many high temperature applications. Specific applications are varied and include the use of SiC as a monolithic structural component, the reinforcing fiber and/or matrix material in advanced composites, and a protective coating for ceramic and carbon/carbon composite systems. Many of the proposed uses involve employing SiC in high temperature gaseous hydrogen environments. Examples include the Stirling engine, advanced earth-to-orbit propulsion systems, and hypersonic vehicles. In these varied systems the moisture content can be expected to range from near pure hydrogen to hydrogen plus steam, and operating pressures may range from below 1 atm to greater than 50 atm.

As a consequence of the recent interest and varied potential applications of SiC in hydrogen-containing environments, a number of investigations have been reported [1-5]. Fischman et al [1], Hallum and Herbell [3], and Kim and Readey [5] all used computer programs based on free energy minimization to predict reaction products [6,7]. However, in each case only selected conditions were evaluated and verified with experimental work.

This paper evaluates the thermodynamic stability of stoiciometric SiC in H_2-containing environments in a manner similar to those previously discussed, but for a wider range of variables. The results of the calculations are illustrated using thermodynamic maps. The maps are presented and discussed using the variables of temperature, moisture content, and pressure. The range for these parameters are; 1100°C-1400°C; 0-50 volume percent moisture; and 1-30 atmospheres total system pressure. Interactions at lower temperatures are discussed elsewhere [8,9]. Since the thermodynamic results do not consider kinetics of reactions, they are not meant to predict specifics of actual performance of the material, but rather set a conservative limit or bound to the material's use.

To predict a material's performance in a particular environment it is necessary to understand the thermodynamics and kinetics of reactions, and the resulting morphology from the reactions. For this study, theoretical calculations for two conditions were verified using a 5% H_2/Ar mixture and a commercially available sintered α-SiC. The kinetics of the reactions were measured for one condition and scanning electron microscopy was employed for analyzing morphological characteristics resulting from reactions in both environments.

Procedure

All of the equilibrium calculations were performed using the computer program SOLGASMIX-PV [6]. The program was originally developed by Eriksson [10] and later modified by Bessmann [6]. The computer program is based on the minimization of the Gibbs free energy of the system. For calculations involving moisture, vapor pressures of the various species were calculated as a function of P_{H_2O}/P_{H_2}. Specific details of the calculations are contained elsewhere [8].

Experiments were conducted to verify the thermodynamic predictions for two conditions. The first condition was exposure of a sintered α-SiC sample* at 1300°C, 1 atmosphere pressure, and approximately 100 ppm (by volume) moisture. The sample was contained in a mullite furnace tube, and exposed to a flowing 5% H_2, 95% argon gas for 24 hours. The sample was exposed to flow rates of 100, 200, and 400 cm³/min, to obtain information on the kinetics of reaction. A zirconia oxygen sensor was utilized to measure oxygen - and thus indirectly, moisture - content. The 5%H_2/Ar mixture was dried over a zeolite. It was found that a repetitive procedure of evacuating the system and back-filling with 5%H_2/Ar gave a P_{O_2} of about 10^{-22} atm. This is the edge of the useful range for the zirconia sensor, but was reproducible. This value corresponds to a moisture content of approximately 100 ppm in a H_2/H_2O system at 1300°C.


*Carborundum Hexoloy, Niagara Falls, NY.

The second experimental condition was again for 1 atm total system pressure and 1300°C, but for a lower moisture level. The goal was to expose the SiC in an environment of less than 30 ppm moisture. Equipment did not permit measuring the oxygen or moisture content at this level. To achieve the desired level, the same procedure used in the first experiment was repeated. However, in this case the α-SiC sample was held in a zirconia crucible and configured such that the gas would pass through loosely packed zirconium turnings prior to reaching the sample to facilitate removal of oxygen. The experiment was again conducted for 24 hours with a single gas flow of 200 cm³/min.

Results and Discussion

Thermodynamic Stability in Pure Hydrogen

Thermodynamic calculations show that SiC would decompose in pure H_2. This is consistent with that previously reported [1,3]. The predicted equilibrium partial pressures of CH_4, SiH and SiH_4 as a function of temperature are seen in Figure 1. Although there are other possible gaseous species, calculations show these to be the predominant ones. The only stable solid phase is silicon.

Since the partial pressures of the Si-H species are at least an order of magnitude less than that of CH_4 for these conditions, the primary reaction is the decomposition of SiC:

$$SiC + 2H_2 = Si + CH_4. \tag{1}$$
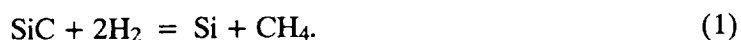
The effect of total system pressure at 1400°C in pure H_2 is shown in Figure 2. The partial pressures of all three gaseous species increase with increasing system pressure. Silicon carbide could therefore be expected to decompose at an increasing rate with increasing system pressure in a pure H_2 environment.

Thermodynamic Stability in H_2 + H_2O mixtures

Temperature Effects: The calculated equilibrium partial pressures of the major gaseous species and the stable condensed phases for SiC in H_2 + H_2O environments at 1 atm total system pressure are shown in Figures 3 - 6. The temperatures considered are 1400°C, 1300°C, 1200°C, and 1100°C, respectively. The results shown at 1400°C are similar to those obtained by Kim [4]. Distinct stability regions, each identified by the stable condensed phases, are shown in the diagrams.

Region I is present in approximately the same magnitude at all of the temperatures considered and corresponds to low moisture levels (<30 ppm) in the atmosphere. The stable solids are silicon (Si) and SiC. This region is similar to the previously discussed case for SiC in pure H_2 in that the predominant vapor species is CH_4 and decomposition occurs primarily by reaction (1).

Region II is identified by the single stable solid phase of SiC. Similar to Region I, this is a region of active attack of SiC by the environment. The predominant gaseous species in this region are SiO, CO, and CH_4. The width of this active oxidation region decreases with decreasing temperature.

Region III has two solid stable phases: SiC and SiO_2. Formation of SiO_2 on the SiC is likely to provide protection against further oxidation, and this region may be called the domain of passive oxidation. With decreasing temperature, the boundaries of Region III shift towards lower moisture levels and eventually encompasses all of what was Region II at higher temperatures.

Region IV is present at higher moisture levels in the environment and at temperatures less than 1300°C. The stable solid phases present at equilibrium in this region are SiC, C and SiO_2.

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<u>Pressure Effects</u>:   Figures 3 and 7 - 9 show the effect of total system pressure on the stability of SiC in the H_2 + H_2O atmosphere at 1400°C.   It is seen that an increase in total system pressure from 1 → 5 → 10 → 15 atm is very similar to the previously discussed decrease in temperature at 1 atm.   That is, the same general regions exist, and the region of passive oxidation region (Region III) increases in width at the expense of the active oxidation region (Region II).

Figure 10 shows the moisture levels required for transition from Region II to Region III as a function of temperature.   This is the moisture level required for the protective SiO_2 layer to be formed on the surface of the SiC.   At one atmosphere total pressure, the moisture level required for SiO_2 formation decreases with temperature up to 1100°C, and then increases with further decrease in temperature.   The inflection point or *minimum* in the moisture versus temperature curve is shifted towards the right (i.e., towards higher temperature) with increase in total pressure. For 20 atm or 30 atm total pressure, the minimum occurs at a temperature greater than 1400°C. As a protective layer, the stability of SiO_2 in H_2 + H_2O atmospheres determines the upper use temperature for SiC.   Calculations for the stability of SiO_2 in H_2 + H_2O are reported elsewhere [8].

<u>Experimental</u>

As a verification of the predicted stable condensed phase regions, two experiments were conducted.   Sintered alpha silicon carbide samples were exposed at 1300°C and 1 atm system pressure for 24 hours in a 5%H_2/Ar atmosphere.   Regions I and II were chosen since abundant literature exists verifying the solid phases predicted in regions III and IV [11,12], and Kim and Ready [5] performed testing in Region II using hydrogen without any dilution from an inert gas.

Figure 11 shows a representative photomicrograph of the SiC after exposure in the environment defined as Region I (< 30 ppm moisture).   The photomicrograph was obtained using backscattered electron imaging.   The large light colored areas were determined to be iron-silicide by EDS.   One as-received sample of the commercial SiC was analyzed and iron was determined to be present as an impurity at the level of 500 ppm.   The formation of the iron-silicides was seen to be a surface effect.   This provides some evidence for the prediction that free silicon is a stable condensed phase since this would enable the reaction with iron to form iron-silicide.

In contrast, Figure 12 shows a SEM photomicrograph of SiC subsequent to treatment in the active oxidation environment of Region II (≈ 100 ppm moisture).   Extensive grain boundary attack is indicated in this region of active attack of the SiC.   In some cases, the attack resulted in pitting. This is consistent with observations reported in the literature [3,13], and would result in strength degradation.

Thermogravimetric tests were also conducted on SiC in Region II.   Specifics of the tests and detailed results are contained elsewhere [14].   The SiC exhibited linear weight loss with time for three gas flow rate conditions.   The linear weight loss rates indicate that either gas phase diffusion or surface reaction is rate controlling.   The measured reaction rates are plotted as a function of the square root of linear gas velocity in Figure 13.   The linear relationship between reaction rate and square root of gas velocity points toward gas phase diffusion as the rate controlling step [15]. Kim and Ready [5] have shown that the primary reactant is H_2O oxidizing the sample to form $SiO(g)$ and $CO(g)$ products.   This is consistent with Region II.   Thus the rate controlling step is most likely $H_2O(g)$ mass transport to the sample.

<u>Summary</u>

Thermodynamic calculations for SiC in H_2 + H_2O environments predict distinct reaction regimes in the temperature range of 1100°C-1400°C.   The primary regimes are carbon removal (Region I), active oxidation (Region II), and passive oxidation (Region (III and IV).   Using the thermodynamic predictions, the temperature, moisture level, and total pressure required for passive oxidation of the SiC surface were estimated.

Experimental studies were conducted in regions I and II at 1300°C and 1 atm total system pressure on a sintered α-SiC. In the carbon removal regime (Region I), iron-silicides are observed. These are likely from formation of free silicon and subsequent reaction of iron with this silicon. In Region II, the active oxidation region, no iron-silicides were observed and the sample exhibited significant grain boundary attack. In this active oxidation regime, a mass transport step is rate limiting--very likely the transport of $H_2O(g)$ to the sample.

Conclusion

Critical experiments confirm the thermodynamic predictions for active attack by oxidation or decomposition of SiC at low moisture levels in hydrogen.

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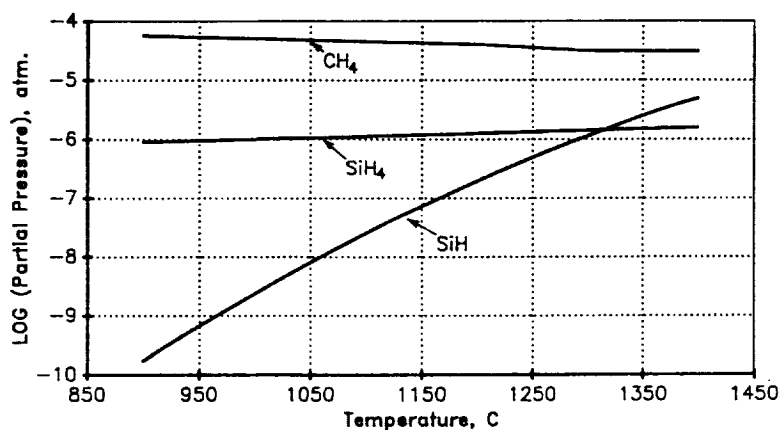
Figure 1 - Equilibrium partial pressures of reaction product gases for reaction of SiC with pure H_2 at 1 atm.
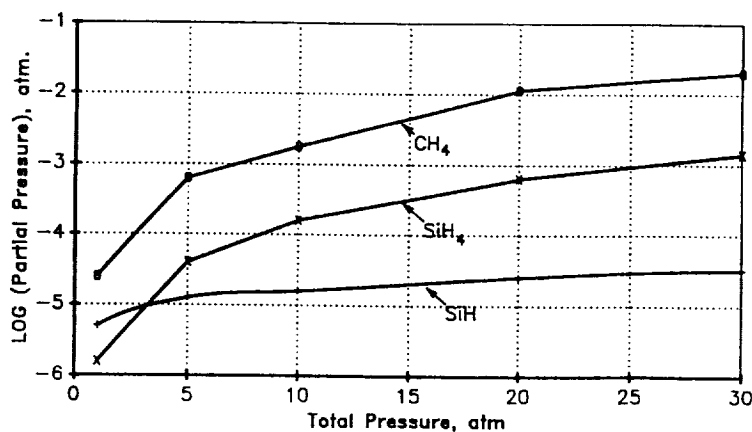
Figure 2 - Effect of total system pressure on partial pressures of reaction product gases for reaction of SiC with pure H_2 at 1400°C

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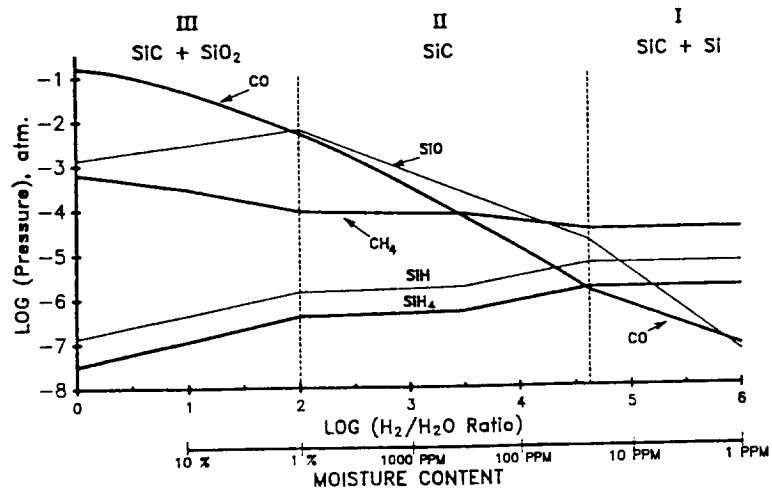
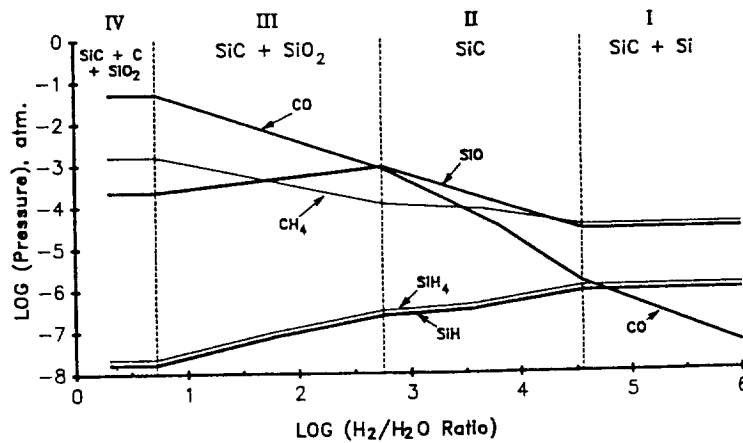Figure 3 - Stability of SiC in $H_2 + H_2O$ atmospheres at 1400°C for 1 atm total pressure.

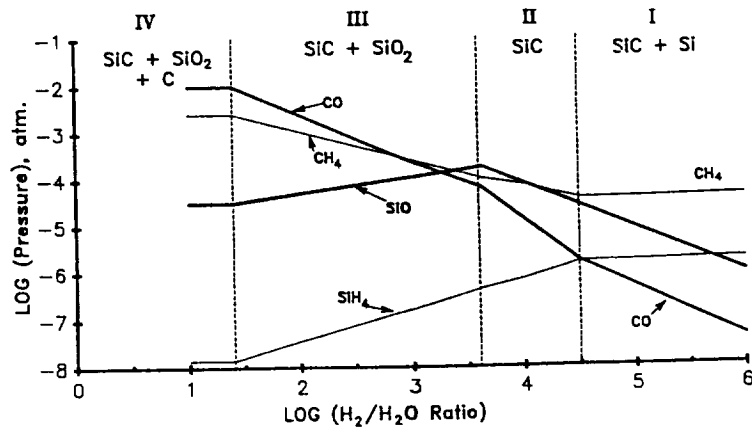Figure 4 - Stability of SiC in $H_2 + H_2O$ atmospheres at 1300°C for 1 atm total pressure.

Figure 5 - Stability of SiC in $H_2 + H_2O$ atmospheres at 1200°C for 1 atm total pressure.

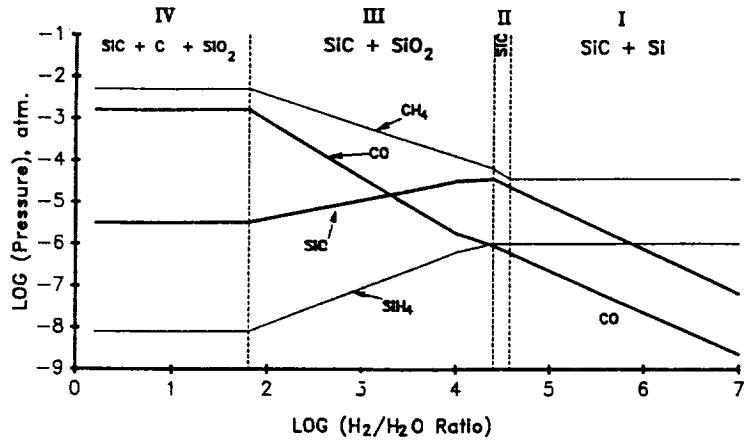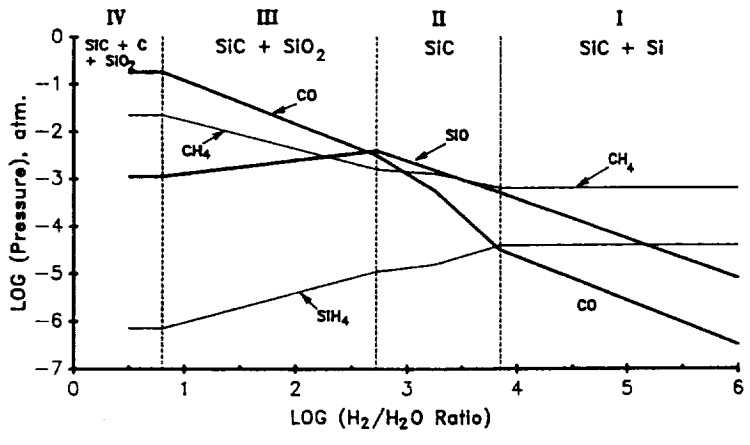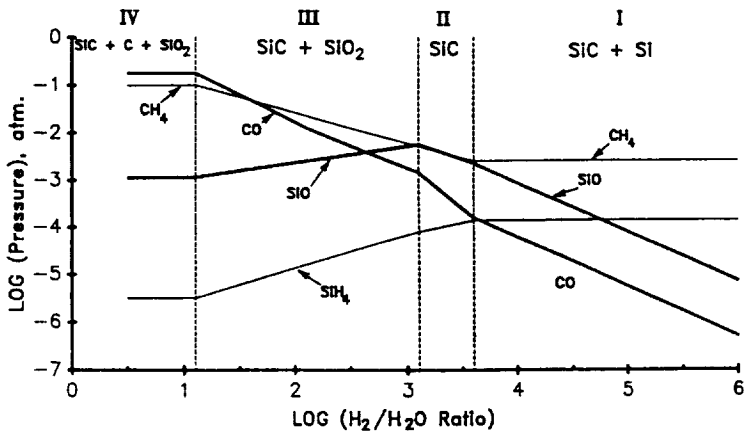Figure 6 - Stability of SiC in H_2 + H_2O atmospheres at 1100°C for 1 atm total pressure.

Figure 7 - Stability of SiC in H_2 + H_2O atmospheres at 1400°C for 5 atm total pressure.

Figure 8 - Stability of SiC in H_2 + H_2O atmospheres at 1400°C for 10 atm total pressure.

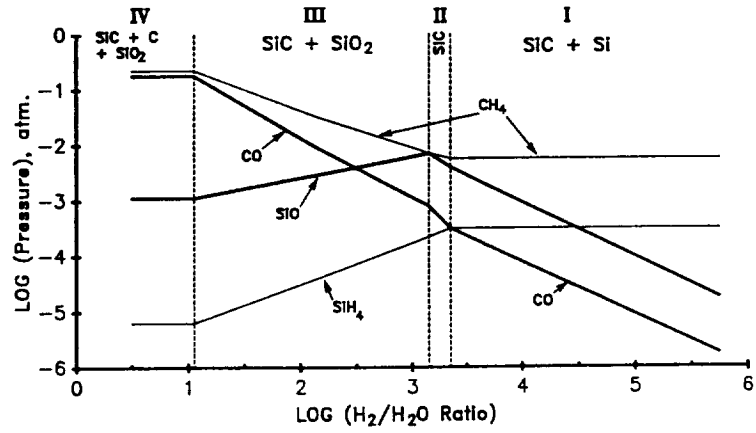Figure 9 - Stability of SiC in H_2 + H_2O atmospheres at 1400°C for 15 atm total pressure.
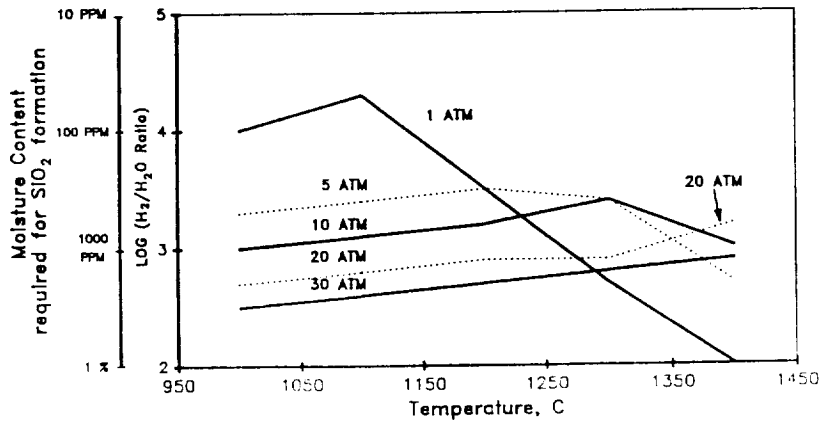

Figure 10 - Minimum moisture levels required for SiO_2 formation on SiC in H_2 + H_2O environments.
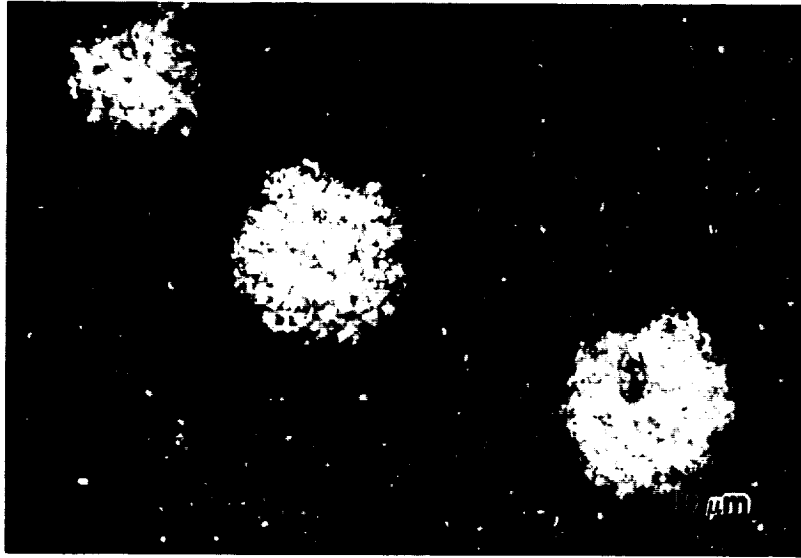
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Figure 11 - SEM backscatter micrograph of SiC after exposure at 1300°C to environmental conditions of Region I.

Figure 12 - SEM photomicrograph of SiC after exposure at 1300°C to environmental conditions of Region II.
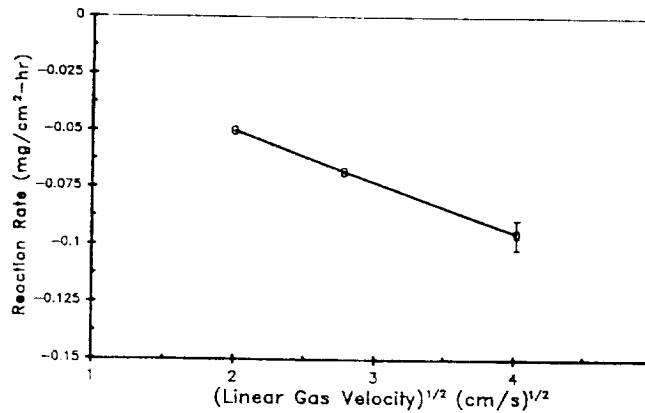

Figure 13 - Effect of flow rate on linear reaction rates for SiC reaction with 5% H_2/Ar at 1300°C.

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16. Abstract

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