

Corrosion of Ceramics in Halogen-containing Atmospheres*

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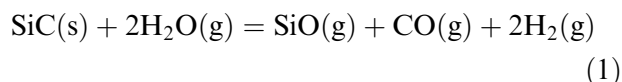
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Abstract

Most single component oxide ceramics undergo active corrosion in halogen-containing gases such as HCl to form gaseous corrosion products only. At high temperatures, such corrosion reactions are controlled by gaseous diffusion of the product gases away from the solid surface. As a result, the reaction kinetics and the corrosion rate can be predicted if the thermodynamics of the reaction are known. Similar behaviour is expected for nitride ceramics. However, several multicomponent oxides, typified by $NiAl_2O_4$, and carbides may react to form a porous solid product layer through which diffusion takes place and controls the corrosion rate. Nevertheless, even in these cases, if gaseous diffusion still controls, the rate of corrosion can be modeled and predicted.
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1 Introduction

Active corrosion usually means atmospheric degradation with the formation of gaseous, non-passivating, corrosion products such as SiO and CO which result from oxidizing SiC in water vapor:¹



Kinetic data on this system¹ and on the active corrosion of SiO₂ in hydrogen²



show that, at high temperatures, diffusion of the product gases away from the corroding surface controls the rate of corrosion. As a result, the kinetics of the reaction can be easily modeled and quantitative comparisons can be made with experimental data to confirm diffusion control.²

In fact, thermodynamic data for the reaction provide the necessary information to permit quantitative prediction of corrosion rates. Of course, if one of many possible surface reactions controls the rate of corrosion, then prediction of corrosion rates without experimental data is impossible. In any event, for any given material, there should be a temperature regime sufficiently high so that gas diffusion will control the corrosion rate and predictions of corrosion behaviour and corrosion rates can be made.

The corrosion of ceramics in halogen-containing gases such as Cl₂, HCl, F₂, and HF is of interest for several reasons, both scientific and technical. First, the number of ceramic compounds that can undergo active gas corrosion in halogens is much larger than those that react to form only gaseous species in either reducing or oxidizing environments. Therefore, the active gas corrosion of a wide variety of ceramics (oxides, carbides, nitrides, borides, etc.) can be studied to determine the systematics, similarities, and differences in their behaviour.

In addition, gas corrosion of ceramics by halogens is technologically important and becoming increasingly so. Chemicals such as TiO₂ pigments and fluorocarbons are processed in halogen environments at high temperatures where refractory corrosion is a problem. Ceramics are being used more frequently as supports and furnace fixturing for silicon wafers in integrated circuit manufacturing. Many of the processing steps are carried out in halogen-containing gases either at high temperatures or in plasmas. Not only is corrosion resistance important, but also the mechanism of degradation is critical in these applications. For example, preferential attack of the glass phase in a high alumina ceramic by a reactive atmosphere can release alumina particles which would pose a serious problem in subsequent wafer processing. The behaviour of ceramics in incinerators is important since the existence of halogens in the combustion gases is assured by the presence of polyvinyl chloride and other halogen-containing polymers in the waste stream. Not only can ceramics corrode

under the atmosphere and temperature conditions in an incinerator, but the corrosion of metal components in the same environment depends critically on the resistance of any passive oxide to the halogen gases that are present. Finally, high temperature systems operating near salt water ingest NaCl from the atmosphere and produce halogen-containing gases that can cause ceramic and passive oxide degradation.

In another area of technical importance, the presence of reactive atmospheres, such as HCl, during sintering leads to enhanced vapor transport, little shrinkage, and significant grain growth.³ Reactive vapor phase sintering can be used to fabricate materials with controlled porosity and pore size that have applications as filters, sensors, biomaterials, and the backbone for ceramic-metal composites.⁴ Knowing whether vapor transport is controlled by gas diffusion or by a surface reaction is important in understanding the kinetics of vapor phase sintering and other applications of reactive vapor transport.

In what follows, based on previous experimental data^{1,2} that demonstrate the ability to model gas diffusion-controlled corrosion, thermodynamic calculations are used to predict high temperature, gas diffusion-controlled corrosion of several different oxides and nonoxides.

2 Thermodynamics and Kinetics

For a reaction such as:



available thermodynamic data⁵ permit calculation⁶ of the gas species in equilibrium. Figure 1 gives the results for MgO in HCl and shows that eqn (3) is the dominant reaction. Since the reaction does not go to completion, it can be shown² that the rate of corrosion, $J(\text{MgO})$ (moles $\text{cm}^{-2} \text{s}^{-1}$), in very dry HCl is:

$$J(\text{MgO}) = -[h(\text{MgCl}_2)h(\text{H}_2\text{O})]^{1/2} K_e^{1/2} p_o(\text{HCl}) \quad (4)$$

where $h(\text{MgCl}_2)$ and $h(\text{H}_2\text{O})$ are the mass transfer coefficients for MgCl_2 and H_2O , respectively, K_e is the equilibrium constant for the reaction, and $p_o(\text{HCl})$ is the ambient HCl pressure. Conversely, in wet HCl the corrosion rate is:

$$J(\text{MgO}) = -\frac{h(\text{MgCl}_2)K_e p_o^2(\text{HCl})}{p_o(\text{H}_2\text{O})} \quad (5)$$

where $p_o(\text{H}_2\text{O})$ is the water vapor pressure in the ambient gas. The mass transfer coefficients are given by:

$$h = \frac{DSh}{dRT} \quad (6)$$

where D is the gas diffusion coefficient, d is a sample dimension, and Sh is the Sherwood coefficient that takes into consideration fluid convection. Since the mass transfer coefficients can be accurately calculated from the kinetic theory of gases,⁷ eqns (4) and (5) show that the corrosion rate is predicted by the ambient HCl and H_2O pressures, $p_o(\text{HCl})$ and $p_o(\text{H}_2\text{O})$, and the equilibrium constant for the reaction which in this case is:

$$K_e = \frac{p_s(\text{MgCl}_2)p_s(\text{H}_2\text{O})}{p_s^2(\text{HCl})} \quad (7)$$

where the subscript 's' refers to the pressures at the MgO surface. Since K_e can be calculated from thermodynamic data, the rates of corrosion can be calculated and predicted. Furthermore, eqns (4) and (5) show that in dry hydrogen, $J(\text{MgO}) \propto \exp -\Delta H^\circ/2RT$ while in wet hydrogen, $J(\text{MgO}) \propto \exp -\Delta H^\circ/RT$; that is, the apparent activation energy for corrosion is twice as large in wet HCl than it is in dry HCl and its value can be calculated from tabulated enthalpy values and compared to experimental data.

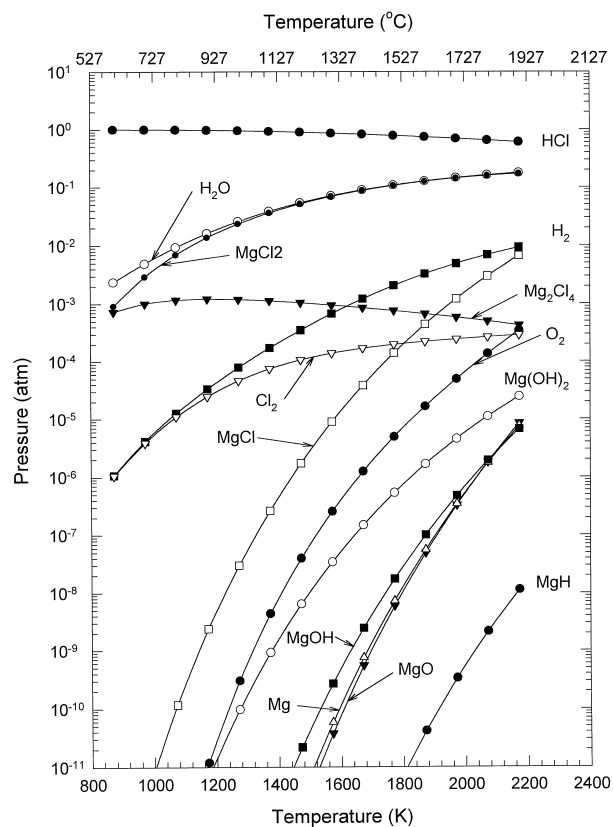


Fig. 1. Pressures of the gaseous species over MgO in HCl.

3 Halogen Corrosion of Ceramics

Thermodynamic calculations for several single oxides, multiple oxides, carbides and nitrides in atmospheres containing HCl as the corroding halogen gas have been carried out. In all cases, the predicted results are similar to those described above. The reactions do not go to completion so product gas diffusion controls the corrosion rate.² Also, product gas pressures sufficiently high for appreciable corrosion are predicted down to low temperatures where a surface reaction will undoubtedly dominate the rate of corrosion.

4 Single Oxides

They are all very similar and typical of that described above for MgO. Figure 2, which shows the gas pressures in HCl over Al_2O_3 , is another typical example of a single oxide in HCl.

5 Ternary Oxides and Solid Solutions

In corrosion of multicomponent oxides, two limiting cases are possible. Take for example, NiFe_2O_4 . In this case, both constituent oxides, NiO and Fe_2O_3 , have high product pressures in HCl. In addition, the pressures of NiCl_2 and FeCl_2 are also both high over NiFe_2O_4 , as Fig. 3 shows, and not very different from those over pure NiO and Fe_2O_3 , respectively. Therefore, NiFe_2O_4 will

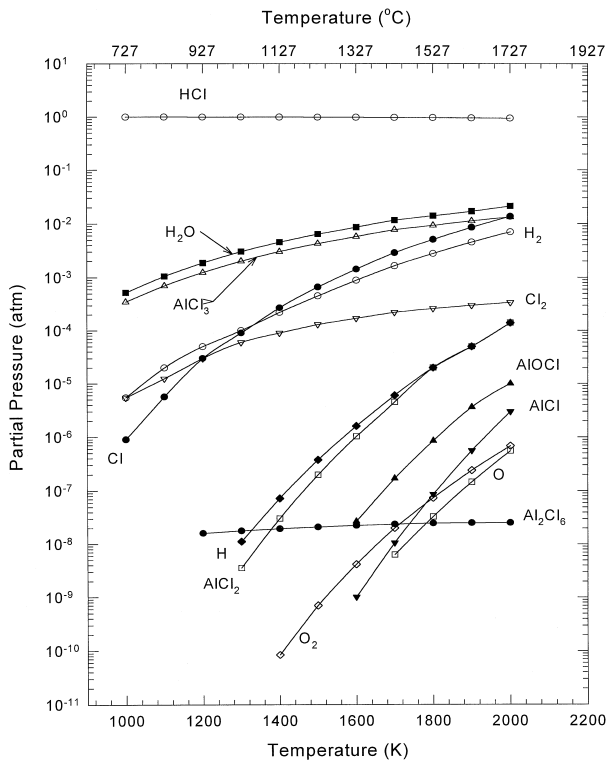


Fig. 2. Pressures of the gaseous species over Al_2O_3 in HCl.

probably corrode congruently in HCl. In contrast, the AlCl_3 and NiCl_2 pressures over NiAl_2O_4 are very different (Fig. 4). As a result, NiO will be preferentially corroded from NiAl_2O_4 leaving porous Al_2O_3 behind. Continued corrosion will depend on

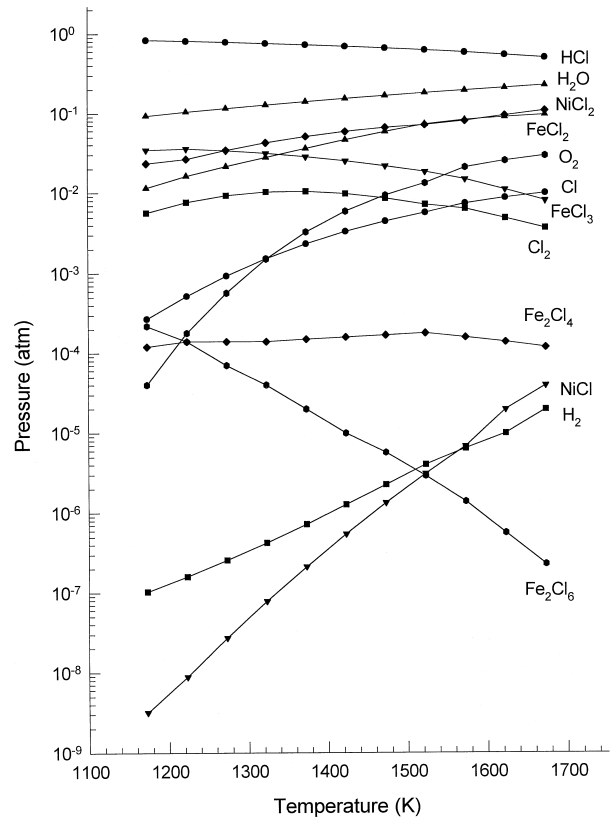


Fig. 3. Pressures of the gaseous species over NiFe_2O_4 in HCl.

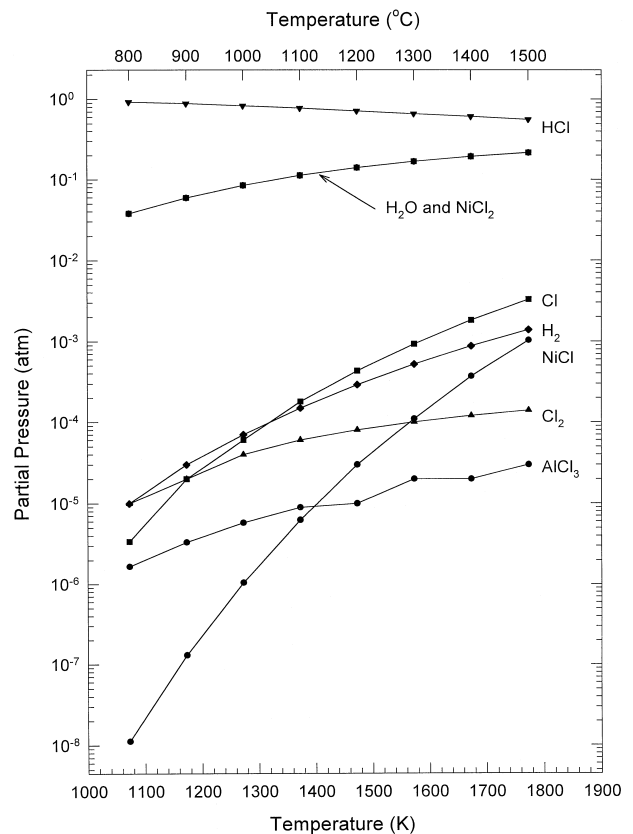


Fig. 4. Pressures of the gaseous species over NiAl_2O_4 in HCl.

gaseous diffusion of NiCl_2 through the residual porous Al_2O_3 as schematically depicted in Fig. 5. One of the features of gas transport control is that the gas diffusion coefficient, D_{AB} , can easily be calculated from kinetic theory with the Chapman-Enskog equation:⁶

$$D_{AB} = 1.8583 \times 10^{-3} \left(\frac{1}{M_A} + \frac{1}{M_B} \right)^{1/2} \frac{T^{3/2}}{P\sigma^2\Omega_{D,AB}} \quad (8)$$

where P = total pressure, σ = collision diameter, $\Omega_{D,AB}$ = collision integral, and M_A and M_B are the molecular weights of A and B. For diffusion through pores whose diameter is on the order of the mean-free-path of the gas atoms, Knudsen diffusion must be considered. The Knudsen diffusion coefficient, K_A is given by:⁸

$$D_{KA} = 9.7 \times 10^3 \bar{r} \sqrt{\frac{T}{M_A}} \quad (9)$$

where \bar{r} is the mean pore radius. Typically, for pores with diameters on the order of a micrometer, as might be expected for the incongruent corrosion of NiAl_2O_4 ,⁹ the molecular and Knudsen diffusion coefficients are of the same magnitude so an effective diffusion coefficient must be used, $D_{A,\text{eff}}$:

$$\frac{1}{D_{A,\text{eff}}} = \frac{1}{D_{KA} + D_{AB}} \quad (10)$$

Depending on the equilibrium product gas pressures and the diffusion coefficients, the thickness of the porous layer may reach a 'steady state' and the multicomponent oxide can continue to corrode congruently. Another alternative is that the less volatile species may simply be left behind as 'ash.' In the case of NiAl_2O_4 , the difference in partial pressures is sufficiently large that in virtually all

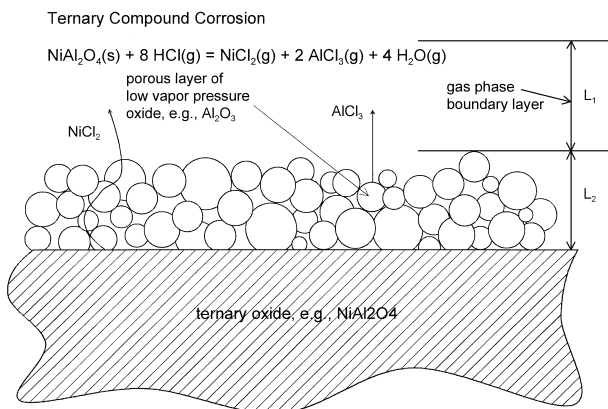


Fig. 5. Schematic representation of incongruent corrosion of NiAl_2O_4 with the formation of NiCl_2 gas and a residual porous layer of Al_2O_3 .

cases the NiO would be preferentially volatilized leaving behind Al_2O_3 .

6 Carbides

The corrosion of SiC in HCl typifies the expected behaviour of most carbides. Figure 6 shows the equilibrium partial pressures in a starting gas of one atmosphere HCl over, what becomes, a

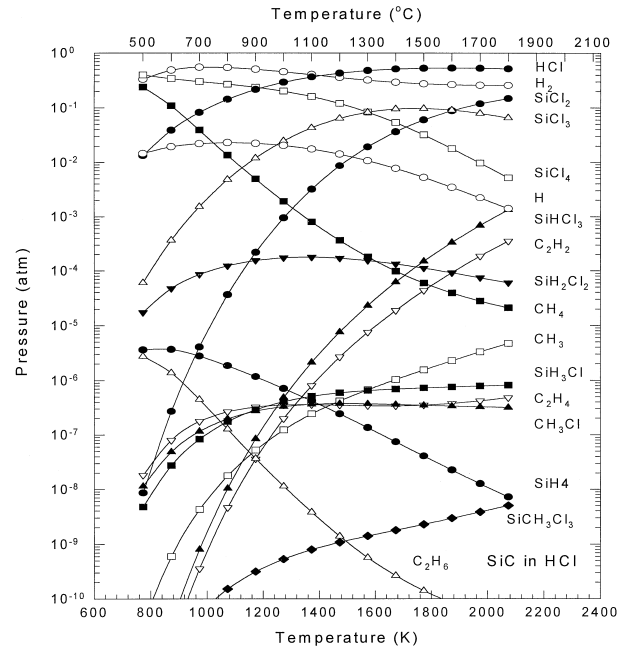


Fig. 6. Pressures of gaseous species over SiC in HCl .

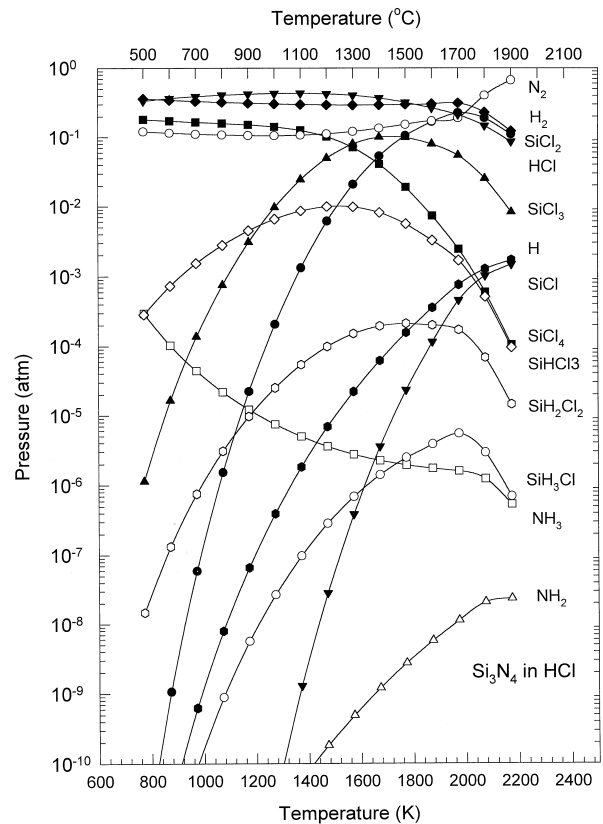
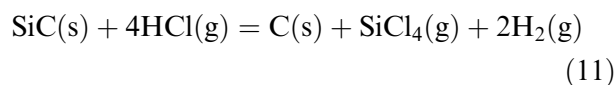


Fig. 7. Pressures of the gaseous species over Si_3N_4 in HCl .

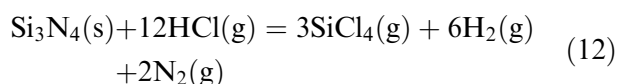
mixture of C and SiC. Even at the lowest temperatures where CH₄ is an important gas species, the primary reaction appears to be:



As the temperature increases, the equilibrium CH₄ pressure decreases further. So in this case, residual porous carbon (or graphite) is left behind and the kinetics will depend on gas diffusion through this layer as discussed above. It is also interesting to note that the reaction goes essentially to completion at low temperatures so that diffusion of HCl to the solid surface could control the rate of corrosion. However, at low temperatures, surface reaction is far more likely to be the rate controlling process. Other carbides should behave similarly. A similar thermodynamic analysis has been carried out for several carbides under hydrothermal conditions and the presence of residual carbon was both predicted and found experimentally.¹⁰

7 Nitrides

In contrast, Si₃N₄ reacts to form completely gaseous products as shown in Fig. 7. In this case the main equilibrium reaction over a large temperature range is:



and other silicon chloride species become more important at higher temperatures. Interestingly, for this reaction the equilibrium pressures virtually do not vary for almost 1000°C. As a result, surface reaction and gas transport control should be easy to separate experimentally.

8 Summary

At high temperatures, ceramics (e.g. SiC in H₂O¹ and SiO₂ in H₂²) have been shown to corrode by gas diffusion control. In halogen-containing atmospheres such as HCl, most ceramics at sufficiently high temperatures will corrode by gas phase diffusion with the rate controlled by the ambient gas pressures and the thermodynamics of the reaction. Thus, the general corrosion behaviour for a specific ceramic can be predicted. Even for cases in which corrosion is incongruent, resulting in a residual porous product, the theory of gas diffusion can be used to quantitatively predict corrosion rates. Experiments are necessary to determine when specific ceramic materials corrode by gas phase diffusion and how well the model predicts rates and congruent or incongruent corrosion.

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