

Corrosion of Silicon-Based Ceramics in Combustion Environments

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Silicon-based ceramics and composites are prime candidates for heat engine and heat exchanger structural components. In such applications these materials are exposed to combustion gases and deposit-forming corrodents. In this paper combustion environments are defined for various applications. These environments lead to five main types of corrosive degradation: passive oxidation, deposit-induced corrosion, active oxidation, scale/substrate interactions, and scale volatility. Each of these is discussed in detail. The key issues in oxidation mechanisms of high-purity silicon carbide (SiC) and silicon nitride (Si_3N_4) in pure oxygen are discussed. The complicating factors due to the actual combustion environment and commercial materials are discussed. These discussions include secondary elements in the ceramics; additional oxidants, such as water and carbon dioxide (CO_2); combustion environment impurities; long-term oxidation effects; and thermal cycling. Active oxidation is expected in a limited number of combustion situations, and the active-to-passive transition is discussed. At high temperatures the limiting factors are scale melting, scale volatility, and scale/substrate interactions. Deposit-induced corrosion is discussed, primarily for sodium sulfate (Na_2SO_4), but also for vanadate and oxide-slag deposits as well. In applying ceramics in combustion environments it is essential to be aware of these corrosion routes and how they affect the performance of a component.

I. Introduction

MANY potential uses of silicon-based ceramics and composites involve exposure to combustion gases. These applications range from hot-section structural components of gas turbines and piston engines to heat exchanger tubes for industrial furnaces. Gas turbines are used in aircraft and electric power generation and have been tested for automobiles.¹ Potential ceramic components of these engines include combustor liners and, perhaps some day, turbine blades.^{2,3} The location of these components in a gas turbine engine is shown in Fig. 1(a). In piston engines the potential ceramic components include

valves and piston heads,⁴ as shown in Fig. 1(b). The use of ceramic tubes as heat exchangers has been proposed for industrial furnaces, such as glass remelt furnaces, steel soaking pits, and aluminum reclamation furnaces.⁵ An example is illustrated in Fig. 1(c). In addition, ceramics are under consideration for heat exchangers in coal-fired combustors.⁶ A more developed application is the use of ceramic tubes for indirect heating, where hot combustion gases pass through the tube, heating a process on the outside.⁷ The structural components of the hot sections are subject to a range of chemical attack processes, depending on the temperature, pressure, and chemical environment.

The focus of this paper is on the silicon-based ceramics silicon carbide (SiC) and silicon nitride (Si_3N_4). These materials are inherently unstable in air and form a thin layer of silicon dioxide (SiO_2) in an oxidizing environment. SiO_2 has the lowest permeability to oxygen of any of the common oxides and forms an effective reaction barrier.⁸ Therefore, silicon-based ceramics have the potential of substantially better high-temperature oxidation behavior than metals. The protective oxide scales on silicon, SiC, and Si_3N_4 are shown schematically in Fig. 2. Note that Si_3N_4 forms a silicon oxynitride ($\text{Si}_2\text{N}_2\text{O}$) layer below the SiO_2 layer.⁹ SiC may also form an oxycarbide layer, but there is only limited evidence for this.¹⁰ The analogous protective layers on superalloys for high-temperature applications are alumina (Al_2O_3) and chromia (Cr_2O_3).¹¹ Extensive work has been done on the performance of Al_2O_3 and Cr_2O_3 scales in combustion environments. In general, our knowledge of the behavior of SiO_2 scales lags behind that of Al_2O_3 and Cr_2O_3 .

The purpose of this paper is to review our current state of knowledge of the interaction of SiO_2 with combustion environments. Because the focus is on the interaction of SiO_2 with the environment, many of the conclusions apply to all SiO_2 -protected materials. This includes composites of SiC and Si_3N_4 , such as SiC-fiber-reinforced SiC matrices and SiC-fiber-reinforced Si_3N_4 matrices, and SiO_2 -forming alloys, such as molybdenum disilicide (MoSi_2). In this paper the major chemical degradation routes are discussed. Particular emphasis is on the mechanisms of corrosion and the key questions involving them.

II. Environments

Combustion environments vary widely, depending on fuel, temperature, pressure, and oxidizer. Fuels are complex mixtures of hydrocarbons, and they are classified by boiling points. Lower-boiling-point fuels include automotive gasoline, and higher-boiling-point fuels include aviation fuel and fuel oils.¹²

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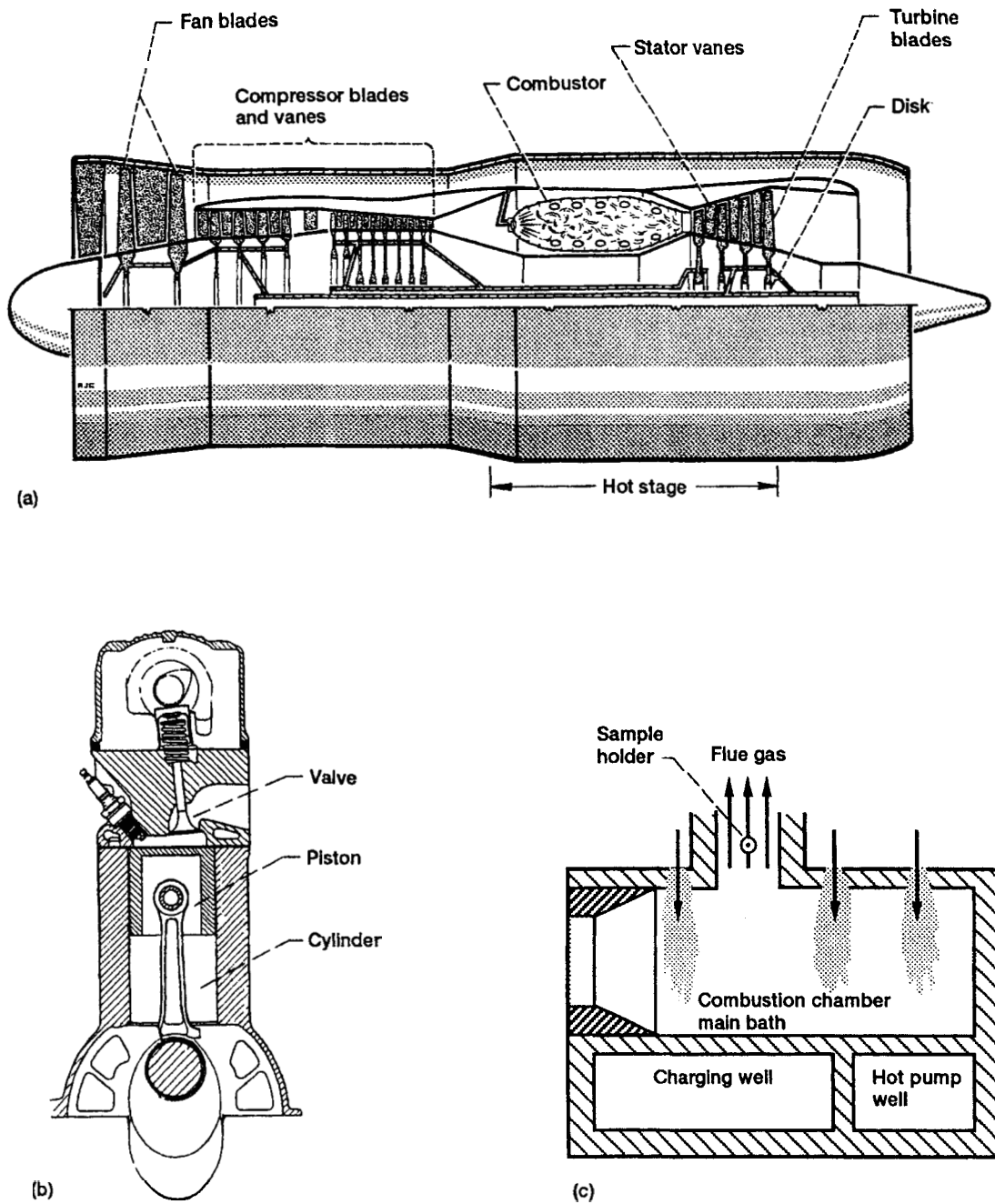


Fig. 1. Schematics of proposed applications for ceramics where ceramics will be subjected to combustion environments: (a) gas turbine engine, (b) piston engine, and (c) aluminum reclamation furnace (see Ref. 5).

Table I lists some common fuels and their approximate impurity contents.¹³⁻¹⁶ Note that all fuels have some amount of sulfur, which may lead to corrosion. The last category of fuel oils contains more sodium, potassium, and vanadium than the other fuels. These lower-purity fuels are likely to be utilized more in the future as petroleum resources decrease. Impurities have a major influence on corrosion. Table I does not include coal-derived fuels, which generally have even higher impurity levels.

Combustion is the oxidation of these fuels to the stable products carbon dioxide (CO_2) and water (H_2O). Equilibrium combustion products can be calculated by mixing the fuel and the oxidant together in a free-energy-minimization computer code.¹⁷ Figure 3(a) shows the equilibrium combustion products for a standard aviation fuel (Jet A— $\text{CH}_{1.0185}$) as a function of

equivalence ratio of 1 is stoichiometric, an equivalence ratio of less than 1 denotes a fuel-lean region, and an equivalence ratio greater than 1 denotes a fuel-rich region. Most gas turbines operate in the fuel-lean or stoichiometric regions. These regions contain large amounts of oxygen with the CO_2 and H_2O . Most corrosion studies have been performed in the fuel-lean region. However, some novel combustor designs may involve the fuel-rich region, which produces larger amounts of carbon monoxide (CO) and hydrogen gas (H_2). However, this region also contains the combustion products CO_2 and H_2O . Note that these are equilibrium calculations; if equilibrium is not attained, other species, such as elemental carbon, may form. The goal of a corrosion study is to understand the chemical reactions that occur between these combustion products and the proposed hot-gas-path structural materials.

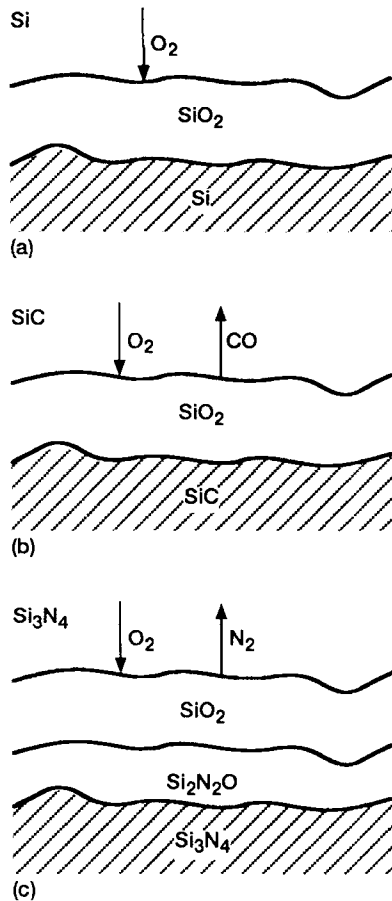


Fig. 2. Schematic of protective oxide scales: (a) on Si, (b) on SiC, and (c) on Si₃N₄.

the net heat loss equal to zero.¹⁷ This is an idealized case that assumes no heat loss through the walls of the combustion chamber. It does give the maximum temperature of the flame, however. In general, the wall materials and the components downstream from the flame are at lower temperatures.

Corrosion occurs not only by gaseous combustion products, but also by deposits. Perhaps the most common deposit is sodium sulfate (Na₂SO₄), which forms when sodium reacts with sulfur fuel impurities.¹⁸ The sodium may originate from a marine environment, from a salted roadway, or as a fuel impurity. Corrosion by Na₂SO₄ is termed "hot corrosion" and is discussed in detail herein. Other types of deposit-induced corrosion originate from vanadium fuel impurities and from oxide slags.

In some ways the piston chamber of an internal combustion engine is a more complex environment than the hot section of a gas turbine.¹⁹ Pressures and temperatures vary through the stroke of the piston. Adiabatic flame temperatures and combustion gas product compositions can be calculated by the same free-energy-minimization program described previously with propane (C₃H₈) as a model fuel. The results of this calculation are similar to those for Jet A aviation fuel. Current automotive engines run slightly fuel rich to allow proper operation of pollution control devices.

In addition to heat engines, silicon-based ceramics are also prime candidates for heat exchanger tubes in industrial furnaces. The environment encountered by a heat exchanger varies widely. Again, one would expect large amounts of CO₂ and

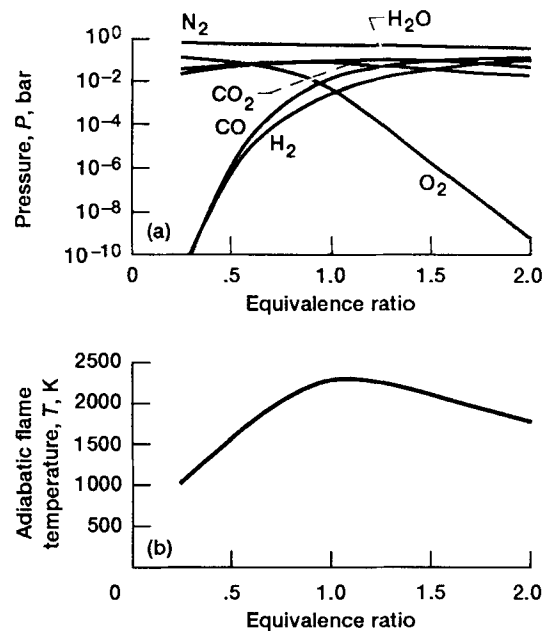


Fig. 3. Calculated gas composition and flame temperature as a function of equivalence ratio: (a) equilibrium gas composition and (b) adiabatic flame temperature.

H₂O, but now the impurities play a key role. An aluminum reclamation furnace and a glass remelt furnace may involve alkali-metal salts that can deposit on the heat exchanger.⁵ In a coal-fired furnace the atmosphere may be more reducing.⁶ In addition, a mixture of oxides may form a slag deposit, which can be quite corrosive, on the tubes.

Table II summarizes the composition of these combustion environments. This list is by no means exhaustive. As noted, specific applications generate specific corrodents. For example, combustion of municipal wastes may generate hydrogen chloride (HCl).²⁰ In summary, combustion environments are complex, involving not only the combustion products CO₂ and H₂O, but a variety of other gases and possible deposits as well.

Temperatures and pressures are again quite dependent on the particular system. The ranges are listed in Table II. An important issue to consider is thermal cycling. Some applications, such as a utility turbine or industrial furnace, involve essentially isothermal exposures for long periods. Other applications, such as an aircraft gas turbine, involve thermal cycling.

III. Types of Corrosive Attack and Experimental Techniques

Figure 4 shows the major types of corrosive attack as a function of pressure and reciprocal temperature. The major types of corrosive degradation are passive oxidation, deposit-induced corrosion, active oxidation, oxide/substrate interactions, and scale vaporization. The temperature boundaries between these types are only approximate and are dependent on the specific system. Furthermore, rarely is one mechanism operative. In practice, several mechanisms operate simultaneously.

Laboratory studies of corrosive degradation fall into two main categories: burner rig studies and laboratory furnace studies. Burners more accurately model the actual combustion situation. Figure 5 shows a typical high-velocity burner rig.

Table I. Properties of Some Common Hydrocarbon Fuels

Fuel	Boiling range (K)*	H:C molar ratio [†]	S content (wt%) [‡]	Na + K content (ppm) [§]	V content (ppm) [¶]
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Table II. Summary of Combustion Environments

Application	Temperature (K)	Pressure (bar) ¹	Gas atmosphere	Potential deposit
Heat engines				
Gas turbine	1173–1673	1–50	Fuel lean: N ₂ , O ₂ , CO ₂ , H ₂ O; fuel rich: N ₂ , CO ₂ , H ₂ O, CO, H ₂	Na ₂ SO ₄ , Na ₂ V ₄ O ₁₅
Piston	1273–1873 ²	1–10	N ₂ , CO ₂ , H ₂ O, O ₂	
Heat exchanger	1273–1873	~1	Oxidizing	Alkali halides, Na ₂ SO ₄ , transition-metal oxides
Coal combustion	1473–1673	1–10	Reducing	Acidic or basic coal slags

¹1 bar = 10⁵ Pa. ²Cycling.

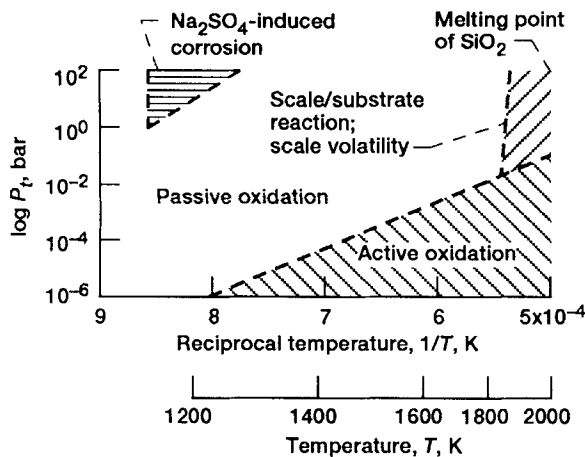


Fig. 4. Major types of corrosive attack and degradation as an approximate function of reciprocal temperature ($P_{\text{total}} = P_{\text{oxidant}}$).

However, burner rig tests are expensive, and it is difficult to precisely control all the operating parameters. Laboratory furnace tests offer much more accurate control of system parameters. Gas composition, pressure, and temperature can be accurately controlled. The extent of corrosion can be monitored by following the weight gain with a microbalance or by measuring scale thickness with various optical techniques. Figure 6 shows a standard laboratory microbalance apparatus for isothermal oxidation studies. Standard electron-optical techniques have been useful for characterizing corroded specimens. In general, burner rig tests are helpful for an overall assessment of behavior in the actual environment. Laboratory furnace tests complement burner rig tests by permitting isolation of individual effects so that they can be understood on a fundamental basis.

IV. Isothermal Oxidation

(1) General Considerations and Pure Silicon Oxidation

A large amount of research has been performed on the isothermal, passive oxidation of silicon-based ceramics. This research is complex because of the various secondary effects, such as other oxidants and impurities in the ceramics and the environment. These effects are noted in Fig. 7. Fundamental studies are at the center of the circle—pure materials and pure oxygen environments. Eliminating the complicating factors allows detailed studies of the basic oxidation mechanism. Actual combustion environments are more complex, involving the various factors on the outer circle in Fig. 7.

The focus of this section is on fundamental studies of SiC and Si₃N₄ oxidation. These studies provide an atomistic understanding of the mechanism of SiO₂ scale growth. These include determining the slow reaction step (or steps) and understanding the diffusion mechanism. Despite the large number of papers in

SiO₂ has some unique properties that influence its performance as a protective oxide. In most oxidation experiments, SiO₂ forms as an amorphous film and then crystallizes to either cristobalite or tridymite. This is significant because these phases have very different physical and chemical properties.²¹ It is generally accepted that the mobile species is oxygen, not silicon. For this reason the chemical reaction occurs at the SiO₂/Si or SiO₂/ceramic interface.^{22,23} Transport through SiO₂ can occur by diffusion of molecular oxygen as interstitials or by network exchange of ionic oxygen.^{24,25} The latter is referred to as either “network exchange diffusion” or “ionic diffusion” in this paper. Molecular oxygen diffusion coefficients are measured by examining permeation through a SiO₂ membrane;²⁶ network exchange diffusion coefficients are measured by an isotope exchange technique.^{27–29} Table III lists both types of diffusion coefficients. The molecular oxygen diffusion coefficient is roughly 10⁶ times greater than the ionic oxygen diffusion coefficient. There have been attempts to correlate these two types of diffusion coefficients;²⁴ however, Cawley³⁰ has reported the difficulties with such a correlation due to network/interstitial exchange and mobile network ions. These issues and the disparity of the diffusion coefficient measurements (Table III) indicate there are still some unresolved issues in these fundamental transport quantities.

Before discussing the oxidation of SiC and Si₃N₄, it is appropriate to discuss the oxidation of pure silicon. Because this process is critically important to the semiconductor industry, it has been extensively studied. The classic paper in this area is by Deal and Grove.³¹ They view oxidation as consisting of three distinct steps, as shown in Fig. 8. The three steps are transfer of the gaseous oxidant to the outer surface of the oxide film, diffusion through the oxide film, and reaction at the oxide/silicon interface. From these steps they derive the following linear-parabolic equation:

$$x^2 + Ax = B(t + \tau) \quad (1)$$

where x is the scale thickness, B the parabolic rate constant, t the time, and τ the time shift corresponding to the presence of an initial oxide layer. The quantity B/A is the linear rate constant. The parabolic rate constant is given by

$$B = 2D_{\text{eff}}C^*(\text{O}_2)/N_0 \quad (2)$$

where D_{eff} is the diffusion coefficient through the film, $C^*(\text{O}_2)$ is the equilibrium concentration of oxidant in the scale, N_0 the number of oxygen molecules incorporated into the SiO₂ scale per unit volume. Note that N_0 must be modified for SiC oxidation due to the formation of CO. For short oxidation times, oxidation follows a linear rate law. The physical interpretation of this linear region is still controversial; it has been attributed to interface control³¹ or to diffusion control which is nonparabolic due to strain effects in the oxide.³² For longer times, oxidation follows a parabolic law, and diffusion through the thicker oxide is rate controlling. An activation energy can be determined from a plot of $\ln B$ vs $1/T$. The magnitude of the activation energy can reveal useful information about the diffusion process. Deal and Grove³¹ report that care must be taken to inter-

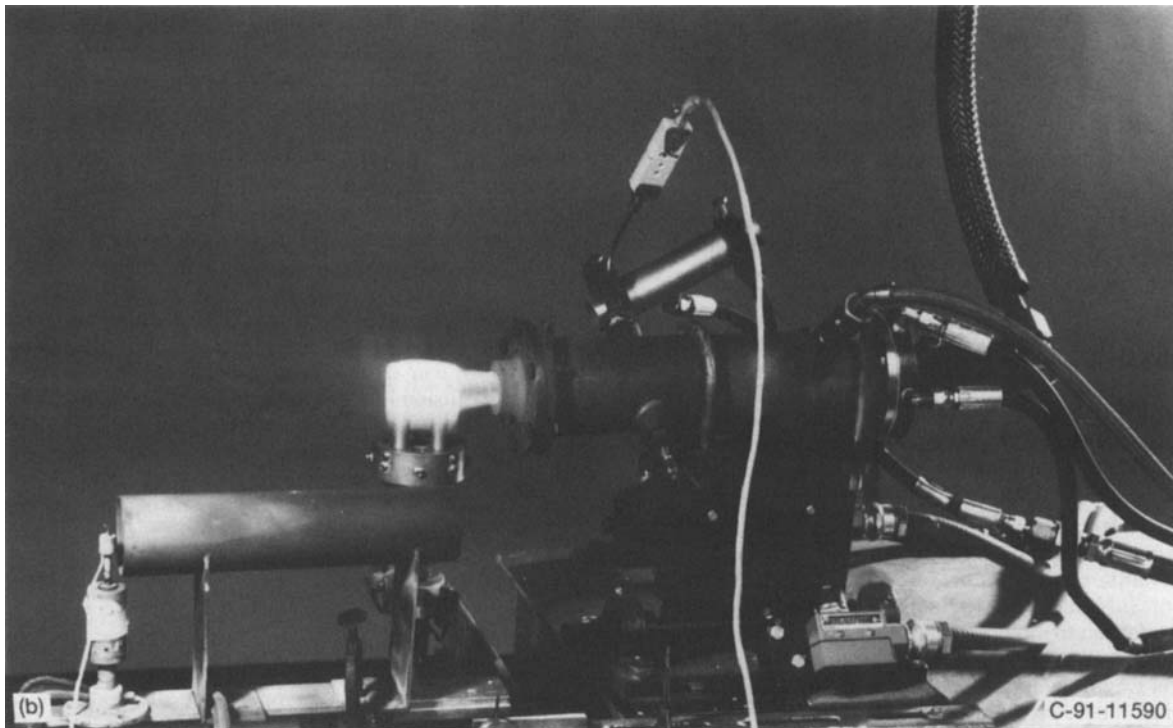
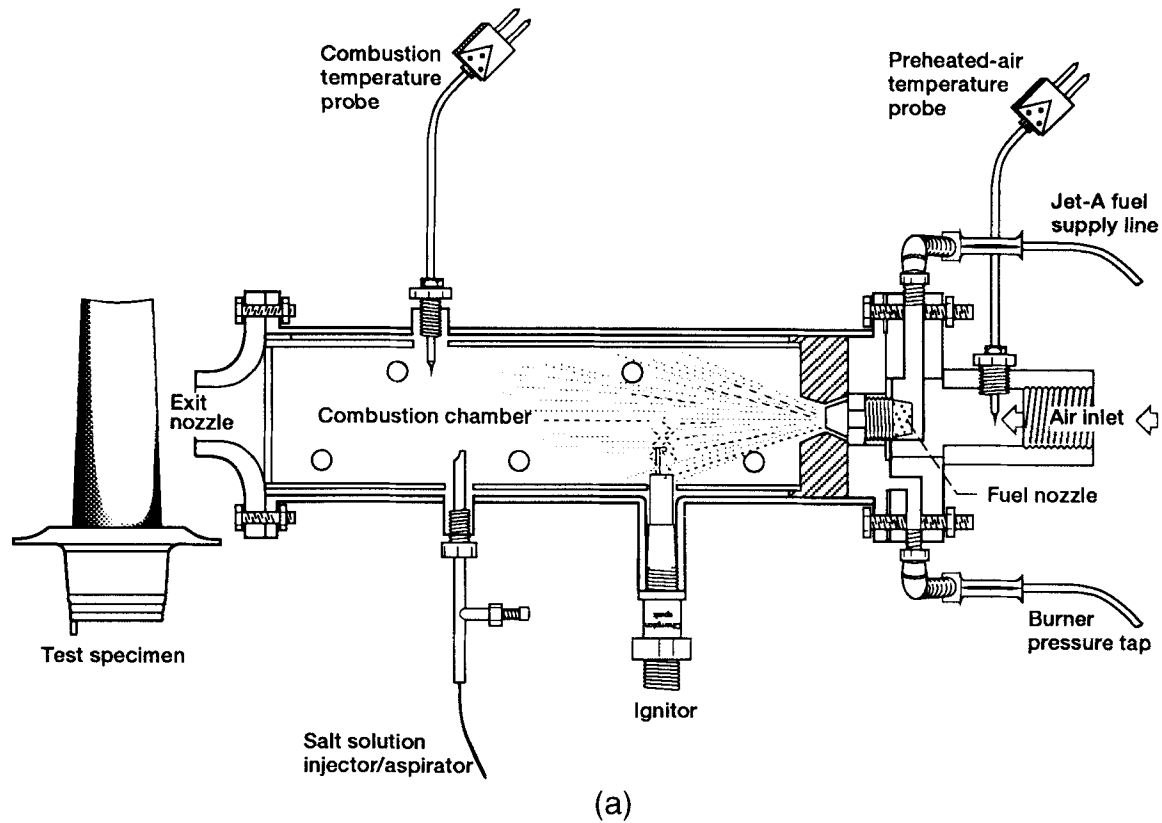
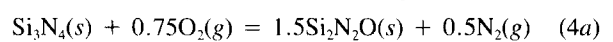
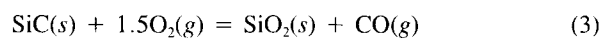


Fig. 5. Mach 0.3 burner rig. (Courtesy of M. Cuy, NASA Lewis.)

wide range of oxidation data. Calculations of the parabolic rate constant that are based on the molecular oxygen diffusion coefficient of Norton²⁶ show good agreement with the measured values, and the activation energy for parabolic oxidation is close to that for molecular oxygen diffusion through SiO_2 . Thus, it is generally accepted that molecular oxygen diffusion through the

there is a countercurrent of gas. The following reactions are generally accepted:



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