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High-Temperature Corrosion Resistance of Ceramic Materials

By T. A. Clancy

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CONTENTS

HIGH-TEMPERATURE CORROSION RESISTANCE OF CERAMIC MATERIALS

by

T. A. Clancy [1]

ABSTRACT

Since many new mineral processing systems under development can impose severe corrosive conditions on construction materials, the Bureau of Mines reviewed and assessed the literature on corrosion resistance of ceramic materials. Corrosive conditions were categorized as: (1) acids and aqueous solutions, (2) glass and slag/metal melts, and (3) gases. Information on the corrosion resistance of ceramic materials, generally, is disseminated by many sources, each of which is interested in specific corrosive environments. Based on this survey, it was noted that (1) the development of standardized tests is needed to study solution-type corrosion of ceramics, (2) slag/melt corrosion data are the most comprehensive of the available data, and (3) better definition of corrosion mechanisms in gaseous environments is needed.

INTRODUCTION

Part of the Bureau of Mines Mineral Resources Technology research program is aimed at solving ceramic materials problems associated with mineral processes that include corrosive environments. Operation at high temperature in corrosive environments is often required in order to achieve energy efficiency. In most cases research is done in small laboratory equipment that can be discarded after one or more experiments. However, when the scale of the research is increased to provide reliable engineering and economic data, inadequate materials performance can become a major problem. Materials are generally selected based on data for only one set of operating parameters or without adequate knowledge of material behavior under actual operating conditions. Changing parameters, as is often done when process scale-up is accomplished, results in new conditions where no data are available and material integrity is unknown. The Bureau's efforts in developing new extractive technology has shown that various ceramic materials are candidates for service in high-temperature corrosive environments. Ceramic materials often have higher corrosion resistance to certain chemicals than metallic compounds and have the possibility of replacing alloys containing critical elements such as chromium,

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nickel, or cobalt. It is advisable, therefore that data regarding the corrosion behavior of ceramic materials be available.

As part of its ceramics research, the Bureau's Tuscaloosa Research Center has reviewed literature sources to determine what information is available on corrosion of ceramic materials. Much of the information found relates to the use of refractory ceramics in more traditional areas such as steelmaking, and petrochemicals. This literature review and technical assessment includes information developed over many years in these traditional areas, as well as current information being generated in the development of new minerals processing technology. This report summarizes the findings of a review of 58 pertinent references, with 44 being cited in the text and the remainder included for supplemental information.

BACKGROUND

Van Vlack (42)[2] defines corrosion as the deterioration and loss of material due to chemical attack. The simplest form of corrosion is by means of chemical solution. Generalizations regarding chemical solution are—

1. Small molecular and ions dissolve most readily.

2. Solution occurs more readily when solvent and solute are structurally similar.

3. The presence of two solutes may produce greater solubility than only one.

The most common type of corrosion involves the electrochemical process of metal oxidation. All metals differ in their tendency to release electrons and form ions. The production of ions and electrons when a metal goes into solution builds up an electrode potential that depends on the nature of the metal and the nature of the solution. The particular potential is measured by determining the voltage difference between the metal and a standard hydrogen electrode. Measurements have been made for a whole series of metals, commonly called the electromotive series.

Electrochemical corrosion is less important in ceramic systems, because the complex nature of ceramic systems makes it difficult to define the conditions of electrode potentials and because oxide-type materials are also more thermodynamically stable. Only in the case of glass tank refractories has electrochemical corrosion been widely reported for ceramic systems (24).

Information on corrosion of ceramic materials is disseminated over sources that are principally interested in specific corrosive environments or operating conditions. Very few sources are available that compare corrosion resistances of ceramic materials. Campbell (6) compares resistances of 17 commercial refractories. Compared with most metals and alloys, ceramic

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[2]Underlined numbers in parentheses refer to the list of references at the end of this report.

materials are very corrosion-resistant, particularly when compared at high temperatures. This is true largely because oxidized, or combined, state of most metals, except the precious metals, is the thermodynamically stable state. It is possible to determine from the relative free energies of a metal and its oxide (or a material and its corroded state) whether or not the corrosion reaction is to proceed. A classic comparison is that both iron and aluminum will oxidize, but aluminum forms an adherent oxide layer that greatly impedes further reaction.

Standardized corrosion testing of ceramic materials, other than slag tests described later, has been established by the American Society for Testing and Materials (ASTM) for only three types of ceramic materials:

1. ASTM C225-54, Resistance of Glass Containers to Chemical Attack.

2. ASTM C279-54, Chemical-Resistant Masonry Units.

3. ASTM C301-78C, Vitrified Clay Pipe.

The test for glass containers involves placing bottles containing: (a) acid or (b) water in an autoclave at 121° C. The amount of attack is reported as the amount of: (a) acid consumed or (b) acid required to titrate the water solution. In cases where bottles are too small for testing, pieces of glass are autoclaved in water. The tests for masonry (fired brick) and clay pipe involve placing pieces of the material in acid (boiling temperature for the bricks) for 48 hours. The amount of corrosion attack is expressed as a percentage of weight loss by the sample.

Corrosion of ceramics has generally been categorized as to the corrosive environment of concern. Therefore, it is easiest to list three broad areas of corrosion as--

1. Aqueous solutions.

2. Glass and slag melts.

3. Gas atmospheres.

However, there is often an overlapping of environments, as in coal gasifiers and steelmaking processes that involve both slag/metal and gaseous conditions. The effects of these three types of corrosion on ceramic materials will be reviewed separately.

CORROSION BY AQUEOUS SOLUTIONS

Probably the simplest form of ceramic corrosion to understand is that by acids or aqueous solutions. The bulk of such corrosion work has been done with glass and enamels and, to a lesser extent, with acid-resistant brick or tile. Morey ([27]) has reviewed the basic nature of chemical attack of glass by water, acids, and alkaline solutions. He states that while water and acids attack only constituents other than silica, alkaline solutions and

hydrofluoric acid attack the silica. Water and other acids extract alkali oxides leaving a hydrated porous layer at the surface, which is mostly silica and through which further reactants must pass. Therefore, the rate of attack in water and all acids except HF will decrease with time. Alkaline solutions, in addition to attacking modifying oxides, also dissolve the high-silica porous layer. The depths to which this layer can extend depends on the relative solution rates of silica and the other oxides in the alkaline solution. When this condition becomes stabilized, the rate of attack tends to become constant. As in the case of other chemical reactions, the rate of attack increases rapidly with temperatures. In general, the increase is of the order of 2.5 times for each increase of 10° C.

Tests for glass corrosion have generally been of two types. In one case, glass is immersed in water or a corrosive solution, and the corrosion rate is measured in terms of the alkali constituents removed from the glass in a given time. In the other case, a piece of glass is exposed to a corrosive reagent for a definite time. The rate of reaction is measured in terms of the weight lost per unit of area exposed.

Because many commercial applications employ enameled metals for containers or similar shapes, the corrosion resistance of enamels is important. While glass shapes can be formed of high-silica (>90 pct SiO_2) and Pyrex-type[3] glasses that are resistant to water and acids, enamels contain more modifying oxides to permit fusing on metal surfaces. Cook and Andrews (8) evaluated the corrosion resistance of eight varied enamels to different concentrations of inorganic acids, alkalies, organic acids, and salt solutions at both room and boiling temperatures. All the enamels were resistant at room temperature to alkali and salt solutions. Acid-proof enamels were resistant to inorganic and organic acids at room or boiling temperatures. All enamels showed low resistance to boiling alkali solutions, and some were marked by boiling salt solutions.

Priest (31) determined the corrosion resistance of glassed steel, which is, (1) applied in greater thicknesses than enamels, (2) more resistant to mechanical damage at thicknesses of 40 to 80 mils, and (3) fired at higher temperatures than enamels. The glassed steel's corrosion resistance to hot acids, hot water, steam, or alkali solutions at moderate temperatures was an order of magnitude greater than that of enamels. He concluded that all acids except HF and H_3PO_4 can be handled in glassed steel up to 150° C and often higher. Resistance to alkalies is lower, but solutions to pH of 12 at 100° C can be handled. Concentrated alkali may be used in glassed steel below 40° C. Corrosion resistance to pure water is limited at temperatures above 95° C.

Nordberg (28) has rated a number of commercial glasses (Corning Glass types) as to resistance to water acid solutions, and alkaline solutions. These ratings are shown in table 1.

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[3]Reference to trade names is made for identification only and does not imply endorsement by the Bureau of Mines.

TABLE 1. – <u>Resistance of glasses to attack by acids and alkali</u>

Designation	Weight loss, mg/cm^2	
	24 hr, 5 pct HCl, 100° C	6 hr, 5 pct NaOH, 100° C
96 percent silica..............	0.0004	0.9
Borosilicate-chemical.........	.005	1.4
Soda lime-bulb.................	.01	1.1
Lead glass-electrical.........	.02	1.6
Borosilicate-tungsten sealing.	Leached	3.9
High lead.....................	Disintegrated	3.6
Aluminosilicate...............	.35	.35
Alkali-resistant..............	.01	.09

Rauch (32) evaluated the resistance of glass-ceramic materials, considered for use in gas turbine heat exchangers, to both sulfuric acid and sodium. Acid resistance was evaluated by immersing samples in concentrated H_2SO_4 at 300° C for 2 hours, followed by heat exposure for 2 hours at 320° C, reimmersion in hot acid, heat exposure for 2 hours at 650° C, reimmersion in hot acid, and heat exposure for 2 hours at 1,000° C. Therefore, each sample received a total immersion time of 6 hours in hot acid. Sodium resistance was evaluated by placing samples in a 100 cm^3 platinum crucible, covering the sample with dry sea salt powder, and placing the crucible in a furnace heated to 750° C. As the salt melted, more was added to maintain the liquid level above the sample during the 2 hour test. The percentage of weight change was determined for each material after these exposures. The acid corrosion resulted in weight losses for the glass-ceramic materials to various degrees, with a cordierite base type showing the least loss. The salt corrosion resulted in weight gains in all the materials except one.

Honeycomb shapes of the heat exchanger candidate materials were exposed to 1.0 percent H_2SO_4 followed by three heat cycles at 300° C and were then immersed in boiling NaCl solution followed by heat soaking at 800° C for 3 weeks. Since the heat exchanger requires low expansion materials, change in length of the shapes was determined after the acid-heating cycles and during the boiling NaCl solution exposure. These results indicated that a glass-ceramic containing a mixture of petalite and cordierite materials retained the lowest thermal expansion.

Cooke (9) determined the chemical durability of eight lead borosilicate glasses containing 60 or 65 mole-percent SiO_2. The compositions were chosen so as to include glasses lying both inside and outside the region in which liquid-liquid immiscibility occurs. Durability measurements were carried out on granular samples of both heat-treated and quenched glasses using solutions of various pH values for 4 hours at 70° C.

It was found that, besides chemical composition, microstructure had an effect on durability. In phase-separated glasses, the durability is determined by the location of the less durable phase. If it is contained as droplets within a stable place, durability will be high. In other cases, durability is low. The addition of Li_2O to some glasses eliminated phase

separation and increased durability. Data are also presented showing that extraction of SiO_2 increases as pH increases, particularly around pH 12, and that lead and silica extraction increase greatly as the B_2O_3 content of the glass increases.

The thermodynamic stability and effect of pH of the solution on durability of glasses are discussed. The very limited solubility of silica in water is one of the main factors in the corrosion resistance of silicate glasses. Silica reacts with water to form H_2SiO_3, and the thermodynamic stability of SiO_2 in water at 25° C is characterized by an activity versus pH plot. This curve can be divided into three sections: one at pH 7 to 10, where solution of H_2SiO_3 occurs; one at pH 10 to 12, where solution is due to formation of $HSiO_3^-$; and a third at pH 12 or over, where solution is by formation of SiO_3^{-2}.

The effect of pH on solution of lithium silicate glasses is then illustrated. Unlike pure silica, in the case of lithium silicate glass, the activity of H_2SiO_3 (glass) or the extent of ion exchange between the silicate and water will depend on the activity of lithium ions in the solution. If lithium ions are allowed to build up in the solution, almost a complete removal of lithium silicate glass is possible even up to pH 14. Since the H_2SiO_3 (glass) becomes ionized and will dissolve above pH 9 or 10, lithium silicate glasses are not durable in water. This is also the case with other alkali (potassium, sodium) silicate glasses.

Similar aqueous reactions are presented for PbO and B_2O_3 in aqueous solutions. Stability versus pH for PbO shows lead dissolves as Pb^{+2} and PbOH in the acidic range, and the Pb^{+2} has much higher activity. While in the alkaline range lead forms $HPbO_2$, and the activity of $HPbO_2$ is greater than that of Pb $(OH)_2$ only at pH above 14. Thus PbO in a glass will increase alkaline durability but decrease acid durability. Boron trioxide forms orthoboric acid in aqueous solutions, which then ionizes in various ways depending on solution concentration and pH. Stability diagrams for B_2O_3 indicate that the stability is much less than that for SiO_2. Normal substitution of B_2O_3 for SiO_2 in single-phase oxide glasses will cause the durability in water to deteriorate. However, glasses containing boron can be produced having good durability by controlling the phase-separated microstructures, as in the case of Pyrex-type glasses.

While the general behavior of common glasses in corrosive solution environments has been investigated fairly thoroughly, this is not true for other ceramic products even though many are used in chemical construction applications. Very limited quantitative data on the behavior of such materials under corrosive solution conditions are available. Robbins (33) has reviewed the use of concretes, cements, acid-proof brick, porcelain, and stoneware under corrosive solution conditions. All these materials are generally more resistant to acid solutions than to basic ones.

Portland cement concretes are readily attacked by weak acids and even by many organic compounds. Alumina concretes are more chemically resistant than

Portland cement concretes and will resist solutions at a pH above 4 or 5. Silicate cements are resistant to many acids, but not to alkaline conditions.

Porcelain and stoneware are very similar in chemical resistance properties. Porcelain is usually made from higher purity material and can usually withstand more severe conditions. These products withstand acids very well, with the exception of hydrofluoric acid. At high temperatures, concentrated phosphoric and sulfuric acids attack porcelain or stoneware. Steam will also cause degradation of these materials. Robbins (33) presents a table comparing the resistance of porcelain and stoneware to 14 different chemicals, but provides no information on the effect of increased temperatures.

Acid-proof brick or tile are characterized by high silica contents and low porosities. They will resist most acids, except hydrofluoric, and are reasonably resistant to bases. While the brick are impervious to solutions, the mortars necessary to join them together are not and can provide a path for penetration.

A review of literature on corrosion by solutions has indicated that nearly all the data available are limited to glass materials. The corrosion data available on other industrial ceramic products are very limited and primarily based upon supplier information which is often not oriented towards the specific conditions of interest. This lack of definitive data may partly be a result of the wide variation in industrial products and applications involved. Therefore, in order to properly compare the chemical resistance of these ceramic materials, standardized descriptions of material classes are required. Also, standardized testing, similar to that used for glass materials, is required.

New mineral processing techniques being investigated such as hot acid or base leaching, chloride leaching, and fused salt baths may require the use of ceramic materials that have superior corrosion resistance. Therefore, engineering data on the corrosion resistance of candidate materials to such corrodents are necessary. These data could be collected in a manner that would provide rates of attack, as is done with corrosion attack data for metals.

CORROSION BY GLASS AND SLAG MELTS

The majority of work on corrosion of ceramic materials has been directed toward corrosion by melts of glasses, slags, and metals. The basic principles of dissolution of ceramic materials by such melts have been covered by Cooper and Kingery (10). They have shown that the rate of dissolution can be controlled by three types of reaction mechanisms. For stationary specimens, the rate of dissolution can be controlled by molecular diffusion; that is, diffusion in the absence of fluid flow. This mechanism is common for ceramic systems, and the rate is dependent on diffusion of solute through a stagnant boundary layer at the specimen surface. Also for a stationary specimen, dissolution by free convection can be the controlling mechanism. This convection is dependent on the rate of bringing fresh slag to the specimen. In the case of forced convection, the dissolution is controlled by the rate of transport in the solution and depends on the velocity of the forced

convection. In the first case, the dissolution rate is proportional to the square root of time, while in the other cases the rate is directly proportional to time. Cooper and Kingery found that for dissolution of sapphire in $CaO-Al_2O_3-SiO_2$ slag, the corrosion rate was dependent on transport in the melt.

McGee (26) has reviewed slag tests for refractories and discusses three types: (1) reaction test, (2) static slag test, and (3) dynamic slag test. The first consists merely of heating a slag in contact with a refractory for a given time and observing the amount of reaction. This test is good for certain applications, particularly as a screening method. The second type is usually a cup or a pencil test. A cup test involves drilling a hole in a brick, filling it with slag, heating it for a given time, sectioning the brick after cooling, and observing the reaction. Pencil tests are conducted by inserting a long, narrow specimen into a slag contained in an inert crucible. ASTM procedure C-621 describes a method for glass tank refractories. Some disadvantages do exist with static tests. If the quantity of slag is small, its composition may change during testing. In the case of small crucibles, convection current effects can be overlooked. Dynamic slag tests are intended to reproduce conditions of an actual process. Typical dynamic slag tests are ASTM procedures C-768 and C-622. The first is a drip slag test in which a known weight of a slag is dripped onto a refractory specimen. In the second, a refractory tank of the test specimens containing a known glass composition is heated for 96 hours at a glass-melting temperature of 1,230° to 1,565° C, then drained of its contents; the depth and volume of corrosion are then measured at the metal line. Such tests are useful when they simulate actual corrosion. In the case of the drip slag test, the velocity of the slag is not well defined, and the results may or may not be in the appropriate regime of mass transport. It is obviously difficult to simulate intermittent processes that have different slag attack mechanisms at different parts of the process. McGee cautions that deliberately making a slag test too severe by producing results in a shorter time may lead to the wrong results. He concluded that it is usually better to increase the flow rate of the slag than to alter the composition or increase its temperature.

The Bureau of Mines' Tuscaloosa Research Center has conducted various dynamic slag corrosion studies using a rotary chamber lined with refractories. Slag melts have included glass wool, steel slag, and coal ash-slag compositions. The refractories are exposed to flowing slag at a desired temperature for periods of 5 to 8 hours. The chamber is heated with an oxygen-propane torch and slag material is fed continuously as the chamber rotates horizontally. Eroded area for each refractory is determined at the conclusion of the run. An application of this test is described by Pahlman (29).

One of the most severe corrosion environments exists in the basic oxygen furnace (BOF) steelmaking process. Kappmeyer and Hubble (17) have presented a review of the slag corrosion effects in this environment. Refractories used in this process are exposed to temperatures up to 1,650° C in contact with liquid steel and fluxing slags—chiefly lime, fluorspar, and mill scale—plus an atmosphere created by the reaction of carbon from the metal with oxygen injected through a lance. They present data indicating that the CO/CO_2 ratio

varies through the vessel and the basicity (CaO/SiO_2 ratio) varies as the temperature increases during the heat. The refractories predominantly used in the BOF vessel are carbon-containing MgO-based types, either pitch-bonded or fired, pitch-impregnated ones. Slag erosion tests are conducted to compare these refractories and to determine what refractory properties are most important. Standard bricks compose the sidewalls of a laboratory furnace in which oxygen is blown onto molten pig iron containing additions of slag formers. Following the heating, the degree of erosion is measured and a slag erosion value is determined. Testing has shown that low erosion levels for specimens are consistent with higher MgO contents, higher hot strengths, higher bulk densities, and higher residual carbon contents. It is generally believed that the carbon inhibits deep slag penetration and thus lowers erosion levels. Thus, a careful balance must be drawn to obtain the best slag erosion resistance through maximum brick density and, at the same time, the maximum amount of residual carbon within the minor pore volume.

One of the most complete discussions on corrosion of glass tank refractories is by Litvakovskii (24). Besides considering the standard effects of diffusion and dissolution of refractories, he discusses the effects of electrochemical corrosion. With regard to chemical reactions, it is noted that dissolution may occur with or without preliminary chemical reactions occurring within the refractory. Generally, the corrosion rate is not limited by a chemical reaction, but by the rate of diffusion between the reactants. One factor greatly affecting this diffusion rate is the thickness of the melt contact layer with the refractory. The thicker this contact layer, the slower is the corrosion. The rate of formation and duration of maintenance of the contact layer are the most important factors for the corrosion resistance of materials. This is analogous to situations with metals where strength and durability of the oxide film on the metal are the most important conditions of resistance to corrosion.

Litvakovskii mentions several cases that substantiate the electrochemical effect on corrosion. Investigations have shown that a certain difference of potentials exists at high temperatures between the glass mass and the refractory oxides. These potentials are due to the contact between electrolytes of different concentration and different temperatures, as well as to the different oxidizing and reducing characteristics of the contacting substances. These potentials can establish anodic and cathodic conditions between a refractory and a glass melt and, as in metals, if the refractory is anodic, it is the material that will corrode. This electrochemical effect is used to explain the case of melting sheet glass in which the refractory is cathodic and only dissolves at the melt line where anodic portions can form. Conversely, in melting borosilicate glass, the whole refractory surface is anodic and dissolves intensively, but more uniformly. Data are given for electrode potentials based on measurements made using a Pt-oxide-sheet glass-Pt cell at 1,100° C. A curve is given showing that, with an increase in potential difference between glass and refractory, corrosion is intensified. The conclusion is made that a refractory and glass should be matched so that the potential difference between them should be positive and have a minimum value.

Kennedy and Peoppel (18) exposed about 50 commercial refractories to a variety of acidic coal ash slags similar to slags expected in coal gasifiers. Such slags consist mainly of SiO_2, CaO, Fe_2O_3, Al_2O_3, MgO, and alkalies. The eutectic temperatures for these slags are low, and the prospect of finding a refractory that will last for years is dim. It may, in fact, be necessary to utilize water cooling as has been done with blast furnace linings. Therefore, slag corrosion tests were run both with and without water cooling. The three most predominant components of the slags used were SiO_2, CaO, and Al_2O_3, creating base/acid ratios of between 0.5 and 0.8. The refractory samples were arranged around the circumference of the furnace shell to form a ring, into which up to 75 kg of slag was charged. While the furnace was not rotated, some rotary action was induced by the three burner flames, which were fired tangential to the furnace circumference.

In the first three runs, no water cooling was used and the furnace temperature was held at 1,450° to 1,500° C for 200 hours. The most corrosion-resistant sample was a fused-cast chrome-spinel refractory, which showed almost no penetration. A fused-cast alumina and a sintered chrome-alumina refractory also showed good resistance.

Subsequent runs were made using water cooling to produce thermal gradients through the walls of the furnace. Water temperatures were monitored so that heat flux could be calculated. The fourth test run included: (1) nitride bonded SiC, (2) silicate bonded SiC, (3) oxynitride bonded SiC, and (4) a silicon oxynitride product. The temperature was held at 1,410° to 1,450° for 500 hours. All the silicon carbide bricks showed little attack, contrary to a previous run without water cooling. The silicon oxynitride product was much less resistant than the silicon carbide types.

The fifth test run included four direct-bonded basic brick of a nominal 60 pct MgO content, with the temperature held at about 1,500° C for 500 hours. The four brick exhibited similar resistance to corrosion. The sixth test run evaluated three fused-cast and one sintered product. The fused-cast products showed better resistance, but developed thermal shock cracks. The seventh test run exposed alumina-chrome and alumina-silica products. A chemically bonded alumina-silica type corroded badly, but a chemically bonded alumina-chrome type did not.

In conclusion, a fused cast chrome-spinel refractory exhibited superior corrosion resistance, while alumina, alumina-chrome, and magnesia-chrome types formed spinel reaction layers at the slag interface. Increased chromia content resulted in increased resistance. Silicon carbide products showed good corrosion resistance when water cooled, but gaseous corrosion problems remained unresolved.

Kim (19) investigated the attack of a 95 pct MgO fired refractory in contact with Al_2O_3-containing slags. A master slag of composition 46 CaO · 30 SiO_2 · 17 FeO · 7 MnO was used as a reference. Cylindrical rods 4-1/4 inches long by 3/4-inch diameter were cut from the refractory and suspended into the slag, contained in a platinum crucible at a furnace temperature of 1,600° C. The slags used could be divided into four categories; that is, the master

slag, the master slag plus MgO, the master slag plus Al_2O_3, and the master slag plus MgO plus Al_2O_3. Two slag immersion times were used, 30 seconds and 5 minutes. Following immersion, the samples were raised from the furnace and sectioned for petrographic examination.

The results of the slag tests may be summarized as follows. The Al_2O_3-containing slags produced the greatest amount of attack. No specimen survived for 5 minutes in slags containing 10 pct or more Al_2O_3. For Al_2O_3-containing slags, the addition of MgO in small amounts did not reduce attack. However, with the addition of 13 pct and 15 pct MgO to these slags, the attack was reduced. A specimen immersed in a low-basicity slag (C/S = 1.0) necked to failure in 5 minutes, while a specimen immersed in the master slag (C/S = 1.5) survived 100 minutes before failing. Both this low basicity slag and slags with high contents of Al_2O_3, demonstrated strong tendencies to penetrate and climb above the slag line in the specimens. The mechanisms of slag attack on the magnesite by Al_2O_3-containing slags is by disruption of the silicate matrix rather than by dissolution of MgO grains. Increased Al_2O_3 contents resulted in greater attack because of the formation of highly fluid Ca-Al silicates. The low-basicity slag was also detrimental to the magnesite refractory, but the higher viscosities of the reaction products and their localized nature cause less disruption than do the Al_2O_3-containing slags.

In another paper, Kim [20] investigated the formation of a dense MgO layer on carbon-containing magnesite-slag interfaces. There have been three mechanisms suggested for the improved slag resistance by carbon-containing magnesites: (1) a decreased slag penetration resulting from an increase of wetting angle between the brick and slag; (2) the generation of internal brick gases and pressure buildup retarding slag penetration; and (3) the carbon reduction of MgO and subsequent oxidation of magnesium at the hot face to produce a dense impervious layer of MgO. Slags of C/S ratios of 1.0, 1.5, and 2.0, and containing the FeO, MnO, Al_2O_3, and MgO components, were melted in crucibles cut from a 95 pct MgO, pitch-impregnated brick. The crucibles contained 50 grams of the slag and were held at 1,600° C for 2 hours in an air atmosphere. After this exposure, the crucibles were sectioned for petrographic examination. Also, microprobe analysis scans were made across the slag-refractory interface.

The following is a summary of the test results. A dense MgO layer does form on the refractory hot face and is effective in reducing slag penetration. This dense layer is not able to form, however, in iron oxide-free slags. The slag should have a high CaO/SiO_2 ratio or should contain MgO if the layer is to survive. The thickness of the layer observed increases as the CaO/SiO_2 ratio and MgO content of the slag increase.

Alumina was used as in the slag as a tracer, and the silicates behind the dense MgO were found to be native to the brick since they contain no detectable Al_2O_3. A mechanism of intermittent destruction and reconstruction of the dense MgO layer is suggested based on slag penetration, magnesium vapor oxidation, MgO dissolution, and rebuilding of the layer at the resultant limit of renewed slag penetration.

Binns (4) reviewed the use of special ceramics in handling molten iron and steel. The nature of the steelmaking environment is described, and those ceramic materials that are widely used in steelmaking are discussed. The properties such as wettability, atmospheric stability, and mineralogy, which make these materials useful for containing molten iron and steel, are described. The factors that tend to impair the performance of, or lead to the deterioration of, these materials are listed as--

1. Reactions with constituents of molten steel.

2. Reaction with oxidation products of steel and with steelmaking slags.

3. Attack by hot reducing or oxidizing gases at atmospheric or low pressures.

4. Damage by steady state or transient thermal stresses.

5. Excessive heat conduction, leading to freezing.

The physical and chemical properties of commercially available oxides and several mixed oxides are presented. The materials included were Al_2O_3, BeO, MgO, CaO, ZrO_2, Cr_2O_3, CeO_2, ThO_2, HfO_2, $MgO \cdot Al_2O_3$, $ZrO_2 \cdot SiO_2$, and $CaO \cdot ZrO_2$. These materials are compared in terms of stability in steelmaking conditions and in contact with molten iron and steel. At present, MgO and ZrO_2 offer the best combinations of properties, although the zirconates may offer some potential.

Properties of nonoxide materials are presented in a manner similar to that for the oxides. The materials included were carbides, borides, nitrides, silicides, and sulfides. The only nonoxides considered to be truly commercially available for large-scale usage are silicon carbide, silicon nitride, and zirconium diboride. The usefulness of SiC and Si_3N_4 is strongly dependent on the particular bonding phase employed as well as the fabrication techniques. The ZrB_2 material usually exists as a mixture with SiC or graphite, which tends to increase oxidation and thermal shock resistance.

Bates (3) reviews the requirements for materials to be used in MHD generators. The corrosion problems in these units are great and are due primarily to coal ash slag and potassium seed liquid, which provides a current flow. Temperatures will range from 600° to 1,800° C, and the added problem of erosion compounds the problem. The slag and seed can react with MHD refractories by direct chemical reaction with vapor or liquid, penetration of vapor or liquid into pores or cracks, or diffusion of elements from the slag or seed. Corrosion by liquid K_2SO_4 seed appears to be more severe than that by vapor phase K_2SO_4. Porosity, as has been mentioned by others, has a profound effect on the corrosion rate. Data are presented indicating that at near zero porosity, corrosion rates for MgO and Al_2O_3 are about 1 cm/year. The logarithm of the corrosion rate increases linearly with porosity. Impurities are known to enhance corrosion rates. The attack on commercial oxide refractories, which occurs at grain boundary-located impurity phases, is greater than for high-purity materials.

A description of two coal slags is given. One type (Montana) is basic, while another (Pennsylvania) is acidic. This wide difference in acidity will undoubtedly require the use of different refractories. Seed material can also be absorbed into the slag (up to about 30 pct), which can alter the corrosiveness of the slag. Also, iron can readily diffuse from the slag into alumina or magnesia refractories. The consequence of this penetration under MHD conditions has not yet been determined. Although emphasis on MHD refractories has been placed on Al_2O_3 and MgO, other oxides such as ZrO_2, BeO, and ThO_2 have shown good resistance to potassium seed slags.

Zborowska (44) investigated the corrosion resistance of dense strontium zirconate ($SrZrO_3$) material in contact with Al_2O_3, CaO, MgO, SiO_2, and K_2CO_3, as well as coal ash. The zirconate material is a candidate for use in MHD generators and would be exposed to coal ash slags. Strontium zirconate has a melting point of about 2,900° C and has good corrosion resistance against alkalies.

Synthesis of $SrZrO_3$ was carried out by prefiring pellets of $SrCO_3$ and ZrO_2 powders, grinding the product, adding a polyvinyl alcohol binder and die pressing crucibles. The corrosion tests were carried out by placing approximately 1 gram of the substances in crucibles and exposing the crucibles to 1,700° C in a gas furnace for 2 hours. After cooling, the crucibles were examined microscopically and by X-ray microanalysis.

No trace of corrosion effects was seen for crucibles containing Al_2O_3, CaO, or MgO. Considerable corrosion occurred when SiO_2 was used. A reaction layer was formed that was rich in zirconium and silicon. The coal ash corrosion produced a similar effect, but produced a reaction layer of only about one-half the thickness of that by SiO_2 corrosion.

Pahlman (29) evaluated the stability of alumina-base refractories in Western lignite ash slag environments. The refractories tested were (1) high-alumina types (50 to 99 pct Al_2O_3), (2) fire clays, (3) high-alumina castables (93 to 95 pct Al_2O_3), (4) regular castables (60 to 70 pct Al_2O_3), and (5) a high-alumina plastic type. Both static and dynamic slag tests were conducted. The lignite ashes used for slag testing were a high-alkali type and a low-alkali type. Besides the chemical components of SiO_2, CaO, Al_2O_3, MgO, Fe_2O_3, and SO_3, the high-alkali type contained 9.3 pct alkali ($Na_2O + K_2O$), and the low-alkali type contained only 1.4 pct alkali.

Static slag tests were run by immersing bars of each refractory in the ash and heating at 1,300° C for 4 hours in an alumina crucible. The reduction in cross-sectional area was determined for each refractory. The degree of corrosion attack by these static tests could be related closely to the phase composition present. Alumina refractories composed of mostly mullite, some α-Al_2O_3, and no cristobalite performed better than refractories of similar alumina content but containing α-Al_2O_3, mullite, and cristobalite. The presence of cristobalite, as a result of sintering that did not permit sufficient mullite formation, resulted in excessive expansion due to formation of alkali silicates. Tests conducted in which cristobalite-containing samples were exposed only to alkali vapors indicated that vapor-phase reaction is

sufficient to cause corrosion effects. Chemically bonded high-alumina samples did not perform as well as did sintered ones.

Dynamic slag tests were run by placing cut refractory specimens around the perimeter of a steel drum. The drum was rotated at about 6 rpm, and the interior faces of the specimens were heated with a propane-oxygen torch at 1,400° C. Ash pellets were fed into the exit end of the drum once temperature equilibrium had been reached. Ash pellets (100 grams each) were fed into the drums every 10 minutes for the duration of an 8-hour run. At the end of the run, the slag pool was poured out of the drum, and the average area change for each specimen was determined. In general, the dynamic corrosion resistance increased with increasing Al_2O_3 content. However, one fused-cast type of only 92 pct Al_2O_3 performed as well as the 99 pct Al_2O_3 types. Bloating of specimens in the dynamic tests did not occur, as had been seen in the static tests. This is likely due to alkali vapors not being able to penetrate the rotating slag layer and the containment of cristobalite-alkali reactions at the slag interface. The dynamic tests indicated that tar-impregnated refractories performed much better than conventional sintered ones of similar chemistry and mineral phase composition. However, it was not clear whether chemical bonding enhanced corrosion resistance of these alumina refractories. In general, corrosion resistance for monolithic refractories was lower than for sintered ones of similar chemistry. It is recommended that, for use in alkali slag and alkali vapor environments, refractories of 90 to 99 pct Al_2O_3 be used.

One refractory application area that is exposed to considerable alkali slag attack is the regenerator checkers of a glass tank furnace. These brick are exposed to the action of alkaline dust carried over from the raw batch and, while checker temperatures are not as high as tank temperatures, checkers may reach 1,370° C. Basic refractories have largely replaced fireclay and high-alumina refractories, especially in the hotter section of the checkers. Many of the studies of effects of alkali on these refractories have been post-service examinations of checkers. Van Dreser and Cook (41) examined three types of used checker refractories--(1) periclase or magnesite, (2) forster-ite, and (3) chrome-magnesite--after 2 years of service. The conclusions reached were that (1) the periclase and magnesite materials exhibited some growth and recrystallization at the hot face, but were still serviceable; (2) grain growth and volume changes in the spinel grains of the forsterite refractory caused a general cracking and friable condition; and (3) the chrome-magnesite exhibited the most carryover penetration, resulting in numerous voids and disintegration.

Steinhoff (38) developed a testing method to determine the degree of corrosion of refractories by alkalies. A cylindrical test sample with a hole drilled in the axis is exposed to corrosion by alkali vapors evolved in the hole from a mix of fine fireclay plus Na_2CO_3, Na_2SO_4, Na_2S, $Na_2B_4O_7$, or mixes of these salts. Magnesite brick showed a minimum of penetration, and no reaction melts were observed. Fireclay refractories are easily covered in the alkali vapors with a glaze that acts as a protecting layer against penetration by alkalies. Sillimanite-type refractories scale under the influence of

penetration by alkali vapors. For checker brick with a service temperature of 1,200° C, ordinary firebrick may be satisfactory, but for higher temperatures, magnesite is necessary.

Schulte (36) describes the corrosion of magnesite refractories in checkers operating in the range 700° to 1,000° C. Chemical changes in composition of brick zones are noticeable, and CaO and MgO are markedly removed by diffusion, or possibly by vaporization. The cross section of the brick is decreased, but usually no loosening of the structure or disintegration is observed. Experiments are described for reproduction of corrosion of magnesite by sulfates and SO_3, but no clear corrosion effects were observed by the action of a gas atmosphere containing SO_3 or in a Na_2SO_4 melt. This is explained by the short reaction time and absence of periodic formation and decomposition reactions that occur in actual checker conditions.

Touhig (40) has evaluated various ceramic materials as components for lithium-sulfide batteries. The materials would be in contact with molten lithium alloys at temperatures of between 375° and 425° C. Free energies of reaction for several technical ceramics indicate that Al_2O_3 and ZrO_2 are unstable with lithium, but no reaction is anticipated with AlN, BeO, MgO, Si_3N_4, Y_2O_3, and BN. Impurities contained in these materials may, however, cause some reaction to occur.

Screening tests on the above materials, consisting of exposure to molten lithium at 400° C, indicated that the most promising candidate materials were Y_2O_3, MgO, and BeO. The first two oxides were slightly discolored, suffered some loss in weight, and remained nonconductive. The BeO specimen exhibited no evidence of any reaction. A similar study in a molten mixture of LiAL-LiCl-KCl produced less degradation but produced comparable qualitative compatibilities. Overall, the BeO and Y_2O_3 materials appear to be the most promising for use in the lithium-sulfur battery.

Singh (37) evaluated the resistance of Si_3N_4 and a 50 pct Si_3N_4 + 50 pct Al_2O_3 material to molten lithium and molten sodium. Both ceramics are expected to be compatible as a result of the positive free energy for the reaction:

$$1/4 \ Si_3N_4 + 3 \ (Na \ or \ Li) = (Na_3N \ or \ Li_3N) + 3/4 \ Si.$$

Tests for sodium compatibility were performed at 550° C in a closed type 316 stainless steel capsule under argon. Similar tests for molten lithium were conducted at 400° C in a closed style 304 stainless steel crucible under helium. Exposures were for 300 hours.

No appreciable weight change was noted in the samples exposed. X-ray diffraction patterns obtained before and after the tests were identical, and no reaction products were detected. The samples exposed sodium showed evidence of attack at the grain boundaries. After exposure to lithium, all samples exhibited an extensive crack network. Crack kinetics tests were run by inspecting samples after exposure for both 1 and 10 hours. Samples exposed for 10 hours appeared the same as those after 300 hours. Materials exposed

only 1 hour showed cracking, but retained their integrity to a greater extent than those exposed for 10 hours.

Robinson (34) detailed the effect of alkali attack on carbon refractories. It is noted that the mechanism of alkali attack on carbon is different than that on alumina-silica refractories. Compounds of potassium were used to evaluate attack, although sodium compounds will produce similar reactions. It is possible for the carbon to react with gaseous, liquid, or solid alkali. A variety of carbon materials were tested. These were categorized as to graphite content, ash content, and apparent porosity.

The first investigation concerned the effect of alkali on carbon oxidation. Carbon refractories were impregnated with KOH, and weight loss (TGA) runs were made. As the KOH content of the refractory was increased, the amount of weight loss increased and the initiation temperature was lowered. Dilatometric determinations on alkali-impregnated specimens showed that alkali increases the expansion that occurs in argon or CO_2.

The corrosive reaction of carbon was investigated by exposing a carbon rod above a charge of molten alkali in a fireclay crucible for 6 hours at 1,315° C. To offset the effects of air leaks, a flowing gas atmosphere was used. It was found that a CO_2 atmosphere resulted in significant alkali attack, while argon and CO atmospheres produced no attack.

Since alkali vapors do cause softening, but not the cracking that has been associated with alkali attack, it was desired to determine if molten alkali would produce carbon cracking. Test samples were cut from carbon refractories and a cavity drilled in each. The cavity was packed with a selected alkali and the specimens were heated at various temperatures in a tube furnace with controlled gas atmospheres. Both KOH and K_2CO_3 were used to produce molten alkali. Molten KOH penetrates the pores of the carbon and reacts with carbon to form K_2CO_3 in an argon atmosphere. The attendant expansion is sufficient to crack the refractory when saturation by liquid is complete. Melts of K_2CO_3 behave similarly, except that temperatures above 900° C are necessary because K_2CO_3 melts and reacts with carbon above 900° C. Atmospheres of CO_2, CO, and air will prevent or retard absorption of the melt by the refractory. Also, a slow rate of heating favors reaction of the hydroxide external to the refractory, while rapid heating rates encourage absorption. The reaction of the alkali with alumina-silica ash material produces a high viscosity melt that does not penetrate the refractory.

Information on slag-melt corrosion of ceramic materials is the most comprehensive for any corrosive environment. This is probably a result of the large-scale use of ceramics and the amount of ceramic experience in the slag-melt area. Therefore, the greatest volume of data is available in this area, and anyone requiring data on specific processes has many sources of information.

This summary of slag and melt corrosive attack on ceramic materials has shown that testing is normally formulated to simulate actual processing practice as closely as possible. Of course, any investigation evaluates

candidate materials under conditions that may not fully represent actual practice. Considering the complex nature of most of the slag or melt processes, full simulation is difficult. In this type of testing, complete definition of test variables such as melt chemistry, refractory properties, melt viscosity and feed rate, atmosphere conditions, and other pertinent variables must be defined. Only by defining these conditions as completely as possible can proper simulation be accomplished. Then, for any specific slag-melt system being evaluated, meaningful data will be obtained regardless of the process of interest.

CORROSION BY GAS ATMOSPHERES

Corrosion of ceramic materials by gases should be considered as similar to corrosion by liquids in that the mechanisms of diffusion, reaction, and dissolution are still pertinent. However, because of the nature of gaseous flow, boundary layers are very thin and corrosion rates may be very high. Also, in gaseous processes, replenishment of the corroding medium is usually rapid so that a condition analogous to a saturated corrosive slag is not likely to occur.

The problems of gaseous corrosion of ceramic materials have, in the past, been limited primarily to processes in the petrochemical industry and the iron and steel industry. However, the recent demand for energy generation from coal and fossil fuels has created interest in processes in which high-temperature, gaseous environments are prevalent. Bakker and Crowley (1) have produced an excellent review of processes in which gaseous corrosion problems are common. They review petrochemical, blast furnace, and coke oven processes that create gaseous corrosion problems and describe refractory experience and selection in those areas.

Petrochemical processes cited are (1) catalytic cracker units, (2) catalytic reformers, and (3) secondary reformers. In catalytic cracker units, operating temperatures are generally 540° to 760° C and conditions vary from oxidizing to reducing throughout the complete unit. Refractory linings in the reactor section are typically filled with carbon. Problems in the units are mainly confined to the transfer lines and cyclones where erosive wear is a real possibility. These areas are typically lined with a high-alumina, erosion-resistant castable. In catalytic reformers, temperatures are only around 540° C, but operating pressures may reach 300 psi. The atmosphere is rich in hydrogen, which can reduce silica at temperatures above 980° C. However, silica-free refractories are not necessary, and concretes containing 50 to 70 pct Al_2O_3 perform well. Conditions in secondary reformers most closely approximate coal gasification conditions. The gas composition is rich in hydrogen, carbon monoxide, and steam. Operating temperatures are about 1,095° C, and pressures are in the 200 to 300 psi range. Because of silica reduction problems, U.S. practice prefers the use of essentially silica-free, 95 pct alumina concretes.

Historically, blast furnaces have been lined with fireclay refractories. Gaseous corrosion failure mechanisms in blast furnaces are a result of either carbon monoxide disintegration or alkali bursting. Carbon monoxide

disintegration occurs around 500° C and is the result of catalytic reduction of CO to carbon in the pores of a refractory in the presence of free iron or iron oxide. It is pointed out that only iron or iron oxides act as catalysts and iron silicates do not. Thus, carbon monoxide disintegration resistance can be built in by high-firing the refractory to insure formation of iron silicates. Alkali bursting is caused by the vaporization of alkali compounds in the lower section of the furnace. Alkali vapors then travel up the stack and reoxidize and react with silicates in the refractory. The alkali silicates have higher specific volumes, and the refractory is disrupted. Most alumina-silica refractories are subject to alkali attack and, in some cases, carbon-containing refractories are used instead.

Bakker and Crowley (1) also discuss the corrosive effects of gases that are found in coal gasification units. The reduction of silica or silicates by hydrogen is a possibility. This reduction is lessened in the presence of steam and so may not be a real problem in some gasifiers. Corrosion by steam leaching may also be a problem in gasifiers. It appears that steam leaching is more pronounced in refractories that have high contents of glassy phases, such as normal fireclay bricks. Carbon disintegration may be a problem if calcium aluminate concretes are able to form a $CaCO_3$ phase. Corrosion by alkali vapors will depend on the conditions of gas atmosphere and types of alkali compounds in the coal ash.

Crowley (11-12) has documented the reduction of silica in refractories by hydrogen. His studies showed that weight loss, due to the formation of gaseous SiO, increased with hydrogen partial pressure, gas flow rate, and temperature. In the presence of steam, this weight loss was retarded. The results indicated that this weight loss will occur at temperatures above 925° C. Refractories having silica contents ranging from 8 to 95 pct were evaluated. Recommendations for use in reducing conditions as encountered in reformer units are that phosphate bonded 85 pct alumina brick, 99 pct alumina brick, and calcium aluminate concretes low in silica be selected.

Wistrom (43) investigated the properties of a dense, 94 pct Al_2O_3 castable after exposure to a 47.5 steam - 52.5 CO (vol-pct) atmosphere at 465 psia and 199° C for 6, 12, and 18 days. Within 6 days, the calcium aluminate cement phase decomposed to calcium formate, Ca $(HCO_2)_2$ and boehmite, AlO(OH). Other than the amount of calcium formate formed, there was no apparent difference in the decomposition of the castable or of three calcium aluminate cements. All of the CaO in the castable and a majority of the CaO in the cements (excepting one) was converted to calcium formate. The weight gain, decrease in porosity, and general increase in modulus of rupture can be explained by the reaction of the cement with the steam-CO atmosphere to form calcium formate and boehmite. Whether the castable had been prefired or only dried prior to exposure had no major effect on these chemical reactions. These data indicate that the bonding provided by the boehmite in castables exposed as described can replace that which is lost by the decomposition of the original cement phases. However, the boehmite will decompose at increased temperatures. Basically all the reaction of the castable is confined to the cement phases, and the alumina aggregate is essentially unreactive.

Ballard (2) investigated the effect of steam-CO atmospheres on refractory bond phase in--(1) a dense-fired alumina brick, (2) a phosphate-bonded ramming mix, and (3) a calcium aluminate cement castable. These materials were exposed to mixtures of steam and CO and to 100 pct of both steam and CO at 385, 750, and 1,015 psia at 260° and 950° C. After exposure, the bulk density, apparent porosity and modulus of rupture (MOR) of the materials were measured. The phosphate- and cement-bonded samples were also analyzed by DTA/TGA and X-ray diffraction (XRD). The dense alumina samples were also examined by Auger electron spectroscopy.

The dense alumina material exhibited a reduction in MOR that was a function of steam pressure and coincided with segregation of calcium at grain boundaries. The phosphate-bonded material showed good corrosion resistance to the atmospheres, except for the case of saturated steam. The strength loss in this material is attributed to attack of the $AlPO_4$ bond phase, although no reduction in the quantity of $AlPO_4$ was detectable by XRD. The calcium aluminate cement bond phases displayed more chemical reactivity than either of the two other types. Reactions occurred between the cement phases and steam-CO atmospheres below 300° C. Calcium formate and especially boehmite provide additional bonding, since samples containing these phases showed an increase in MOR. Above 900° C, no evidence was found for reactions of the cement bond phases with the test atmospheres.

Sadler (35) has conducted a continuing program directed toward selection of suitable refractory liner materials for nonslagging high- and low-Btu coal gasifiers. Fourteen commercial refractories have been tested before and after exposure to a variety of atmospheres ranging from 760° to 1,100° C, pressures from 400 to 1,000 psi, and gas velocities from 0.04 to 1.4 ft/min for periods up to 1,000 hours. Atmospheres include typical high- and low-Btu coal gasifier atmospheres as well as steam, H_2, CO, and CO_2. An exposure of refractories to high-Btu gases containing sodium and potassium hydroxide vapors as well as an exposure to alkali-impregnated refractories to high-Btu gas at 980° C were conducted. The major results can be summarized as follows:

1. Steam is the most corrosive gaseous component of the coal gasifier environment toward the refractories tested.

2. Silica loss, due to volatilization, from intermediate-alumina concrete containing high-purity cement is negligible in high-Btu coal gasifier environments below 1,000° C.

3. High-alumina concretes made from tabular alumina and high-purity calcium aluminate cements lose strength when exposed to steam atmospheres at 1,000 psi and 760° C or above.

4. Brick containing 45 to 60 pct alumina show adequate resistance to coal gasifier environments, and some phosphate-bonded concretes are unaffected while other gradually lose strength.

5. Silicon carbide refractories are aggressively corroded (converted to silica) by atmospheres containing high partial pressures of steam.

6. The presence of saturated alkali vapors at 980° C seem to have no effect on cold crushing strength of alumina refractories, while all refractories suffer deterioration when exposed to molten NaOH and KOH at 980° C.

Swaroop (39) has reviewed the feasibility of using ceramic coatings on metal structures in a coal gasifier environment. Tables are given which indicate the relative amounts of NH_3, CO_2, CO, H_2, CH_4, H_2O, and H_2S to be expected in a coal gasifier operating in the temperature range 800° to 1,200° C. The most corrosive gas is expected to be H_2S. Therefore, the sulfidation and oxidation of potential ceramic coatings are discussed. Five types of coatings that conceivably could be used to coat metallic structures: (1) intermetallic compounds that form compact oxide layers, (2) intermetallic compounds that form glassy oxide layers, (3) alloy coatings that form compact oxide layers (4) noble metals and alloys, and (5) stable oxides that provide a barrier to the corrosive environment. The only one of interest in the report is the fifth type.

The protective capability of an oxide layer may be estimated by the Pilling-Bedworth (P-B) ratio, which relates the specific volume of the oxide formed to the specific volume of the corresponding metal. If this ratio is below 1.0, an unprotective layer is formed, and if it is over 1.0, a protective layer is formed. However, for large values, the layer develops internal stresses and will scale. The ratios presented for potential coating materials indicate that carbides and nitrides of Ti, Si, and Zr should have the highest resistance to scaling.

Besides this P-B ratio for compounds, one should also consider the stability of the compounds in coal-gas environments. Free energy of reaction values are given at 1,026° C for a number of ceramic compounds in coal-gas mixture. It is noted that most of the coating compounds will resist sulfidation. Also, the listed compounds (except for SiC) form an oxide layer that is protective from further oxidation. Silicon carbide will not oxidize at 1,026° C at the oxygen pressure of a coal gasifier. Also, oxides such as Al_2O_3, ZrO_2, and Cr_2O_3 will not undergo sulfidation.

Four methods are noted as suitable for applying these ceramic coatings: (1) chemical vapor deposition, (2) vitreous enameling, (3) plasma spraying, and (4) physical vapor deposition (sputtering, vacuum evaporation, etc.). Conclusions are that ceramic compounds of the type Al_2O_3, ZrO_2, or Cr_2O_3; SiC, HfC, or ZrC; Si_3N_4, TiN, or HfN; and TiB_2, ZrB_2, or HfB_2 have the desirable properties that could offer corrosion resistance to coal-gas conditions. It would be best if these compounds could be graded with suitable alloys to match the base metal. Also, plasma spray techniques are probably best for application since vapor deposition techniques are not well-enough developed for these materials.

Kraner (21) reviewed the effects of various atmospheres and gaseous constituents on the life of steelplant refractories. The fluxing ability of alkali compounds and accessory materials such as lead compounds, zinc compounds, sulfides, chlorides, and fluorides is discussed. Many of these

compounds have significant vapor pressures at steelmaking temperatures and
will migrate throughout a furnace and react with refractories.

The influence of oxygen content in these atmospheres is illustrated by
the role played by iron oxides. Hematite, Fe_2O_3, will lose oxygen and form
Fe_3O_4. The Fe_3O_4 is relatively refractory and will not drastically affect
refractory performance. However, if reducing conditions are allowed to exist
(as by formation of CO), the Fe_3O_4 will be reduced to FeO, which is a strong
flux for alumina-silica refractories.

Kraner also discusses the CO disintegration problem in blast furnace
walls and the alkali bursting problem. Although the alkali contents of ores
and coke are not high, after long periods of operation the refractory may con-
tain up to 20 pct alkalies. The formation of minerals such as nephelite,
$Na_2O \cdot Al_2O_3 \cdot 2SiO_2$, results and such minerals are not refractory.

The use of basic refractories in open hearths is discussed. Chrome-
containing bricks are subject to expansion effects because of the oxidation-
reduction of iron oxide. Therefore, chrome-containing bricks are not used in
contact with liquid metal, but are used in roofs. Magnesia refractories are
preferred for areas in contact with liquid metal.

The effects of oxidation-reduction reactions in carbon-containing MgO BOF
refractories have been reported by Leonard (23), Pickering (30), and
Carniglia (7). These papers show that the reaction:

$$MgO + C = Mg + CO$$
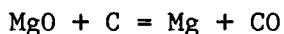
can be predicted by comparing the free energies of formation at temperature
for both MgO and CO. At steelmaking temperatures of about 1,600° C, the CO
equilibrium pressure is about 1.0 atm and the magnesium pressure at equi-
librium would be about 0.01 atm. Therefore, any carbon in the refractory not
oxidized would react with MgO until the magnesium pressure reached 0.01 atm.
Removal of magnesium vapor by flowing gases would cause the reduction reaction
to continue.

As Mg vapor diffuses out of the brick, oxygen diffuses in and a dense
layer of MgO is produced about one-fourth to one-half inch into the brick.
This type of oxidation-reduction reaction continues as the BOF undergoes heat-
ing cycles. The reaction rate increases with temperature and decreases with
increasing Mg or CO pressure at constant temperature. The dense MgO layer
dissolves quickly in low lime-silica slags, but is quite impervious to high-
silica slags.

The effect of vanadium attack on refractories has been reported by Jones
and Hardy (16), Lehmann (22), and Gottardi and Bonetti (14). These studies
indicate that vanadium in oil ash used in furnaces is very corrosive to
refractories because of the formation of low melting vanadates (melting point
about 1,050° C). The first reference states that fuels containing vanadium
are very destructive to fireclay refractories, and the second states that

magnesite refractories show less resistance to vanadium attack than do fire-clay refractories.

A recent paper by Havranek ($\underline{15}$) compares cup slag testing to a new method of evaluating alkali attack. The refractories tested were blast furnace types and were first tested in a standard slag cup test (DIN 51069) under controlled CO/CO_2 atmospheres at 1,000° C, 1,200° C, and 1,400° C for 5-hour periods. The degree of attack and amount of cup expansion were determined. A total of 103 cup tests were run at various temperatures. The results obtained were quite variable and difficult to reproduce, and it was concluded that this type of test was unsuitable for selection of alkali-resistant refractories.

Therefore, a more precise method based on the change of a physical parameter of the refractory was desired. A method based on the hot modulus of rupture after alkali attack was developed. Six, 25- by 25- by 150-mm test bars are cut from each refractory. The hot modulus of rupture at a selected temperature is then determined on three bars. Bulk density and porosity are determined on the other three bars. These bars are then dried and placed in a silicon carbide box measuring 250- by 170- by 250-mm after the bottom has been covered with 50 to 60 mm of fine coke. The test bars are then covered with 500 g of potassium carbonate, and the lid is cemented on the box with refractory cement. The box and contents are then held at the selected test temperature for 5 hours.

The test bars are examined visually after the test, after which soluble alkali salts are removed by boiling until a neutral pH is obtained. The hot modulus of rupture of these bars at 1,250° C is then determined. After cooling the bars, bulk density and porosity are determined. Refractories that had good resistance to alkali at 1,250° C were (1) brick with low porosity and excess silica glass, (2) alumina or silicon carbide brick with a mullite bond, and (3) silicon carbide brick with an oxynitride bond. After exposure to alkali at 1,400° C, only the latter two types showed good resistance. These results appear consistent with experience in the use of blast furnace refractories.

Brooks ($\underline{5}$) investigated the corrosive effects of fuel oil combustion products on silicon nitride and silicon carbide. The silicon materials were exposed in a burner duct to combustion gas and in crucibles to molten sodium sulfate and vanadium pentoxide. The gas environment tests were run at 900°, 1,000°, and 1,400° C, while the melt tests were run at 900° C only.

The test results indicated that fuel oils containing 50 ppm sodium produced a deposition of Na_2SO_4, which reacted with the silicon materials to form $Na_2Si_2O_5$. This reactant, which is molten above 780° C, severely attacked both self-bonded SiC and reaction-bonded Si_3N_4. Corrosion by vanadium was less severe and was only noted when sodium salts were present so that the protective SiO_2 layer was destroyed. Localized corrosion could be related to areas of low O_2 pressure, which would result in the formation of SiO. Hot-pressed Si_3N_4 demonstrated better corrosion resistance. Instead of exhibiting deep penetration of deposits, the reaction with the hot-pressed material was

limited to a narrow layer. The corrosion is dependent on the sodium content of the fuel, and this fact may affect the use of such materials in gas turbines.

Information on engineering properties of ceramic materials compiled by Lynch (25) includes corrosion or oxidation resistance on most of the common oxides, carbides, nitrides, and silicides. The information is quite general or is limited to single data points, except in a few cases. The data on these groups of materials are summarized below.

Oxides

Aluminum oxide is chemically one of the most stable refractory compounds and up to the 1,700° – 1,815° C range is resistant to all gases, except moist fluorine. It may be used in either oxidizing or reducing atmosphere as high as 1,925° C for short periods.

Beryllium oxide is stable in all dry atmospheres, but undergoes considerable weight loss above 1,095° C in even low concentrations of water vapor. The weight loss is attributed to formation and volatilization of $Be(OH)_2$.

Magnesium oxide is unaffected by neutral or oxidizing atmosphere even above 1,980° C, but is easily reduced. The powder dissolves slowly in water unless highly sintered, but dense material is stable in presence of water vapor.

Calcium oxide reacts readily with water at room temperature and also hydrates in air. It will react with CO_2 and SO_2 on heating.

Zirconium oxide is stable in oxidizing and moderately reducing atmospheres, but will decompose at 2,200° C in contact with carbon, nitrogen, or hydrogen.

Titanium oxide may be reduced and is restricted to oxidizing environments.

Chromium oxide is resistant to reduction by carbon and hydrogen.

Calcium and strontium zirconates are stable in air at high temperatures, but will react with silica or alumina.

Carbides

Silicon carbide is the most stable of the carbides up to about 1,650° C. It is stable below 980° C and above 1,150° C owing to a protective silica coating. Between these temperatures, the oxidation is a function of the physical state of this silica. The rate of oxidation above 1,150° C is affected by a decrease in viscosity of the silica due to impurities, formation of volatile SiO in vacuum or reducing conditions, and the mass velocity of the oxygen-bearing environment.

Appreciable oxidation of titanium, hafnium, and zirconium carbides occurs as low as 430° C. Increased oxidation rates of HfC and ZrC coincide with phase changes of the oxide coatings. These carbides are reportedly attacked by nitrogen at high temperatures. However, samples of TiC and ZrC were non-reactive with hydrogen at 2,200° C.

Chromium carbides are not significantly affected in air up to 1,270° C, although carbides of tungsten and molybdenum are less stable. Oxidation occurs with these materials between 540° and 815° C, and oxidation becomes catastrophic at slightly higher temperatures. Carbides of uranium, thorium, and plutonium react with water and moist air to form hydrogen, hydrocarbons, and hydrated oxides.

Nitrides

Nitrides are poor in oxidation resistance except for BN and Si_3N_4 up to 1,095° C. Most nitrides are stable in reducing atmospheres and, of course, nitrogen. Controlled oxidation of Si_3N_4 above 1,700° C produces an oxynitride. Less weight change in Si_3N_4 occurs in the higher density, hot-pressed material. Silicon nitride is stable in neutral or reducing atmospheres up to 1,870° C. It is attacked very slowly in boiling water and is slightly soluble in water at 1,500 psi and 315° C.

Boron nitride is only slightly oxidized in air at 980° C and is insoluble in water, but hydrolyzes in boiling water and aqueous solutions. It is stable in inert atmospheres, but reacts with carbon above 1,980° C. In hydrogen, it can be used above 1,980° C and will resist chlorine up to 700° C.

Silicides

Oxidation of the silicides decreases as the silicon content increases. Tantalum silicide is relatively stable in air up to 1,650° C. Chromium silicide oxidizes in air, and the brittle oxide layer offers little protection. Molybdenum disilicide resists oxidation up to 1,700° C. Above 1,755° C and an oxygen pressure of 10 torr, oxidation increases owing to formation of gaseous SiO. Tungsten disilicide oxidizes to form WO_3 and SiO_2. Above 1,040° C, WO_3 volatilizes, and a stable SiO_2 coating forms.

The review on gaseous corrosion of ceramic materials indicates that this area has been investigated heavily in recent years. These recent investigations have dealt with more complex and more severe gas conditions than were encountered previously. As in the case of slags and melts, the intent has been to simulate process conditions, and this can be difficult to accomplish. While actual simulation of O_2, CO_2, CO, H_2, and steam conditions has been conducted extensively, testing has been directed towards oxide ceramics and only limited data are available on carbides, nitrides, silicides, or borides. Also, the effects of environments of nitrous oxides, sulfurous oxides, volatile metal oxides, halogen gases, etc., are not well known. Of course, as in the case of slag-melt corrosion, the specific conditions of the process of interest will dictate the corrosion information that is necessary. As processes lead to environments containing various other gaseous components, the

corrosion effects of such components must be determined. A major aim of any gaseous corrosion testing should be to determine the attack mechanisms predominating so that judicious selection of materials may be made. Testing to determine mechanisms requires that standardized and accepted test procedures be developed.

SUMMARY

The information available on the corrosion behavior of ceramic materials is disseminated by many sources, each of which are principally interested in specific corrosive environments. In the case of corrosion by acid as well as basic solutions, it was noted that quantitative corrosion information is available only for glass materials. Information for other classes of ceramic products is only qualitative and generally is supplied by the manufacturers. Standardization of both material classifications and test procedures would be required to better describe the corrosion resistance of ceramic materials. Ideally, it should be possible to quantitatively define the rates of corrosion attack by specific reagents and conditions on different classes of ceramic products. One advantage in solution corrosion testing is that exposure conditions are probably the simplest to define of the three types being considered, since solution concentration and temperature are the prime variables.

The area of slag-melt corrosion contains the most comprehensive information of the three general areas of corrosion. This type of corrosive attack is difficult to fully simulate at the test level because of the many variables that must be defined. Complete definitions of the refractories being tested and the slag or melt material are necessary to obtain meaningful data. The aim of most slag-melt corrosion investigations is usually to determine what particular refractory will best contain a specific slag or melt. This type of evaluation serves well to assess new developments in refractory materials. The data collected in regard to existing mineral or energy conversion processes should aid in selection of suitable materials for new processes.

The area of gaseous corrosion has received a great deal of study in recent years. Systems such as coal gasification, gas turbines, and MHD have led to much of this interest. Simulated testing in O_2, CO, CO_2, H_2, and steam environments has resulted in a large amount of data on gas-refractory reactions, but primarily for oxide ceramics and not for carbides, nitrides, silicides, etc. The mechanisms of many of these reactions are not well known, and standardized tests are required to establish the corrosion behavior in various gaseous environments. As future energy conversion processes lead to corrosive gas environments such as nitrous oxides, sulfurous oxides, and volatile metal vapors, the effects of such environments on ceramic structural materials will need to be determined.

An effort directed toward establishing the relative importance of the materials performance problems associated with evolving metallurgical processes, critical materials substitution, and energy conversion processes is needed to ascertain what areas demand the majority of investigative work. Once this importance is established, the specific problems of corrosion attack on ceramic materials can be evaluated and means taken to improve their

performance. The information in this review indicates that data are available for a limited number of corrosive environments, but quantitative data are needed in certain areas in which ceramic materials will potentially be exposed to new, untested service conditions.

Research at the Bureau's Tuscaloosa Research Center has been initiated to evaluate the resistance of commercial ceramic materials to hydrochloric acid solutions. Work also is underway to evaluate the relative resistance of commercial refractories with regard to slag attack in the production of glass wool from mineral waste materials such as slate wastes and porphyry copper tailings. Future research is being directed toward developing quantitative data on the resistance of ceramic materials to acids such as H_2SO_4, HNO_3, H_3PO_4, and HF; bases such as NaOH and NH_4OH; and various gaseous environments encountered in the roasting and/or reduction of low-grade, complex refractory ores.

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