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Abstract
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STABILITY OF ZIRCONIUM OXIDE IN GRAPHITE SURROUNDINGS

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Ames, Iowa
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ABSTRACT

Zirconium oxide specimens which have been fired at high temperatures in graphite enclosures are known to fail mechanically upon oxidation. A review of the literature failed to completely explain such failure. Possible causes of failure, arising both from internal and external influences, are discussed. Experimental investigation established the presence of zirconium carbide in all specimens where failure later occurred. Compressive strengths were measured both before and after oxidation and are discussed. Limitations and recommendations for graphite firing of zirconium oxide are given.

INTRODUCTION

Zirconium oxide, due to its high melting point and other refractory properties, has become a popular high temperature furnace material within the past few years. The crystallographic inversion which takes place is the only major defect in its refractory properties and its effect has been minimized by the use of stabilizing additions of other refractory oxides.

While using zirconium oxide, it was noted that reaction with graphite destroyed some of its more desirable physical properties. After zirconia had been fired in a graphite susceptor induction furnace and oxidized to remove carbon, complete failure often occurred. Considering the lack of information in the literature and the otherwise excellent properties of stabilized zirconia, a short study of the cause of such failure was made.

PREVIOUS WORK

A review of the literature failed to yield sufficient information to explain the problem. Prescott (1) found an equilibrium pressure of 1 atmosphere of CO gas at 1930°K (1657°C) in the reaction
between carbon and zirconium oxide. The reaction was reported as very slow. George (2) reported reaction at as low a temperature as 1500°C. In direct contradiction to this, Wainer (3,4) was issued two patents on a method of producing zirconium oxide refractory articles employing a mixture of the oxide and up to 5% of another oxide and silica. The mixture was fired in reducing atmosphere to 2200°C. Jennings (5) also patented a zirconium oxide-silica mixture which was fused in a carbonaceous atmosphere at 2200°C. The zirconia was reported to be completely stabilized by this treatment.

Kroll and Schlechten (6) found zirconium oxide reacted with carbon at 1300°C under high vacuum and at 1400°C at atmospheric pressure. Zirconium carbide was formed and found to be stable.

Schofield and co-workers (7) reported loss of strength or complete failure of specimens fired to 3500°F and 3900°F (1930°C and 2150°C) respectively when oxidized at 1800°F (982°C). A carbon resistance furnace with argon atmosphere was employed for the high temperature firing.

Whittemore and Marshall (8) described the use of stabilized zirconia insulating grain around graphite tubes. They claim absence of carbide at 2300°C. At a temperature of 2600°C, no loss of lime was noted, indicating no decrease in the stabilizing agent at high temperatures.

In a study of hot pressing of refractory oxides, Murray, Rodgers, and Williams (9) found zirconium oxide could be hot pressed in graphite molds at temperatures of 1200°C to 2000°C. A thin skin was observed on all specimens but presence of carbide was not reported. Extremely rapid heating was employed.

Thus the literature search does not predict or explain failure of graphite-fired zirconia. The information is somewhat contradictory and does not indicate any clear solution.

POSSIBLE CAUSES OF FAILURE

There are several possible causes of failure of a refractory material, some due to external influence and others due to the nature of the refractory itself. It is wise to consider the latter carefully before examining external causes of failure.

Zirconia, in its pure form, has a monoclinic structure which changes to tetragonal upon heating to approximately 1000°C. Other higher temperature inversions have been reported by Cohn (10) but have not been fully confirmed and accepted. The transformation at 1000°C is accompanied by a volume change which is sufficient to eliminate the possibility of a pure zirconia refractory.
Fortunately, it has been found that small additions of other oxides, usually lime or magnesia, cause the formation of a predominately cubic structure at about 1700°C. This structure is stable and excellent refractories may be made in this manner. Zirconia with additions of this type is termed stabilized. It has been noted by several workers that a small amount of monoclinic material is desirable as it gives a structure with a lower coefficient of expansion than that obtained by an entirely cubic form. Considerable work has appeared in the literature concerning stabilized zirconia, notably a paper on additions by Geller and Yavorsky (11) and a bibliography by Kreidl (12).

From the above discussion, it may be concluded that if the stabilizing influence is removed from the cubic zirconia structure, failure would be expected to occur on heating. This would be failure from the action of the material itself, although influenced by external factors.

Thermal shock may cause failure of the type observed, i.e. severe spalling. As stabilized zirconia is reasonably resistant to thermal shock, oxidation had been carried out by placing the carbon fired specimens in a hot furnace. This was a possible cause of failure which was easily eliminated by the use of a low firing rate during oxidation.

The formation of another compound whose structure or volatilization would be detrimental to the stability of zirconia was next considered. The most obvious of these was zirconium carbide which, having a cubic structure, would be expected to be reasonably compatible with cubic zirconia. However, on oxidation, this carbide might be expected to cause a disturbance in the zirconia structure.

EXPERIMENTAL PROCEDURE

To determine which of the above factors, or all three, caused failure, a small graphite induction furnace was constructed. A four inch tube of vitreous silica, forming the outer shell of the furnace, was placed inside a four inch water-cooled induction coil. This coil was activated by a 6 Kw Ajax mercury arc high frequency converter. A graphite slug, 2½ inches in diameter and six inches in length, was cut and fitted to form a tight enclosure for three specimen bars, each ½ x ½ x 3 inches. This slug was packed in the silica cylinder with graphite powder. A small alumina tube was placed on the top of the slug and positioned so it was possible to see into a ¼ inch opening drilled into the center of the susceptor. Graphite powder was packed around this tube, insuring reducing conditions all around the zirconia. The furnace temperature was measured with an optical pyrometer sighted on the center opening in the susceptor. This furnace was found to be very satisfactory for operation up to temperatures of 2400°C.
The zirconia used for this study was a commercial grade of stabilized material, supplied by the Norton Company, for which production methods have been described elsewhere (8,13). Spectrochemical analysis of this material showed the presence of iron, titanium, silicon, and slight amounts of alkalies as well as calcium, the stabilizing agent. This oxide was ball milled in a steel mill revolving at 60 rpm for 28 hours, then washed with hydrochloric acid to remove the iron. Analysis showed no contamination from the ball mill after washing. The particle size distribution of the ground material, as determined by the hydrometer method (14), is given in Figure 1. The curve is the result of two individual analyses.

Specimens, \( \frac{1}{3} \times \frac{1}{3} \times 3 \) inches, were made by both slip casting and dry pressing. The slip cast pieces were cast at a pH of 4.0 and at a specific gravity of approximately 3.5. In all cases the slip cast bars were extremely fragile and difficult to handle. It was found that dry pressing at 3,000 to 4,000 psi with 5 to 10% moisture gave excellent specimens with good handling qualities. These were fired to 1200°C in air before firing in the graphite induction furnace. After this pre-firing, all mold stains and surface defects were carefully removed with sandpaper so surface effects could be more accurately observed.

Compressive strength measurements were made using the fired specimens described. They were cut to approximately one inch lengths and the ends ground parallel. Loading was with a Baldwin hydraulic testing machine at no more than 40 lb./sec.

RESULTS AND DISCUSSION

The physical results observed after firing are given in Table I.

The induction furnace was heated at approximately 1900°C/hr. The oxidation firing rate was approximately 100°C/hr., with a one hour soaking period at 700°C.

In addition to the tabulated observations it was noted that where the bars were in direct contact with loose graphite, as in the bottom of the holes where they were set, reaction occurred locally at temperatures as low as 1600°C. This was uniform in all specimens, with the amount increasing only slightly with increase in temperature.

The results of the compressive strength measurements are given in Figure 2. All specimens failed with a splintering fracture which is characteristic of brittle materials of this type. The upper curve in Figure 2 shows the ultimate strength of unoxidized specimens. There is an appreciable increase in strength at about 1850°C which reaches a maximum at about 1975°C. This increase and maximum occurs in the region of decreasing strength of oxidized material. This would indicate a similar cause for both conditions. Such a cause is changed by oxidation at 700°C.
FIGURE 1 PARTICLE SIZE DISTRIBUTION BALL MILLED ZrO₂

DIAMETER (MICRONS)

FINER %

100 80 60 40 20 0

0 60
### Table I

Description of Specimens after Firing and Oxidizing

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Induction firing</th>
<th>After graphite firing</th>
<th>Appearance</th>
<th>After oxidation at 700°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td><strong>Slip Cast Specimens</strong></td>
<td></td>
</tr>
<tr>
<td>1750</td>
<td>white to grey</td>
<td></td>
<td>red-brown core, yellow</td>
<td></td>
</tr>
<tr>
<td>1800</td>
<td>slightly darker</td>
<td></td>
<td>surface</td>
<td></td>
</tr>
<tr>
<td>1900</td>
<td>medium grey</td>
<td></td>
<td>same, smaller core</td>
<td></td>
</tr>
<tr>
<td>1950</td>
<td>some black, grey</td>
<td></td>
<td>same, much smaller core</td>
<td></td>
</tr>
<tr>
<td>2000</td>
<td>black, charred appearance. Homogeneous.</td>
<td></td>
<td>no core present</td>
<td></td>
</tr>
<tr>
<td>2100</td>
<td>same as 2000°C</td>
<td></td>
<td>badly spalled</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td><strong>Dry Pressed Specimens</strong></td>
<td></td>
</tr>
<tr>
<td>1600</td>
<td>light grey</td>
<td></td>
<td>yellow, cored as above</td>
<td></td>
</tr>
<tr>
<td>1700</td>
<td>light grey</td>
<td></td>
<td>yellow, cored as above</td>
<td></td>
</tr>
<tr>
<td>1800</td>
<td>medium-light grey</td>
<td></td>
<td>yellow (repeated oxidation had no effect)</td>
<td></td>
</tr>
<tr>
<td>1900</td>
<td>medium grey</td>
<td></td>
<td>yellow, smaller core</td>
<td></td>
</tr>
<tr>
<td>1950</td>
<td>dark grey</td>
<td></td>
<td>yellow-brown</td>
<td></td>
</tr>
<tr>
<td>2000</td>
<td>very dark</td>
<td></td>
<td>no core, yellow-brown</td>
<td></td>
</tr>
<tr>
<td>2050</td>
<td>very dark</td>
<td></td>
<td>no core, some spalling</td>
<td></td>
</tr>
</tbody>
</table>
FIGURE 2  ULTIMATE COMPRESSIVE STRENGTHS OF ZrO$_2$
The above curves are not to be considered fundamental but were made on a qualitative basis and are to be used for comparison only. Much higher strength values have been reported in the literature and are not to be confused with the information presented above.

To determine whether or not zirconium carbide was formed during the graphite firing, x-ray analyses were made of the raw material, bars fired to 2000°C, bars fired to 2100°C and later oxidized at 700°C, and zirconium carbide. These were exposed to nickel filtered CuK\(_\alpha\) radiation in a Debye-Scherrer camera. As may be observed in Figure 3, numerous carbide lines are notably prominent in the film of the specimen which had been fired to 2000°C and had not been oxidized. This gives positive evidence of the existence of carbide in the fired pieces which later failed in the oxidizing cycle. The oxidized bars exhibit the same structure as the original material, indicating no loss in stabilization due to the high firing. This information was checked by actual measurement of the line spacings.

Spectrochemical analysis of the specimens failed to show any change in the amount of calcium, i.e., the stabilizing agent, between various specimens. It did, however, give excellent reasons for the coring effect noted in Table I. The iron content decreased from 0.150\% Fe at the center of one of these cores to 0.028\% at the surface. This coring effect was unchanged during the oxidizing cycle, as illustrated by repeated oxidations.

CONCLUSIONS

From the data and observations presented on the zirconia-graphite reaction, it is possible to make the following conclusions:

1. Zirconium carbide is formed when zirconia is heated in graphite surroundings at temperatures above 1600°C.

2. The ultimate compressive strength increases with heat treatment but decreases when the carbide is removed by oxidation.

3. Specimens have been found to disintegrate completely when oxidized after firing to temperatures above 2000°C. This is likewise attributed to the formation and oxidation of zirconium carbide.

4. A core, the dimensions of which decrease with increasing temperature, may be observed in the specimens. This is thought to be due to the presence and volatilization of iron. Sufficient volatilization occurs to produce a uniform color throughout the specimen at about 2000°C, i.e., the core disappears.
Stabilized Zirconia (Norton Company)

Stabilized Zirconia (2000°C)

Zirconium Carbide

Stabilized Zirconia (2100°C + 700°C)

Figure 3
5. Graphite firing does not decrease the amount of stabilizer present in the zirconium oxide nor change the crystallographic structure.

6. For best results, zirconium oxide should not be fired in graphite enclosures at temperatures above 1900°C nor in direct contact with graphite at temperatures above 1600°C. Carbide formation at these temperatures is sufficient to cause failure on oxidation.

ACKNOWLEDGMENT

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LITERATURE CITED
