Comparative Strengths of Refractories versus Corundum in Furnace Linings

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Refractory manufacturers have spent countess hours selling the virtues of the high crushing strengths and flexure strengths exhibited by their products. An aluminum producer could become convinced that the greater these values are, the better the refractory product. Here is an argument that refractory strength is not as important to cleaning and furnace maintenance as is commonly thought.

Introduction

The causes and consequences of corundum formation in the production of aluminum are well known. It has also been documented that specific characteristics of refractories can contribute to aluminum penetration and the formation of corundum, specifically surface tension, porosity and availability of reducible oxides.[1]

Certain operating practices, like blankets of inert gases, can slow the formation of corundum on refractory surfaces, but do nothing to eliminate corundum formation internal to the refractory due to capillary influx of molten aluminum and subsequent reduction of available oxides.

The potential for corundum formation and aluminum penetration are ever present in the production of aluminum, but should refractory strength be such a critical aspect of product selection? This article acknowledges the need for refractory strength in furnace areas where materials handling practices are harsh, and examines the perception that high strength refractories are required to handle furnace cleaning practices.

The Need for Strength

Strength measurements on refractory ceramics are typically measured by applying a force to a sample at a defined and constant rate until the sample fails. The measured load is then related to the cross-sectional area to which the load was applied resulting in a strength measurement expressed in typical English units of lb/in^2 (psi) or kg/m^2 in Metric units. For most U.S. companies these test methods are defined by ASTM International[2]. In the end, the resulting values give a reasonable method for comparing the strengths of like refractory products.

This is useful when deciding what refractory to use in designing or relining a furnace. For example, let's assume a refractory furnace wall must support its own weight. If we assume this refractory is a standard 60% alumina castable with a dried density of 160 lb/ft^3 and the wall dimension is 10 feet long x 1 foot thick by 4 feet high (volume = 40 ft^3); the weight of this wall would be 40 ft^3 x 160 lb/ft^3 or 6,400 lb. So, picking the worst case; the bottom of our wall will need to support the entire 6,400 lb. This weight will be distributed over the area of the wall's 10 ft^2 footprint which is 1,440 in^2. So each square inch of refractory at the bottom of the wall is going to see a pressure of 6,400 lb / 1,440 in^2 or 4.4 lb/in^2 of applied compression. A typical 60% alumina low cement castable has a crushing strength exceeding 10,000 psi. So, lining weight is a relatively minor force acting on our wall.

In another example assume this furnace holds 100,000 lb of molten aluminum. Also assume there are two long walls as defined in our first example and two short walls of 4 feet in length. Together these make a simple box with a total wall length of (4+4+10+10) 28 feet holding the aluminum. We will assume that all 100,000 lb of load from the aluminum pushing out on the lowest 1 inch of the wall. In this worst case example a total of (28 ft x 12 in/ft x 1 in) 336 in^2 is exposed to this load. Each square inch is seeing 100,000 lb / 336 in^2 = 298 psi of bending force. A typical 60% alumina low cement castable has a flexure strength (MOR) of approximately 1650 psi, far in excess of the strength needed to contain the aluminum.

As we can see from our examples great strength in refractory ceramics is not necessitated by the structural forces or the mass of the melt. What then seems to be driving the perceived need for strength?

One reason a high strength refractory might be needed is the charging practice for the furnace. In many operations charge materials are either shoved or dropped into furnaces with little regard for the added stresses on the refractory lining. If high refractory strength is coincident with good impact resistance and abrasion resistance, furnace lining life can be improved for those areas experiencing mechanical abuse.

If your facility is like most operations handling and processing molten aluminum you've been exposed to corundum formation at the top of your melt and attached to the refractory lining. If you are tasked with cleaning this furnace you know the force required to remove corundum buildup from the lining, and it is obvious as to why a stronger refractory is perceived as a better choice.

The question becomes: Is stronger really better for these operating practices?

With regards to the stresses added due to material handling, the answer is yes.

But with regards to corundum removal the answer is not so clear. This article examines the inherent strength of corundum material formed during aluminum processing, how and why this material forms and why it seems impossible to remove without damaging the refractory lining. With this information we can make a judgment about the requirement for refractory strength relative to cleaning practices.

Experimental

Corundum samples were collected from various aluminum process vessels. These samples were analyzed for mineral composition, structure, and strength (flexural and compressive) at room temperature and at 1000 ^{o}F, typical of the measured temperatures of the corundum prior to removal.

Background

Aluminum is much more stable as an oxide than as an elemental metal.[3]

At high temperatures the rate and degree of aluminum oxidation increases as the metal becomes the more stable form Al_2O_3. In order to prevent oxidation many aluminum producers will use a low reactive or inert gas like nitrogen or argon, respectively, as a 'cover' gas to prevent air coming in contact with the hot aluminum bath. Although this practice reduces the potential for corundum formation it does not eliminate it.

Figure 1 shows typical corundum buildup on a holding furnace. Typical cold cleaning practice would be to remove this buildup by physically separating the corundum from the refractory lining. The damaging effects of previous cleanings can be seen as the refractory shows rough corners and thinning along the length of the wall.

Figure 1. Corundum build up on refractory sidewall.

Molten aluminum is extremely fluid. It is significantly less viscous than water at room temperature and consequently has a much lower surface tension.[4] This allows molten aluminum to enter into the inherent porosity of the refractory walls used to contain the metal, resulting in capillary action allowing aluminum to 'pull itself' or travel through the porosity of the lining. As long as the aluminum remains in a liquid state it can be wicked though the refractory not only where it is in contact with metal but also to a point several inches above the metal line. If the aluminum is solidified within the refractory, attempts to remove the surface corundum/aluminum mix during a cold cleaning often results in damage to the penetrated refractory.

Complicating these issues, most refractory products contain a variety of mineral and chemical raw materials that contribute accessory oxides, including SiO_2, TiO_2, and Fe_2O_3. Most oxides are susceptible to an oxidation/reduction reaction with aluminum but because they tend to be part of a larger mineral structure they are generally protected from this reaction. This is typically the case with TiO_2 and Fe_2O_3. On the other hand SiO_2 can be a ready source of oxygen that can contribute to internal corundum formation. At elevated temperatures the aluminum metal can take or 'strip' the oxygen molecules from silica to form corundum.[5] Internally developed corundum that blooms out of the refractory surface is virtually impossible to remove without damaging the refractory lining.

Fine alumina (Al_2O_3) that is not combined with another element or compound within the refractory system lowers the 'energy barrier' for corundum formation, by acting as the perfect 'seed' crystal for corundum crystal growth in molten aluminum in the presence of oxygen.[6]

Fume silica (very fine SiO_2) is used in the production of many refractory castables. Because it is very small (<1µm, with a large surface area) and because the energy required to break the silicon-oxygen bond is far less than the energy released on formation of the aluminum-oxygen bond[5], corundum (Al_2O_3) readily forms when silica (SiO_2) comes in contact with molten aluminum and no other oxygen source is available. If fine Al_2O_3 in the refractory acts as a seed crystal, a bad situation becomes worse.

Results

Figure 2 shows photos of several samples of corundum which were removed from furnaces and sectioned for strength testing and analysis. It can be seen that corundum growth manifests itself in many forms from wavy formations to those which look like heads of cauliflower. Regardless of the surface appearance, upon sectioning all samples seem to contain metallic aluminum as shown in Figure 3.

Figure 2. Corundum Surface Formations

Figure 3. Interior of samples showing metal / oxide mix.

This is confirmed by Figure 4 which shows the X-ray diffraction patterns for a sample taken. It can be seen that the sample is a mixture of the aluminum metal and oxide of aluminum (corundum). Also present is the silicon metal which is part of the 300 series alloy produced by this manufacturer.

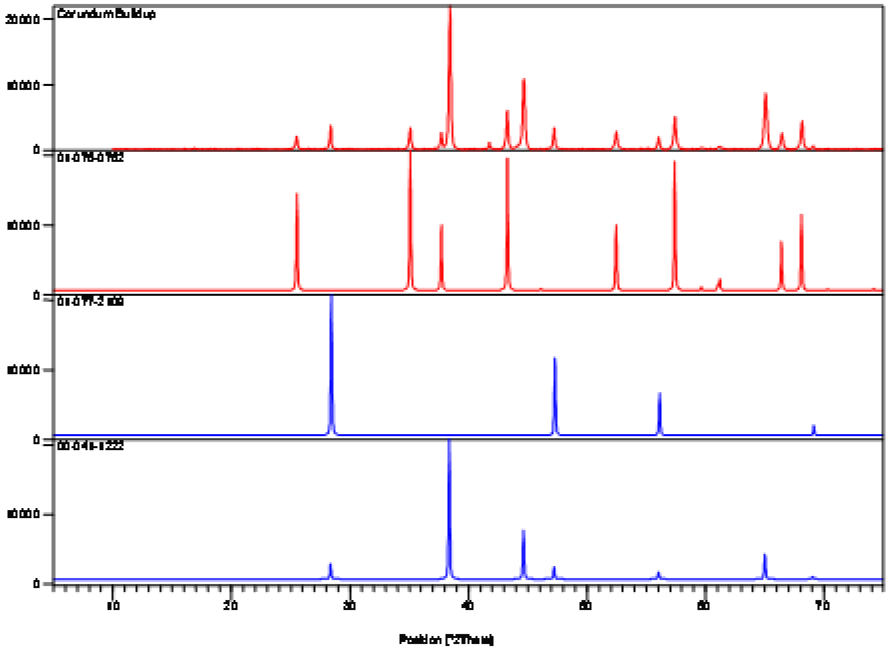

Figure 4. X-Ray diffraction pattern for corundum formation

Figure 5 shows the sample after acid etching to remove some metal. As can be seen this had the effect of increasing the size of the corundum peaks indicating a higher concentration. However, both aluminum and silicon metal were still detected.

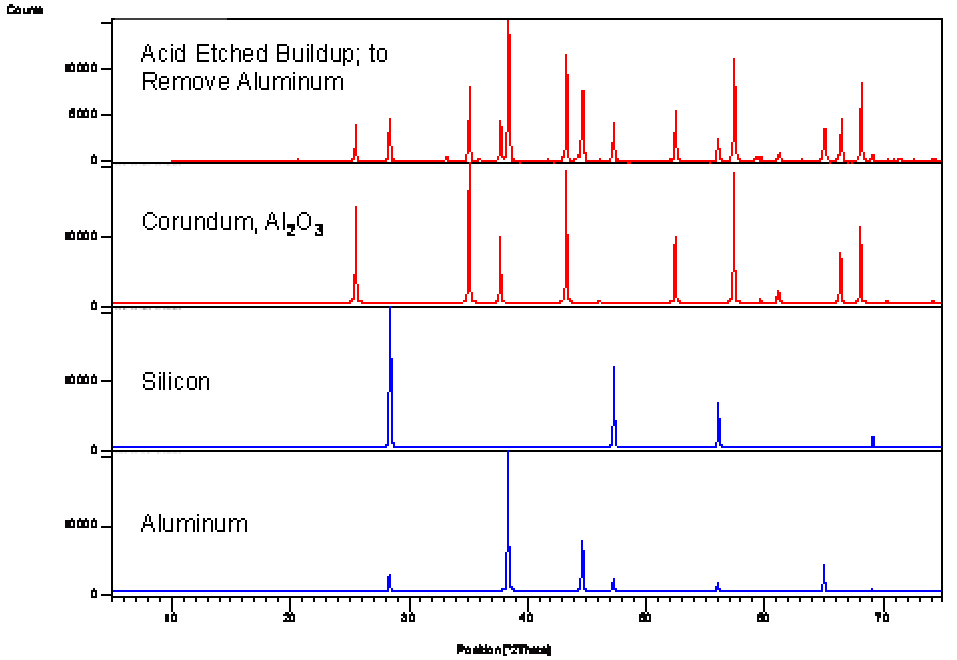

Figure 5. X-Ray diffraction pattern for sample after acid etching.

Figure 6 shows the typical chemical analysis of a 300 series alloy being produced in the furnaces at this facility. This is a shop utilizing silicon alloys and this chemistry is representative of the metal found in the samples.

Aluminum, Al	85.3 - 91.4 %
Copper, Cu	3.00 - 4.00 %
Iron, Fe	<= 1.00 %
Magnesium, Mg	0.100 - 0.600 %
Manganese, Mn	<= 0.500 %
Nickel, Ni	<= 0.350 %
Other, total	<= 0.500 %
Silicon, Si	5.50 - 6.50 %
Titanium, Ti	<= 0.250 %
Zinc, Zn	<= 1.00 %

Figure 6. Typical chemical analysis of a 300 series alloy[7] from www.matweb.com.

Bars and cubes were cut from the corundum/metal matrix in order to determine strengths of the material. One sample contained a large void and its results were discarded. Care was taken not to use samples containing refractory as this would skew the test results toward higher values. Figure 7 shows some of the bars used to determine the bending strength (MOR). An average of ten samples was used to determine strength values at room temperature and 1000^{o}F. The bars measured at 1000 °F show oxidation on the cut surfaces. Cubes (not shown) were used to determine crushing strength.

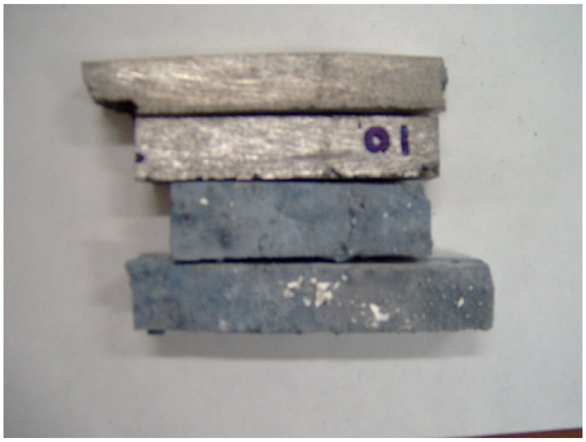

Figure 7. Bars used for MOR testing.

Figure 8 shows the bending strengths (MOR) of samples at room temperature. Figure 9 shows hot bending strengths (HMOR) at 1000^{o}F. Figure 10 shows crushing strengths (CCS) at room temperature and Figure 11 shows hot crushing strengths at 1000^{o}F (HCS).

Sample	MOR (psi)	Deviation (psi)
1	13163	8914
2	9324	12753
3	20679	1398
4	20723	1354
5	10043	12034
6	29092	7015
7	33145	11068
8	25262	3185
9	21826	251
10	37514	15437

Average MOR = 22077 +/- 7341psi Low = 9324psi High = 37514psi

Figure 8. Room temperature Modulus of Rupture data.

Sample	HMOR (psi)	Deviation (psi)
1	void	void
2	14084	3923
3	14752	3255
4	14828	3178
5	24485	6478
6	11113	6894
7	25982	7976
8	28127	10120
9	21305	3299
10	7383	10624

Average HMOR = 18006 +/- 6194psi Low = 7383psi High = 28127psi

Figure 9. 1000 F Hot Modulus of Rupture data.

Sample	CCS (psi)	Deviation (psi)
1	52413	3631
2	51748	4297
3	57512	1467
4	49039	7005
5	56251	207
6	53918	2126
7	60502	4458
8	62752	6707
9	61999	5955
10	54307	1737

Average CCS = 56044 +/- 3759psi Low = 49039psi High = 62752psi

Figure 10. Room temperature Cold Crushing Strength data.

Sample	HCS (psi)	Deviation (psi)
1	21554	16212
2	36810	956
3	47013	9247
4	38551	785
5	43120	5354
6	21058	16708
7	49315	11549
8	38976	1210
9	48668	10902
10	32595	5171

Average HCS = 37766 +/- 7809psi Low = 21058psi High = 49315psi

Figure 11. 1000 F Hot Crushing Strength data

Figure 12 shows published MOR and CCS values for several common refractory compositions used in aluminum contact applications, both castable and brick. Values shown are for burned brick and after 1500°F reheats for castables unless stated otherwise. Hot strength values were not available for most compositions. In general hot strengths are lower than strengths at room temperature. The castables contain aluminum penetration inhibitors.

Type	castable	castable	castable	castable	castable	brick	brick	brick	brick
Alumina content	60% alumina	70% alumina	80% alumina	92% alumina	65% alumina	60% alumina	70% alumina	80% alumina	90% alumina
bond	cement bond	cement bond	cement bond	cement bond	acid/base bond	pressed sintered	pressed sintered	pressed sintered	pressed sintered
CCS (psi)	12000*	13350	12700 230°F	10800	5000	8410	8500	9000	11350
MOR (psi)	3000*	2420	2170 230°F	1330	1450	2640	1700	1600	2330

*maximum reported value in a range.

Figure 12. Published strength data for several commercially available refractories.

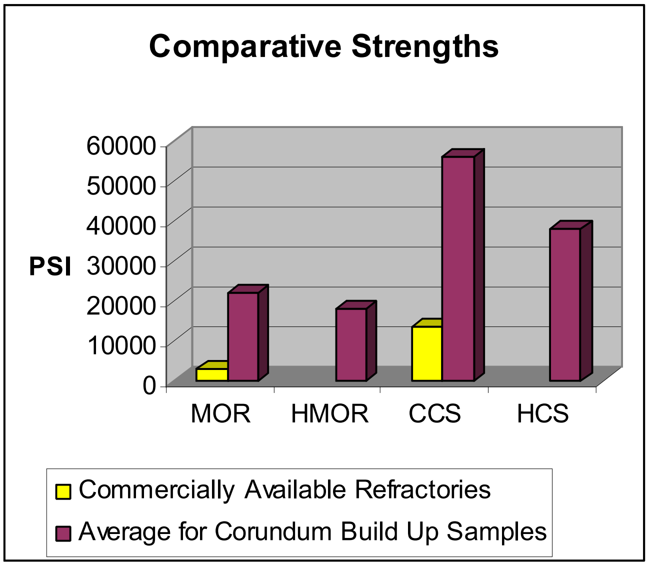

Figure 13. Strength comparison for corundum build up samples versus available published data for commercially available refractories. The highest available data published for MOR and CCS were used for the refractory products, irrespective of brand, manufacturer or type. Hot MOR and hot crushing strength data was not published for any products reviewed.

<u>Discussion of Results</u>

Examination showed that ‘growth’ in the furnace was primarily composed of a mix of corundum and the metal produced by this manufacturer.

Corundum growth samples were surprisingly strong at both room temperature and at 1000°F. The lowest measured MOR at 1000°F is approximately 2.5 times the greatest room temperature MOR reported for the refractories evaluated (Figures 12 and 13).

Average room temperature MOR is over 7 times as great as the highest reported for the refractories. CCS of the corundum/metal matrix is 4.2 times the highest reported CCS for refractory compositions. At 1000^{o}F it is still 2.8 times that value.

A search of published data for refractory products from several manufacturers did not yield any products with a reported MOR or CCS that would be comparable to that of the corundum growth samples in this study.

The implication of this data for the furnace cleaning process is fairly straight forward.

When attempting to mechanically remove corundum growth from a refractory lining, the refractory is always going to suffer the mechanical failure before the corundum growth. This cycle of refractory damage and loss ends up in the need to repair the vessel with a new refractory lining. Refractory damage will have a direct and negative effect on the thermal efficiency of the furnace since there is less insulation to keep heat in the metal bath.

While the necessary strength requirements for simple containment of molten aluminum and support of lining structure are well within the reported values of most currently available refractory materials including lightweights, no currently available refractories exceed the strength of corundum and corundum metal matrices as demonstrated by the research discussed here.

Addressing the Root Causes

Since refractories sufficiently strong to withstand the mechanical cleaning process either are not available or are not cost effective, the use of a refractory lining with characteristics that deal with the root causes of aluminum penetration and internal corundum formation is a desirable alternative.

Such a refractory would feature:

- A micro-porous mineral composition that eliminates molten aluminum penetration and limits adherence of corundum formed on the surface of the molten aluminum bath.[8]
- An absence of compounds such as SiO_2 which contribute to internal corundum formation.
- Inherently high insulating value.

If internal corundum formation and aluminum penetration are eliminated, the strength of the refractory material only needs to be that required for structural support of the vessel lining and the containment of the molten aluminum bath.

One recently patented and commercially available refractory product provides the molten metal contact qualities necessary to limit aluminum penetration and eliminate internal corundum formation. WAM® AL II from Westmoreland Advanced Materials™ forms no bond to externally formed corundum buildup, which is easily removed without damage to the refractory. This technology has been proven successful in several long term trials. The micro-porous nature of this product provides significant resistant to aluminum penetration as well as about 3 times the thermal efficiency of commonly used, “high strength” metal contact refractories.[9] Because vessels utilizing this technology are not damaged by removal of corundum; the thermal efficiency of these vessels has not diminished with time.

Conclusions

1. The strength of corundum formed in the production of aluminum greatly exceeds the strength of available refractories, even those touted as ‘high strength’ compositions.
2. Removal of the bonded corundum damages the refractory thereby decreasing the vessel’s thermal efficiency and physical integrity. Once corundum is removed, the growth process repeats itself, further damaging the vessel.
3. In order to resist damage caused by corundum removal, the refractory needs to have MOR values >15,000 psi and CCS values >30,000 psi based on the measured strength of the formed corundum. Refractories with strengths exceeding these standards either are not available or do not offer cost effective service.
4. Alternatively, refractories that do not allow penetration by molten aluminum, do not contain oxides which promote corundum formation and will not bind with formed corundum on the metal surface are commercially available, and avoid the conditions that make exceedingly strong linings necessary. One such product is available from Westmoreland Advanced Materials™.
5. Strength in the refractory lining is important if the refractory is going to be used in an impact area where solid pieces of aluminum would be dropped, dragged, or pushed onto a lining; for example in the sill and hearth area of reverbs. Resistance to mechanical forces due to cleaning procedures is not necessary if the refractory is not susceptible to aluminum penetration or interior corundum formation; buildup is easily removed without hammering or chiseling.