# Solid-state chemistry of alumina–chrome refractories

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Incorporating chromium(III) oxide in alumina refractories improves resistance to thermal-shock damage and slag attack. In manufacturing alumina–chrome refractories, the chromium(III) oxide can be added to a coarse alumina as a fine chrome ore [1] or to corundum as a purified chrome ore [2]. When preparing ethyl-silicate-bonded alumina–chrome refractories [3] the source of chromium is usually chromium(III) oxide. In our earlier work [4, 5] on alumina–chrome refractories the effect of powder preparation procedures and composition, compaction pressure, and temperature and time of sintering, on the formation of solid solutions in sintered compacts prepared from two aluminium(III) oxide materials (MA95, average particle size 4 μm angular; A17, reactive average particle size 2 μm round) and a chromium(III) oxide material (M100, average particle size 0.4 μm) was studied. These results are summarized in Table I. The low density of some sintered compacts prepared from MA95 material may be due to loss of chromium, which could occur by the reaction

$$Cr_2O_3(s) + \frac{3}{2}O_2(g) \rightarrow 2CrO_3(g)$$
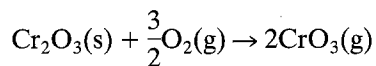
Chromium loss is consistent with the large primary particle size of MA95 material, suggesting that loss of chromium by volatilization is faster than solid-solution formation. The results of a similar study in which the aluminium(III) oxide material (AMS 9, average particle size 0.55 μm) and the chromium(III) oxide material (M100) have a similar particle size are given in Table II. The expected result is the change in grain structure in the range 10–15 wt % chromium(III) oxide. The system aluminium(III) oxide–chromium(III) oxide is a simple binary system, with formation [6] of solid solutions of aluminium(III) oxide and chromium(III) oxide. For A17 reactive and MA95 materials, our previous

work [4, 5] showed that the corundum lattice dimensions of sintered compacts prepared using varying amounts of M100 chromium(III) oxide decrease with 7 wt % chromium(III) oxide, other compositions giving lattice expansion. For a given time of sintering the ratio of the lattice parameters (c/a) depends on the composition and on the temperature of sintering. For AMS9 material (similar particle size to M100 chromium(III) oxide) the results [7] given in Table III show only a small variation in c/a with composition and temperature of sintering, although a minimum occurs at about 7.5 wt % chromium(III) oxide. In general, for all of the aluminium(III) oxide materials, the corundum peak width in the X-ray diffraction pattern increases with chromium(III) oxide content, consistent with solid-solution formation.

TABLE II Densification, microstructure and grain growth of sintered compacts prepared from M100 chromium(III) oxide and AMS9 alumina with compaction at 310 MPa

Chromium(III) oxide (wt %)	Observations
> 5	Decreased densification of compacts sintered at 1600 °C for 1 h or less. Increasing sintering temperature and time of sintering increases density
10 or 15	Grain structure changes from polygonal grains (in AMS9) to tabular grains

TABLE III c/a values for compacts prepared from AMS9 alumina and M100 chromium(III) oxide, compacted at 310 MPa and sintered for 6 h

Chromium(III) oxide (wt %)	Sintering temperature (°C)	c/a
15.0	1600	2.721
15.0	1650	2.726
15.0	1700	2.721
10.0	1600	2.720
10.0	1650	2.719
10.0	1700	2.716
7.5	1700	2.714
5.0	1600	2.719
5.0	1650	2.733
5.0	1700	2.727
2.5	1600	2.719
2.5	1650	2.733
2.5	1700	2.727
Nil	1600	2.721
Nil	1650	2.726
Nil	1700	2.721
Corundum standard[a]		2.730

[a] American Society for Testing and Materials ASTM 10-173.

TABLE I Densification, microstructure and grain growth of sintered compacts prepared from M100 chromium(III) oxide and MA95 or A17 reactive alumina with compaction at 310 MPa

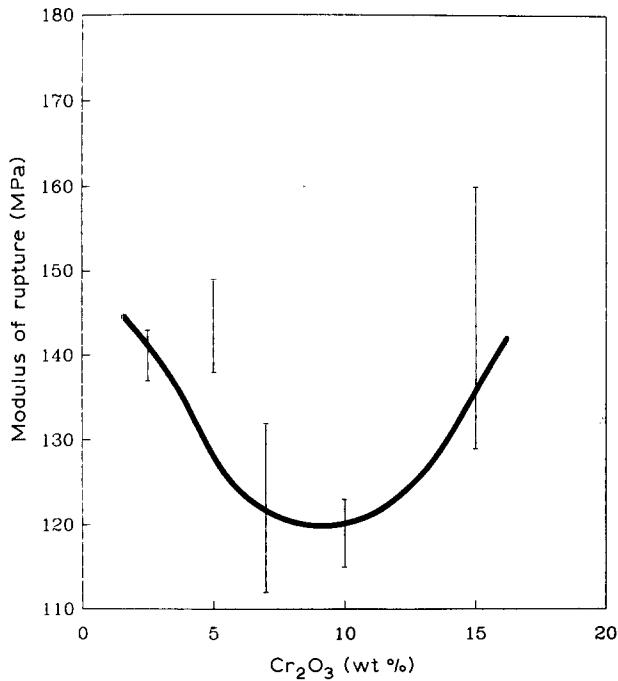| Chromium(III) oxide (wt %)	Observations
3	Fine-grained, porous microstructure at 0.5–1 h sintering time. At 8 h sintering time, densification and formation of large grains by selective grain growth
7 or 14	Grain growth more uniform and equiaxial. MA95 gives low density, consistent with loss of chromium by volatilization

Figure 1 Modulus of rupture at ambient temperature of sintered compacts prepared from AMS9 aluminium(III) oxide with varying amounts of M100 chromium(III) oxide. (Compacted at 310 MPa, sintered at 1700 °C for 6 h).

Previously we showed [5] that the hot (1150 °C) modulus of rupture of a series of ethyl-silicate-bonded alumina–chrome refractories is minimum at 7 wt % chromium(III) oxide. The modulus of rupture at ambient temperature of a series of sintered compacts prepared from AMS9 and M100 materials (compacted at 310 MPa and sintered at 1700 °C for 6 h) has now been determined and the results shown in Fig. 1 show that the modulus of rupture at ambient temperature is minimum at 8–10 wt % chromium(III) oxide. A change in corundum lattice parameters could alter the elasticity, thereby altering the modulus of rupture. Analysis [5] of modulus-of-rupture measurements at ambient temperature of

sintered compacts prepared from M100, MA95 and A17 reactive materials showed that powder mixes that were thoroughly blended and had the finest particle size gave the highest value of modulus of rupture (205 MPa) and Weibull modulus (17.5). The addition of boehmite improved the packing and mouldability.

The role of the matrix binder grain in the behaviour of a refractory body is critical; the various compositions reported here represent matrices of alumina–chrome refractories. The modulus-of-rupture results show the importance of a small and uniform particle size in the matrix. This gives uniform grain growth and densification, which leads to consistency of the mechanical properties. This type of matrix microstructure is found in alumina–chrome refractories that resist thermal-shock damage and slag attack.

The experimental procedures for the preparation and characterization of the sintered compacts were described in [5]. The modulus of rupture at ambient temperature of the sintered compacts prepared from AMS9 and M100 materials was determined [8] by diametrical compression of cylindrical compacts.

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