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Preparation and properties of some alumina–chrome refractories

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Preparative procedures, grain growth, densification and change in corundum lattice dimensions in sintered compacts made from chromium(III) oxide/aluminium(III) oxide mixtures were evaluated in a study of some alumina–chrome refractories. High-energy milling using "A17 reactive" alumina gave densification at low temperature and rapid grain growth, also a low variability in modulus of rupture. X-ray diffraction studies confirmed solid solution formation, the corundum lattice dimensions decreasing with 7 wt% chromium(III) oxide, other compositions giving lattice expansion. The modulus of rupture at 1150 °C for a series of ethyl silicate-bonded alumina–chrome refractories containing 5 to 12 wt% chromium(III) oxide was also minimal at 7 wt% chromium(III) oxide. The composition of this series is typical of ethyl silicate-bonded alumina–chrome refractories used in the steel industry.

1. Introduction

Resistance to thermal shock and reduction of slag attack can both be achieved by adding chromium(III) oxide to refractory bodies. The chromium(III) oxide is often added as a chrome ore. Examples are the addition of fine chrome to coarse alumina or mullite to reduce slag attack [1] and mullite–chrome systems [2] in which an iron–chrome ore containing about 46 wt % Cr_2O_3 is the source of chrome. Incorporating fine chromium(III) oxide in ethyl silicate-bonded refractories [3], especially ethyl silicate-bonded alumina refractories, reduces slag attack and improves resistance to thermal shock. The fine material (chrome or chromium(III) oxide, together with any "fines" fraction present in the refractory grain mix) form the "matrix" in a refractory body. The matrix binds the grain from which the body is made and is crucial in determining the properties of the refractory body obtained. The system aluminium(III) oxide (solid)–chromium(III) oxide (solid) is a simple binary system known [4] to show formation of solid solutions of chromium(III) oxide in aluminium(III) oxide.

Alkyl silicates, particularly ethyl silicate, can be used [5] to prepare refractory binders which do not contain fluxing agents. Intricate shapes having good refractoriness and thermal shock resistance can be made to close dimensional tolerances. In the production of ethyl silicate-bonded alumina–chrome refractories, the source of chromium is usually chromium(III) oxide [3] rather than a chrome ore. The inner nozzle of a sliding-gate system for the continuous casting of steel is an example of a refractory shape requiring close dimensional tolerances, resistance to slag attack and resistance to thermal shock. The nozzles are made from a grain mix comprising coarse "tabular" alumina with a "fines" fraction consisting of chromium(III) oxide plus aluminium(III) oxide. Two typical ethyl silicate-bonded alumina–chrome inner nozzles are shown in Fig. 1.

In the present work, preparative procedures, densification, grain growth and change of corundum (α-alumina) lattice dimensions in sintered compacts made from chromium(III) oxide–aluminium(III) oxide mixtures were evaluated in a study of some alumina–chrome refractory bodies [6–9]. The results showed that high-energy milling using "A-17 reactive" alumina powder produced a mixture which, after compaction, densified at low temperature giving rapid grain growth and the least variability [10] in modulus of rupture. The formation of chromium(III) oxide solid solutions in aluminium(III) oxide was confirmed by X-ray diffraction (XRD) observations, the corundum (α-alumina) lattice dimensions contracting with 7 wt % chromium(III) oxide, other compositions giving lattice expansion. The modulus of rupture at 1150 °C for a series of ethyl silicate-bonded alumina refractories containing 5 to 12 wt % chromium(III) oxide and fired at 1700 °C was also minimum at 7 wt % chromium(III) oxide; these compositions represent ethyl silicate-bonded alumina–chrome refractories used in the steel industry.

2. Experimental procedure

2.1. Materials

The aluminium(III) oxide materials were "A17 reactive" alumina (Alcoa, average particle 2 μm, round) and "MA95" (B.A. Chemicals Ltd, average particle size 4 μm, angular). Major impurities were Na_2O (0.55% max) and SiO_2 (0.07% max). The chromium (III) oxide material was "M 100" (British Chrome and Chemicals Ltd, average particle size 0.4 μm, soluble impurities 1.0 % max). Boehmite was "GC

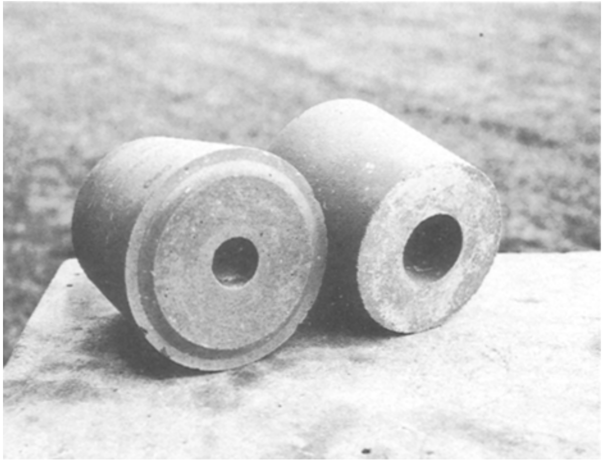

Figure 1 Ethyl silicate-bonded alumina–chrome inner nozzles.

powder" (Keith Ceramic Materials Ltd). These are representative of materials used in refractories manufacture.

2.2. Preparation and characterization of powder mixes

Three milling and mixing procedures were used, to break down particle aggregates and to blend the powder components.

(a) High-energy milling (hem), using a chrome–steel pot containing hardened chrome–steel balls. The powder mix was vibrated at high frequency, producing high impact energy between powder and balls, giving a rapid decrease in particle size and highly deformed particles.

(b) Ball milling (bm), using chrome–steel balls in a mill of hardened rubber. The predominant mechanism for particle size reduction is wear and abrasion, giving a round particle shape.

(c) Tungsten carbide milling (tcm), using a tungsten carbide–6% cobalt mortar and pestle, mechanically driven to provide a steady force on the powder. The action is a mixture of shear fracture, abrasive wear and particle rolling.

Each aluminium(III) oxide material was milled for 2 h to break down particle aggregates. Then the required amount of chromium(III) oxide was added and the mixture blended for 4 h. Mixes containing boehmite ("GC powder") for modulus of rupture determinations were prepared similarly.

X-ray diffractometry was used to assess the effect of milling and powder blending on the aluminium(III) oxide materials. A Philips PW 1033 X-ray diffractometer was used to obtain X-ray diffraction data. The corundum lattice constant a was calculated using the (1 1 0), (0 3 0) and (2 2 0) reflections. The corundum lattice constant c was calculated using the reflections (0 1 2), (1 0 4), (1 1 3), (0 2 4), (1 1 6), (0 1 8), (1 2 4), (1. 0. 10).

2.3. Preparation and characterization of powder compacts

Compacts for evaluating microstructure, grain growth and densification were prepared by compacting the powder mix in a tungsten carbide-lined die to give cylindrical compacts diameter ~10 mm, and height ~3 mm. Compaction was at 97.5, 155 or 310 MPa. Densities were determined before and after firing by weighing and measuring. Compacts were sintered at 1600, 1650 or 1700 °C for 0.5, 1 or 8 h, and cooled in the furnace. The grain structure was observed by scanning electron microscopy (Philips 505 scanning electron microscope) and grain size was determined from the scanning electron micrographs or by optical microscopy (specimens polished on diamond layers, then etched for 0.5 to 1 min in hot concentrated phosphoric acid).

Compacts for evaluating mechanical properties were prepared from aluminium oxide materials milled (hem) for 2 h. The required amount of chromium(III) oxide ("M 100" material) was added and the powder mix prepared by blending (bm, hem or tem for 4 h, see Section 2.2). Test bars for the determination of modulus of rupture were prepared by compacting the powder mix in a rectangular punch and die to give bars of approximate size 7.5 cm × 1.5 cm × 1.5 cm. Compaction was at 310 MPa. The bars were sintered at 1650 °C for 5 h. Grain structure and grain size were assessed as previously described.

2.4. Determination of mechanical properties

Modulus of rupture determinations, by three-point loading, were made on an Instron testing machine. A minimum of six bars from each powder mix was made and tested. Prior to testing, the density of each bar after sintering was determined.

Ethyl silicate-bonded alumina–chrome refractory bricks were prepared by the standard procedure [5] for base hydrolysis and gelation of ethyl silicate and fired at 1700 °C. The bricks were made from a grain mix (supplied by Zedmark Refractories Ltd, Dewsbury, UK) consisting of coarse "tabular" alumina with a "fines" fraction comprising fine aluminium(III) oxide plus varying amounts of fine chromium(III) oxide (5, 7, 10 or 12 wt % M100 material). At least six test bars 7.5 cm × 1.5 cm × 1.5 cm were cut from each batch of bricks. The modulus of rupture by three-point loading was measured at temperatures up to 1150 °C in air.

3. Results and discussion

3.1. Powder milling

Table I gives the effect of milling on the corundum lattice parameters, showing substantial lattice distortion and strain induced in the particles during comminution. For "MA95" material the milling is essential to reduce the large primary particle size of this material. Examples of the effect of powder composition plus milling and mixing procedure on powder particle size distribution are shown in Figs 2 to 5. Scanning electron micrographs of other powder mixes are given in [9]. Figs 2 and 3 show powder mixes of 7 wt % chromium(III) oxide, prepared by the same milling and mixing procedure, from "MA95" and "A17 reactive" materials, respectively, the "A17 reactive" mater-

TABLE I Effect of milling on corundum lattice parameters. Milling time 2 h

Powder	a (nm)	c (nm)	c/a
A17 as-received	0.476 44	1.300 87	2.7304
A17 hem	0.476 44	1.296 72	2.7217
A17 bm	0.475 75	1.306 85	2.7463
A17 tcm	0.476 19	1.298 71	2.7273
MA95 as-received	0.476 19	1.304 76	2.7400
MA95 hem	0.475 90	1.304 15	2.7404
MA95 bm	0.475 90	1.303 15	2.7383
MA95 tcm	0.476 82	1.293 56	2.7129
Corundum standard (ASTM 10-173)	0.475 8	1.299 1	2.7303

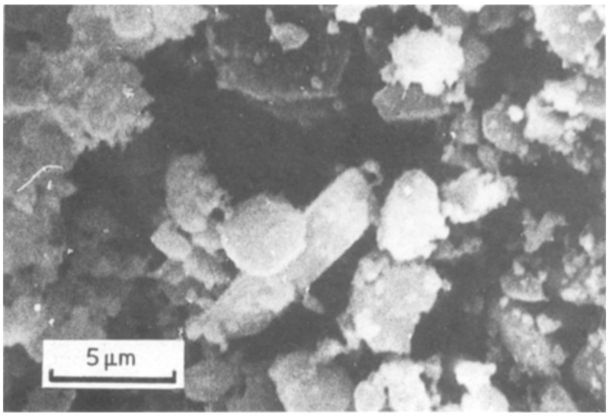

Figure 2 Particle size distribution in 7 wt % Cr_2O_3, 93 wt % "MA95" Al_2O_3 (2 h tcm), blended 4 h hem.

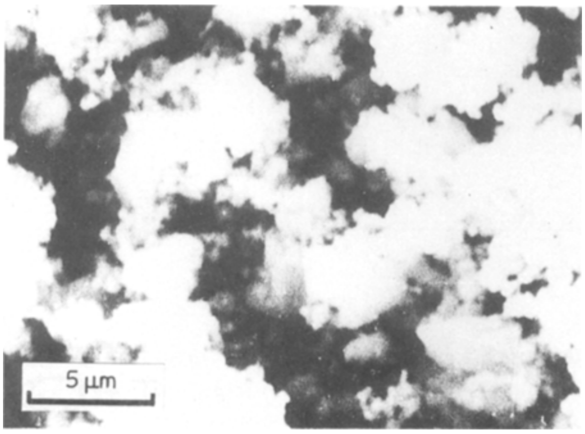

Figure 3 Particle size distribution in 7 wt % Cr_2O_3, 93 wt % "A17 reactive" Al_2O_3 (2 h tcm), blended 4 h hem.

ial giving a more uniform particle size. Increasing the chromium(III) oxide content gives better blending and homogenization of mixing for each material. The improvement may be seen by comparing Fig. 4 where the chromium (III) oxide content is 14 wt %, with Fig. 5, where the chromium(III) oxide content is 3 wt %. Tables II and III give the effect of powder composition and preparation procedure on the corundum lattice parameters in powder mixes prepared from "A17 reactive" material and "MA95" material, respectively, showing further lattice distortion and strain induced during the preparation of the powder mix.

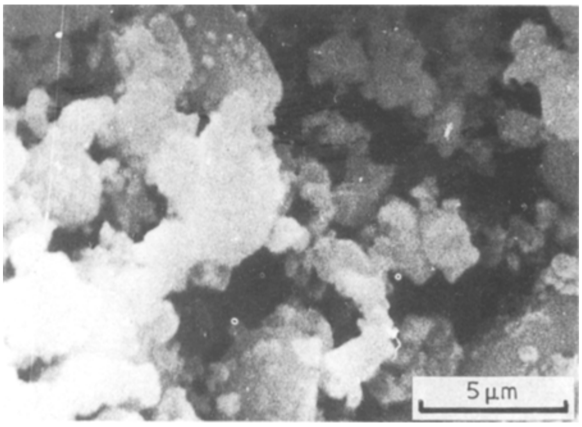

Figure 4 Particle size distribution in 14 wt % Cr_2O_3, 86 wt % "A17 reactive" Al_2O_3 (2 h tcm), blended 4 h hem.

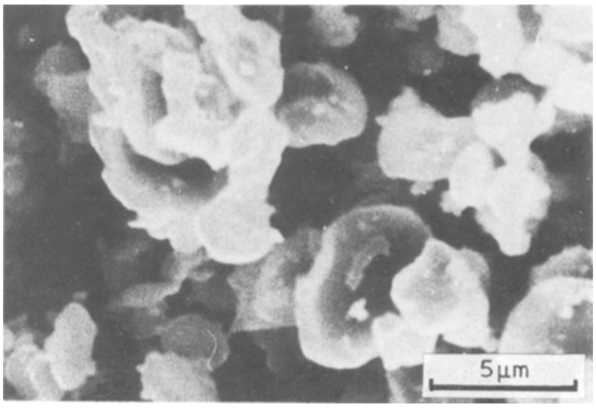

Figure 5 Particle size distribution in 3 wt % Cr_2O_3, 97 wt % "MA95" (2 h bm), blended 4 h bm.

3.2. Properties of compacts

Tables IV, V and VI give the properties of compacts prepared from the various powder blends and sintered for varying time and temperature. The XRD results confirm solid solution formation from chromium (III) oxide and aluminium(III) oxide, agreeing with the results of Spriggs and Bender [4]. Results show that the effect of chromium(III) oxide additions on the corundum lattice parameters is to produce small changes which are probably the consequence of compaction, densification and subsequently grain growth during sintering; the corundum crystals will have been severely elastically stressed and microfractured during the milling and blending operations.

Compacts prepared from "A17 reactive" material with 14 wt % chromium(III) oxide sintered at 1600 °C for 0.5 h contained free chromium(III) oxide, whereas other compositions did not. Occasionally, small amounts of impurities were detected, possibly due to small amounts of silica and/or sodium present in the starting materials.

3.2.1. *Densification, microstructure and grain growth*

The highest green densities are obtained with 14 wt % chromium(III) oxide, because the fine chromium(III)

TABLE II Effect of powder composition and preparation procedure on corundum lattice parameters in "A17 reactive" alumina–chromium(III) oxide mixture

Alumina (wt %) and milling method	Chromium(III) oxide (wt %)	Mixing time (h) and method	*a* (nm)	*c* (nm)	*c*/*a*
97 hem	3	4 bm	0.47545	1.31742	2.7709
97 bm	3	4 bm	0.47597	1.30406	2.7398
97 tcm	3	4 bm	0.47545	1.31742	2.7709
93 hem	7	4 bm	0.47566	1.29658	2.7265
93 bm	7	4 bm	0.47566	1.30012	2.7333
93 tcm	7	4 bm	0.47566	1.30264	2.7386
86 hem	14	4 bm	0.47512	1.30553	3.7478
86 bm	14	4 bm	0.47566	1.30074	2.7346
86 tcm	14	4 bm	0.47566	1.30235	2.7380
97 hem	3	4 hem	0.47643	1.30070	2.7301
97 bm	3	4 hem	0.47574	1.30110	2.7349
97 tcm	3	4 hem	0.47618	1.30768	2.7462
93 hem	7	4 hem	0.47561	1.29941	2.7321
93 bm	7	4 hem	0.47572	1.29957	2.7318
93 tcm	7	4 hem	0.47618	1.29059	2.7103
86 hem	14	4 hem	0.47700	1.30054	2.7265
86 bm	14	4 hem	0.47628	1.30343	2.7367
86 tcm	14	4 hem	0.47641	1.30107	2.7310

TABLE III Effect of powder composition and preparation procedure on corundum lattice parameters in "MA 95" alumina–chromium(III) oxide mixtures

Alumina (wt %) and milling method	Chromium(III) oxide (wt %)	Mixing time (h) and method	*a* (nm)	*c* (nm)	*c*/*a*
97 hem	3	4 bm	0.47604	1.30634	2.7442
97 bm	3	4 bm	0.47501	1.30243	2.7373
97 tcm	3	4 bm	0.47498	1.29736	2.7314
93 hem	7	4 bm	0.47557	1.31266	2.7602
93 bm	7	4 bm	0.47566	1.30026	2.7336
93 tcm	7	4 bm	0.47597	1.29887	2.7289
86 hem	14	4 bm	0.47645	1.30099	2.7306
86 bm	14	4 bm	0.47657	1.29736	2.7223
86 tcm	14	4 bm	0.47541	1.30400	2.7429
97 hem	3	4 hem	0.47659	1.30480	2.7378
97 bm	3	4 hem	0.47268	1.30062	2.7308
97 tcm	3	4 hem	0.47641	1.30345	2.7263
93 hem	7	4 hem	0.47651	1.29927	2.7127
93 bm	7	4 hem	0.47659	1.29284	2.7127
93 tcm	7	4 hem	0.47574	1.29705	2.7264
86 hem	14	4 hem	0.47643	1.30308	2.7351
86 bm	14	4 hem	0.47654	1.30333	2.7350
86 tcm	14	4 hem	0.47684	1.30196	2.7304

oxide particles fill the interstices between the "MA95" or "A17 reactive" particles. In general, higher green density and better blending are obtained when the chromium(III) oxide content is increased. As expected, a high compaction pressure gives a high green density. No attempt was made to optimize the particle size distribution in the powder mixes prior to compaction. No binders (fugitive or permanent) were added, as it was considered that these might alter the microstructure.

The microstructures were evaluated in terms of composition, powder preparation procedure, sintering temperature and time. Densification at low temperatures and the most rapid grain growth are obtained with "A17 reactive" material, hem, which had the smaller primary particle size. When the sintering time is short, irrespective of temperature, changing the preparation procedure does not produce a very different microstructure. With 3 wt % chromium(III) oxide, the sintered compact has a fine-grained porous structure (Fig. 6) at 0.5 or 1 h sintering time at 1600 °C. Increasing the sintering time to 8 h results in densification and formation of large grains by selective grain growth (Fig. 7), but with 7 or 14 wt % chromium(III) oxide a more uniform equiaxial grain growth is observed (Fig. 8).

The low density of some sintered compacts prepared from "MA95" material may be due to loss of chromium, which is consistent with the larger primary particle size of this material, suggesting that volatilization is faster than solid solution formation. This gives a structure of the type shown in Fig. 9. Chromium(III) oxide is known [11] to volatilize when heated above 1000 °C in air or oxygen, due to the reaction

$$Cr_2O_3(s) + 3/2\,O_2(g) = 2\,CrO_3(g)$$

TABLE IV Effect of composition, preparation procedure and sintering conditions on density and grain size of sintered compacts (mixing time 4 h, uniaxial compaction at 310 MPa)

Alumina material (wt %) and milling procedure	Mixing	Sintering temp. (°C)	Sintering time (h)	Green density ($kg\,m^{-3}$)	Density after sintering ($kg\,m^{-3}$)	Grain size (±1 μm)
97 A17 tcm	bm	1600	0.5	2781	3447	4
97 A17 tcm	bm	1600	1	2765	3514	4
97 A17 tcm	bm	1600	8	2768	3808	6
93 A17 tcm	bm	1600	8	2795	3542	6
86 A17 tcm	bm	1600	8	2841	3719	6
97 A17 tcm	bm	1650	8	2764	3688	35
93 A17 tcm	bm	1650	8	2789	3725	42
86 A17 tcm	bm	1650	8	2851	3636	28
97 A17 tcm	bm	1700	8	2745	3752	40
93 A17 tcm	bm	1700	8	2800	3565	35
86 A17 tcm	bm	1700	8	2846	3290	12
97 MA95 hem	hem	1600	8	2611	3500	5
97 MA95 bm	hem	1600	8	2610	3731	22
97 MA95 tcm	hem	1600	8	2581	3599	19
93 MA95 hem	hem	1600	8	2712	3547	4
93 MA95 bm	hem	1600	8	2669	3027	3
93 MA95 tcm	hem	1600	8	2681	3356	5
86 MA95 hem	hem	1600	8	2807	3633	5
86 MA95 bm	hem	1600	8	2802	3344	4
86 MA95 tcm	hem	1600	8	2797	3253	5
97 MA95 tcm	hem	1650	0.5	2589	3675	18
97 MA95 tcm	hem	1650	1	2585	3733	23
97 MA95 tcm	hem	1650	8	2601	3635	12
93 MA95 tcm	hem	1650	8	2693	3600	15
86 MA95 tcm	hem	1650	8	2779	3515	8
97 MA95 hem	hem	1700	1	2612	3342	7
97 MA95 hem	hem	1700	8	2613	3380	12
93 MA95 tcm	hem	1700	1	2683	3723	15
93 MA95 tcm	hem	1700	8	2691	3697	8
86 MA95 bm	hem	1700	1	2808	3788	18
86 MA95 bm	hem	1700	8	2812	3714	16
97 MA95 tcm	bm	1600	8	2408	3052	2
93 MA95 tcm	bm	1600	8	2511	3271	3
86 MA95 tcm	bm	1600	8	2611	3370	3
97 MA95 hem	bm	1650	1	2518	3585	9
93 MA95 hem	bm	1650	1	2576	3562	8
86 MA95 hem	bm	1650	1	2693	2870	5

TABLE V Properties of shapes made by blending and compacting chromium(III) oxide and milled "A17 reactive" alumina uniaxially at 310 MPa
(alumina milling, tcm; mixing, bm or hem 4 h; sintering time 8 h)

Al_2O_3(wt %) and blending	Corundum lattice parameters			Green density ($kg\,m^{-3}$)	Sintering temperature (°C)	Density after sintering ($kg\,m^{-3}$)	Average grain size (±1 μm)	Corundum lattice parameter change after firing (%)		
	a (nm)	*c* (nm)	*c*/*a*					*a*	*c*	*c*/*a*
97 bm	0.475 45	1.317 42	2.7709	2768	1600	3808	6	0.15	−3.69	−3.84
93 bm	0.475 66	1.302 65	2.7386	2795	1600	3502	6	0.32	−1.64	−1.96
86 bm	0.475 66	1.302 35	2.7380	2841	1600	3719	6	0.45	−1.13	−1.58
97 bm	0.475 45	1.317 42	2.7709	2764	1650	3688	35	0.18	−0.70	−0.88
93 bm	0.475 66	1.302 64	2.7386	2789	1650	3725	42	0.02	0.93	0.92
86 bm	0.475 66	1.302 35	2.7380	2851	1650	3636	28	0.41	−0.38	−0.78
97 bm	0.475 45	1.317 42	2.7709	2745	1700	3752	40	0.06	−1.05	−1.10
93 bm	0.475 66	1.302 64	2.7386	2800	1700	3565	35	−2.13	6.28	8.59
86 bm	0.475 66	1.302 35	2.7380	2846	1700	3920	12	−0.61	0.30	0.91
97 hem	0.476 18	1.307 68	2.7462	2793	1600	3902	20	0.03	−0.92	−0.95
93 hem	0.476 18	1.290 59	2.7103	2795	1600	3895	9	0.06	4.30	4.23
86 hem	0.476 41	1.301 07	2.7310	2920	1600	3830	8	0.37	−0.34	−0.71

TABLE VI Properties of shapes made by blending and compacting chromium(III) oxide and "MA 95 alumina" uniaxially at 310 MPa (hem 4 h, sintering time and temperature 8 h at 1600 °C)

Al_2O_3 (wt%) and blending	Corundum lattice parameters			Green density ($kg\,m^{-3}$)	Average grain size (±1 µm)	Density after sintering ($kg\,m^{-3}$)	Corundum lattice parameter change after firing (%)		
	a (nm)	*c* (nm)	*c/a*				*a*	*c*	*c/a*
97 hem	0.476 59	1.304 80	2.7378	2611	5	3500	−0.09	1.08	1.17
97 bm	0.476 28	1.300 62	2.7308	2610	2	3731	0.04	5.31	5.27
97 tcm	0.476 41	1.303 45	2.7360	2581	2	3599	0.01	5.09	5.07
93 hem	0.476 51	1.299 37	2.7263	2717	4	3547	0.11	−6.86	−6.90
93 bm	0.476 59	1.292 84	2.7127	2669	3	3027	1.77	−5.07	−6.72
93 tcm	0.475 74	1.297 05	2.7264	2681	5	3356	0.13	3.28	3.15
86 hem	0.476 43	1.303 08	2.7351	2807	5	3633	0.08	−0.21	−0.29
86 bm	0.476 54	1.303 33	2.7350	2802	4	3449	0.18	−0.10	−0.28
86 tcm	0.476 84	1.301 96	2.7304	2797	5	3253	−0.35	0.54	0.89

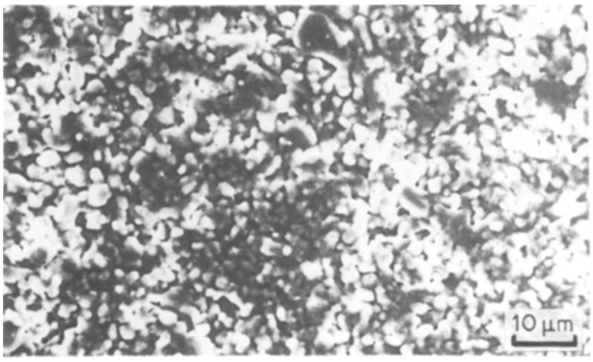

Figure 6 Microstructure of powder mix 3 wt % Cr_2O_3, 97 wt % "A17 reactive" Al_2O_3 (2 h tcm), blended 4 h hem, sintered at 1600 °C for 1 h. Grain size 3 µm, density 3686 $kg\,m^{-3}$.

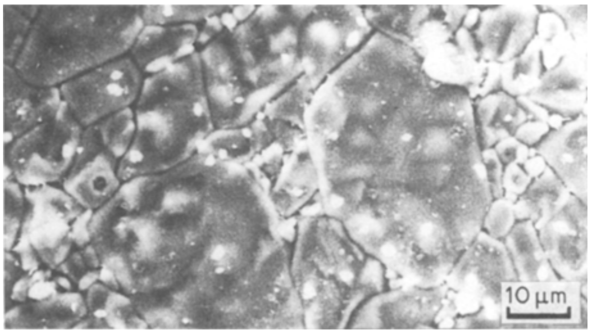

Figure 7 Microstructure of powder mix 3 wt % Cr_2O_3, 97 wt % "A17 reactive" Al_2O_3 (2 h tcm), blended 4 h hem, sintered at 1600 °C for 8 h. Grain size 20 µm, density 3902 $kg\,m^{-3}$.

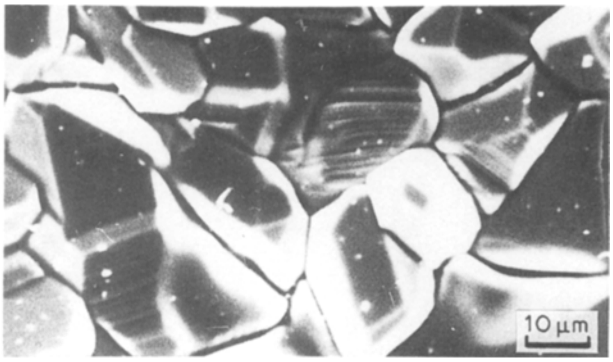

Figure 8 Microstructure of powder mix 14 wt % Cr_2O_3, 86 wt % "A17 reactive" Al_2O_3 (2 h tcm), blended 4 h bm, sintered at 1650 °C for 8 h. Grain size 28 µm, density 3636 $kg\,m^{-3}$.

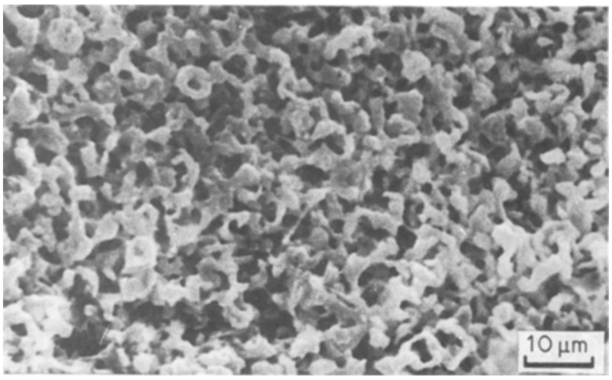

Figure 9 Microstructure of powder mix 14 wt % Cr_2O_3, 86 wt % "MA95" Al_2O_3 (2 h tcm), blended 4 h bm, sintered at 1600 °C for 8 h. Grain size 3 µm, density 3370 $kg\,m^{-3}$.

Figs 6–9 are from compacts prepared at 310 MPa. Micrographs of other compacts are given in [7] and [9].

3.3. Mechanical properties of alumina–chrome refractories

The modulus of rupture of a series of test bars sintered at 1650 °C for 5 h was determined at ambient temperature. The details are given in Table VII, which includes a Weibull analysis [10] of the data. In some mixes, boehmite was added to improve the packing and mouldability of the powder and to increase the 'green' strength of the moulding (12). The results given in Table VII show that, as expected, the modulus of rupture increases as the density after sintering increases. An increase in the Weibull modulus value corresponded to a decrease in the average value of the modulus of rupture. The results show that the high energy milling route gave the best Weibull modulus value. These powders have the finest particle sizes, showing the importance of a small and uniform particle size in optimizing the consistency of mechanical properties, as well as in obtaining the uniform equi-

TABLE VII Mechanical properties of aluminium oxide–chromium(III) oxide mixtures (Compaction 310 MPa, sintered at 1650 °C for 5 h)

Aluminium oxide material (wt %)			Cr_2O_3 (wt %)	Powder mixing	Density after sintering ($kg\,m^{-3}$)	Modulus of rupture (MPa)	Weibull modulus	Stress at 99.5 % survival probability (MPa)
GC powder	MA95	A17 reactive						
6.5	65.6	24.9	3	hem	3730	205	17.3	155
6.5	65.6	24.9	3	bm	3540	152	4.4	48
Nil	Nil	97	3	hem	3870	243	8.8	140
Nil	Nil	97	3	bm	3880	245	8.4	138
Nil	Nil	97	3	tcm	3870	245	7.4	125
31	45	10	14	tcm	3040	70	6.7	35
31	45	10	14	hem	3230	137	15.1	95
31	45	10	14	bm	3220	90	6.7	45

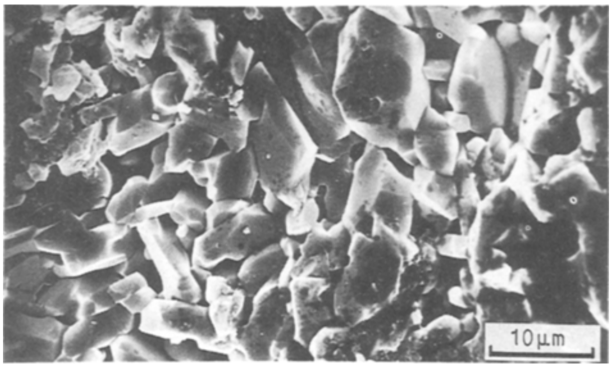

Figure 10 Test bar microstructure. Fractograph of powder mix 3 wt % Cr_2O_3, 97 wt % alumina derived from “MA95” “A17 reactive” and “GC boehmite” (4 h hem), blended 4 h hem, sintered at 1650 °C for 5 h. Grain size 6 µm, density 3730 $kg\,m^{-3}$.

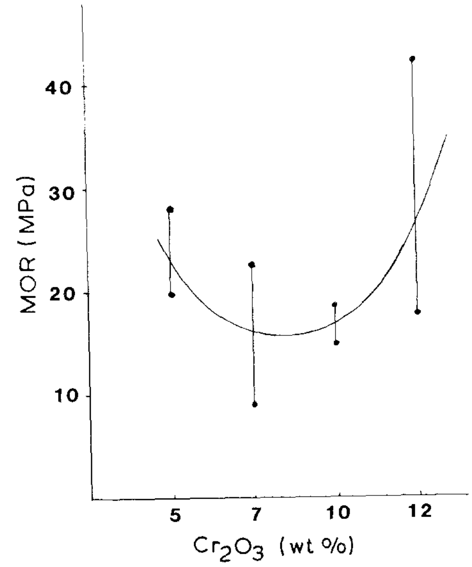

Figure 11 Variation of the hot (1150 °C) modulus of rupture (MPa) with wt % chromium(III) oxide for ethyl silicate-bonded alumina–chrome refractory.

axial grain growth and good densification considered to be the reason for the resistance to slag attack and thermal shock damage found in ethyl silicate-bonded alumina–chrome refractories. The microstructure giving the highest Weibull modulus and a modulus of rupture of 205 MPa is shown in Fig. 10. Comparison of Fig. 10 with Figs 6 to 9 shows the effect of boehmite (added to increase the green strength) on the microstructure. Weibull modulus values of 5 to 20 are usual [13] for ceramic materials, the higher value showing less strength variability. The strength values are reasonable; for comparison a value of ~200 MPa is given [14] for the strength of mullite ceramics.

The effect of chromium(III) oxide content on the modulus of rupture, measured at 1150 °C, of a series of ethyl silicate-bonded alumina–chrome refractory compositions is shown in Fig. 11. The composition of these refractory bodies and the firing schedule closely resemble those used in the production of the inner nozzles shown in Fig. 1. The modulus of rupture is minimum at ~7 wt % chromium(III) oxide. This coincides with the change in corundum lattice parameters noted in the powder blends containing 7 wt % chromium(III) oxide.

4. Conclusions

1. High-energy milling of the aluminium oxide starting material, to break down clusters of primary particles, followed by high-energy milling to mix with chromium(III) oxide is the preferred method of preparing powder mixes which, after compaction and sintering, give consistent mechanical properties, uniform grain growth and good densification.
2. XRD results confirm solid solution formation between aluminium(III) oxide and chromium(III) oxide.
3. The uniform grain growth and good densification observed after compaction and sintering of powder mixes containing 7 or 14 wt % chromium (III) oxide suggests why ethyl silicate-bonded alumina–chrome refractories resist slag attack and damage by thermal shock.
4. Loss of chromium from powder mixes prepared from aluminium oxide material of large primary particle size suggests that volatilization of chromium is faster than solid solution formation.
5. The effect of chromium(III) oxide on corundum (α-alumina) lattice parameters is, with 3 or 14 wt %, to increase *a* and *c* by 0.02 % to 0.45 % depending on sintering conditions, and with 7 wt % to decrease the lattice parameters.
6. The hot modulus of rupture of a series of ethyl silicate-bonded alumina–chrome refractories containing varying amounts of chromium(III) oxide is minimum at 7 wt % chromium(III) oxide. The change in

lattice parameters could change the elasticity of the refractory body, altering the modulus of rupture.

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