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The mechanical properties of ceramics from bauxite waste

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This paper summarizes the development of engineering ceramics made from bauxite waste ("red mud") produced in the alumina industry in Jamaica. Test specimens are fabricated from powders by sintering. For a particle size distribution of less than 75 μm in the starting powders and firing temperatures in the range of 1000 to 1100° C various mechanical properties are measured. These include fracture toughness (K_{Ic}), modulus of rupture (MOR), compression strength (σ_c) and Brinell hardness. While apparent porosity varies between 40 and 48%, K_{Ic} is found to vary between 0.39 and 0.68 MN m$^{-3/2}$. The values are compared with those measured for commercial ceramic tiles and also with ceramics of magnesia and calcium zirconate. Within the fabrication temperature range studied the MOR ranges between 17.23 and 27.09 MN m^{-2}, compressive strength between 42.0 and 83.9 MN m^{-2} and Brinell hardness between 26.2 and 59.9 kg mm^{-2}. With the aid of scanning electron microscopy and a basic knowledge of the physicochemical properties of the mud an attempt is made to explain the high strength and toughness achieved. The ready availability of raw material and the relatively low firing temperatures required for suitable engineering products should keep the production costs low for "red mud ceramics".

1. Introduction

Much has been said about the possibility of using Jamaican bauxite waste ("red mud") as a cheap source of raw material for the manufacture of low-cost ceramic products such as building blocks, floor and wall tiles, sanitary ware, etc. [1, 2]. However, what has been said is of a speculative nature revolving around economic feasibility. Hence very few technically useful data are available to aid in an assessment of the potential of red mud ceramics as suitable engineering materials. In particular, previous studies seem to have neglected the fact that the mechanical properties of engineering materials are determined primarily by their microstructure. Because of this no studies have systematically investigated microstructures (dependent on fabrication parameters) for optimum values of mechanical properties commensurate with the proposed applications.

Such an oversight is unfortunate, since it is expected that the microstructure, and hence mechanical properties of a ceramic component will vary depending on factors such as sintering temperature, sintering time and particle-size distribution in the initial starting powder, and the use or non-use of a bonding agent.

In addition, early studies of mechanical properties have concentrated on the tensile strength of the ceramics. But this may not be the most important parameter relevant to applications such as floor and wall tiles and sanitary ware. In ceramics, which are inherently brittle and thus susceptible to stress concentration and impact damage, the development of tough (as distinct from strong) materials should, perhaps, be of paramount importance. Thus fracture toughness (a good quantitative measure of the resistance of the material to fracture or of brittleness) along with other mechanical properties may be more significant to a meaningful assessment of the potential of red mud ceramics for the envisaged applications.

Of further interest is the fact that most ceramic products fabricated by conventional techniques (e.g. sintering, hot pressing, reaction bonding) contain varying degrees of residual porosity. The polycrystalline ceramic microstructures are often multiphase (as is the case for most clay bodies and hence is expected for red mud ceramics) and even when raw materials consist of a simple single-phase material, they are rarely ever 100% pure. When formed, impurity minor phases tend to segregate to grain boundaries. This often affects the mechanical and physical properties significantly, particularly if the grain-boundary phases are glassy and thus soften at much lower temperatures than the primary phase(s) when exposed to elevated temperatures. There is at present some understanding of the effects of porosity and second phases on the mechanical properties of ceramics (e.g. [3, 4, 5]) but much of it is of an empirical nature and relevant to specific microstructures. This, coupled with the statistical nature of the mechanical properties (e.g. fracture stress) of ceramics, makes it difficult to predict or generalize the mechanical properties of porous, multiphase ceramics from literature data.

In view of the points raised so far it seems justifiable and necessary to undertake an experimental programme directed specifically at red mud ceramics, not

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TABLE I Chemical analysis of typical Jamaican red mud [6]

Compound	Fe_2O_3	Al_2O_3	SiO_2	TiO_2	CaO	Na_2O	P_2O_5	Loss on ignition
Content (wt %)	51.50	15.00	1.70	6.70	7.0	0.97	0.83	9.30

only to determine their potential as possible practical engineering materials, but also to generate data from which a theoretical formulation may be attempted.

2. The physico-chemical properties of Jamaican red mud

The first comprehensive study of bauxite waste directed towards its utilization was instituted by the US Bureau of Mines and is reported by Parekh and Goldberger [6]. In this study one finds a detailed characterization of Jamaican red mud. This mud is very high in haematite and low in silica content [7] (see Tables I and II). This is distinct from most of the other Bayer process wastes. Also the data on grain size analysis shows that Jamaican bauxite waste is finer than muds from other places, with most of the particles being less than 0.5 micrometres in size (Fig. 1). These make the mud a potential raw material for the production of ceramics as engineering materials.

A more recent study [8, 9] describes the physical and chemical properties and the amorphous content in the red mud, used for this study (Tables II and III). The amorphous content is very high and is clearly visible in SEM photographs of the dry mud (see Fig. 5a below).

From Tables I and II one can see that Jamaican bauxite waste consists of several oxides such as SiO_2, P_2O_5 and CaO which can form glassy phase after sintering. One can exploit this property to develop strong ceramics from this material. The high amorphous content may, however, reduce the strength. But it is known that amorphous haematite crystallizes in the heating and cooling cycles. This motivated us to attempt a development of ceramic material using the red mud.

From a commercial point of view, the availability of a continuous supply of red mud with the same physicochemical properties is an important requirement. In this regard, an extensive characterization of the mud at various locations and depths (down to 9 m) was carried out in the Alcan Kirkvine disposal pond. The details of the study are given by Yong and Wagh [8, 9].

3. Experimental procedure

3.1. Fabrication of test pieces

The fabrication of the test pieces involved grinding dried red mud taken from the red mud disposal pond into a fine powder, then forming a "dough" with suitable addition of water. This dough was then moulded into rectangular bars using specially constructed moulds. Moulding was done at a pressure of 32.2 kg cm^{-2} (460 psi) and room temperature in a hydraulic press. The size of each bar was 3.8 mm × 10.5 mm × 60.4 mm. After excess water was allowed to evaporate the bars were placed in an electric furnace (AIM Kiln Model 2318, Ramona, California, USA) and fired for 3 h at the soaking temperature, which was attained at the rate of 300° C h^{-1}, with the necessary precautions taken to ensure uniform heating and to offset warping. Firing temperatures ranged between 1000 and 1100° C in steps of 25° C.

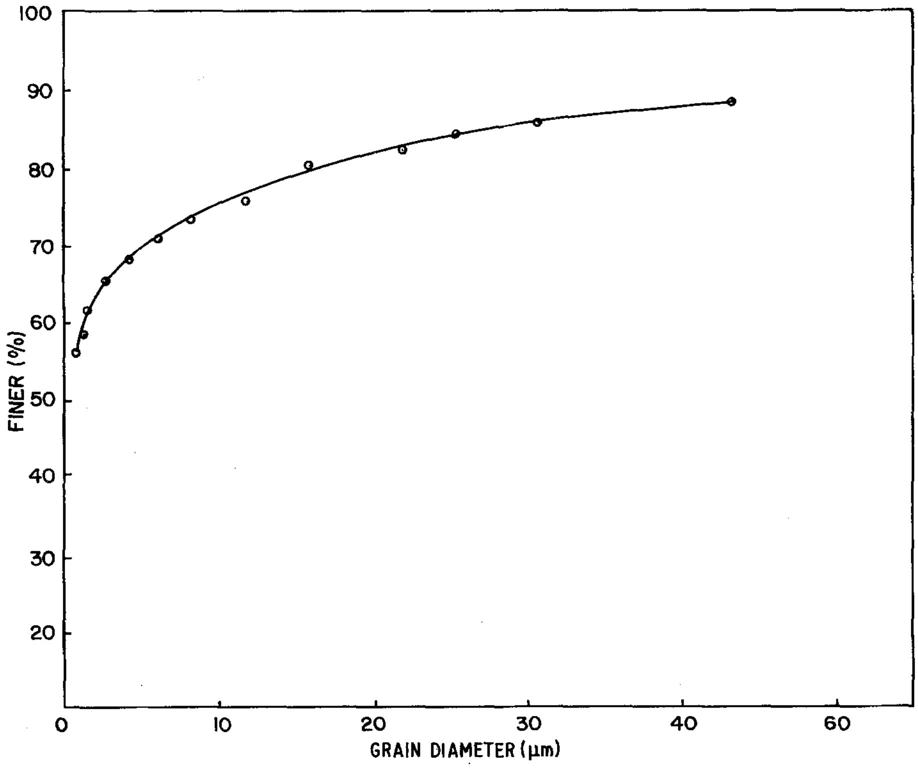

Figure 1 Grain-size analysis of Alcan (Jamaica) red mud. 70% of the particles are finer than 5 μm.

TABLE II X-ray fluorescence studies on dry Jamaican red mud

Element	Atomic No.	Content (wt %)
Al	13	9.8
Si	14	1.7
P	15	0.9
S	16	0.25
K	19	0.07
Ca	20	4.55
Ti	22	5.10
Cr	24	0.26
Mn	25	0.78
Fe	26	31.5
Ni	28	230 p.p.m.
Cu	29	120 p.p.m.
Zn	30	380 p.p.m.
Rb	37	8 p.p.m.
Sr	38	290 p.p.m.
Pb	82	40 p.p.m.

3.2. Microstructural investigation

The microstructures of the fired materials were studied using scanning electron microscopy. The samples were gold–palladium coated and imaged in the secondary electron mode at 25 kV. Open porosity and bulk density were determined gravimetrically using a technique based on the Archimedes principle and involving vacuum impregnation of the specimens with water.

3.3. Mechanical tests

The fracture toughness of the fired specimens was measured using the K_{Ic} concept. Briefly, it stems from the fact that with the advent of linear elastic fracture mechanics (LEFM) the energy-balance approach to brittle fracture [10] has been further developed by the introduction of the stress intensity factor K ($= K_{\mathrm{I}}$ for Mode I, opening-mode loading). According to LEFM, which essentially considers a specimen with an automatically sharp crack being loaded until a rapidly moving crack is initiated, fracture occurs in a brittle body when K_{I} reaches a critical value K_{Ic}. But under plain-strain conditions the critical strain energy release rate G_{Ic} is related to K_{Ic} by the equation (e.g. [11, 12])

$$K_{\mathrm{Ic}} = \left(\frac{EG_{\mathrm{Ic}}}{1 - \nu^2}\right)^{1/2} \tag{1}$$

where E is Young's modulus and ν the Poisson ratio. Since K_{Ic} is so related to G_{Ic}, K_{Ic} is generally taken as a measure of the materials fracture toughness.

Several attractive points are associated with the K_{Ic} approach when applied to the testing of brittle materials. For example:

(a) It is a better method of measuring toughness than the impact test because of better experimental control and greater accuracy.

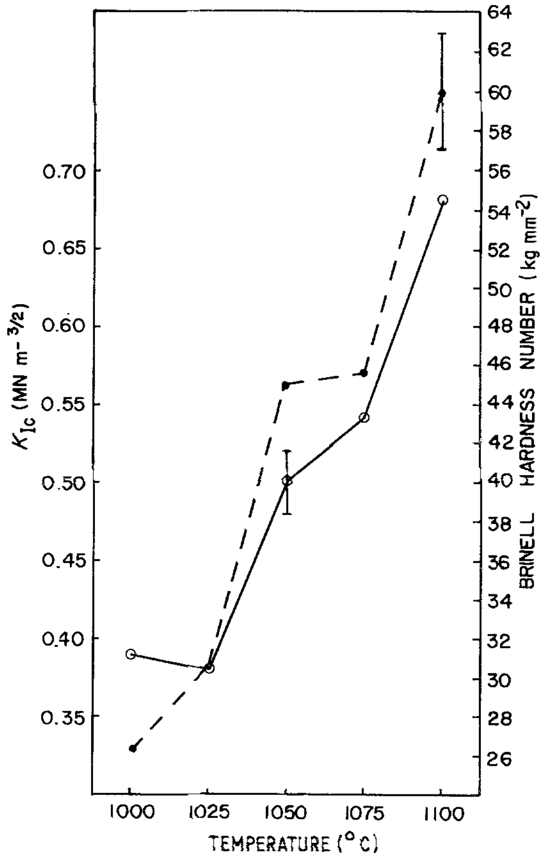

Figure 2 The variation of (●) Brinell hardness number (BHN) and (○) fracture toughness with firing temperature.

(b) K_{Ic}, unlike fracture strength, is a basic materials property, whose value should ideally be independent of specimen geometry and test technique (e.g. bending or torsion).

(c) Given any stress system (e.g. simple tension or bending) it is theoretically possible to calculate the fracture stress for a given defect size, or for a given stress to determine the maximum defect size to cause failure. This can be done, as shown by Paris and Sih [13], by means of the generalized equation

$$K_{\mathrm{Ic}} = y\sigma_{\mathrm{f}}a^{1/2} \tag{2}$$

where a is the maximum defect size to cause failure, or the depth of an introduced crack (or notch), y is a geometric factor and σ_{f} the fracture stress.

In this study K_{Ic} values were calculated using Equation 2 after σ_{f} was determined in three-point bending using single-edge notched bending specimens of dimension 57.6 mm × 10.2 mm × 3.8 mm with a depth of 2.0 mm. Tests were done in a Hounsfield Tensometer (Monsanto Ltd., Swindon, Wiltshire) fitted with a three-point loading arrangement.

MOR values were measured by the three-point bend test in a Hounsfield Tensometer using beam specimens of dimensions 3.8 mm × 10.2 mm × 57.6 mm. The compressive strength was also measured in the Hounsfield Tensometer using specimens of

TABLE III Some physical and chemical characteristics of Jamaican red mud [8]

pH	Amorphous content (mg/g soil)			Specific gravity (dry solids)	Organic content (wt %)
	Iron	Aluminium	Silica		
12.4	50 to 60	40 to 60	< 1	3.3	0.2

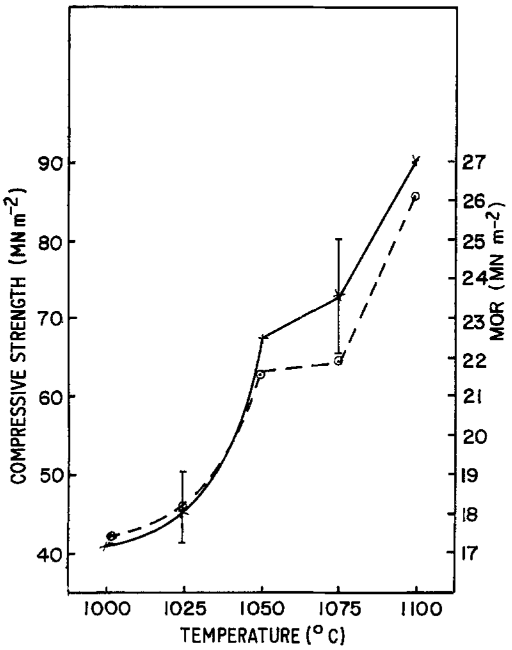

Figure 3 The variation of (○) compressive strength and (x) modulus of rupture with firing temperature.

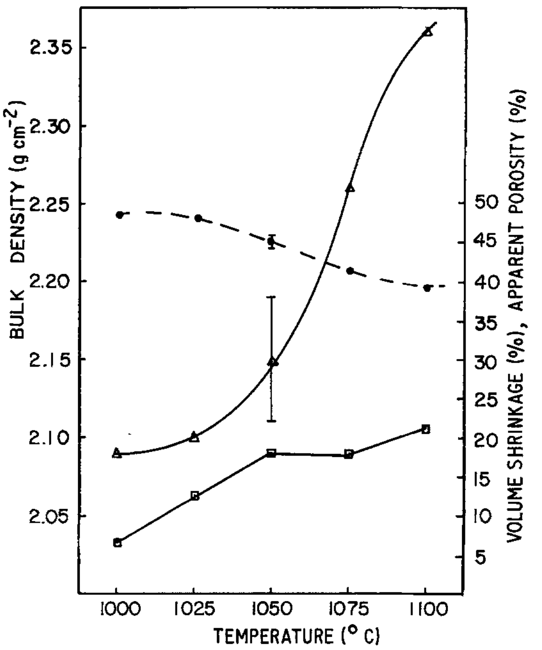

Figure 4 Basic physical properties of the various specimens: (△) bulk density, (●) apparent porosity, (□) volume shrinkage.

length 28.9 mm and cross-sectional area 38.8 mm^2. A 5 mm diameter ball was used for the measurement of the Brinell hardness.

4. Results

The results of the above-mentioned measurements are presented in Figs 2 to 4 as a function of the firing temperature. In Fig. 2, the fracture toughness (K_{Ic}) and the Brinell hardness number (BHN) are presented, while in Fig. 3 we have the modulus of rupture (MOR) and the compressive strength. Fig. 4 shows the variation in bulk density, apparent porosity and the percentage volume shrinkage.

In all the tests for mechanical properties (Figs 2 and 3) the general trend is an increase in the value with increase in firing temperature. The increase is not, however, uniform. In particular a slower rate of increase is noted between 1050 and 1075° C. However, overall K_{Ic} increase from 0.39 to 0.68 MN m$^{-3/2}$, BHN from 26.2 to 59.9 kg mm^{-2}, compressive strength from 42.0 to 83.9 MN m^{-2} and MOR from 17.23 to 27.09 MN m^{-2}, thus exhibiting almost a doubling of the value between the lowest and highest firing temperature in each case. The temperature range chosen here is the most interesting range, since the mechanical properties in this range compare well with those of commercial ceramics. For the sake of comparison, Table IV summarizes some of the toughness measurements on commerical and also high-strength ceramics. The toughness achieved with our material is certainly higher than the commerical building material and closer to Pyrex and other high-strength ceramics. It is in fact possible to raise the toughness further by reducing the initial particle size and raising the firing temperature. At present these are being studied by us systematically. However, it suffices to state here that the present data clearly indicate that the required toughness of the ceramics can be achieved even at a temperature as low as 1050° C. As expected, bulk density and percentage shrinkage increase with increasing firing temperature, while the porosity decreases (see Fig. 4). Both the shrinkage and the porosity are higher than in commerical tiles. However, after glazing and surface treatment we believe the porosity can be further reduced.

5. SEM investigations

Fig. 5a is a typical micrograph of a specimen before

TABLE IV Toughness of typical sintered ceramics

Material*	Measured by*	Porosity (%)	K_{Ic} (MN m$^{-3/2}$)
"Ceramic" Trinidad Ltd. (glazed on one side)	UWI	19.04	0.42 ± 0.02
Hungarian red mud ceramics (UNIDO) (Floor tiles, unglazed)	UWI	38.4	0.55 ± 0.02
UWI Tiles (unglazed)	UWI	40-48	0.39 to 0.68 ± 0.02
MgO	Knight *et al.* [5]	31.2	1.10
CaZrO$_3$	Knight *et al.* [5]	33.2	1.00
Borosilicate glass (Pyrex)	Wedderhorn *et al.* [14]	—	0.75

*UWI: University of the West Indies; UNIDO: United Nations Industrial Development Organization.

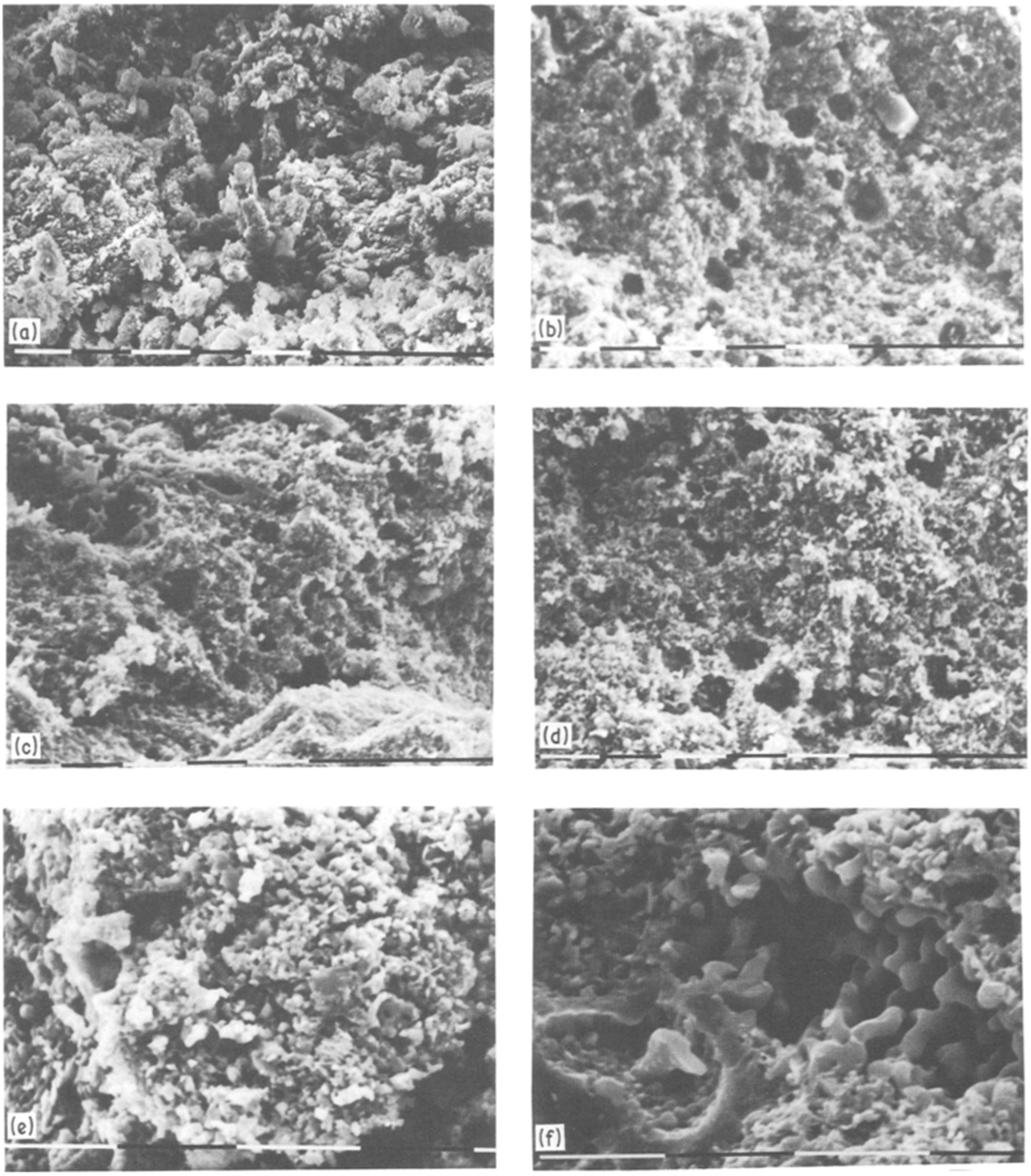

Figure 5 SEM micrographs of the samples (bars $= 10\,\mu m$): (a) unfired sample; (b to f) fired at (b) 1000° C, (c) 1025° C, (d) 1050° C, (e) 1075° C and (f) 1100° C.

firing while Figs 5b to f are typical of the microstructures of ceramics fired between 1000 and 1100° C. In Fig. 5a, rod-like crystals coated with amorphous material are clearly visible. Spheroidal particles are also common features of the microstructure. Presumably the rod-like particles are goethite ($Fe_2O_3 \cdot H_2O$) while the spherical ones are haematite (Fe_2O_3) particles. This belief is based on the fact that iron oxides form the larger part of the aggregate and also, as presented in Table III, a good part of it is amorphous. When this material is fired, one expects two transitions to take place: the amorphous material will reduce to crystalline, and also the water of crystallization will escape from geothite and several other crystals leading to better bonding and better strength, as normally expected in any ceramic [15]. The outstanding difference between the microstructures shown in Figs 5a and b is the absence of rod-like crystals and the amorphous material in Fig. 5b. As the sintering temperature is raised, there is hardly any observable difference in the microstructure, possibly because these temperatures are too close for any visible change. One does however see a marked difference between the microstructures of samples fired at 1050 and 1075° C (see Figs 5d and e), where now the agglomerates are bigger and a clear bonding between the particles is visible. The particles fuse further and at 1100° C (Fig. 5f) all the particles appear to be interconnected.

Thus overall the general trend seems to be an increase in agglomerate size with increasing temperature. At 1100° C the smooth nature of the surface of an agglomerate is quite distinct from the powdery (amorphous) surface seen in Fig. 5a.

6. Discussion

"Red mud" is a very complex material. It is a mixture of several oxides and minerals which respond in a complex way to heat treatment. As such one can only be guided by the behaviour of the prominent constituents of the mud in any analysis.

In this respect, iron oxide, titania, alumina and limestone form the major components of Jamaican red mud. None of these softens at the temperatures considered here. It is, however, possible that some of the known constituents of some low softening-temperature glasses such as SiO_2, CaO, Na_2O and P_2O_5 may be responsible for the glassy phase, leading to the network-like structure seen at 1075 and 1100° C (Figs 5e and f). This is consistent with the idea that as the temperature is increased the viscosity of the glassy phase would be sufficiently reduced, above a certain temperature, for it to flow and disperse in the microstructure. On cooling it would act to bind the agglomerates of the major constituents, thus increasing the fracture toughness and other mechanical properties. This softened, high-viscosity glassy phase could also be responsible for coating the surface of agglomerate particles, thus rendering them smooth in appearance (Fig. 5f). At present attempts are under way to identify the bonding phases.

It should, however, be noted that in Figs 2 and 3 one observes almost a plateau or a slow increase in the mechanical properties between 1050 and 1075° C. Just beyond 1050° C a solid solution [15] is formed between haematite and rutile (TiO_2). Also soda felspar ($Na_2O \cdot Al_2O_3 \cdot 6SiO_2$) and silica form a binary eutectic [16] at 1062° C. These transformations are probably responsible for the "discontinuity" in most of the curves.

To summarize, the following important conclusions may be drawn from the data and observations presented in this work:

(i) The particle size and the mineralogy of Jamaican bauxite waste allow one to develop ceramics of high strength and toughness.

(ii) The toughness of this red mud ceramic is comparable or superior, depending on sintering temperature, to values obtained for other porous ceramics.

(iii) The microscopic cause of the high toughness is not clear. However, it appears that the dispersion of a glassy phase in the microstructure is mainly responsible for bonding and toughening.

(iv) It is now possible to make ceramic material with sufficiently high toughness for practical engineering applications from 100% red mud, unlike previous attempts [1, 2] where a number of additives, organic or otherwise, were added.

References

1. "Utilisation of Red Mud Wastes for Lightweight Structural Building Products", IITRI Project No. G6015 (US Bureau of Mines, Washington D.C., 1968).
2. "Jamaica–Pilot scale Testing of representative samples of Bauxite residues (red mud) for profitable utilisation in the building materials industry", Draft Final Report of Project No. SI/JAM/81/802, (Jamaica Bauxite Institute, Kingston, Jamaica, 1983).
3. F. L. KNUDSEN, *J. Amer. Ceram. Soc.* **42** (1959) 376.
4. R. W. DAVIDGE and A. G. EVANS, *Mater. Sci. Eng.* **6** (1970) 281.
5. J. C. KNIGHT, T. F. PAGE and J. E. WESTON, *Proc. Br. Ceram. Soc.* **32** (1982) 291.
6. B. K. PAREKH and W. M. GOLDBERGER, "An Assessment of Technology for Possible Utilisation of Bayer Process Muds", EPA (USA) 600/2-76-301 (Washington D.C., 1976).
7. A. S. WAGH, C. G. C. DOUGLAS and P. V. D. PRASAD, "The Status and Requirement of Bauxite Slime Disposal Problem of Jamaica", UWI Physics Department Report No. 131 (1982).
8. R. N. YONG and A. S. WAGH, "A Study of Jamaican Bauxite Waste – First Annual Report" (International Development Research Centre, Ottawa, Canada, 1984).
9. *Idem*, "A Study of Jamaican Bauxite Waste–Second Annual Report" (International Development Research Centre, Canada, 1985).
10. A. A. GRIFFITH, *Phil. Trans. R. Soc.* **221A** (1920) 163.
11. A. G. EVENS and T. G. LANGDON, *Prog. Mater. Sci.* **21** (1976) 187.
12. B. R. LAWN and T. R. WILSHAW, "Fracture of Brittle Solids" (Cambridge University Press, 1978) p. 65.
13. P. C. PARIS and G. C. SIH, ASTM STP 381 (American Society for Testing and Materials, Philadelphia, 1965) p. 30.
14. S. M. WEDDERHORN, H. JOHNSON, A. M. DINESS and A. H. HEUER, *J. Amer. Ceram. Soc.* **5** (1974) 336.
15. J. L. RENDON and C. J. SERNA, *Clay Minerals* **16** (1981) 375.
16. W. A. DEER, R. A. HOWIE and J. ZUSSMAN, "Introduction to Rock-forming" (Longman, London, 1976).
17. "Materials and Technology; a systematic encyclopaedia", Vol. 2 edited by J. H. de Bussy (Amsterdam, 1971) p. 320.

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