Ceramic joining through reactive wetting of alumina with calcium aluminate refractory cements

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Abstract. Compositions in CaO–Al$_2$O$_3$ system have been prepared by gel–to–crystallite conversion method. Reactive powders of 1 : 2, 1 : 1, 2 : 1 and 3 : 1 of CaO and Al$_2$O$_3$ compositions were obtained by calcining the product at 800–1200°C. Fine grained powders were used as refractory cement for joining alumina ceramics. An optimum temperature of 1450°C for 4 h produced joints of satisfactory strength. The microstructure and X-ray phase analysis of the fractured joint surface clearly indicate reactive wetting of the alumina ceramics. This wetting enhances the joining of alumina substrates and can be attributed to the formation of Ca$_{12}$Al$_{14}$O$_{33}$ liquid phase. The results are explained by using CaO–Al$_2$O$_3$ phase diagram.

Keywords. G → C conversion; reaction bonding; alumina ceramics; calcium aluminate; high temperature cements.

1. Introduction

Many complex ceramic joining techniques have been developed for ceramic–to–metal and ceramic–to–ceramic joining. The electronic, mechanical, crystallographic and thermodynamic changes occuring in the interfaces of the joints have resulted in development of unique joining techniques like diffusion bonding (Bates *et al* 1990), brazing (Loeman and Tomsia 1988), glass frit joining (Walls and Ueki 1992), fusion and friction welding (Fernie 1997) and microwave joining (Meek and Blake 1986; Palaith and Silberglitt 1989). Most of the ceramic joining investigations are carried out in non-oxide ceramics such as AlN, Si$_3$N$_4$, SiC etc while ZrO$_2$ and Al$_2$O$_3$ are the usually considered oxide materials for many applications. The literature about alumina joining is very much limited when compared to other ceramics like Si$_3$N$_4$ and SiC.

Alumina, both as single crystal and in polycrystalline form, has remarkable properties in comparison to the conventional porcelains and other oxide ceramics. Application of alumina ceramics can be greatly enhanced and fabrication costs reduced if simple and reliable joining techniques are developed. One possibility of doing this is to use refractory cements for joining. Binary compounds of CaO–Al$_2$O$_3$ system have long been known as refractories especially in furnace lining applications (Parker and Sharp 1982).

Wet chemical methods of preparation is a preferred route for obtaining homogeneous and reactive powders, producing relatively small particle size compared to that

prepared using the solid state reaction. The gel to crystallite (G → C) conversion route can yield highly reactive powders as the desired phase can be formed at relatively low temperatures. Reactive powders of various aluminates have been prepared by earlier workers using this method (Kutty and Padmini 1992, 1995; Padmini and Kutty 1994; Kutty *et al* 1996; Nayak and Kutty 1996; Jayaraman *et al* 1998). In the present investigation, G → C conversion method has been used to prepare reactive refractory cement compositions in CaO–Al$_2$O$_3$ system. Joining of alumina ceramics using these cements has been optimized. The joint region has been investigated by XRD, SEM and mechanical pull test.

2. Experimental

G → C conversion method involves the reaction of a hydrated gel such as hydrated alumina gel (Al$_2$O$_3 \cdot x$H$_2$O) with M^{n+}(OH)$_n$, (where M = Ba^{2+}, Ca^{2+}, Mg^{2+} etc) in presence of a hydrophilic solvent, such as ethanol, at 80–100°C for 4–6 h. Often, the as-prepared form is a crystalline metastable hydroxylate which acts as a precursor. The precursor decomposes on calcination giving rise to the desired end product. Different stoichiometric calcium aluminates were prepared using this method by precipitating the gel using either AlCl$_3$ (Qualigens-LR) or Al(NO$_3$)$_3 \cdot$4H$_2$O (Qualigens-GR grade). The aqueous aluminum nitrate solution was analysed by gravimetry for Al$_2$O$_3$ content. Stoichiometric amount of calcium ion was added in the form of either Ca(OH)$_2$ or CaO freshly prepared by decomposing CaCO$_3$ at ≈ 900°C.

TG/DTA was used to find out the reaction sequence of the calcium aluminates from the precursor to final

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compound and to find the temperature at which the precursor becomes volatile-free. The TG/DTA curves were recorded in air at a heating rate of 15°C/min using an automated simultaneous thermal analyser STA/1500 of Polymer Laboratories. The characterization of the compounds was done using a Scintag/USA X-ray Diffractometer employing Cu-K$_\alpha$ radiation and Ni filter. Scanning electron micrographs (SEM) were obtained using a S360 Cambridge scanning electron microscope on fractured surfaces sputtered with a thin layer of gold.

A commercial alundum cement procured from Fisher Scientific, USA was used for comparison of the alumina joining property of prepared cements. The alumina ceramic specimens for reaction studies were prepared in the cylindrical form (10 mm dia and 15 mm length) by compacting and sintering submicrometer sized reactive alumina powder. Alumina powder (Alcoa, A-16 grade) is seen to have spherical shape and the average size as calculated from the SEM is about 0·4 μm. Most of the joining studies were conducted on the alumina substrates sintered at 1450°C for 4 h and having the density of ≥ 90·5%.

The joining possibilities were investigated by varying the joining temperature from 1200 to 1550°C. Calcium aluminates of the composition $CaAl_4O_7$ (CA$_2$), $CaAl_2O_4$ (CA), $Ca_{12}Al_{14}O_{33}$ (C$_{12}$A$_7$) and Ca_3AlO_6 (C$_3$A), heat treated at 800–1200°C for 4 h, were made in the form of paste using distilled water and then applied to the alumina test specimen surfaces. The pairs of alumina specimens to be joined were kept in the vertical position with the joining surfaces in contact and allowed to dry up in the open atmosphere for 6–10 h before subjecting them to heat treatment. A home-built pull test apparatus was extensively used for evaluating the comparative strength.

3. Results

Most of the as prepared precursor powders were either X-ray amorphous or showed broad peaks. TG/DTA data showed a typical residue of 60–70% after all the volatiles were lost up to 700°C. TG/DTA run in figure 1 shows the decomposition of the precursor of C$_3$A powder prepared using G → C conversion method. The initial weight loss at < 200°C varies depending upon the drying condition. The weight loss at 315°C can be attributed to the decomposition of aluminium hydroxide. The decomposition of calcium hydroxide begins at 450°C and goes to completion only at 750°C. These compositions were calcined between 800 and 1200°C for the purpose of getting crystalline refractory cements. Table 1 gives the nominal starting composition, phase identifications as well as the structural and thermal data of the heat-treated compounds. XRD analysis of the calcined powders indicated complete crystalline phases. These phases remain stable on heating up to 1500°C except C$_2$A, which melts at 1415°C.

The strength of the joints was evaluated by the pull test and the results tabulated (table 2). As seen from table 2, at 1200°C no joining is observed in any of the calcium aluminates and at temperatures > 1400°C, C$_3$A joined alumina specimens display comparable strength with that of joints made with commercial alundum cement. The other two compositions viz. CA$_2$ and CA do not show any joining even at 1500°C. C$_{12}$A$_7$ composition, however, showed some joining above 1500°C. The fractured surface was extensively studied for composition analysis. In all cases, multiphasic XRD spectra were obtained indicating chemical reaction taking place at the joint region. Solid state reaction occurs between C$_3$A and Al$_2$O$_3$ to form C$_{12}$A$_7$, which is a liquid phase at the reaction temperature and reacts with the Al$_2$O$_3$ substrates to form CA. The CA formation could be due to the mechanism of interstitial migration of Al^{3+} ions. In general, the reaction product was richer in alumina contents than the starting Ca : Al ratio. Though the relative amounts of the crystalline phases varied, presumably due to the exact location of cleavage surface with respect to the substrate, a common phase formed in all cases was C$_{12}$A$_7$. A typical XRD analysis of the fractured region of CA joined alumina ceramics by heat treating at 1450°C for 4 h is shown in figure 2 wherein, the interface shows the presence of crystalline phases of C$_{12}$A$_7$ and CA. Figure 2b shows the presence of CA$_2$, CA and C$_{12}$A$_7$ along with α-alumina of the substrate. Histograms of the joint strengths obtained with C$_3$A at different temperatures are shown in figure 3. Temperatures > 1450°C were not helpful in preparing stronger joints.

Figure 4 is an SEM picture of the joint with C$_3$A cement showing the bottom substrate, joint region and top substrate. The thickness of the joint region is about 10–30 μm and the evidence for the melting nature of the cement is also seen. There is no difference in the interfaces of the joint in between top and bottom substrates. In figure 5 the three cements CA, C$_{12}$A$_7$ and C$_3$A are compared by presenting SEM pictures of the respective fractured surfaces. Melting of the cement occurs in all the three cases but is more pronounced in the case of C$_{12}$A$_7$.
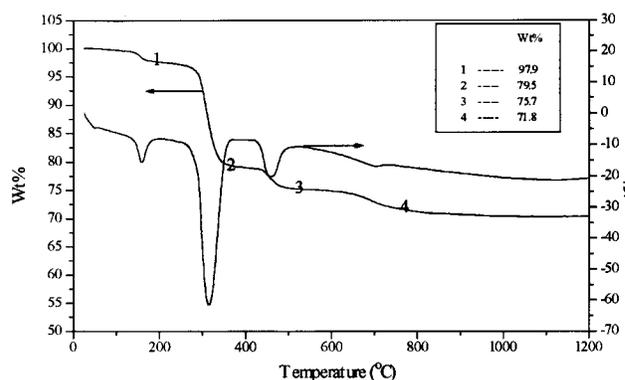

Figure 1. TG/DTA curves of C$_3$A prepared by G → C conversion route.

Table 1. Refractory cement compositions and the crystalline phases obtained upon high temperature heat treatment.

| Nominal composition[†]	Crystalline phases identified*	Unit cell structure	Unit cell parameters (Å)	Density (g/cm³)	Melting point (°C)
$CaAl_4O_7$ (CA_2)	$CaAl_4O_7$	Monoclinic	$a = 12.94$ $b = 8.91$ $c = 5.45$ $\beta = 107°$	2.86	1762
$CaAl_2O_4$ (CA)	$CaAl_2O_4 + Ca_{12}Al_{14}O_{33}$ (minor quantities)	Orthorhombic	$a = 8.74$ $b = 8.10$ $c = 15.13$	2.98	1605
$Ca_2Al_2O_5$ (C_2A)	$Ca_{12}Al_{14}O_{33} + C_3A$ (minor quantities)	Cubic	$a = 11.98$	2.68	1415
$Ca_3Al_2O_6$ (C_3A)	$Ca_3Al_2O_6$	Cubic	$a = 7.62$	3.03	1540

*Crystalline phases identified after heat treatment at 1200°C in open air.
[†]Cement chemistry notation: C = CaO and A = Al_2O_3.

Table 2. Joint strength as obtained by pulling strength measurement (kg/cm²).

Cement used	Temperature (°C)				
	1200	1400	1450	1500	1550
CA_2	not joined	not joined	not joined	not joined	not joined
CA	not joined	not joined	not joined	very weak joint	not joined
C_2A	not joined	very weak joint	very weak joint	20–40	10–15
C_3A	not joined	20–60	30–60	30–60	20–60
Alundum cement	very weak joint	50–70	20–35	40–55	weak joint

The molten microstructure indicates the reaction between cement and alumina substrate. Figure 5b shows the solidification fronts on cooling in the samples joined using $C_{12}A_7$. At the temperature of joining (1450°C) only $C_{12}A_7$ phase is expected to melt. All the other phases CA_2, CA and C_3A have much higher melting points. To confirm the above observation, pellets made out of these three cements were heated separately on a platinum foil to 1450°C. While $C_{12}A_7$ melted, there was no evidence of melting or decomposition of the CA and C_3A phases. This is in agreement with the published CaO–Al_2O_3 phase diagram (Taylor 1990), a portion of which is given in figure 6. This reveals that $C_{12}A_7$ has the lowest melting point at 1415°C while C_3A melts at 1540°C and CA at 1605°C. Two eutectic points at 1400°C and 1390°C for (C_3A and $C_{12}A_7$) and ($C_{12}A_7$ and CA), respectively covering a wide range of compositions from C_3A to CA are indicated in the phase diagram. This could explain the small amount of joining observed in some cases at 1400°C.

The extent of reaction happening at different temperatures can be analysed from the XRD patterns of the alumina joints prepared using C_3A at temperatures of 1400–1550°C as given in figure 7. At 1400°C, mainly the
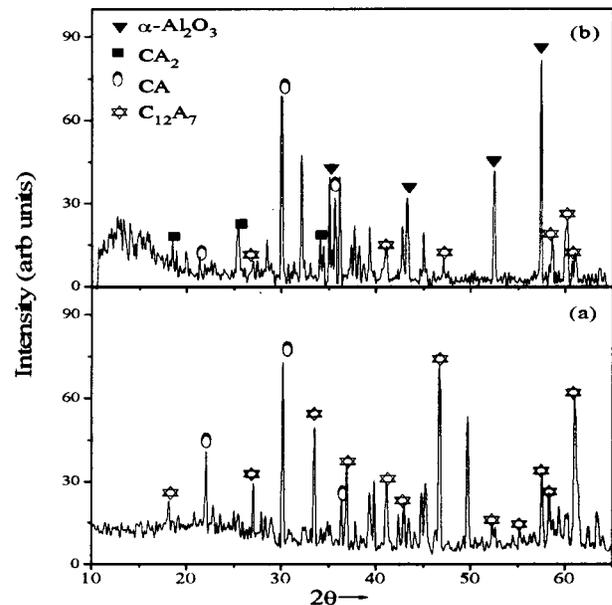
Figure 2. XRD patterns of the fractured region of alumina joints prepared using calcium aluminate of the composition CA by heating at 1450°C for 4 h (**a**) middle region and (**b**) surface of the joint.

C_3A and $C_{12}A_7$ phases are seen while CA is present only in small amounts. At 1450°C, the CA and $C_{12}A_7$ are of almost equal amounts, along with some C_3A. At 1500°C onwards, the CA phase dominates in comparison to $C_{12}A_7$.

4. Discussion

From the above results it can be clearly concluded that calcium aluminates applied as cement on the alumina surfaces react with the substrates to form alumina-rich compounds at high temperatures. Out of the phases considered, calcia rich C_3A takes up more Al^{3+} from the substrate. Diffusion of Al^{3+} occurs through the HCP layers of O^{2-} anions by the mechanism of interstitial migrations. The solid state diffusion of Al^{3+} ions at 1400°C is accompanied by its reaction with C_3A to give products $C_{12}A_7$ and CA. At temperatures > 1400°C, $C_{12}A_7$ melts and wets the alumina substrate surface, further enhancing the chemical reaction with that. The diffusion occurring at the interface to give the reaction products can be diagrammatically expressed as in figure 8 with a possible continuous variation in the calcium content. The reactions occuring at the interface, in the case of C_3A, can be written as
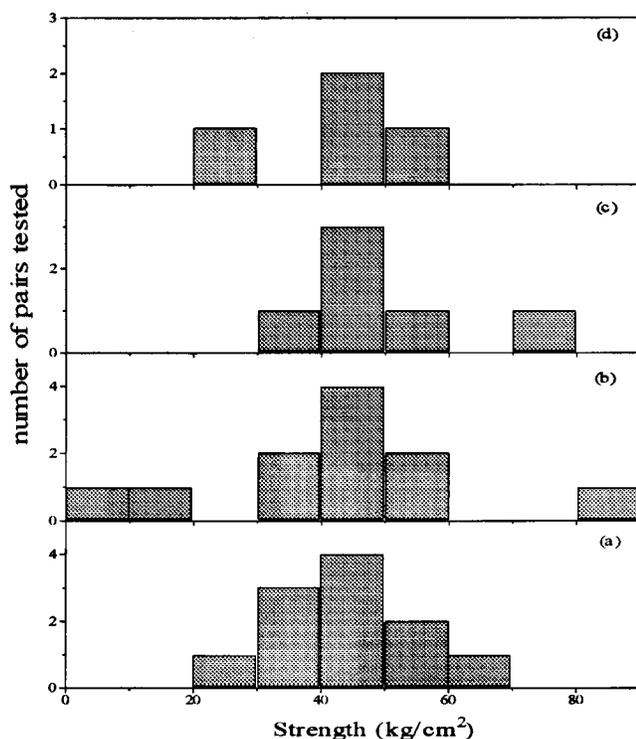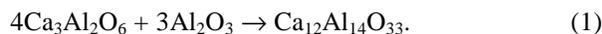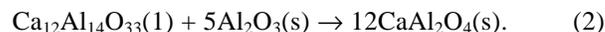
(i) Reaction by solid state diffusion at 1400°C:

$$4Ca_3Al_2O_6 + 3Al_2O_3 \rightarrow Ca_{12}Al_{14}O_{33}. \qquad (1)$$

(ii) Reaction involving a liquid phase at > 1400°C:

$$Ca_{12}Al_{14}O_{33}(1) + 5Al_2O_3(s) \rightarrow 12CaAl_2O_4(s). \qquad (2)$$

In the case of C_2A cement, $C_{12}A_7 + C_3A$ being the evolving crystalline phases while heating, the reaction (2) can directly take place when applied to the alumina surface and heated to temperatures > 1400°C. Since $C_{12}A_7$ melts by itself at these temperatures, the wetting can be self-initiated. However, due to difference in the calcium cation concentration in cement (50 mole%) and the alumina substrate (0 mole%), the reaction of $C_{12}A_7$ with the alumina can take place to give an alumina richer compound as well.

The formation of liquid phase is minimal in the case of CA. However, the SEM microstructures and XRD patterns show evidences of partial melting and reaction respectively. Presence of small quantities of $C_{12}A_7$ along with the nominal CA composition may be the reason for this. The liquid phase, though in minor quantities, can still provide partial wetting and hence the observed joining for CA composition.

SEM result of the C_3A joined alumina essentially shows a molten phase in the joint region. Wetting of the alumina substrates is observed thereby restricting the debonding at the substrate–joint interface. The reactions result in the formation of different phases of calcium aluminates, which wet the alumina specimen surface. This wetting of the alumina substrate by the reaction products result in the filling up of all pores giving rise to strong joints. The different phases in the joint surface, all being calcium aluminates, can have similarity in properties and this composite mixture gives a chemical gradient, which is much better than having abrupt boundary due to a single phase. The temperature range around 1450°C is found to be the most optimum for producing good joints. This temperature is
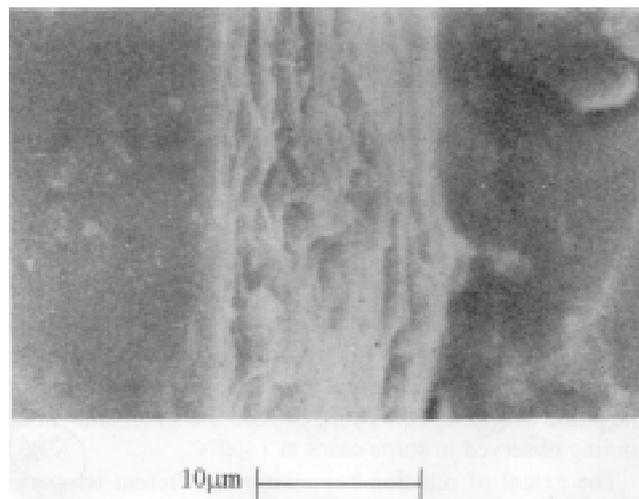

Figure 3. Histogram representing the strength of C_3A joined alumina specimens heated at (**a**) 1400, (**b**) 1450, (**c**) 1500 and (**d**) 1550°C.

Figure 4. Scanning electron micrograph showing both the joint and base alumina specimens.

just above the eutectic points of C_3A and $C_{12}A_7$ and hence the joining is assisted by the wetting of the alumina surface by the liquid phases thus formed.

Even though the eutectic point of $C_3A + C_{12}A_7$ lies at 1400°C, there may not be much liquid phases or the melt may be too viscous. Hence, the joining obtained at this temperature may not be the optimum. Higher temperatures of 1500 to 1550°C do not seem to have any significant advantage in improving joint strength because, as observed in figure 7, higher temperature treatment seems to
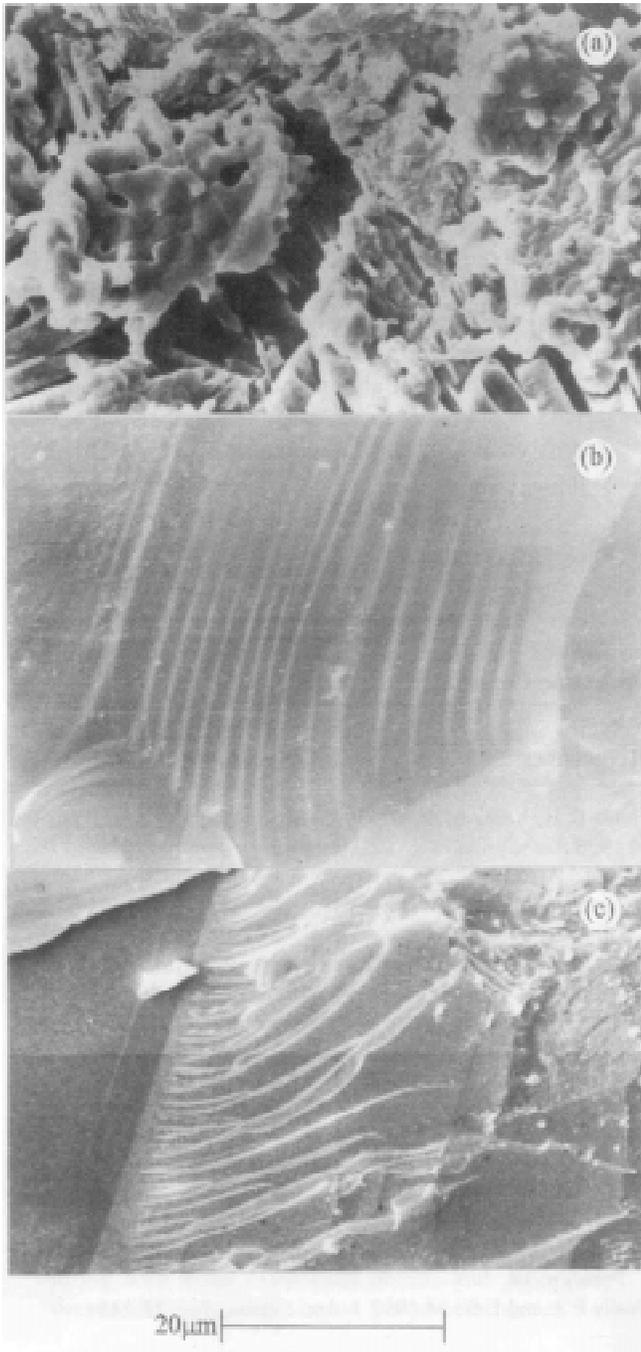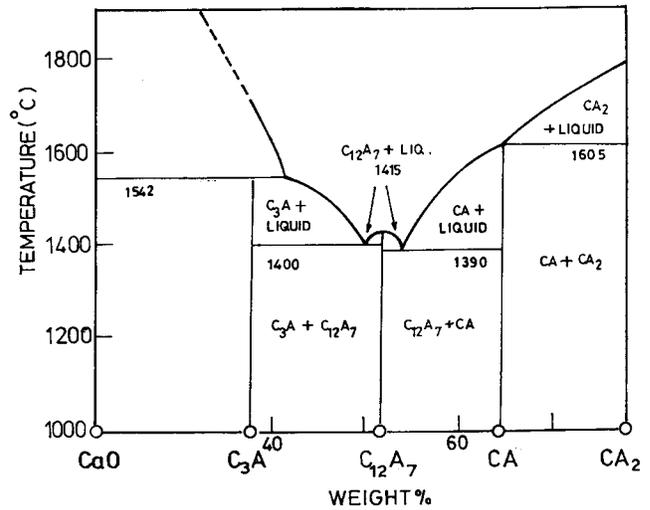

Figure 6. Expanded central region of calcia–alumina phase diagram in the presence of small amounts of H_2O and CO_2 (Taylor 1990).

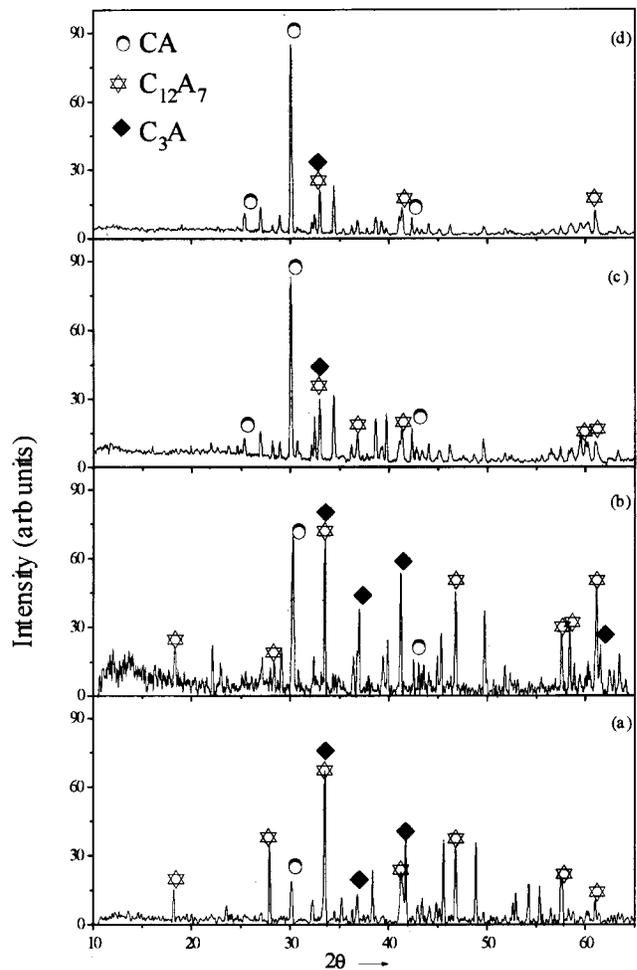**Figure 5.** Scanning electron micrographs of the fractured surfaces of the joints (**a**) CA, (**b**) $C_{12}A_7$ and (**c**) C_3A.

Figure 7. C_3A applied alumina joined at different temperatures for the duration of 4 h (**a**) 1400, (**b**) 1450, (**c**) 1500 and (**d**) 1550°C.
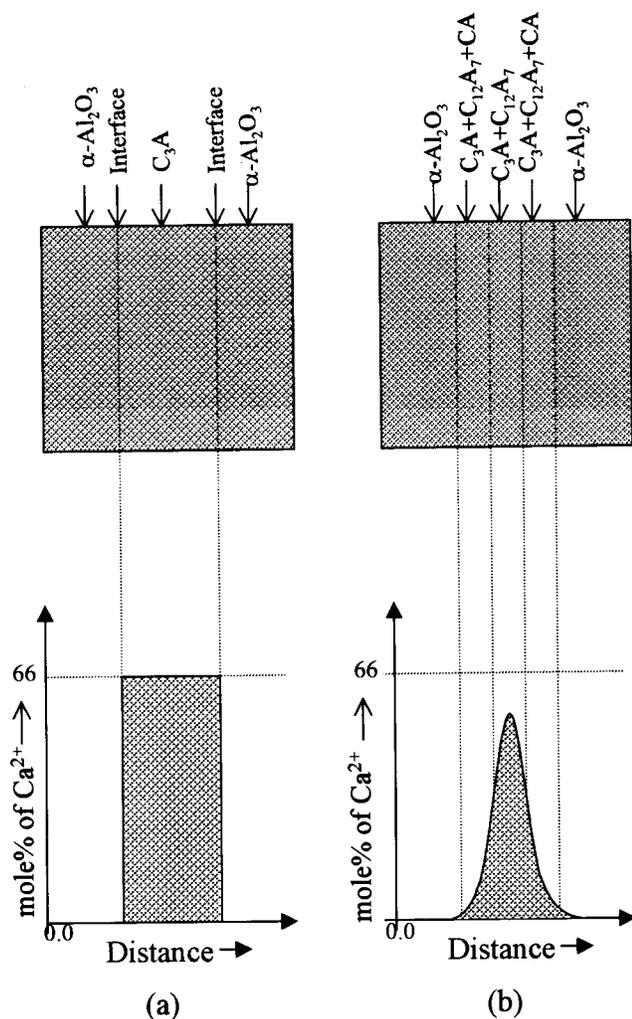
Figure 8. Schematic expression of calcium concentration at the alumina substrate–C₃A interface (**a**) before and (**b**) after heat treatment for joining.

one, as further reaction with the substrate should yield CA which does not by itself melt up to 1600°C. Thus, apart from temperature, time duration at the joining temperature also plays an important role in controlling different solidification products and residual liquid present in the joint area; thereby influencing strength of the joints at room temperature.

5. Conclusions

$G \rightarrow C$ conversion method has been used to prepare fine-grained refractory cements of different materials and compositions. Successful cements could be obtained by calcining these powders at 800 to 1200°C. Out of the various refractory cements tried, the C_3A composition is found to be the most advantageous for alumina joint formation at 1450°C. The study of fractured surface of the resultant alumina joints formed by heating at 1450°C for 4 h indicate the reaction of C_3A composition with the alumina substrate. The SEM shows clear melting and solidification. The XRD analysis shows the existence of reaction products of Al_2O_3 with the refractory cement. Thus the mechanism of alumina joining obtained here can be termed as the reaction bonding. These observations are discussed on the basis of the binary $CaO–Al_2O_3$ phase diagram.

produce a predominantly single phase (CA), which can be counter productive by way of enhanced brittleness. Further if the melt becomes less viscous at temperatures > 1400°C at the initial state of joining, as it can also happen at shorter time durations of joining, it can prove to be disadvantageous for retaining the physical strength of the joined region.

The relatively better performance of C_3A over $C_{12}A_7$ and CA refractory cements could depend on the mole percentage of calcium ions present. C_3A with cation concentration of 66 mole% Ca^{2+} will have higher reaction potential with alumina as compared to $C_{12}A_7$ (46 mole%) and CA (33 mole%). The reaction bonding of C_3A can then be more effective in producing eutectic liquid phase along with other crystalline phases and generating a gradient composite. The liquid phase is however a transient

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