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An Attempt to Develop Sulfate Bonded Alumino–Silicate Refractories

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Abstract

The prospect of sulfate bonding in Alumino Silicate has been investigated. The result of bond formation with calcined clay and calcined bauxite based refractories has been presented. It has been found that small quantity of bond id effective in developing good refractory properties. Apparent porosity, cold crushing strength, RUL, PLC etc. have been studied. DTA studies have also been made to investigate the possible mechanism of bonding.

Introduction

Chemically bonded refractories of various types have wide applications in different industries like ferrous, non-ferrous, glass and cement. These chemically bonded refarctories have advantages over fired refractories particularly with respect to abrasion and thermal shock resistance. The different properties of chemically bonded alumino-silicate refractories bonded with various phosphates, phosphoric acid and chromic acid have already been reported[1-4]. These refractories exhibited strength retrogression for a certain temperature range due to decomposition of bond material followed by improvement in strength through ceramic bonding.

Water soluble sulfate forms a gel like mass by reacting with microfine hydrated alumina. In the present investigation this mass is utilized as a bond for preparing alumino-silicate refractories by mixing with calcined clay and calcined bauxite separately. On heating of this refractory body, the dehydration slowly starts through the conversion of boehmite [γ-AlO(OH)] into γ-Al_2O_3 keeping the topotaxy phenomenon undistributed[5]. Finally the lattice of oxide compound breaks an alumina takes part in ceramic bond formation. The bond mechanism of sulfate bonded alumino silicate refractories may be cited in the following way:-

a) Room temperature Bond formation Step — Microfine hydrated alumina reacts with sulfate solution to form oxysulfate and strength develops through hydrogen bond

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b) Low temperature dehydration step	Existing hydrogen bond of sulfate bonded sample gradually breaks (decrease strength)
c) Moderately high temperature decomposition step	Residual hydrogen and oxysulfate bond decompose and release of various forms of alumina occurs. Simultaneously cation and anion vacancies are created and mass transport between reactive alumina and aggregate in sulfate bonded samples occur (decrease of strength continues)
d) High temperature sintering step (>1000^{o}C)	Ceramic bond formation in sulfate bonded sample starts and continues to elevated temperatures

The relevant properties of sulfate bonded alumina-silicate refractories like apparent porosity, C.C.S, R.U.L and PLC results are presented in this paper. DTA curves are shown to understand dehydration & decomposition behavior of sulfate bond present in the refractories.

Experimental:-

Different raw materials were intimately mixed following the batch composition given in Table -2. Test samples of 7.5cm cube were fabricated by manual ramming. The samples were air dried for 24hrs followed by heating at 110^{o}C, 1000^{o}C & 1400^{o}C for 4hrs. The cold crushing strength of heat treated samples were measured. Bulk density and apparent porosity of the samples were determined as per BIS test methods. DTA of selected samples were performed at a heating rate 10^{o}C/min.

Table 1: Chemical composition of raw materials

		Constitutes (%)						
		Al_2O_3	SiO_2	Fe_2O_3	TiO_2	CaO	Na_2O	LOI
1)	Plastic Clay	29.3	49.0	1.6	-	-	1.2	18.8
2)	Calcined Clay	38.6	59.9	1.1	-	-	-	Trace
3)	Calcined bauxite	86.2	9.1	1.8	0.8	1.3	-	Trace

Table 2: Batch composition of samples

Sample No	Constituents (%) Calcined Clay / Calcined bauxite 1-3mm	0-1mm	BMF*	Plastic Clay	Microfine hydrated alumina	Sulfate compound (parts)
Calcined clay based						
CC1	40	25	25	5	5	5
CC2	40	25	25	5	5	6
CC3	40	25	25	5	5	7
Calcined bauxite based						
CB1	40	25	25	5	5	5
CB2	40	25	25	5	5	6
CB3	40	25	25	5	5	7

BMF* = Ball Mill Fine

Table 3- Properties of Alumino-Silicate Refractories

Properties	Sample Nos.					
Bulk Density (gm/cc)	CC1	CC2	CC3	CB1	CB2	CB3
At 110^{o}C	2.07	2.05	2.04	2.9	2.8	2.7
At 1400oC	2.00	1.99	1.97	2.4	2.3	2.1
Apparent Porosity (%)						
At 110^{o}C	20.2	19.6	20.5	17.3	17.5	17.2
At 1000oC	24.2	24.3	24.8	21.5	21.9	22.6
At 1000oC	22.5	23.1	23.6	23.4	23.8	24.4
Cold crushing strength (kg/cm^{2})						
At 110oC	143	170	180	242	220	220
At 1000oC	132	154	160	330	310	335
At 1000oC	231	270	291	560	435	510
RUL	1380	1390	1410	1450	1490	1510
PLC% at 1400oC for 2h	-1.9	-2.1	-2.5	-1.4	-1.6	-1.9

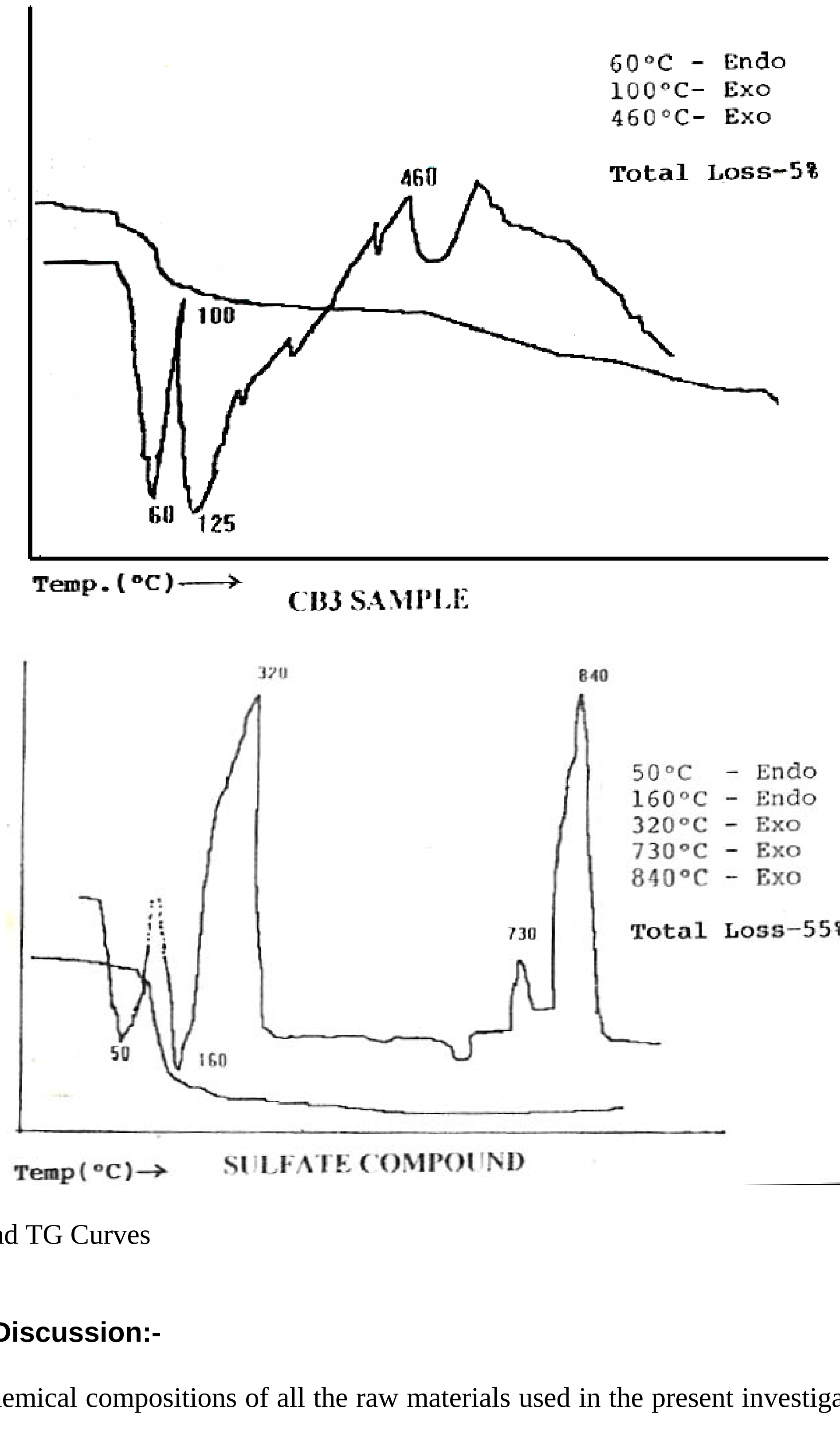

Fig 1: DTA and TG Curves

Result and Discussion:-

The chemical compositions of all the raw materials used in the present investigation are shown in Table 1. Table 2 indicates the different batch formulations of sulfate bonded refractories prepared in the present study. It is found from Table 3 that bulk density and porosity values of all the samples are more or less comparable with the burnt alumino-silicate refractories having similar alumina content. The CCS values are quite good indicating the effective bond formation between oxysulfate mass and aggregate grains.

The strength retrogression tendency heat treatment is found in case of calcined clay based refractories but this trend is not very much prominent. On the contrary mechanical strength gradually increases in case of calcined bauxite based refractories. It may be said that oxysulfate bond acts effectively in bauxite based refractories.

The mechanical strength of oxysulfate bonded refractories is dependent on following three factors.

(a) The bonding force existing in oxysulfate compound itself
(b) The bonding force existing between oxysulfate bond and aggregate grain
(c) The ceramic bond exists between crystalline phase and glassy phase in aggregate grains and the ceramic bond develops between generated reactive alumina and aggregate grains.

Upto 1000oC, (a) and (b) are the controlling factors and beyond 1000oC factor (c) is to be considered. R.U.L results are quite satisfactory and the values do not vary appreciably with the variation of sulfate compound. It is found that bauxite based refractories have higher RUL values than calcined clay based refractories and this is quite expected. PLC values are little higher which are not desirable but this can be reduced by using pneumatic ramming technique instead of manual ramming during fabrication of body.

DTA and TG curves of sulfate compound and CB3 sample are shown in Fig 1. The stepwise release of water molecule (dehydration) could be observed upto 400^{o}C and decomposition of anhydrous salt continues upto 900^{o}C[6]. It may be noticed that peak temperatures (60, 125, 460) found in case of CB3 sample are different from peak temperatures of sulfate compound indicating the stepwise dehydration and decomposition of oxysulfate bond materials. It is clear that ceramic bond formation starts well below 1000oC and strength improves and this is supported by CCS values of CB3 sample.

Conclusion:-

1) The oxysulfate bond develops by interaction of hydrated microfine alumina and sulfate compound may be considered as a prospective bond of alumino-silicate refractories.
2) The desired properties of fired alumino-silicate refractories can be achieved in sulfate bonded refractories provided fabrication pressure and proportion of bond material are controlled. This will be studied in details in our future study

3) These sulfate bonded refractories may be efficiently used in different parts of ladle and furnace related to ferrous industry.

References:

1) Kingery W.D, Fundamental study of phosphate bonding refractories, J. Am. Ceram. Soc. 33 (8), 239-50 (1950).
2) Mitrs S.K, Ghosh b.N and Swaminathan K.S, Development of phosphate bonded high alumina monolithics, Trans Ind. Ceram. Soc. 32(6) 25-31 (1973).
3) Webber R. A. Et al, Effect of water vapor on gel formation in ethyl silicate bonded alumina, Bull Am. Ceram. Soc. 54(9) 792-94 (1975).
4) Roy A.K and Sircar N.R, Phosphate bonding of aluminous aggregates and thermomechanical characterization of the monolithics, Trans Ind. Ceram. Soc., 37(6) 231-241 (1978).
5) Hlavac Jan, The technology of glass and ceramics: An introduction, Elsevier Scientific Publishing Company, Vol 4, 25 (1993).
6) Kirk and Othmer, Encyclopedia of Chemical Technology, Vol 2 , 3rd Ed, 228 & 245.