

Phosphate bonded monolithics for reheating furnaces

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Introduction

Use of monolithic construction in reheating furnaces for roofs, hearths and burner blocks is gradually on the increase.^{1,2} Phosphate bonded sintered corundum and electro corundum have been reportedly used with considerable success in U. S. S. R. N. V. Pitak³ et al observed that such ramming mass for the bottoms of soaking pit furnaces offered high resistances to thermal shock and to action of ferruginous slag at elevated temperature. According to S. R. Zamyatin⁴ et al phosphate bonded fireclay blocks could be recommended for use in blooming soaking pits. The use of monolithics for lining soaking pit has been described⁵ as a success in Japan. The high temperature properties of phosphate bonded monolithics containing chromic acid have been evaluated by Mitra⁶ et al. Martin J. O. Hara et al⁷ also observed that the strength and stability of phosphate-bonded alumina can be enhanced through the use of chromic acid as a partial replacement of phosphoric acid. They concluded that chromic acid facilitate growth of stable phases which did not undergo inversions as in the case of aluminium phosphate

With a view to developing improved ramming masses for applications in critical areas of reheating furnaces and soaking pits, compressional creep tests were conducted on phosphate bonded alumina products. The effect of chromic oxide addition, as a partial replacement of phosphoric acid, has been investigated. The results show that hot strength of the system is enhanced with gradual replacement. The study was carried out upto an extent of 30% addition. Arrhenius equation, has been applied to determine the energy of activation of the creep rate. A probable mechanism has been suggested to elucidate the improvement of hot strength.

phases. Hearths and burner blocks are the positions where chemical attack by slag as also mechanical abrasion and compression are operative at elevated temperature. Monolithic components in small sections are extensively used for repair and replacement of the wornout refractory parts in such regions. The critical role of anchor design, fabrication and characteristics have been elucidated by Viswanathan⁸.

An effort has been made in the present investigation to develop some suitable ramming masses in which fused and calcined alumina grains have been used as filler and phosphates were employed as chemical bond. The work has been extended by adding chromic acid as a partial replacement for bonding alumina with a view to enhancing high temperature strength. The effect of such addition has been evaluated by compression creep determination.

Experimental

Technical alumina was calcined to 1650 °C for 5 hours and ground to—270 mesh in vibro-energy mill using sinttered alumina as grinding media.

Orthophosphoric acid used was of E. Merck G. R. quality having density 1.7 g/cc and chromic acid used was of L. R. quality of S. M. Brand. The creep test specimens of 20 mm in diameter and 45 mm in height have been formed under a total pressure of 300

kg the samples were dried at 110 °C overnight and were kept in desiccator before creep tests were under taken. The different compositions included in this investigation are given in Table I.

Creep tests were conducted in an apparatus fabricated at the Central Glass & Ceramic Research Institute. The experiments were carried out at 1200 °C, 1250 °C and 1300 °C and the load applied was 3 kg/cm² on the test pieces.

The samples were heated at the rate of 6 °C per minute and were held for 30 minutes at the maximum temperature of each test. On being applied the load, the deformation was noted at different intervals of time. True strain was calculated on the basis of corrected height of the test specimen. This was done by taking into account the slight expansion observed in the test pieces before the application of load.

TABLE—I
Compositions of the test pieces for compressional creep study and energy of activation as per Arrhenius equation

Sample number	Calcined alumina (Al ₂ O ₃)	Acid orthophosphoric (H ₃ PO ₄)	Chromic acid (CrO ₃)	Water used in ml for dissolving CrO ₃	Energy of activation K. Cal/Mole
C0	90	10.0	—	—	27.54
C1	—do—	9.5	0.5	0.5	37.33
C2	—do—	9.0	1.0	1.0	45.71
C3	—do—	8.0	2.0	2.0	48.98
C4	—do—	7.0	3.0	3.0	54.95

Creep apparatus : A schematic diagram of the apparatus is shown in Fig. 1. The furnace tube of 5 Cm in diameter and 15 Cm in length and made

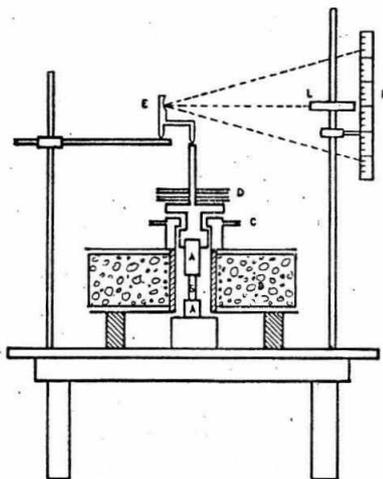


Fig 1 **COMPRESSIONAL CREEP APPARTUS**

- A. Recrystallised alumina
- B. Alumina bubble
- C. Water jacket
- D. Load
- E. Mirror
- F. Scale
- S. Sample
- L. Light source

of crystallised alumina (Morgan) is wound around with Pt/Rh (20.0%) heating element. The hearth on the furnace is covered with a recrystallised alumina with a slit for the insertion of Pt-Pt Rh (13.0%) thermocouple. The top of the thermocouple was just at the centre of the test piece under test. Towards the upper portion of the furnace, there is a cooler dish through which water is circulated continuously. This is fitted with a sliding top having a rod pointed upwards to denote the sharp end used for measurements. The top carries the applied load and

rests on the thrust rod of recrystallised alumina (Morgan). The rod carries a circular plate on which the front leg of the optical mirror of lamp and scale arrangement rests, and the other two legs are in contact with the rigid support. The rod has a sharp end on which a cathetometer is focussed to note its vertical movement. Thus, in addition to the direct reading of the cathetometre, the accuracy of the reading is enhanced by lamp and scale device providing a magnification of 50 times.

Results and discussion

The thermal sensitivity of the creep process like other rate processes is determined by thermal activation energy. The rate of strain at a constant stress is related to the temperature by Arrhenius equation

$$\frac{dE}{dt} = Af(S) f(P) e^{-Q/Rt} \dots (1)$$

where, E-true strain, f(S) and f(P) are some functions of structure and stress Q = thermal activation energy, R gas constant and T absolute temperature.

On integration and rearranging, the above equation become

$$\frac{1}{t} = Af(S) f(P)/\delta e^{-Q/RT} \\ = A'.e \dots (2)$$

where A' is constant and is equal to

$A = (Af(S) f(P)/\delta) =$ a constant, The value of activation energy now could be calculated from equation (2), by multiplying the slope of the plot by 2.303R, at constant strain.

In the present study, the sample contains both glassy and crystalline phase. It is likely that the creep rate will be steady only after a long period of time. So, a short-time creep test was conducted, and the energy of activation of the creep rate for a particular strain has been evaluated (Table I) by utilizing Arrhenius equation.

Each test piece was tested at 1200°C, 1250 °C and 1300 °C at the same stress of 3 kg/cm². From the creep curves, time required by the test piece to reach the constant strain were found out. The creep curves and plot of $\log_{10} t$ to $VS \frac{1}{T}$ are shown graphically (Fig. 2)

Analysis of curves : Plots of strain against time Fig. (3a), (3b) and (3c) show that for all the samples, the creep rate increases relatively with increase of test temperature. It is further observed that the replacement of orthophosphoric acid by chromic acid has resulted in decrease of creep rate (Fig. 3)

The highest creep was observed at 1300 °C in the case of samples bonded only with orthophosphoric acid (Fig. 3c). This is ascribed to segregation of the highly viscous aluminium phosphate. It is also observed that upto a strain of .022, the creep rate is more or less constant. Thereafter it exceeds the critical level. And the result is, an

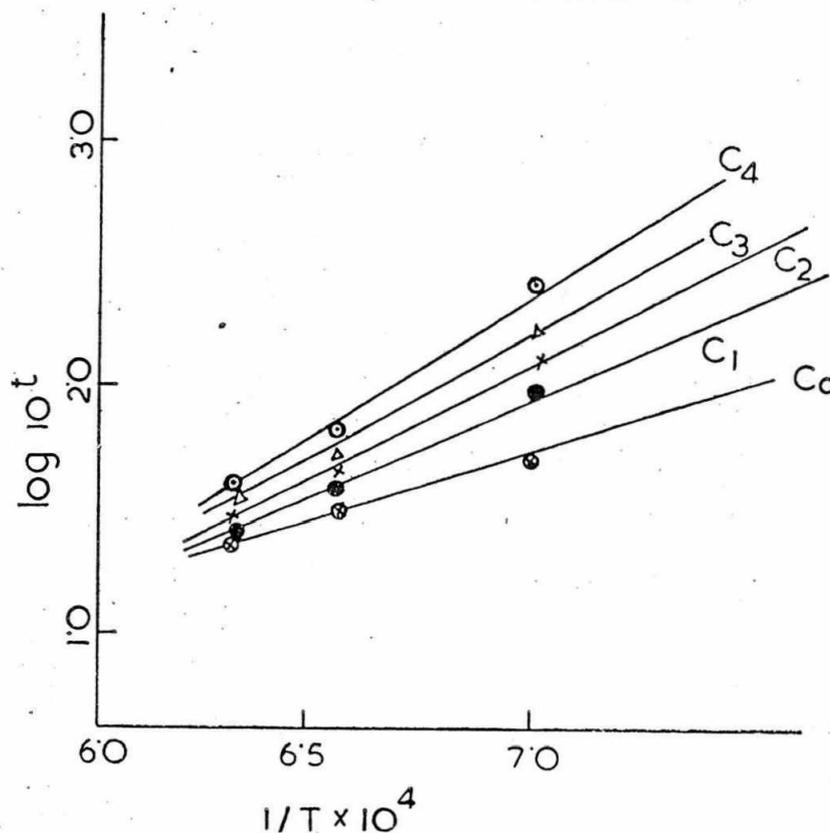


Fig. 2 Curve of $\log_{10} t$ VS absolute temperature.

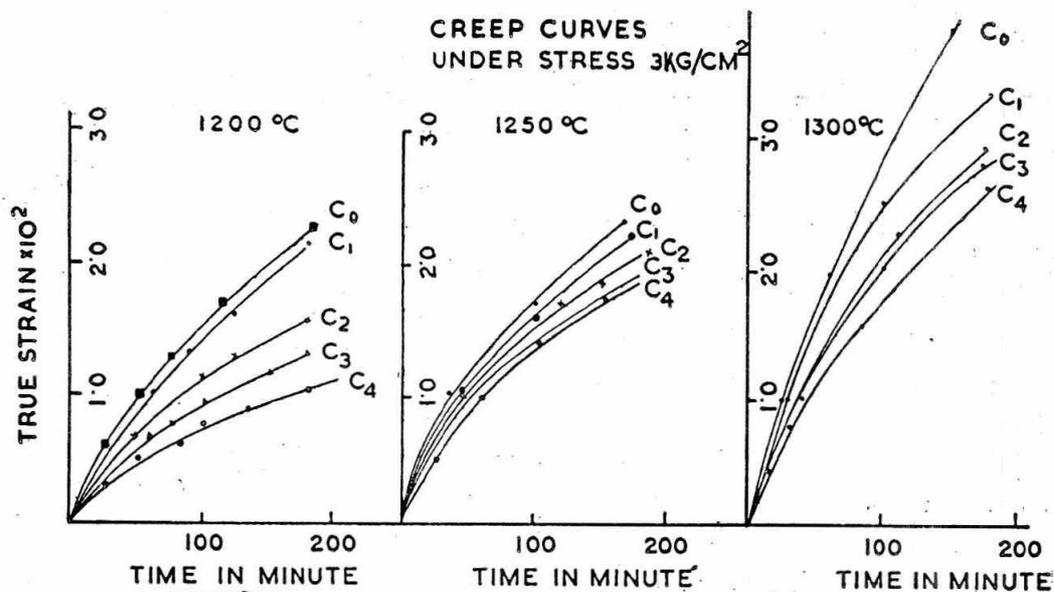


Fig. (3a)

Fig. (3b)

Fig. (3c)

acceleration of creep rate (Fig. 3c). The conversion of amorphous aluminium phosphate to non-bonding aluminium orthophosphate and polymorphic transformation thereof within this temperature region are considered to be contributing factors for the enhancement of creep of these samples. In Fig. 3 the plot of $\frac{1}{T}$ against $\log_{10} t$ gives a slope which in energy of activation 27.54 K. cal/Mole.

The creep rate has been found to decrease gradually with the incorporation of chromic acid, stepwise. The activation for the strain 0.01 as per Arrhenius plot (Table I) shows an increase from 37.33 K. cal/Mole to 54.95 K. cal/Mole. Thus, replacement of phosphoric acid by chromic acid can be considered to resist the flow of the bond. As per Grigerov⁸, the principal phase in the thermal transformation

products of aluminium chromium phosphate above 1200 °C is chromium pyrophosphate $\text{Cr}_4(\text{P}_2\text{O}_7)_3$ with a small amount of $\text{Cr}(\text{PO}_3)_3$ glass and aluminium ortho phosphate in cristobalite form. X-ray analysis, in the present investigation, of one of samples after test at 1300 °C shows that the phases present are $\alpha\text{-Al}_2\text{O}_3$ and aluminium phosphate. Such an assemblage implies that either alumina has reacted with chromium phosphate to form aluminium chromium phosphate glass or that chromium has undergone solid solution with alumina. The electron micrograph of sample no. C4 shows segregation rather than uniform distribution of Cr_2O_3 in Al_2O_3 lattice.

It is established that glass becomes semicrystalline in nature when crystals are present in contact with it. So, from the analysis of the creep curve, it appears :

- (I) Aluminium phosphate has retained its glassy form in aluminium chromium phosphate.
- (II) Reinforcement of partly crystalline aluminium phosphate with either aluminium chromium phosphate glass or chromium meta phosphate $\text{Cr}(\text{PO}_3)_2$ (glass) are the reasons for the enhancement of hot strength.

Conclusions

High temperature strength of monolithics bonded with orthophosphoric acid or acid phosphate is seriously affected in the temperature region of 1200°C—1300 °C because of crystallisation of aluminium phosphate and its polymorphic inversion. This is evident from short temperature creep carried out at different temperatures in the range of 1200 °C to 1300 °C. This short-coming is overcome by introduction of chromic acid. The combination of such bonds with sintered or fused alumina can produce some monolithics with improved mechanical strength and related properties which will help resisting the severe conditions prevailing in soaking pits and reheating

Acknowledgements

The authors are grateful to Shri K.D. Sharma, Director Central Glass & Ceramic Research Institute for his kind permission to present/publish this

work. Thanks are also to Shri R. C. Chaudhuri, Senior Foreman for cooperation during the fabrication of the creep apparatus

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