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DEVELOPMENT OF LOW TEMPERATURE CLAY BONDED GRAPHITE CRUCIBLES

M. Latif, M. Yousaf, M.A. Baig and F. A. Faruqi

PCSIR Laboratories Lahore, Pakistan

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Low temperature clay bonded graphite crucibles have been developed from Ceylone graphite. The exact firing technique has been evolved to control the oxidation of graphite crucibles. A glaze has also been developed which assists in the control of oxidation of graphite crucibles.

INTRODUCTION

Low temperature clay bonded graphite crucibles are used in foundry work and in the non ferrous alloy industries as well as in the smelting and refining of such metals as copper and zinc and of precious metals. The requisites of good crucible are strength, refractoriness, good heat conduction, the capability of being used for many melting of metals and resistants to the action at high temperatures of the molten materials with which it comes in contact. The graphite[1,2] used in the development of low temperature clay bonded graphite crucible has a low content of mineral matter and a suitable texture. The ash content does not exceed 5 to 10% and is infusible and has no tendency to combine with the clay to from fusible mixture. Locally available minerals such as feldspar, clay quartz, pitch, tar and sodium silicate have also been utilized in the development of these crucibles. Chemical analysis of Ceylone graphite, KD_{10} clay, KD_{10} grog, feldspar, Quartz and Sieve analysis of KD_{10} Grog are given in Table 1. Pakistani graphite was not suitable for this specific purpose because of low content of carbon and higher content of ash and other impurities which tend to accelerate the rate of oxidation of graphite crucibles. The main problem in the fabrication of low temperature clay bonded graphite crucibles is to control the oxidation of graphite during firing operation and to develop a suitable bond. Clay has been as successful bonding material and various compositions having clay contents ranging between 30-50% have been tried. The exact firing technique has been evolved to put a check on the oxidation of graphite crucibles. A glaze composition which gives promising results and covers evently the surface of the crucible has also been developed. Run trial tests of these crucibles have also been carried out at these laboratories and copper was melted. The crucible withstood 12 firing cycles.

EXPERIMENTAL

Following procedure was adopted in the preparation of graphite crucibles are as follows:

Clay and feldspar are weighed and charged into a pebble mill together with water. It is allowed to run for 6 to 8 hours to ensure thorough mixing. At this stage graphite powder is introduced into the pebble mill which is further made to run for at least 2 hours to homogenise the mass. The mixed material is than caused to pass through pug mill which further mixes and eliminates air from the mass. It is made just softly plastic by the addition of water and kneaded to a uniform consistency. It is than set aside to age. The lumps of the kneaded material are allowed to season for a week. When the mass commences to show a dry surface crust, it is again worked up into a pug mill until all parts are homogenous. The material after seasoning is ready to be worked up into crucible.

Preparation and Biscuit Firing of the Crucibles. A weight of the mixture is taken, kneaded by hand into a ball and placed into a mold. The crucibles are formed by pressing the mass in a hand press and then allowed to dry in open air for at least 2 days. The dried crucibles are subjected to biscuit firing at about 1100°C raising the temperature at the rate of 100°C/hour.

Glazing and Firing of the Crucibles. The glaze composition tried in making clay bonded graphite crucibles being sodium silicate 40-50%, Quartz 35-45% and aluminium phosphate 10-20%. The whole composition was mixed with water for about 4 hours in a pebble mill and the glaze thus obtained was applied to the crucibles either by spraying or dipping. The glazed pieces were dried and fired at 1350°C maintaining the temperature for two hours. The firing consumed from 15 to 20 hours after which the furnace was allowed to cool off for 24 hours.

RESULTS AND DISCUSSIONS

Graphite contributes towards the refractoriness and heat conductivity of the mass [3]. At the same time it produces a smooth surface for pouring. It has long been recognized that incorporation of carbon with the clay of crucible diminishes their tendency to break with sudden changes of temperature without lowering the refractoriness. Carbon is incorporated in the form of graphite with the fire clay in the crucible compositions in the range of 40-60% as shown in Tables 2A, 2B and 2C and any deviation from it leads to various defects. Where high refractory qualities are demanded, the graphite percentage may be as high as 80 and over. Such high proportion, however, result in crucibles which are structurally too weak to be glazed. Less than 30% quantity of graphite in the compositions suggests the likeli-hood of poor refractoriness and lower thermal conductivity.

The fuction of the clay is tha of a bonding material which makes possible the forming of the crucible and the cementing of the graphite flakes.[4] At the same time, it covers and prevents their oxidation. It has been introduced into the graphite crucibles from 30-50% as shown in Table 2A, 2B and 2C . As the crucibles are fired in the furnace, the fire clay present in the composition shrinks considerably and exerts a pressure which ultimately holds firmly all the graphite grains and develops good strength. If less than 30% clay is used in the crucible compositions, it undergoes partial oxidation because of insufficient quantity of clay which fails to cover and coat fully all the graphite grains. If more than 50 percent clay is used in the composition, it lowers refractoriness because of it high flux content and its tendency to yield a glassy product with poor apalling resistance. Composition No. 11 in Table 2A containing 40% clay yields the best results. It is not oxidise at all. It develops good strength and withstands 12 firing cycles at 1250°C. KD_{10} grog has been introduced in the graphite crucible compositions in order to combat with the shrinkage.

Organic binders such as pitch and tar are also tried in some of the compositions[5,6] . On firing the crucibles at 1350°C (a temperature distinctly higher than they are likely to experience when in use, otherwise the crucibles might shrink and collapse), the coal tar gets decomposed and the volatile constituents are given off leaving the residual carbon which serves as the binder of graphite. In all these compositions partial oxidation of graphite takes place during firing leaving the crucibles weak and porous.

R.H. Stone considers that the presence of certain amount of flux (Feldspar) in clay accounts for its suitability for graphite crucibles. Feldspar is added up to 10% to each composition of graphite crucibles to favour vitrification and thus diminishes the risk of permeation crucibles. More than 10% feldspar in the crucibles composition tends to decrease the refractoriness of the crucibles. Less than 10% amount of feld-spar does not serve the purpose as the glassy melt produced on firing is quite insufficient to hold tightly and cement all the graphite grains and other constituents in the crucibles.

Oxidation of the graphite is effectively checked by glazing the crucibles. Such glazes are feasible only on graphite whose thermal expansion characteristics match that of the glazes quite closely. But graphite is the material which in not easily wetted by ordinary melts or glaze. Most of the glass forming oxides and other oxides used in glass compositions have such angles of contact that coatings formulated from these oxides do not cover the graphite surfaces properly and crawling takes place. Continued diffusion of oxygen into the body subsequently causes oxidation which results in violent blistering and bubbling of the glaze. It is found that the introduction of molybdenum in the form of the oxide causes the glaze to wet and to flow out into a smooth continuous coating that effectively products the carbon bond from all oxygen except that which diffuses through the glaze [8]. The coating thickness ranges from 0.001 to 0.050 inch or more [9]. The thinner the glaze coating , the less trouble with the creacking from differential expansion but harder to achieve freedom from pores and pinholdes. Thickness between 0.010 to 0.030 inch appears to be the most practical.

For firing graphite crucibles there should be hermetically sealed, medium sized gas furnace in which uniform temperature could be obtained in all the regions as too large a furnace is inefficient and too small a furnace requires additional care to prevent oxidation of the curcibles [10].

The temperature of the furnace is gradually raised to 1250°C at the rate of 100°C per hour. After 1250°C all the refractories bond become plastic and the risks of crazing and cracking of the crucible is very greatly reduced. Crucibles are fired in reducing atmosphere as an oxidation condition extracts carbon from the crucible wall leaving a porous structure liable to crack. The temperature of the furnace is kept uniform in all the regions as far as possible otherwise different results for the crucibles having the same compositions are obtained. Composition from 1 to 10 in Table 1 are partially oxidised leaving the crucible weak and porous. This may partly be attributed to high difference of temperature in various regions of the furnace. At too

Table 1.

	Chemical Analysis of Feldspar (%)	Chemical Analysis of Quartz (%)	Chemical Analysis of K.D.$_{10}$Clay (%)	Chemical Analysis of K.D.$_{10}$Grog (%)	Chemical Analysis of Ceylone Graphite	
L/I	0.02	0.046	14.70	–	Moist.content.	0.90
Al_2O_3	22.23	1.865	50.26	58.36	Carbon:	93.55
SiO_2	67.90	97.4	33.26	38.62	Ash	5.55
Fe_2O_3	0.10	0.035	0.70	0.81	Sp.gravity	2.345
CaO	0.378	0.85	1.40	1.63		
MgO	0.23	0.15	0.50	0.58		
Alkalis	9.14	–	–	–		

Sieve Analysis of K.D.$_{10}$ Grog -18 + 25 40 % -25 + 50 20 % -50 40 %

high temperature zone, the glaze becomes very fluid and runs off the were leaving some parts bare where oxidations takes place. At too low temperature zone, the glaze is partly fused and the result is unsatisfactory for several reasons.

i) Full protection is lacking.
ii) Bubbles of air remain in the glaze giving an unfinished and unattractive appearance.
iii) Brilliance and glass are not developed. This fault results from the loss of essential fluxes from glaze during firing or when the glaze is applied too thinly. Another cause is under firing.

Composition No. 11 in Table 2A develops good strength and withstands twelve firing cycles. Sometimes pincholes are observed in the glaze. These can be reduced considerably by substituting and equal amount of grog with the ball clay in the body composition. Compositions from 12 to 21 develop some strength but not so good as that of composition No.11. In all these cases the glaze inside the crucibles does not mature. Pinholes are also observed. In Table II-B all the compositions are totally oxidised leaving behind reddish brown porous weak clayey structure. In Table 2C compositions from 1 to 6 do not develop any strength at high temperature. Composition from 7 to 10 were melted at low temperatures. Oxidation was also not controlled.

The correct ratio of the fuel to air is maintained so that there is a neutral and slightly reducing atmosphere at the fuel outlet. The temperature at which the crucibles begin to soften or melt is influenced by the grain size, the finer grains appear to be more fusible and by the characteristics of atmosphere in which they are heated, a reducing atmosphere generally tending to lower refractoriness. Very fine particles of graphite are prone to oxidation because of their increased surface area. Large flakes are, therefore, used in the crucible compositions as they are thicker with less surface per unit weight and a slower burning rate and can be oriented more nearly correctly in the crucibles. Flakes of more than ordinary size that is, much larger than 20 mesh are not desirable as they tend to decrease the density of the crucibles and detract from its strength [11].

Table 2A. Batch composition for low temperature clay bonded graphite crucibles.

Sr.No.	Graphite	K.D.$_{10}$ Clay	K.D.$_{10}$ Grog	Feldspar
1.	40	40	10	10
2.	41	40	9	10
3.	42	40	8	10
4.	43	40	7	10
5.	44	40	6	10
6.	45	40	5	10
7.	46	40	4	10
8.	47	40	3	10
9.	48	40	2	10
10.	49	40	1	10
11.	50	40	0	10
12.	51	39	0	10
13.	52	38	0	10
14.	53	37	0	10
15.	54	36	0	10
16.	55	35	0	10
17.	56	34	0	10
18.	57	33	0	10
19.	58	32	0	10
20.	59	31	0	10
21.	60	30	0	10

A number of heats that crucibles may be expected to stand is dependent on the material of its composition. The care taken in manufacturing and the handling it receives in service. No matter how well the crucible may have been made, it will have its life shortened by careless handling.

Table 2B.

Sr.No.	Graphite	K.D.$_{10}$ Clay	K.D.$_{10}$ Grog	Feldspar
1.	40	41	9	10
2.	40	42	8	10
3.	40	43	7	10
4.	40	44	6	10
5.	40	45	5	10
6.	40	46	4	10
7.	40	47	3	10
8.	40	48	2	10
9.	40	49	1	10
10.	40	50	0	10

Table 2C.

Sr.No.	Graphite	K.D.$_{10}$ Clay	K.D.$_{10}$ Grog	Boro-silicate Glass.
1.	50	40	9	1
2.	50	40	8	2
3.	50	40	7	3
4.	50	40	6	4
5.	50	40	5	5
6.	50	40	4	6
7.	50	40	3	7
8.	50	40	2	8
9.	50	40	1	9
10.	50	40	0	10

Graphite crucibles like all other materials containing clay are hygroscopic and should be freed from moisture by gently heating before being put into use. This disregard of precaution causes the loss of thousands of crucibles annually. Graphite Crucibles are not so porous as those of clay and thus do not absorb so much of the melted as the latter. For this reason they are preferred in the melting of precious metals. The material for crubcibles manufacture, while different in some minor details are particularly the same everywhere. The preparation of the mixture and the preparation of the graphite, clay and grog or sand entering into it are the secrets of the individual makers.

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