Pakistan J. Sci. Ind. Res., Vol. 28, No. 3, June 1985

DEVELOPMENT OF HIGH TEMPERATURE GRAPHITE CRUCIBLES

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

PCSIR Laboratories, Lahore

(Received December 1, 1984; revised, May 9, 1985)

This paper describes some of the studies made on the preparation of high-temperature graphite crucibles used for melting ferrous and non-ferrous metals. Ceylon graphite has been employed in the fabrication of these crucibles as the indigenous graphite possesses a low carbon content and a higher content of ash and other impurities which tend to accelerate the rate of oxidation of graphite crucibles.

INTRODUCTION

Graphite is one of the most widely used high temperature materials because of its unrivalled combination of refractoriness, thermal shock resistance and machinability. Advanced applications [1], especially in the aerospace field, call for improvements in oxidation and erosion resistance and in the mechnical properties of graphite. In metals similar improvements in these directions have been accomplished by alloying. This approach is not effective with graphite. Graphite cannot be melted with any degree of convenience and it cannot readily be dissolved in a solvent.

An approach similar to alloying is that of making composites from powders. By processing such composites at elevated temperatures, some regional alloying takes place, providing coherence of the individual particles.

The constituents of the composite act in an additive manner so that characteristics such as thermal and electrical conductivity of the resulting material are a mean value among the properties of the components. Oxidation resistance is one property where the characteristics of the composite exceed those of any of the constituents and it is here that composite technology has achieved significant success.

Graphite as a refractory has unique properties which distinguish it from other non-metallic refractories chiefly because of its thermal and electrical conductivity. The combination of high thermal conductivity with a melting point of 3800° and a high thermal shock resistance make it indispensable in the manufacture of metling receptacles.

Graphite in combination with a fireclay grog or alone and with suitable binders such as clay or pitch or tar is used in the manufacture of crucibles for melting non-ferrous metals and steel, in retorts for the distillation of secondary zinc, in steel ladle stopper heads and in resistor heating elements. An objection to graphite is its ease of oxidation which takes place readily at 700° in air leaving ash from 5 to 10%. This objection may be largely overcome by protection with a ceramic glaze.

Mechanism of Protection

Graphite oxidizes at elevated temperatures and its oxides are of a gaseous nature. This limitation requires protection against oxidation by means of a suitable surface coating. If the coating is applied to the graphite by conventional means, such as vapour of electro-deposition, any loss of the coating through mechanical or chemical attrition results in rapid oxidation at high temperatures. Catastrophic destruction can be avoided if the coating were generated *in situ* through additions to the graphite of refractory materials, the oxides of which are sufficiently liquid to flow and hermetically seal the exposed surface.

The Role of Binding Material

The starting materials are powdery blends consisting of graphite, pitch and the additives. The blends are moulded into crucibles under hydrualic pressure of 41378.9 KN/m^2 and baked at 1000°. Upon heating these blends, a significant primary compactions is achieved when the pitch melts between 100-200°. This allows the solid particles in the system to arrange themselves into a densely packed array. A carbon-bonded matrix is formed upon the conversion of the pitch to coke. No further densification takes place until the pitch coke assumes a degree of plasticity at temperatures of about 1550°, where a secondary compaction is effected.

In general, the process is carried beyond the temperature where a liquid phase appears in the system because of the melting of additives. Liquid phase penetrates into the pores of the solid phase so that on cooling an impervious body results. Varying amounts of the solid phase dissolve in the liquid phase in accordance with the equilibrium relation. As solubility limits are a function of temperature, processing conditions allow the adjustment of the degree of homogenity within the composite.

Quite a substantial amount off foreign exchange is spent on importing graphite and graphite based products such as graphite crucibles, electrical carbon, electrical carbon brushes, cinema projector electrodes, electrodes for dry cells and are furnaces refractories, lubricant brake liners etc. According to one estimate in the country is spending about Rs. 10 million/annum on the import of graphite and graphite based products.

EXPERIMENTAL

A refractory composition comprises graphite, silicon carbide, a flux and a carbonizing binder, such as tar or molasses. As fluxes, clay salts such as borax, metallic or non-metallic oxides or sulphides may be used. The mixture is thoroughly mixed with water and after drying in the plaster of Paris moulds, it is aged for a week and then moulded into crucibles under a hydraulic pressure of 43178.9 MN/m^2. The crucibles, after carefully drying in the oven, are subjected to biscuit firing at 1000^o.

Glazing and firing of the crucibles: The glaze composition tried and tested in making high temperature graphite crucibles was sodium silicate 30-40%; quartz, 45-50%; and aluminium phosphate, 10-20%. The whole composition was mixed with water for about 4 hr. in a pebble mill and the glaze thus obtained was applied to the crucibles either by spraying or dipping. The glazed pieces were dried in the oven and subsequently fired at 1550^o in the reducing atmosphere of the furnace maintaining the temperature for 2 hrs. The firing took from 15 to 20 hr. after which the furnace was allowed to cool off for 24 hr.

RESULTS AND DISCUSSION

Graphite, as a component of crucible mixtures, has a number of functions including the mechanical one of preventing any general fluxing of the crucible at high temperature. As graphite is a good conductor of heat, it improves heat transfer, minimizes the danger of breakage from heating and cooling strains and reduces the coefficient of expansion. Graphite, being a lubricant, is difficult to bond and requires a clay of high plasticity and adhesiveness with a high drying and heat shrinkage. The shape of the grains of clay is such that the clay when moistened and dried will have a high mechanical strength. A large content of plastic clay in the compositions of graphite crucibles was avoided because of its high flux content and its tendency to yield a glassy product with poor resistance to spalling and poor refractoriness under load.

Plastic clay contents upto 58% have been used in the compositions of Table 3. The function of the clay is that of a bonding material which makes possible the forming of the crucible and the cementing of the graphite flakes. At the same time, it covers and prevents their oxidation. Compositions from 22 to 31 (Table 3) swell up or bloat and numerous pin-holes occur on both the inner and outer surfaces of the crucibles because of the excessive quantity of clay present in these compositions. Sometimes the crucibles becomes deformed and the creep or flow of the glaze takes place. Compositions from 1 to 6 (Table 3) develop good mechanical strength. Some of the crucibles are partially oxidised because of rapid rise in temperature of the furance.

As a common impurity of plastic clays and an addition introduced to reduce overall drying and firing shrinkage, quartz is a prominent phase in graphite crucibles in amounts which run as high as 10%. Quartz grains are frequently shattered as the result of inversion during firing, but no conversion to cristobalite or tridymite is usually evident. Because of high thermal expansion accompanying the quartz inversion, graphite crucible with too high a quartz content may be susceptible to spalling and probably the limit of safety is 10%. Quartz upto 10% has been used in all compositions shown in Table 1. Compositions from 5 to 10

Table 1

Sr.No.	Graphite	Sic	Feldspar	Quartz	Carbonizing binder
1	50	20	17	10	3
2	50	21	16	10	3
3	50	22	15	10	3
4	50	23	14	10	3
5	50	24	13	10	3
6	50	25	12	10	3
7	50	26	11	10	3
8	50	27	10	10	3
9	50	28	9	10	3
10	50	29	8	10	3
11	50	30	7	10	3
12	50	31	6	10	3
13	50	32	5	10	3
14	50	33	4	10	3
15	50	34	3	10	3
16	50	35	2	10	3
17	50	36	1	10	3

(Table 1) yield good results. They develop good mechanical strength and do not shrink.

In all the compositions listed in Table 2 grog has been used upto 7%. The grog [2] was used for two reasons (a) economic, i.e. to salvage costly materials; and (b) to reduce the shrinkage in the final product. The addition of grog gives the crucible a better texture and regidity during firing. Compositions from 9-13 (Table 2) develop good strength and do not shrink at all. Further the crucibles are of better texture.

The inclusion of pitch in the starting material (batch composition) offers the following advantages:

1. It allows dense packing due to extensive lique-faction of the system before its consolidation. Molten refractory additives could accomplish this only when present in a sizable volume.
2. In forming a carbon matrix, it provides the material with a residual strength when exposed to temperatures at which a mloten phase occurs.
3. In forming a carbon matrix, it prevents excessive escape of molten additives by trapping them in pores. This benefit is manifest during processing as well as during use at high temperatures.
4. It improves the machinability of the final product.

In all the compositions of graphite crucibles from 1 to 10 (Table 1) tar has been used as a bonding material. As graphite crucibles are subjected to biscuit firing at 1000° in a reducing atmosphere, the tar decomposes to a char or coke which bonds the graphite particles together.

With increase in temperature at about 1550°, the crystal structure of this char develops some of the greater perfection of the graphite lattice and grains grow together to give something like the structure of polycrystalline metal. The crucibles have excellent strength and good resistance to thermal spalling. They are scarcely wetted by either metal or slags and are not subjected to chemical attack except by oxidizing slags and oxidizing gases, particularly air, CO_2 and H_2O. The graphite in the wall of the crucible begins to oxidise at about 600°. Oxidation increases with temperatures and varies with the composition of the furnace gases. The life of the crucible depends largely on the non-oxidation of the graphite. The glaze on the outer surface delays this oxidation. Hence if the materials be too infusible, the life of the crucible is much shortened, but if it be too fusible, it softens and fails to protect the graphite. The outside of a crucible is usually coated with a mixture more fusible than the crucible wall itself. If the first heat to which a crucible is subjected is high enough to produce this protective glaze, its life at lower subsequent service temperatures is much prolonged.

The formation of a protective layer of silicon carbide has been suggested to improve oxidation resistance.

The carbides possess the highest melting points of all known materials and their extreme hardness suggests very high ultimate strength. These factors make the carbides potentially useful for many high temperature applications. Silicon carbide (SiC) or carborundum has been used under favourable conditions but it tends to decompose in air, Si burning to SiO_2. If this occurs slowly, a glaze forms and

Table 2

Sr.No.	Graphite	Sic	Feldspar	Grog	Binder (Organic)	Sr.No.	Graphite	SiC	Feldspar	Grog	Binder (Organic)
1	70	20	0	7	3	14	57	20	13	7	3
2	69	20	1	7	3	15	56	20	14	7	3
3	68	20	2	7	3	16	55	20	15	7	3
4	67	20	3	7	3	17	54	20	16	7	3
5	66	20	4	7	3	18	53	20	17	7	3
6	65	20	5	7	3	19	52	20	18	7	3
7	64	20	6	7	3	20	51	20	19	7	3
8	63	20	7	7	3	21	50	20	20	7	3
9	62	20	8	7	3	22	49	20	21	7	3
10	61	20	9	7	3	23	48	20	22	7	3
11	60	20	10	7	3	25	47	20	23	7	3
12	59	20	11	7	3	25	46	20	24	7	3
13	58	20	12	7	3	26	45	20	25	7	3

protects the rest of the material but it can start burning very violently if the protection breaks down. As a matter of fact, the oxidation of SiC takes place at 1150-1450°. SiO_2 is liberated which recrystalizes to form cristobalite. Cristobalite sinters and produces a dense outer layer on the surface of the graphite crucibles. This results in marked decrease in further oxidation of the SiC. SiC has been used at upto 0-36% in the compositions (Table 1, 2 and 3). In compositions from 1 to 36 (Table 3). As the amount of SiC decreases, the clay content increases and the melting temperatures of the crucibles as well as their refractoriness

Table 3

Sr. No.	Graphite	SiC	Plastic clay	Feldspar
1	50	20	20	10
2.	50	19	21	10
3	50	18	22	10
4	50	17	23	10
5	50	16	24	10
6	50	15	25	10
7	50	14	26	10
8	50	13	27	10
9	50	12	28	10
10.	50	11	29	10
11.	50	10	30	10
12.	50	9	31	10
13.	50	8	32	10
14.	50	7	33	10
15.	50	6	34	10
16	50	5	35	10
17.	50	4	36	10
18	50	3	37	10
19	50	2	38	10
20	50	1	39	10
21	50	0	40	10
22	49	0	41	10
23	48	0	42	10
24	47	0	43	10
25	46	0	44	10
26	45	0	45	10
27	44	0	46	10
28	43	0	47	10
29	42	0	48	10
30	41	0	49	10
31	40	0	50	10

decreases. Compositions from 1 to 6 (Table 3) having SiC contents ranging between 15 to 20% yield good results. The use of SiC above 30% renders the renders the composition too refractory and weak. This is obvious from the compositions from 12 to 17 (Table 1).

According to Stone [4], the presence of a certain amount of flux (feldspar) in clay accounts for its suitability for graphite crucibles. Feldspar, is therefore, added upto 0-25% in all batch compositions of Tables 1-3 to favour vitrification and to diminish the risk of permeation of crucibles. Less than 10% amount of the feldspare does not serve the purpose as the glassy melt produced on firing is insufficient to hold tightly and cement all the graphite grains and other constituents in the crucibles. Compositions from 14 to 26 (Table 2) bloat due to excessive amounts of fluxes. Complete oxidation of graphite takes place leaving the structure of the crucibles reddish brown, porous and weak.

Bloating in the compositions from 1 to 4 (Table 1) takes place because of their high flux content. Pin holes and blisters are formed in the glaze. Sufficient strength is developed in the crucibles but their spalling resistance and refractoriness are considerably reduced because of the excessive amount of the glassy matrix formed. Some of the crucibles are totally oxidised on their inner and outer surfaces because of the loss of fluxes at high temperatures and their strength is very low. Compositions from 5 to 10 (Table 1) yield rather good results. They develop good mechanical strength and do not shrink. Crucibles are not oxidised at all on the surface of the inner wall but some of them are partially oxidised at their outer surface. This may be attributed to the rapid rate of firing as well as different temperatures at different regions of the furance. Compositions from 12 to 17 (Table 1) do not develop good strength as the glassy melt produced during firing is not sufficient enough to hold tightly all the graphite grains and other constitutents of the crucibles.

The chief advantage [5] of graphite in a crucible arises from its capacity to absorb and transmit heat, but it is also infusible at temperature below that of an electric arc, and its electrical conductivity is comparatively high. Graphite can withstand sudden changes of temperature for it can be heated to white heat and quenched into cold water without any apparent damage.

By increasing the content [6] of graphite in the crucible its refractoriness may be increased. This is impracticable, however, as the greater the graphite content, the lower is the mechanical strength and the higher the thermal conducitivity. These factors are likely to interfere with the normal procedure of steel pouring for if the mechanical

Table 4

	Chemical analysis of feldspar (%)	Chemical analysis of quartz (%)	Chemical analysis of clay (%)	Chemical analysis of grog (%)	Chemical analysis of Ceylon graphite	
L/I	0.02	0.046	14.70	–	Moisture 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
CaO	0.378	0.85	1.40	1.63		
Fe_2O_3	0.10	0.035	0.70	0.81	Sp. gr.	2.345
MgO	0.23	–	–	–		
Sieve analysis of grog:	– 18 + 25	40%	– 25 + 50	20% – 50 40%		

strength of a crucible is low, it will be strongly eroded by the liquid steel. Compositions from 1 to 8 (Table 2) are structurally too weak to be glazed because of their higher contents of graphite and insufficient amount of feldspar.

Ceylon graphite contains from 5 to 10% ash. In a crucible [7] any fluxing action of the ash begins on the surface where carbon is first burned away, and such action proceeds only as fast as the ash is formed. Fluxing action would be retarded by the production of a dense skin resulting from the softening clay and ash mixture.

The batch compositions were aged [8] under constant temperature and high humidity. This operation increased the colloidal content of the constitutents of the batch composition through bacterial action and improved its bonding power and plasticity.

Graphite crucibles [9] that were to transfer heat were made as dense as possible under hydraulic pressure of 41378.9 KN/m^2 so that they should have maximum weight per unit volume and consequently the greatest heat capacity.

Stabbing of the graphite crucibles

Stabbing denotes the crumbling or disintegration which the graphite crucible undergoes when subjected to furnace conditions and thermal shock. Such disintegration is brought about by one or both causes, one being the difference in the temperature and hence in the degree of expansion or contraction of the inner and the outer faces of the crucible, and the other being a difference in the expansion of the component particles of the crucible, such as might occur with a mixture of quartz and clay particles. The characteristic of a spalled crucible is a general looseness of the structure, accompanied by cracking and by the breaking of the edges or faces.

Sometimes graphite crucibles bloat when overfired. This is due to the melting action of the fluxes, together with the evolution of the gases from such impurities as $CaSO_4$. A large number of bubbles and blisters are formed and the article expands, becoming a mass of sealed pores and the bloating continues. Bloating in the compositions from 1 to 4 (Table 1) takes place because of their high flux contents. Pinholes and blisters are formed in the glaze. Sufficient strength is developed in the crucibles but their spalling resistance and refractoriness are considerably reduced because of the excessive amount of glassy matrix formed.

Open pores formed on the outer surface of graphite crucibles during firing are voids which are accessible to penetration by a field. They exist because of the loss of individual particles of the material and also due to the escape of gases during the firing process. Sealed pores are formed on firing when bubbles of gas are frozen into the glassy matrix, or when pores are sealed by molten material.

Composition 22-31 (Table 3) bloat and numerous pinholes are visible on crucibles because of the fluxing action of the excessive quantity of the clay present in these compositions. Sometimes the crucibles are deformed and the crawling of glaze takes place.

Conclusion

This study establishes that compositions containing 50-60% graphite, 15-30% SiC, 10-13% feldspar together with small additions of quartz, fire clay grog organic binder or plastic fire clay have good mechanical and refractory properties. For example, compositions from 5 to 7 in Table 1, 11 to 13 in Table 2 and 4 to 6 in Table 3 can be used for melting ferrous as well as non-ferrous metals. If high temperature graphite crucibles are produced on a large scale in Pakistan, foreign exchange to the tune of Rs. 10 million spent on the import of this item per annum to meet the industrial needs of the country can be saved.

Acknowledgement. The authors owe a debt of gratitude to Dr. M.K. Bhatty, Director, PCSIR Laboratories, Lahore for providing research facilities. They are also thankful to him for his kind permission to publish this paper. Thanks are due to Mr. M. Afzal, Technician and Mr. Javaid Amjad, Senior Technician (S.G), for their help during the course of these investigations.

REFERENCES

1. J.E. Hove and W.C. Riley, *Modern Ceramics,* (Aerospace Corporation, El. Segundo, California).
2. H.K. Richardson, *Graphite as a Refractory,* J. Am Ceram. Soc., **65**, 69, 18 (1935).
3. J.D. Gilchrist, *Fuels and Refractories,* Department of Metallurgy, King's College, Newcastle-upon-Tyne (The University of Durham, Pergamon Press, New York, 1963).
4. M. Latif, M. Yousaf, M.A. Baig and F.A. Faruqi, Pakistan J. Sci. Ind. Res., **26**, 2, (1983).
5. L.W. Brooks, *Graphits* (Mining and Sc. Press. 115, 391, 1917).
6. Bornatsky, M. Kotrovsky and Y. Yargin, *Open Hearth Practice,* (A Hand Book Foreign Language Publishing House, Moscow, 1962).
7. M.C. Booze J. Am. Ceram Soc., **2**, 65 (1919).
8. A report of Bartley Crucible and Refractories Co., Trenton, New Jersey, U.S.A., Chem., Metallur, Eng., **38**, No. 5 (May 1932), p. 282.
9. K.K. Majumdar, J. Sci. Ind. Res. (India), **7B**, 187 (1948).