REFRACTORY MATERIALS FOR FURNACE LININGS.

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The production of electric-furnace products as refractory materials for furnaces, kilns, ovens, etc., as well as for electric furnaces themselves, is likely to develop into an important branch of electrometallurgy. The great range of temperature of the various furnaces, ovens, etc., enables widely differing materials to be used, but the requirements of a good refractory material may be said to be :—

- (a) It should be a relatively poor conductor of heat, so as to reduce to a minimum the amount wasted through the furnace walls.
- (b) It must be mechanically strong and not liable to crack or flake off over a wide temperature range.
- (c) It must withstand the reducing action of the charge, particularly carbon, as this element enters into most furnace reactions.
- (d) When used for electric furnaces it should be as far as possible a non-conductor of electricity.

This last requirement is perhaps as difficult as any to fulfil, because many materials which are non-conductors when cold become fairly good conductors at a high temperature. The filament of the Nernst lamp is an example of this characteristic.

Refractory materials may be roughly divided into—

- I. *Carbon*, for the highest temperatures.
- II. *Silicon carbides*, made in the electric furnace, such as—
 - (a) *Carborundum*, which is pure crystallised silicon carbide.
 - (b) *Siloxicon*.
 - (c) *Amorphous or soft silicon carbide*.
- III. *Crystallised magnesia*, made in the electric furnace.
- IV. Ordinary *firebrick, magnesia brick, cement clinker brick*, etc., for the lower ranges of furnace temperature.

This Paper deals with the second and third groups, and especially with the use of electric-furnace products as furnace washes.

It should be noted that the large majority of furnaces are combustion or gas furnaces, and it is for lining these that most of the above-named electrical products are so useful. For electric furnaces they have also a rapidly extending use, and even for these the less refractory may be used, because the electric arc is very local in its action, and is usually arranged so that it does not play direct on the linings.

It used to be thought that a refractory lining should be homogeneous throughout, but actual experience has conclusively shown that ordinary linings such as firebrick, magnesia brick, etc., may be usefully washed over with a highly refractory material to the depth of half a millimetre or so.

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CARBORUNDUM.

Probably the first material to be used in this way was carborundum, Engels having first suggested its use as a wash in 1899. Although introduced so recently, it has already established quite an excellent reputation. For ordinary furnace kilns, etc., the carborundum is ground up very fine, and mixed in the proportion of three parts by weight of carborundum to one part by weight of silicate of soda (waterglass). After thoroughly brushing the freshly set firebrick to get rid of dust, etc. (the mixture does not stick readily to a surface which has been already fired), the carborundum is painted on to the depth of about half a millimetre. It is then left for about twenty-four hours to dry, and afterwards the firing started up gradually. The result is that a layer of carborundum becomes cemented over the whole surface of the firebrick lining, cracks and all, and if properly done it adheres quite soundly.

It may be mentioned here that carborundum * taken from the core of the furnace is infusible at 7,000° F., and is unaffected by oxygen, ozone, or sulphur at 3,000° F. It is also unaffected by chlorine, bromine, or boiling concentrated sulphuric acid, gaseous hydrochloric, nitric, or hydrofluoric acid.

To show how well this coating will resist high temperatures, it may be mentioned that during the Düsseldorf Exhibition, a welding furnace with coke firing and blast was used for the welding of tubes from nine o'clock until seven at night, for nearly six months, and the carborundum lining was in almost as good a condition at the end as at the beginning of the run.

Where basic slags or basic materials have to be taken into consideration, fireclay is employed as a binder instead of the waterglass, the proportion being usually six parts by weight of carborundum to one part by weight of fireclay. Carborundum mixed with fireclay in equal parts has been used for repairing cracked gas retorts in Berlin with considerable success. This was done whilst they were still hot, and they ran for a considerable time afterwards perfectly gas-tight. For pointing the joints in brickwork of coke ovens for recovery of by-products, a mixture of carborundum and fireclay has been found very useful. The mixture is tamped in, to about half an inch deep, and it completely closes the oven chamber against the flues so preventing any gases from entering through the heating walls.

Carborundum has also been used for lining iron and other metals. In this case three parts by weight of carborundum are mixed with two parts of silicate of soda. Where it is used for this purpose, however, the metal must remain constantly heated, as otherwise the coating will burst off when the metal cools down. Carborundum coatings have proved of considerable value for coating iron, etc., which have to be subjected to considerable heat; thus in the case of some central iron pipes for a particular blast furnace the useful life was increased from 2½ to 9 months.

The temperature limit to the use of carborundum is reached when it decomposes according to the equation

the silicon escaping as vapour, whilst the carbon remains as graphite. When the temperature is so high that this decomposition occurs, it would appear that the only refractory material that can be used is carbon, and the best

* Carborundum or crystallised silicon carbide was first discovered in 1893, by Acheson, when he treated sand and coke in the electric arc at a temperature of 3,300 C., the following chemical action taking place:—

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form of carbon for the purpose is charcoal. Possibly further study of electric-furnace products may produce other highly refractory materials.

The samples of carborundum which Mr. Richard Cremer has kindly sent for exhibition include the following :—

- (1) Three fireclay bricks with carborundum surface for use at the highest possible temperature.
- (2) Piece of Glenboig firebrick coated with carborundum taken from a furnace heated with coal-dust firing. This brick was exposed to a very high temperature, and yet the carborundum surface has protected it exceedingly well.
- (3) An injector furnace, of which one half is coated with carborundum. This furnace was heated with a blow-pipe, and it will be seen that the uncovered part has commenced to flux, whilst the carborundum-covered part is perfectly intact.
- (4) A fireclay crucible coated with carborundum which has been exposed to oxy-hydrogen blow-pipe. The sample shows how efficiently carborundum has acted as a protector.
- (5) Carborundum crucible made from 90 per cent. carborundum and 10 per cent. fireclay.
- (6) Sample of carborundum powder for refractory purposes, and a sample of carborundum crystals as obtained from the electric furnace.

SILICON.*

In 1903 a patent was issued to E. G. Acheson for refractory material containing silicon, carbon, and oxygen, which he called "siloxicon."† He produced it by heating in an electric furnace a mixture of carbon and silica, the latter being in excess of the amount required for the formation of silicon carbide. The resulting substance gave the following analysis :—

SILICON	...	...	...	...	...	57.7
CARBON	...	...	...	...	...	25.9
Iron	...	...	...	...	...	2.1
Aluminium	...	...	...	...	...	0.4
Calcium	...	...	...	...	...	trace
Magnesium	...	...	...	...	...	trace
OXYGEN (by difference)	...	...	...	...	...	13.9

At very high temperatures the oxygen goes off and crystallised carborundum remains.

Siloxicon has a density of 2.73, and is of a grey-green colour when cold, and light yellow when heated to 300° F. It has the property of forming a coherent mass when ground fine, moistened with water, and moulded into a

* See also "Note on the Properties and Use of Siloxicon," by L. Gaster. *Trans. Faraday Soc.*, Jan., 1905, p. 118.

† The first mention of a silicon-carbon-oxygen compound appears to have been by Colson and Schutzenberger in 1881, before the Paris Academie des Sciences, when they described an experiment in which they heated silicon strongly in a porcelain tube, through which a current of carbon dioxide gas was passed. The result was a green-coloured mass which, purified from silicon and silica by heating in potassium hydrate solution and hydrofluoric acid respectively, gave a green-coloured powder, which was unattacked by acids or alkalis, and corresponded to the formula SiCO. It is this SiCO which is now known as siloxicon. In 1892 Schutzenberger described how he obtained a new compound, SiC, by heating powdered silicon mixed with silica in a carbon crucible. This SiC is now called carborundum or amorphous silicon carbide, according as to whether it is crystallised or not.

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form and fired. It is very refractory, and has a neutral action with both acid and basic slags, and is indifferent to all acids except hydrofluoric acid, which attacks it slowly.

With proper mixtures of silica and carbon it forms in the electric furnace at about $2,500^{\circ}\text{C}$. It is insoluble in molten metals. At fusion temperatures it is decomposed by free alkalis, and in the presence of free oxygen it oxidises at about $1,500^{\circ}\text{C}$. In a neutral or reducing atmosphere it is unaffected until its temperature of decomposition is reached, which is about $3,000^{\circ}\text{C}$. Upon decomposition the oxygen is set free, the carbon and silicon uniting to form silicon carbide, which is in itself a very refractory material.

Although to a certain extent self-binding when heated to a high temperature, in commercial work it is advisable to add some form of bond to siloxicon. If it is desired to make up articles which can be baked thoroughly before use, the Siloxicon Company recommend the addition of about 2 per cent. of finely powdered alumina, the mixture to be baked at a temperature slightly below that at which siloxicon oxidises. In certain cases 5 per cent. of finely powdered, refractory, plastic, non-alkaline clay can be used in addition to the alumina, this giving increased strength without detracting from the refractoriness of the article as a whole.

If it is desired to use siloxicon as a lining to some form of furnace, the material is tamped into place and baked in the furnace itself; and for this purpose it may be mixed with either silicate of soda or with coal-tar. If silicate of soda is used it should have a specific gravity of 1.1. This is mixed with the siloxicon until the desired consistency is obtained, and a thin wash is applied as a paint when it is desired to protect some other form of lining.

AMORPHOUS SILICON CARBIDE.

When describing the carborundum furnace before the Franklin Institute in 1893, Acheson referred to a white or grey-greenish looking shell, surrounding the zone of carborundum crystals. This was found to consist of small pieces of the size of the original sand grains, which were soft and easily ground to a fine powder. The powder had the same constituents as the carborundum crystals, and after being heated with hydrochloric acid, caustic soda, water, hot oxygen, and hydrofluoric acid, it gave the following analysis :—

SILICON	...	...	...	...	...	65.42
CARBON	...	...	...	...	...	27.93
Ferric oxide and alumina	...	...	...	...	...	5.09
Calcium oxide	...	...	...	...	...	0.33
Magnesium oxide	...	...	...	...	...	0.21

It is known as amorphous silicon carbide, and the first mention of it as a furnace lining appears to have been in 1899, when, in a patent granted to Benjamin Talbot, he stated he had found carbide of silicon to be very refractory at high temperatures, and able to resist the fluxing action of acid and basic slags. To use the carbide as a refractory material it is mixed with some suitable binding agent and moulded into forms, such as bricks, etc., and he says he prefers to use the *amorphous form of silicon carbide*, since "that has hitherto been deemed a waste product, and is consequently inexpensive."

As silicon carbide is a much better heat-conductor than ordinary fire-bricks, it is best not to use it alone, otherwise there may be serious loss of

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heat, but it may be used as a wash over other bricks ; indeed, this may be said to be true of all silicon carbides. For example, in *Electrochemical Industry* for November, 1904, Fitzgerald mentions a case of a small gas furnace, where siloxicon was substituted for a fireclay lining. Although a steel melt could easily be obtained in the furnace under ordinary conditions with fireclay, yet the heat was conducted away so rapidly by the siloxicon that it was almost impossible to melt copper. This points to the importance of only using this material as a wash over the surface of ordinary firebricks.

Although silicon carbides are fairly good electrical insulators, they are better conductors than ordinary firebricks, heated to the same temperature. Of course, the more porous they are the lower the electrical conductivity.

BINDING MATERIALS.

When a silicon carbide is put directly into place in the furnace, where it will not have to undergo any serious mechanical strains, the mixture may consist of powdered silicon carbide mixed in a solution of hot glue and water. Silica is usually present in commercial silicon carbide, and by fusing at high temperatures it strengthens the article considerably. When no free silica is present, Fitzgerald has found that an article made up with the glue solution becomes weak and crumbles after use ; it is, therefore, advisable to add silica in the form of a small quantity of infusorial earth. When the lining is not exposed to very high temperatures the silicon carbide may be mixed with a dilute solution of sodium silicate, having a density of 1.03 to 1.05, but the higher the temperature the smaller must be the amount of sodium silicate used.

Gas-tar makes a fairly satisfactory bond, but if in the proportion of 4 to 1 a residue of carbon is left in the article, which tends to diminish the insulating properties of the silicon carbide. Where the conditions are such that neither oxidation or current leakage is to be feared, a tar bond is satisfactory, and has considerable mechanical strength.

When an article of great mechanical strength is required, and the use of tar is objectionable, the article may be made by causing the particles of the silicon carbide to frit together by oxidation. To accomplish this result the silicon carbide is mixed with some temporary binding agent, such as a solution of glue in water, and then heated to a high temperature for several hours in a strongly oxidising atmosphere. By this treatment the grains of the silicon carbide are superficially oxidised. In the case of amorphous silicon carbide this would take place according to the equation—

Fitzgerald says that if the article made in this way is examined under a strong lens, the grains of carbide are seen to be superficially oxidised and fused together. This formation of silicon carbide articles by the oxidation method requires prolonged heating, because the rate of oxidation is slow, and proceeds gradually from the outside of the article to the centre.

CRYSTALLISED MAGNESITE.

Most of the magnesite at present used comes from Styria in Austria, the Island of Eubœa in Greece, from California, and from Salem in Southern India. Ordinary calcined magnesite, generally in the form of bricks, is now recognised as the best material for lining *basic* open-hearth furnaces, cement kilns, etc. It may be employed to advantage wherever high temperatures

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and chemical reactions are usually detrimental to dolomite, chromite, and silica. America uses large amounts of magnesite for steel furnaces, whereas in England dolomite is chiefly employed; magnesite is, however, coming into use, although it is double the price. The distinctive characteristics of a magnesite lining are durability, freedom from moisture and silica, and resistance to corrosion when exposed to the action of basic slags and metallic oxides. These qualities make the lining cheaper than most others in the long run.

The usual method of dealing with the native magnesium carbonate, which is found in a more or less pure state, is to drive off the carbonic acid gas as far as possible by calcining in a kiln. The kilns of the Anglo-Greek Magnesite Company on the Island of Eubœa were originally roughly-built for firing with wood, but now modern shaft calciners are employed fired with lignite coal. The temperature, however, is not sufficient to shrink the magnesium carbonate, and it is even doubtful whether rotary kilns would do this satisfactorily.

About two years ago the writer carried out some original experiments in Meraker, Norway, with a view to thoroughly shrinking magnesite in an electric furnace. The furnaces were of the Siemens & Halske type, built for the manufacture of carbide of calcium on the intermittent system, and they were supplied with current from 900-kilowatt three-phase generators, driven by water turbines. The material on which the writer worked was native magnesite brought from Salem in Southern India,* where it is found in a remarkably pure state.

The writer found that it was possible simply to pass the magnesite down the chutes in the same way as the raw materials for making carbide of calcium. When once the arc was fairly started the raw magnesite could be fed in at a fairly rapid rate and completely shrunk (after first driving all the CO₂ off), without the assistance of any carbon or other material.

After a two hours' run with 3,500 amperes at 65 volts a block, about 15 inches cube, was obtained, which was practically pure crystallised magnesia. When broken into pieces with a sledge-hammer the material showed a fine crystalline structure with a beautiful iridescent colour, and it had evidently been in a semi-plastic condition. Attempts were made to mould the half-shrunk material into bricks, and then treat these in the electric furnace, but with poor success.

On returning to England in November, 1902, the writer found that Mr. W. Deighton, of the Deighton Patent Flue and Tube Works, Hunslet, was trying carborundum as a wash in his furnaces and also on the refractory blocks surrounding the water-gas flame used for heating steel tubes. He showed Mr. Deighton the electrically-shrunk magnesia, and suggested that it would probably be as good as and considerably cheaper than carborundum. It has since been tested as a wash over the firebrick lining of a carbide of calcium furnace, and it was found that the bricks lasted for two hundred hours without repair, whereas the unprotected bricks required repair after a five hours' heat. There is no doubt that the crystallised material, without further preparation than being crushed to suitable dimensions, will prove of special value as a refractory material in metallurgical practice, and an important

* These magnesite deposits have been known to the natives for many generations, and they use it for plastering the inside walls of houses. Being absolutely fireproof and self-binding, it is an excellent material for the purpose. It has been suggested to make partition walls for houses from it by smearing it on to a textile fabric as a base, and letting it set in a corrugated shape. The samples of partition walling which the writer has seen, promise well.

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point in connection with its use as a lining for electric furnaces is that magnesia, unlike lime, does not form a carbide with carbon.

In the large open-hearth steel furnaces at the Homestead Steel Works, Pittsburg, the writer found that large quantities of ground calcined or partly shrunk magnesite were used for the underbeds of the furnaces, and it is probable that the electrically-shrunk material would be found to be still more effective for this purpose.

In replying to a letter by the writer in *Electrochemical Industry* for Nov., 1904, Mr. Fitzgerald states "that he considers that the electrically shrunk magnesia is not as refractory as silicon carbides or carborundum, and he instances a case of a furnace in which magnesia was used for part of the lining. The temperature at the inner surface of the magnesia lining was well below that of the formation of the carborundum, but above that of the formation of the silicon carbides. The heat lasted about eight hours, and the magnesia lining, which was about 4 cm. thick, was completely fused."

Probably this was because Styrian magnesite, which is largely exported to America, was used. This magnesite unfortunately contains a high percentage of iron which causes it to flux easily. Further, it would appear that the magnesite was not crystallised but only partly burnt. A very pure magnesite, such as the Indian, when crystallised, certainly does not run at the electrical-furnace temperature. In the writer's experiments at Meraker it was never more than in a semi-plastic condition. Even the temperatures obtained in thermit compounds have no effect on it.

REPORT OF TEST MADE ON MAGNESITE BY THE AUTHOR, OCTOBER 29, 1902.

Twelve bags of partly calcined magnesite were screened through a sieve having meshes about half an inch by a quarter, and the material then fed into the chutes leading down to the furnace. Started furnace with a shovelful of charcoal and allowed some magnesite to run in. The material took longer to heat up than in making calcium carbide, but in about fifteen minutes I was able to raise the top electrode, which showed that it was going to be possible to treat the material *without* coke. Later on I found it was much better to work without coke.

In three-quarters of an hour the handle raising the electrode had been given $8\frac{1}{2}$ turns, which meant that it had been lifted $5\frac{1}{4}$ inches, and in one hour it had been raised $7\frac{1}{2}$ inches.

The process was continued for two hours, by which time all the twelve bags had been used up, and the furnace filled to within 6 inches of the top. The furnace was left to cool, and on the following day the hard core immediately between the electrodes was taken out, and found to weigh about 3 cwts., whilst it measured about 15 inches cube.

The operation throughout was very quiet, this no doubt being partly owing to the absence of coke. Occasionally when the material ran short and the edge of the electrode became uncovered some material would be thrown up with considerable violence.

On breaking the block with a sledge-hammer the centre and bottom was found to be a very dark grey leading off to white on the outside of the block. There was also a considerable amount of yellowish white fused material and some reddish brown.

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Throughout the two hours the pressure was 65 volts, and the current was kept as near 3,500 amperes as possible. To make the 3 cwts. of crystallised magnesia therefore took about 300 horse-power for two hours.