Aug. 3, 1948. J. FLETCHER ET AL 2,446,222

METALLIC STRUCTURES WITHIN HIGH TEMPERATURE FURNACES

Filed July 10, 1942 3 Sheets-Sheet 1

Fig. 1

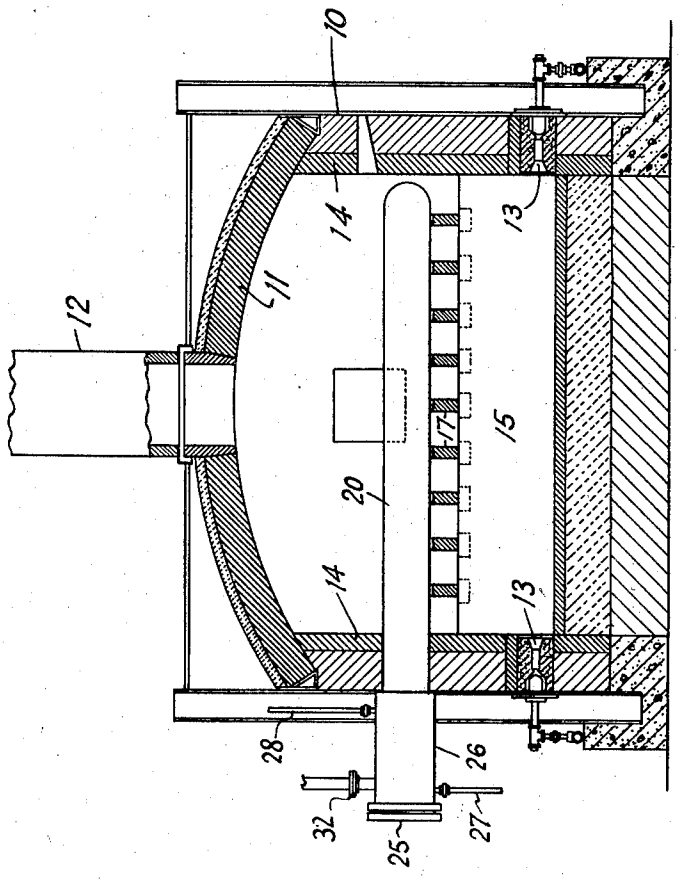
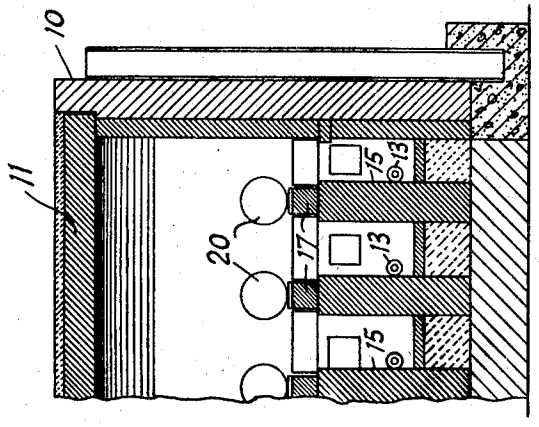


Fig. 2



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Filed July 10, 1942 3 Sheets-Sheet 2

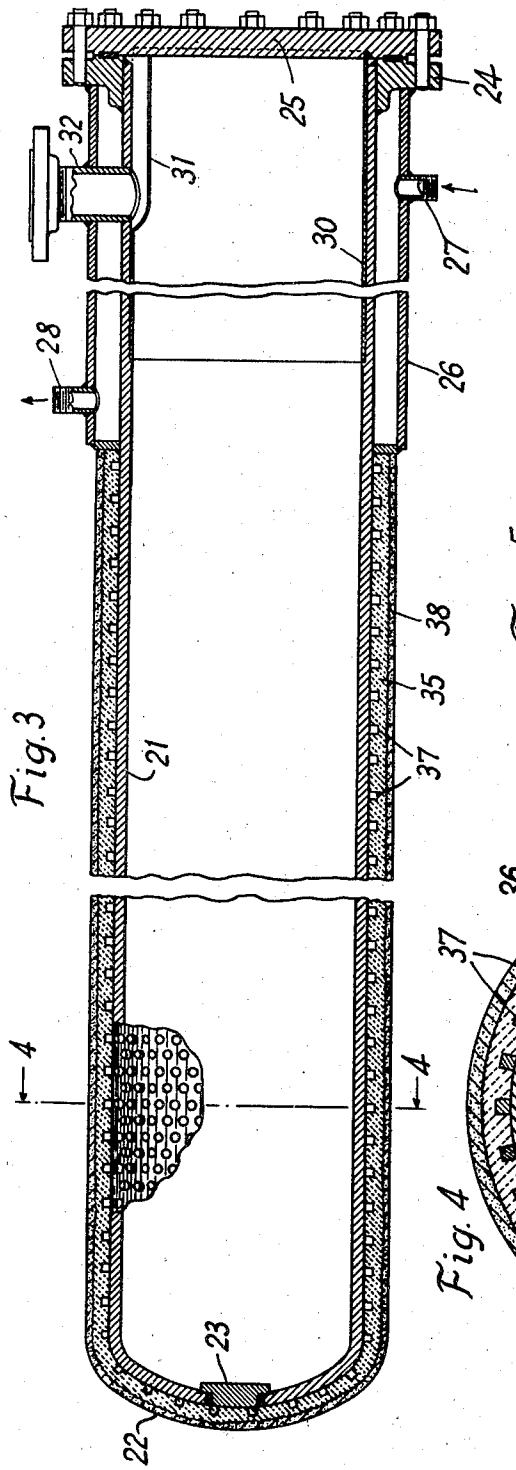


Fig. 3

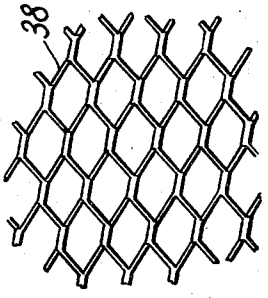


Fig. 5

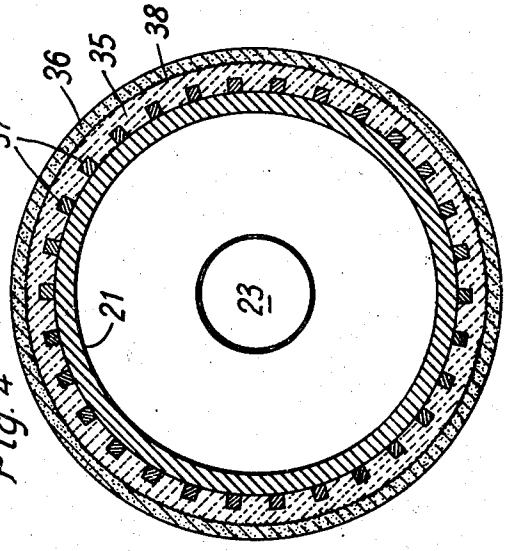


Fig. 4

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METALLIC STRUCTURES WITHIN HIGH TEMPERATURE FURNACES

Filed July 10, 1942 3 Sheets-Sheet 3

Fig. 8

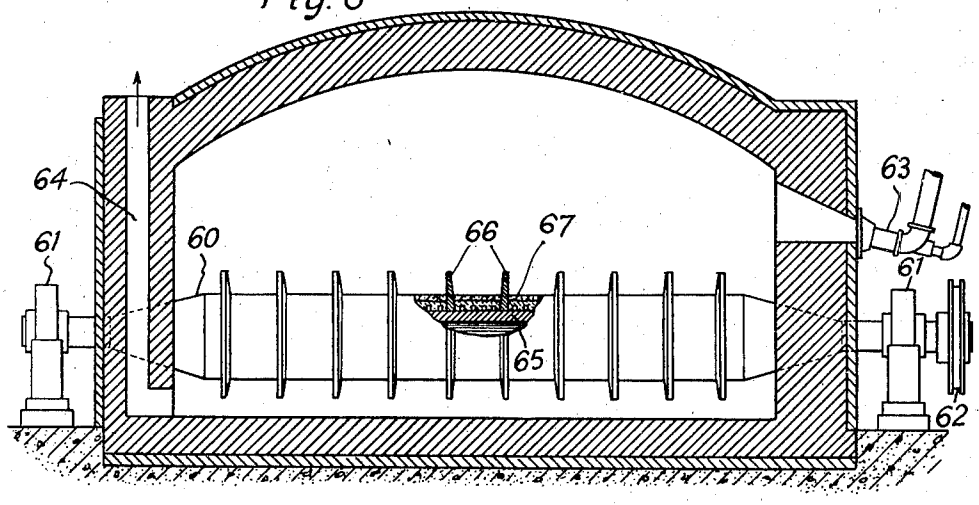


Fig. 6

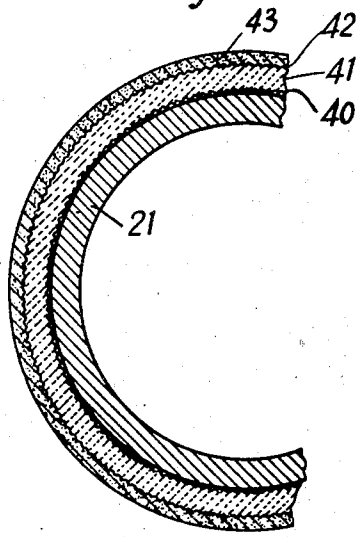
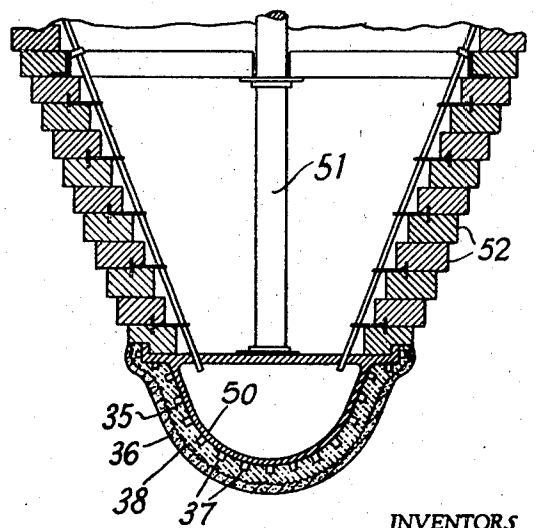


Fig. 7



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2,446,222

UNITED STATES PATENT OFFICE

2,446,222

METALLIC STRUCTURE WITHIN HIGH-TEMPERATURE FURNACES

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Application July 10, 1942, Serial No. 450,472

3 Claims. (Cl. 266—19)

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The present invention relates to the construction of metallic structures adapted for use in a corrosive or oxidizing atmosphere at temperatures approaching the melting point of the metal.

Ordinary iron or steel having a melting point of 2700–2900° F. oxidizes comparatively rapidly at temperatures above 930° F., and the oxide coating formed does not protect the underlying metal from further oxidation. When held for a prolonged period at high temperature in an atmosphere containing corrosive constituents, such as oxygen, carbon dioxide, steam or sulphur dioxide, the metal is gradually converted to the oxide and may entirely waste away much as it wastes away when exposed to particularly corrosive conditions at ordinary temperatures. According to some authorities, the rate of oxidation of iron at a constant high temperature varies directly as the square root of the elapsed time. Due to this progressive scaling of the metal, ferrous structures are ordinarily limited to use under service temperatures below 900° F. For effective resistance to scaling at high temperatures, it has been universally considered necessary to use an alloy steel or iron.

Corrosion of ferrous metal structures at atmospheric or low temperatures can be reduced in various ways, such as by the use of a coating of protective metal like zinc, tin, lead, nickel or copper; the application of protective paints; the production of oxide, phosphate or similar coatings on the exposed surfaces; and passivating the surface. None of these protective methods however is suitable for service use above relatively low temperatures. For higher temperature service conditions, the structure to be protected can be calorized to produce a coating of aluminum and aluminum-iron alloys on the surface which tends to protect the metal against high temperatures because of the formation of aluminum oxide on the surface. A calorized surface has been found to resist continued temperatures up to 1800° F. but begins to burn at approximately 2000° F.

It has also been proposed to cover the otherwise exposed surface of the structure with a layer of highly heat resistant alloy metals, either in the form of a sheet welded to the exposed surface or a deposited layer of alloy weld metal. Such constructions however are expensive to manufacture and require a substantial amount of alloy metal.

It is also well known in the construction of water-cooled furnace walls and the like to cover the furnace side of the water tubes lining the furnace walls with a layer of initially plastic

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refractory cement, such as a silicon carbide or a chrome ore cement, for the purpose of providing a heat radiating refractory surface to increase the furnace chamber temperature and in some cases to protect the tubes from erosion by slag depositing thereon. The refractory layer is usually held in place by metallic projections, such as studs or fins, on the tubes which also serve to increase the rate of heat transmission to the tube walls and contained fluid. The rapid conduction of heat away from the tube walls by the contained fluid holds the tube wall temperatures well below 930° F., even with furnace chamber temperatures of 2500° F.–3000° F. and operating pressures in excess of 2000 p. s. i. No special problem of tube metal oxidation is present under such conditions.

Where the metallic structure is to be subjected to internal or external pressure stresses under service temperatures, alloy steels and special heat-resisting alloys are universally used, in view of the rapidity with which carbon steels lose strength at high temperatures. Another factor of importance is the lower permeability of alloy steels at high temperatures to the infiltration of gases. The attention of investigators therefore has been largely given to the properties of alloy steels at high temperatures, and little is known of the strength and permeability of ordinary iron and steel at temperatures above 1800° F.

The general object of our invention is the provision of a metallic structure adapted for prolonged service in a corrosive or oxidizing atmosphere at temperatures approaching the melting point of the metal. A further and more specific object is the provision of a protective covering for a pressure vessel made of a corrodible or oxidizable metal, permitting the use of the vessel for long periods at temperatures substantially above the temperatures for which the bare metal could safely be used. A further and more specific object is the provision of a retort of a non-alloy ferrous metal capable of use with a substantial vacuum therein under furnace temperature conditions maintaining a metal temperature above 2000° F. for long periods of time.

The various features of novelty which characterize our invention are pointed out with particularity in the claims annexed to and forming a part of this specification. For a better understanding of the invention, its operating advantages and specific objects attained by its use, reference should be had to the accompanying drawings and descriptive matter in which we have illustrated and described several embodiments of our invention.

Of the drawings:

Fig. 1 is a sectional elevation of a retort furnace for the production of metallic magnesium;

Fig. 2 is a partial longitudinal section of the furnace shown in Fig. 1;

Fig. 3 is a longitudinal section, partly broken away, of a furnace retort constructed in accordance with our invention;

Fig. 4 is a transverse section taken on the line 4—4 of Fig. 3;

Fig. 5 is a fragmentary plan view of the expanded metal shown in Figs. 3 and 4;

Fig. 6 is a view similar to Fig. 4 illustrating a modified retort construction;

Fig. 7 is a sectional elevation of the lower part of a furnace baffle constructed in accordance with our invention; and

Fig. 8 is a transverse section of a heat treating furnace containing furnace rolls constructed in accordance with our invention.

While our invention is adapted for a wide field of use wherever a structure of a corrodible or oxidizable metal is subjected to corrosive service conditions at a temperature above that at which the bare metal can safely be used, it is particularly designed for and especially useful in the manufacture of retorts for the production of metallic magnesium by the reduction of a magnesium-containing material.

In this process dolomitic limestone is burned and pulverized to a finely divided condition; it is then mixed with a predetermined amount of a pulverized reducing agent, preferably ferro-silicon. The pulverized dolomite and ferro-silicon are mixed and formed into small briquets. The briquets are charged so as to partly fill an externally heated sealed metallic retort which is kept under a high vacuum by means of a suitable vacuum pump. The charge in the retort is heated to a temperature of approximately 2100–2200° F., i. e. above the vaporization temperature of magnesium which is usually considered as 1958–2048° F. A chemical reaction occurs between the burned dolomite and ferro-silicon resulting in the reduction of the magnesium oxide and the formation of magnesium, calcium silicate, and iron, substantially in accordance with the following reaction:

$$2(MgOCaO)+FeSi=2Mg+Ca_2SiO_4+Fe$$

The operating pressure within the retort is maintained as low as possible, preferably at an absolute pressure of 0.1 mm. Hg. Such a high vacuum has been found to minimize wastage of the silicon by oxidation, formation of magnesium nitride, and discoloration and sponginess of the condensed magnesium. The vaporized magnesium passes into the condenser section of the retort where it is recovered in a solid dense crystalline mass 99.98% pure. The condensed metal is removed from the retort, subsequently melted down under flux, and poured into ingots.

In Figs. 1 and 2 we have illustrated a furnace designed for the described process of reduction of magnesium ore. The furnace 10 is of substantially rectangular cross-section with an arched roof 11 containing gas outlets 12. The furnace is heated by rows of gaseous fuel burners 13 oppositely arranged in the lower part of the side walls 14 and positioned between transverse refractory partitions 15 extending the full width of the furnace. Short firebrick piers 17 are spaced along the top of each partition 15, and serve as supports for a corresponding horizontally elongated retort 20 extending substantially the full width of the furnace chamber. Due to the high retort metal temperatures in operation, the corrosive furnace atmosphere, and the high vacuum maintained within the retort, it has been considered essential to make the retort of stainless steel, such as an alloy of 25% chrome, 20% nickel, and the balance substantially all iron. Such alloy metal however, is expensive, and under war conditions relatively scarce. In accordance with our invention, such stainless steel retorts are economically replaced by retorts made of non-alloy ferrous metal having a protective covering preventing oxidation or corrosion of the retort metal under the service conditions described.

In Figs. 3, 4, and 5, we have illustrated one form of our improved retort, the body or shell of which is formed by an "extra heavy" pipe of mild steel. One end of the pipe is spun inwardly to form a rounded end portion 22 having a circular center opening which is closed by a metal plug 23 conforming in contour to the retort opening and welded therein to form a gas-tight closure. The opposite or outer end of the retort shell is provided with an external peripheral flange 24 welded thereto. An end plate 25 is connected to the flange 24 in any suitable manner to form a gas-tight detachable closure for the retort, adapted to be removed for the charging and discharging of the retort. The outer end portion of the retort is constructed to form a magnesium vapor condensing section by means of a water cooled circumferential jacket 26 having water inlet and outlet connections 27 and 28 respectively, as indicated in Fig. 3. A cylindrical metallic sleeve 30 is arranged to closely fit within the condenser section of the shell with its outer end secured to the end plate 25 in any suitable manner. An outer section of the sleeve 30 is slotted as indicated at 31 to connect the interior of the shell to a short pipe 32 to which the vacuum pump (not shown) is detachably connected. In operation the magnesium vapor condenses on the sleeve 30, which is removed with the end plate 25 at the end of the distillation period and the condensed magnesium removed. A fresh charge of briquets is then placed in the retort and the sleeve and end plate restored to their original position.

With a retort metal temperature of 2100–2200° F., a non-alloy ferrous metal shell has been found to have a service life of only a relatively few hours before the oxidation and scaling of the metal progresses to such an extent that the desired vacuum could no longer be maintained or the thinning of the shell wall and pressure differtial thereon caused the shell to collapse. In accordance with our invention the portion of the shell beyond the condenser section, i. e. the portion which normally extends through the furnace side wall and into the furnace chamber is provided with a protective covering which effectively prevents corrosion and scaling of the ferrous metal shell and which substantially strengthens the retort under the contemplated service conditions.

The preferred covering is preferably made of a highly refractory material or materials, at least the portion of which contacting with the shell is chemically inert with respect to the ferrous metal shell throughout the normal operating temperature range. Certain materials, such as silicon carbide cement, were found to alloy with the shell at temperatures of and above 2050° F. to form a layer of ferro-silicon which progressively pene-

trates the shell wall to a dangerous extent. The material used in the outer portion of the protective covering must also be capable of forming and maintaining a substantially gas tight glaze throughout the exposed surface of the retort over a relatively wide temperature range. Coating the shell with the usual porcelain enamel glazes maturing at approximately 2100° F. was found unsatisfactory as the enamels were rendered porous after a relatively short heating period due to the volatilization of some of the constituents of the glaze. Other coatings of known glaze forming materials were found unsatisfactory as some of the coatings did not flow or fuse while others bubbled excessively and ran off or cracked on drying and split off from the metal. A further desirable characteristic for the covering material is that at least the inner portion in contact with the metal shell should have a thermal expansion rate commensurate with that of the shell metal and/or provisions be made for compensating for thermal expansion differences therebetween to avoid an undesirable amount of cracking of the covering material as the shell and covering expand or contract under varying temperature conditions.

Another feature of our invention is the use of extended metallic surface on the outer surface of the shell in the form of studs, fins, or expanded metal integrally connected to the shell. This extended surface serves several important functions, one being to provide a strong connection between the shell and the contacting refractory layer. This not only aids in holding the parts in their assembled relation but also materially adds to the strength of the retort as a whole. As the higher temperatures are reached, the strength of the ferrous shell tends to decrease substantially while the strength of the refractory layer becomes greater due to its vitrification. The metallic projections on the shell thus aid in forming a composite beam structure of the shell and refractory layer capable of withstanding the forces tending to collapse the retort when operating under the described high vacuum conditions. Such metallic projections are also useful in partly breaking-up the continuity of the layer of contacting refractory material and thus reducing the extent of any shrinkage cracks which may develop during the initial drying and vitrification of the refractory layer as well as minimizing cracking of the refractory due to expansion and contraction of the parts. The parts will also serve to increase the rate of heat transmission from the furnace chamber to the charge within the retort to a substantial extent.

The retort protective covering illustrated in Figs. 3–5 is of a composite type, being formed of an inner layer 35 of neutral refractory material and an outer layer 36 of glaze-forming refractory material, with the layers reinforced and held tightly together by suitable means. The retort shell is provided throughout the area of the covering with staggered rows of short steel studs 37 welded to the outer circumferential and end surfaces of the shell. The studded area of the shell is then covered with a suitable moldable cement of initially plastic neutral refractory material rammed into place so that it will be tightly packed against the shell and studs. This can be done manually with a small headed heavy hammer. Small areas are preferably applied at one time and the previously applied areas kept moist to avoid any drying out. The plastic refractory is

applied with a thickness such that it will completely cover the outer ends of the studs.

We have found a number of plastic refactory cements which are inert with respect to the metal of the retort throughout the operating temperature range and which will vitrify but not fuse under such temperature conditions. One highly suitable material is that known commercially as "B & W 80 Moldable" consisting approximately of 80% crushed dense fire brick or grog, 10% ball clay, 10% bond clay and a small amount of binding material. Another highly suitable material is that known commercially as "Alundum" cement which we believe consists of approximately 90% crushed fused alumina grain and 10% binder. This material appears to set harder and have a more permanent attachment to the shell and studs than most other materials used. Another satisfactory material for the inner layer was plastic chrome ore cement known commercially as "PCO" or "KN" and consisting approximately of 85% finely divided chrome ore, 5% ball clay, and 10% sodium silicate. A further satisfactory refractory cementitious material was a mixture of 65% crushed fire brick or grog and 35% fire clay.

It is usually desirable to clean and sand blast the shell outer surface before applying the refractory to strengthen the attachment of the refractory layer. A thin coat of corrosive resistant paint, such as chrome paint, can also be applied underneath the refractory if desired.

In the service temperature range contemplated, the neutral refractory layer alone would be insufficient to prevent oxidation and scaling of the retort shell and studs. The refractory layer has been found to be pervious and does not prevent the corrosive gaseous constituents of the furnace atmosphere from penetrating the refractory layer and reaching the retort metal. The shell and studs rapidly become pitted and waste away under the corrosive action. In accordance with our invention the outer portion of the covering is a layer of refractory material which will form a substantially gas-tight or impervious surface glaze or outer skin throughout the service temperature range contemplated over the entire exposed surface of the retort, and preferably a glaze which will be semi-fluid, but not run off or blister, at the normal operating temperature. We prefer to use a relatively thick coating of a material which will form a smooth semi-fluid glaze on its exposed surface while the remaining enclosed portion will remain unglazed unless a portion of the glaze is broken off or cracked whereupon the subjacent area then exposed will glaze over and heal the break in the outer skin.

The most suitable glaze-forming material we have found having the foregoing characteristics is a silicon carbide refractory cement known commercially as "Carbofrax 5B" and made from high grade silicon carbide grain, raw clay and a soluble binder containing borax or other glaze forming constituents in the approximate proportions of:

	Per cent
Silicon carbide	84
Clay	12
Binder	4

This cement is tempered with water to a suitable molding consistency. It is believed that the silicon on the exposed surface will oxidize to SiO_2 and then combine with the borax in the binder to form a semi-plastic boro-silicate glassy skin on

the exposed surface of the layer. The remaining Carbofrax in the outer layer appears to remain as an unfused amorphous structure unless the skin is ruptured in some manner whereupon the rupture is healed by the glazing of the newly exposed portion of the outer layer.

Another material which has been found satisfactory for use as the glaze-forming outer layer is a refractory cement having a clay base in the approximate proportions of

	Per cent
Raw clay	28
Crushed heavy fire brick	57
Dry sodium silicate	15

The dry materials are tempered with water to a suitable molding consistency. The crushed fire brick can be replaced in part by silica sand.

In the manufacture of the retort illustrated in Figs. 3–5, the layer of neutral refractory **35** is completely applied to the studded shell to the thickness indicated. We have found it desirable to provide means for holding the refractory layer tightly against the shell and also to facilitate the application of the outer refractory layer thereto. For these purposes, a layer of wire mesh or expanded metal **38** of the character shown in Fig. 5 is tightly wrapped around the retort and secured in place. The expanded metal or metal lath may be in the form of a single sheet wrapped around and the ends tack-welded or otherwise secured together, or one or more narrow strips of such expanded metal wound around the refractory layer with a small overlap between turns. The outer coating **36** was then applied over the expanded metal layer to the desired thickness and smoothed over the entire area. The retort is then heated to approximately the normal operating temperature to vitrify the refractory material and create the glazed outer skin. The initial firing of the retort can be done by inserting the protected part of the retort into an operating retort furnace, as shown in Figs. 1 and 2, and using the normal temperature conditions therein to heat treat the refractory and form the glazed skin, or into a separate heat treating furnace before or after shipment to the point of use.

By way of example and not of limitation, one magnesium furnace retort was made in accordance with the present invention with its shell 8′ 5½″ long and of 10″ ex. hy. seamless forged steel pipe, the wall thickness being ½″. Rows of studs ⅜″ diameter and ⅜″ long were welded on the shell with 1½″ staggered spacing. A ¾″ thick layer of B & W 80 Moldable was rammed on the studs and shell. Metal lath shown in full size in Fig. 5 was then wrapped around the shell and a ¼″ thick layer of Carbofrax 5B added. The retort was then heated to 2300° F. and maintained at that temperature. The surface of the Carbofrax layer begins to glaze at about 1800° F. and remains in a semi-fluid condition throughout a temperature range up to and beyond 2300° F. While the metal lath tends to melt and combine with silicon in the outer layer to form a ferro-silicon, this action does not occur until the refractory materials are vitrified to the desired extent. The inert refractory layer effectively prevents any reaction between the silicon of the outer layer and the ferrous shell or studs, so that these metal parts are maintained intact and reinforced by the surrounding vitrified refractory to withstand the pressure stresses thereon due to the high vacuum normally maintained within the retort. One advantage of the argillaceous base refractory cement outer layer described is its inertness relative to the metal lath. Consequently the intervening layer of metal lath is advantageously maintained intact when such material is used.

Where the covered portion of the retort adjacent the condenser section is not likely to be heated to a glaze-forming temperature under normal furnace operating conditions, it is desirable to preheat the covering in this section to a glaze-forming temperature by a blow torch or other suitable means before installing the retort. Similarly, where the retort normal operating temperature is above 900° F. but below the glaze-forming temperature, adequate protection is obtainable by preheating the retort to a temperature above the glaze-forming temperature to cause the glaze to form.

In the modification illustrated in Fig. 6, the studs on the shell are replaced by a layer of metal lath **40** tack welded to the shell **21**. A layer of Alundum cement **41** is then rammed on the shell and over the metal lath and a second layer of metal lath **42** then wrapped around the Alundum layer. An outer layer **43** of Carbofrax 5B is then added to complete the protective covering, which is then heat treated as previously described.

While our protective covering has been specifically described in connection with a retort of mild steel, it will be obvious that our invention is applicable to other ferrous metals and alloys, such as cast iron and steel, high carbon and alloy steels, etc. and to non-ferrous metals and alloys, such as tungsten and molybdenum, either to prevent corrosion or to increase their ability to withstand high temperatures. Nor is our invention limited to use in retorts or pressure vessels, as many structural parts such as case hardening boxes, cyanide pots, crucibles, furnace supports and other furnace parts can be made in a similar manner. Two of such uses are illustrated in Figs. 7 and 8.

In Fig. 7 a furnace baffle cone of the type disclosed in the Throckmorton et al. U. S. Patent 2,276,527 is shown with a refractory and protected steel construction instead of the usual stainless alloy material. The lower end of the baffle is formed by an hemispherical hollow steel nose member **50** supported by a hanger **51** and in turn supporting overlapping circular rows of insulating fire brick **52** forming the remaining exposed part of the baffle wall. The nose **50** has its otherwise exposed surface studded as previously described and covered with successive layers of neutral plastic refractory, metal lath of expanded metal or similar material and a glaze-forming refractory, as disclosed in Figs. 3–5.

In Fig. 8, we have shown a construction of a rotary supporting roll **60** for a heat treating furnace embodying our invention. Such rolls are horizontally arranged in external bearing supports **61** and with a drive connection **62**. In operation the heating gases from the fuel burners **63** flow down over the rolls and any material supported thereon, and escape through gas outlets **64** in the opposite wall. Instead of the usual 100% stainless steel alloy construction, the roll can be formed by a hollow tube or shell **65** of mild steel having circumferential fins **66** of stainless steel alloy welded thereon at points spaced along its length to directly support the articles to be heat treated. Between the fins, the otherwise exposed steel surface is studded and covered with our protective covering **67** of neutral refractory, metal lath of expanded metal or similar material

and glaze-forming refractory as illustrated. No fluid cooling of the roll is necessary, as the protected shell is capable of withstanding metal temperatures substantially above 1000° F.

While in accordance with the provisions of the statutes we have illustrated and described herein the best forms of the invention now known to us, those skilled in the art will understand that changes may be made in the form of the apparatus and composition of the materials disclosed without departing from the spirit of the invention covered by our claims, and that certain features of the invention may sometimes be used to advantage without a corresponding use of other features.

We claim:

1. A pressure vessel capable of use under corrosive conditions at metal temperatures above 1000° F. which comprises a shell of metal subject to rapid corrosion when exposed to said service conditions, metallic projections on the outer surface of said shell, and a heat resistant protective covering for said shell including an inner layer of initially plastic chemically inert refractory material on the outer surface of said shell and covering said projections, a layer of expanded metal on the outer surface of said refractory layer, and an outer layer of metal-alloying glaze-forming material covering said inner layer and expanded metal and forming a self-sealing substantially gas-tight skin thereon.

2. A furnace retort capable of use under corrosive conditions at metal temperatures above 2000° F. which comprises a shell of non-alloy ferrous metal subject to rapid corrosion when exposed to said service conditions, metallic projections welded to the outer surface of said shell, and a heat resistant protective covering for said shell including an inner layer of initially plastic chemically inert refractory material contacting

with the outer surface of said shell and covering said projections, a layer of pervious metal on the outer surface of said refractory layer, and an outer layer of glaze-forming material covering said pervious metal layer and forming a self-sealing substantially gas-tight skin thereon.

3. A metallic retort for the reduction of magnesium ore under a high vacuum and capable of use under corrosive conditions at metal temperatures above 2000° F. which comprises a cylindrical shell of non-alloy ferrous metal subject to rapid corrosion when exposed to said service conditions, metallic projections welded to the outer surface of said shell, and a heat resistant protective covering for said shell including an inner layer of initially plastic refractory material neutral relative to said shell metal and contacting with the outer surface of said shell and covering said projections, a layer of expanded metal extending around the outer surface of said refractory layer, and an outer layer of initially plastic silicon carbide cement covering said expanded metal layer and forming a self-sealing substantially gas-tight skin thereon at temperatures above 1800° F.

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CHARLES L. NORTON, JR.

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