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METHOD OF PRODUCING CAST REFRACTORY

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This invention relates to a method of producing heat cast refractories free from large voids or pipe and the product obtained thereby.

In the cooling of molten refractories the transition from the liquid to the crystalline state is accompanied by a large decrease in volume. As the casting chills a solid external layer or skin is formed enclosing a molten core, and when the material ultimately completes solidification, the effect of the shrinkage is manifested in a large entirely enclosed void or in a pipe. The extent of this shrinkage is indicated by the fact that the voids or pipe in a block cast in accordance with the general teachings of the Fulcher Patent #1,700,288 may amount to 10% of the total volume of the cast block even though an additional supply of molten material is provided by a font, itself as large as 10% of the block volume.

Both voids and pipes are highly undesirable in certain cases, i. e. those in which the block is so situated in a furnace that the material melted therein may enter the void or pipe initially or as the result of corrosion of the outer surface of the block. Under these circumstances the effective thickness of the block is materially reduced.

According to this invention the above objectionable results are obviated, or at least greatly diminished, without increasing the weight or cost per cubic foot of the refractory, by distributing the shrinkage due to crystallization between a multiplicity of separate and unconnected cellular voids so that a more or less cellular block is obtained, the cells however being of such small diameter that the material being melted in the furnace will not enter them to attack.

We have discovered that a block of this character may be produced by introducing into the molten refractory certain materials which will slowly evolve minute gas bubbles during the solidification. Starting from independent foci, the cells produced are not connected. By control of the amount of added material, just sufficient cell space may be uniformly distributed to offset the normal shrinkage.

In general, in prior attempts to produce light weight material with insulating properties, relatively large cells have been sought and the formation of the relatively large individual cells produced by the agents so far suggested have not been objectionable. In the problem of pipe elimination however a very definite control of the limited cell size required is essential and while heat transmission changes are of minor importance, corrosion resistance of refractories exposed to molten fluxes cannot be sacrificed if an improved product is to result.

In the case of corrosion by molten glass or slag it is found that if cell size can be kept below about 0.5 mm. in diameter then the forces of surface tension will prevent entrance of the flux into the cells when opened and for practical purposes the surface area available for solution attack is not increased by the presence of the cells.

In our efforts to find suitable agents to produce such fine cells and in such large numbers as to nevertheless produce sufficient volume increase to eliminate pipe we have experimented at length with over forty types of gassing agents. Agents as Fe_2O_3, gypsum, limestone, magnesite, coke, and sodium sulphate gave large cells ranging around 3 mm. or larger when the gas was successfully trapped. Hydrates, peroxides, nitrates, sulphites and chlorides of various elements also are ineffective, either giving up their gas too quickly to permit trapping or else producing relatively large cells. In order to produce controlled and uniform cells it is necessary for the gasifier to produce slow and delayed evolution of gas throughout the period of solidification of the refractory and to mix uniformly with the molten refractory before gasification. The latter requirement eliminates those substances which due to low specific gravity or lack of ability to be wetted by the molten refractory do not distribute themselevs throughout the molten mass but rather rise and float on the surface thereof (e. g. coke and graphite) and do not give good results. On the other hand, hydrates, nitrates, sulphites and peroxides are apt to be very unstable thermally and yield their gas too early.

While we have found the sulphates of alkali and alkaline earths which are thermally relatively stable probably due to their basic character; and also alkali bisulphate which is unstable with respect to its acid content but stable with respect to its normal sulphate content all unsatisfactory for our purposes, we have discovered that certain other sulphates will give the fine cells desired and in desired and controllable amounts. While it might be supposed that since all sulphates would be decomposed at the temperatures of molten refractories, all should be more or less equivalent in effect, in practice such is found not to be the case. For one thing the property seems to be definitely associated with the formation of SO_3. Thus cupric sulphate, stannous sulphate, bismuth sulphate and ammonium sulphate which yield SO_2 on decomposition prove to be useless for

the purpose. On the other hand alkali acid sulphates and ammonia alum which yield SO_3 very easily at low temperatures apparently do not permit successful incorporation in the molten refractory before decomposition, and are likewise ineffective.

Between the sulphates which yield SO_3 at too low temperatures to permit preliminary solution and the sulphates such as those of the alkali and alkaline earth elements which are apparently too stable, there is a relatively large group of elements which yield SO_3 with intermediate ease, are capable of mixing with the molten refractory, forming SO_3 in solution and are found in practice to yield cells ranging from 0.3 to 0.5 mm. in diameter. This group comprises those sulphates which yield SO_3 on dissociation and when heated yield that gas in substantial quantities above 400° C. and below 1100° C. and while, from the standpoint of cell size the group is satisfactory, this factor depending on the SO_3 taken into solution, there are other differences. For pipe elimination exact control of the character of the cells is desirable and this in turn depends on the individual properties of the particular sulphates in respect to mixing uniformly with the molten refractory without too much or at least with reproducible loss of SO_3 in the mixing process.

Working specifically with the aluminum silicate refractory disclosed in U. S. #1,615,750 to Fulcher, we have found that the sulphates of aluminum, zirconium, zinc, titanium, chromium, iron, cobalt and nickel are all reasonably reproducible in the volume of cell space produced from a given addition. Beryllium sulphate is also moderately good and offers an interesting test of our theories in that the basic nature of the alkaline earth is opposed by the relatively low decomposition temperature (530–540° C.).

From the standpoint of effects on the casting other than in cell formation the elements combined with the sulphate have their individual advantages. For the aluminum silicate refractories, aluminum sulphate is ideal for it permanently adds no oxide not already present. For use in a glass refractory one would normally avoid such coloring oxides as nickel, chromium, and cobalt while in any non basic refractories the fluxing oxides of iron and titania would likewise be less advantageous though naturally permissible in any refractory already containing the oxides in substantial quantity.

We have found that the hydrated salts are as useful as the anhydrous sulphates, the water of crystallization apparently being dissociated and evolved so quickly that it does not influence the result. It appears to be sufficient that SO_3 be introduced in a form capable of incorporation and dispersion in the molten refractory.

Since the period of crystallization and the amount of pipe to be eliminated will vary with the block size and the font size under given cooling conditions, the amount of gasifier to be added for a given size must be determined experimentally. To illustrate with a specific example, it was found that for a 6 by 12 by 12 inch casting with 10% additional alumina silica refractory in the font, that 10 ounces of $Al_2(SO_4)_3.18H_2O$ or 5 ounces of $Al_2(SO_4)_3$ or 16 ounces $Zr(SO_4)_2.4H_2O$ produced proper cell character with individual cells from 0.3–0.5 mm. diameter to just eliminate the large voids. If less gasifier is used, some void still remains, while with too large an amount, the mold tends to bulge under excess pressure and often the undesirable type of large cells will appear on the outside surfaces from trapping the first too vigorously evolved gas.

The substances before discussed decompose in the molten refractory to yield oxides which happen to be gases at room temperature. Their useful effect however is exerted at high temperatures. There are a certain number of oxides which are solids at room temperature but have a considerable vapor pressure, i. e. volatilize into the gaseous state without decomposition, at the high temperatures of molten refractories. We have investigated such substances as for example the oxides of tin, cadmium, magnesium, boron and phosphorus with the expectation that these might give a more easily controlled gas evolution but without successful production of the desired porosity. It is probable that the vapor pressure is considerably reduced by solution of the oxide in the refractory and this may explain the ineffectiveness of these particular oxides. We heave found however that zinc oxide or salts which yield zinc oxide on decomposition do produce the desired type of porosity. Because of the lack of violent gas release on first contact with the molten refractory, the oxide itself gives easily reproducible results.

In introducing the gasifier into the molten material we prefer to pour a weighed portion of the gasifier in powdered form into the molten stream as it leaves the furnace, starting as soon as the stream is full size and finishing before the refractory rises in the font. In this way the powder disappears into the stream without loss and is apparently well distributed by the turbulence of the metal in filling the mold. However, any other equally efficient method of introducing the powder can be used in practicing this invention.

U. S. Patent #1,700,288 to Fulcher discloses the process of diminishing pipe which consists of breaking open the font scar after a substantial amount of solidification has occurred, placing new font molds and refilling the void. A certain percentage of this refilled volume will also become pipe unless a wastefully large font is used. This process can be combined with the present invention by adding the gasifier to the metal used for refilling, thus obtaining nearly as much solid block as from a single casting but with the core filled with cellular refractory instead of pipe. This technique also has the advantage of eliminating any danger of mold bulging due to excess gas pressure and achieves a completely pipe free block without extra precautions or special handling. Since the time required to set up this additional molten refractory is small compared to the time for a complete casting, a smaller percentage of gasifier will suffice to keep up the evolution, and its precise proportioning is not as essential.

What we claim is:

1. The hereinbefore described method of producing a refractory casting free from large voids which comprises casting the molten refractory and filling the pipe formed by the crystallization thereof with additional molten refractory mixed with a sulphate capable of dissociating sulphur trioxide at temperatures between 400° and 1100° C. and dissociating the sulphur trioxide by the heat present in the refractory prior to its solidification.

2. The hereinbefore described method of producing a cellular heat cast refractory which comprises casting molten refractory mixed with zinc oxide.

3. The hereinbefore described method of producing a cellular heat cast article which com-

prises melting a refractory material, mixing with the material while molten a sulphate capable of dissociating sulphur trioxide at between 400° and 1100° C. and at temperatures between the temperature of the molten material and the solidifying points of the said material, and permitting the molten material to solidify.

4. The hereinbefore described method of producing a cellular heat cast article which comprises melting a refractory material, flowing the molten material into a mold, adding to the molten material while flowing into the mold a sulphate capable of dissociating sulphur trioxide at temperatures between the temperature of the molten material and the solidifying points of the said material and between 400° and 1100° C., and permitting the molten material to solidify.

5. The hereinbefore described method of producing a cellular heat cast refractory which comprises adding an aluminum sulphate to molten material having a temperature above the dissociating point of the aluminum sulphate, and permitting the material to solidify.

6. The hereinbefore described method of producing a cellular heat cast refractory which comprises adding a zinc sulphate to molten material having a temperature above the dissociation point of the zinc sulphate, and permitting the material to solidify.

7. The hereinbefore described method of producing a cellular heat cast refractory which comprises adding a zirconium sulphate to molten material having a temperature above the dissociation point of the zirconium sulphate, and permitting the material to solidify.

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