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ZIRCON REFRACTORIES

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The invention relates to zircon refractories. This application is a continuation-in-part of my copending application Serial No. 296,765 filed July 1, 1952 now abandoned.

One object of the invention is to provide strong zircon refractories. Another object of the invention is to provide a superior composition for "arc barriers" in electrical circuit breakers. Another object is to provide superior refractories for electrical insulating purposes, providing many advantages, i. e. rigidity coupled with strength, maximum insulating properties coupled with high dielectric strength including resistance to electrical breakdown, ready moldability so that intricate shapes can easily be made, coupled with the advantages of small shrinkage during firing, inexpensiveness of the raw materials used to make the refractories and relatively low temperature firing conditions required.

Another object of the invention is to provide a superior refractory porcelain for the spark plugs of internal combustion engines. Another object is to provide zircon refractories for spark plugs that can be fired at relatively low temperatures. Another object is to provide refractories especially adapted for high frequency electrical insulation, as well as for use as radio and radar components. Another object is to provide superior porcelains for coaxial cable terminals, for bushings, for transformers and for capacitor cases. Another object is to provide an electrical porcelain for use at elevated temperatures. Another object is to provide an electrical porcelain for use at extremely high voltages. Another object is to provide an electrical porcelain having high thermal shock resistance.

Another object of the invention is to provide refractories of high thermal conductivity. Another object is to provide refractories of low thermal expansion characteristics. Another object is to provide porcelains having very smooth surfaces. Another object is to provide porcelains having extremely high resistivity in the high megohm-cm. range especially at the lower temperatures. Another object is to provide refractories or porcelains of some or more of the characteristics indicated having a long firing range. Another object is to provide refractories or porcelains having high resistance to abrasion. Another object is to provide zircon refractories having some or all of the characteristics indicated which, during firing, have very little tendency to warp even in thin sections.

Other objects will be in part obvious or in part pointed out hereinafter.

The importance of porcelains in general for the manufacture of electrical insulating parts of various kinds probably needs no extended discussion. Zircon porcelains have long been favored for such parts where high dielectric strength and resistance to electrical breakdown are important. While more expensive than silica, zircon of good grade is not too expensive. But the manufacturers of zircon porcelains have hitherto encountered

the difficulty of excessive shrinkage of zircon porcelains, causing a high percentage of rejections and restricting the permissible shapes to simple ones. I provide a composition which undergoes relatively slight shrinkage in firing, or good strength in the fired pieces and which can be fired at reasonably low temperatures.

My composition ranges from 80% to 95% zircon, by weight. I can use commercial zircon having a purity of from 95% to 99% by weight zircon, $ZrO_2 \cdot SiO_2$. In the above statement any hafnia HfO_2 content is treated as zirconia, ZrO_2, since this is commercial practice, the compounds of hafnium being indistinguishable from the compounds of zirconium by ordinary chemical analysis and having the same physical properties and since all zirconium containing ores contain a minor (but not insignificant) proportion of the element hafnium (in combined form).

I can use either granular or milled zircon or a mixture of the two in any proportions, the one or the other or the proportion being dependent on the fineness of structure or the strength required. For the finer structures I use all milled or a high proportion of milled zircon; for the stronger structures I use all granular or a high proportion of granular zircon. The granular zircon ranges from grit size No. 100 to No. 280 while the milled zircon is 74 microns and finer.

The remainder of my composition is silicate bond and should analyze within the limits shown in the following table.

TABLE I

Oxide	Percentage by Weight
Lime, calcium oxide, CaO	23.3 to 48.2.
Alumina, Al_2O_3	11.8 to 20.0.
Silica, SiO_2	39.2 to 62.2.

The silicate bond should have not more than 10% of oxide material other than calcium oxide, alumina, silica and alkali oxide. I cannot avoid having less than .02% of alkali oxide and I prefer to keep the alkali oxide to .2% and below. However, I can tolerate up to 2.0% of alkali oxide. The silicate bond is practically all oxide, treating silicates as oxides which is permissible, and the material other than oxide material in my composition will at the most be not more than 0.2%. I find it advantageous to have from 6% to 10% of the alkaline earth oxide, magnesium oxide otherwise known as magnesia, MgO, to depress the melting point of the bond which even without the magnesia has a fairly low melting point due to so much of the alkaline earth lime, CaO. For spark plug porcelains, for high frequency electrical insulation and for like uses the alkali oxide content of the bond should be not greater than 0.2%, but for many other uses it can be up to 2.0%.

The alkali oxides present will of course be mainly soda and potash, Na_2O and K_2O respectively. However, within the above limits the alkali oxides can include the other three, lithia, rubidium oxide and cesium oxide. Whereas the alkaline earth oxides are not detrimental to the porcelain with respect to the desired electrical properties, the alkali oxides soda, potash and also those of less frequent occurrence lithia, rubidium oxide and cesium oxide are detrimental to the porcelain, weakening its dielectric strength, lowering its resistivity etc.

According to my present knowledge, for many practical purposes and (understanding that varying the amount of zircon will still permit the manufacture of many different porcelains) for the manufacture of porcelains for

many electrical uses I prefer a silicate bond analyzing about as follows:

TABLE II

Oxide	Percentage by Weight
Lime, calcium oxide, CaO	27
Magnesia, MgO	6
Alumina, Al_2O_3	13.5
Silica, SiO_2	53.5

I can produce the bond of Table II in many different ways, from many mixtures of clays and compounds, but the following examples illustrate two convenient mixtures each of which gives substantially the bond of Table II.

Example I

Ingredient	Percentage by Weight
Eyrite, a clay-like magnesium silicate	43
Whiting, calcium carbonate	14
Kentucky plastic fire clay	43

A typical analysis of eyrite is as follows:

TABLE III

	Percentage by weight
Lime, CaO	30.5
Silica, SiO_2	28.1
Magnesia, MgO	14.4
Fluorine, F (with allowance for the oxygen equivalent)	1.64
Iron oxide, Fe_2O_3	0.5
Alumina, Al_2O_3	0.2
Ignition loss	24.7

A typical analysis of Kentucky plastic fire clay which is a siliceous clay is as follows:

TABLE IV

	Percentage by weight
Silica, SiO_2	66.1
Alumina, Al_2O_3	21.3
Titania, TiO_2	2.6
Iron oxide, Fe_2O_3	1.0
Potash, K_2O	0.6
Soda, Na_2O	0.2
Magnesia, MgO	0.1
Lime, CaO	0.0
Ignition loss	7.4

Example II

Ingredient	Percentage by Weight
Whiting, calcium carbonate	37
Kentucky plastic fire clay	48
Talc	15

As more specific examples of my invention I prepared mixtures as shown in the following table.

TABLE V

	Percentage of Ingredients by Weight							
Granular Zircon	90	50	90	50	95	55	95	55
Milled Zircon	---	40	---	40	---	40	---	40
Bond of Example I	10	10	---	---	5	5	---	---
Bond of Example II	---	---	10	10	---	---	5	5

The above constitutes 10 examples of the invention. In none of these examples was any attempt made to introduce any alkali oxide. However, as impurity there was and there would be in each of these examples a very small amount of alkali oxide as impurity at least as much as .02%.

With each of these mixtures 1% of dextrine and from 1% to 2% of water were added and the resulting mix in each case was pressed into small plates which were dried and fired at cone 12. I prefer that my zircon refractories be fired at firing conditions at least as high as cone 8. All of the plates, after firing, were stronger than a composition of 50% granular zircon, 40% milled zircon, 9% clay and 1% talc fired at cone 16. It thus appears that my composition makes stronger pieces when fired at relatively low temperatures than standard mixtures fired at cone 16 temperatures. In general the higher the firing temperature the stronger should be the piece. The mixture of 50% granular zircon, 40% milled zircon and 10% of the bond of Example II was one of the best and the plates made therefrom were twice as strong as those made from 50% granular zircon, 40% milled zircon, 9% clay and 1% talc.

Articles of zircon refractories according to the present invention have all the advantageous characteristics and features stated in the objects. It will thus be seen that there has been provided by this invention zircon refractories in which the various objects hereinabove set forth together with many thoroughly practical advantages are successfully achieved. As various possible embodiments may be made of the above invention and as many changes might be made in the embodiment above set forth it is to be understood that all matter hereinbefore set forth is to be interpreted as illustrative and not in a limiting sense.

I claim:

1. Zircon refractories consisting essentially of from 80% to 95% zircon, the remainder silicate bond including and analyzing within the following limits:

Calcium oxide from 23.3% to 48.2%
Alumina from 11.8% to 20.0%
Silica from 39.2% to 62.2%
Alkali oxide from .0% to 2.0%

said silicate bond having not more than 10% of oxide material other than said calcium oxide, alumina, silica and alkali oxide and said silicate bond having not more than 0.2% of material other than oxide material, all percentages being by weight.

2. Zircon refractories according to claim 1 in which there is at least 6% of magnesium oxide, MgO.

3. Zircon refractories according to claim 2 in which the alkali oxide does not exceed .2%.

4. Zircon refractories according to claim 1 in which the alkali oxide does not exceed .2%.

References Cited in the file of this patent

Riess: Clays (3rd ed.), 1927, pp. 438–444.