Engineering Journal of Qatar University, Vol. 1, 1988.

"CERAMICS AS MATERIALS OF CONSTRUCTION"

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ABSTRACT

This paper attempts to review the limitations for using the important ceramics in contact with corrosive media. Different types of ceramics are included. Corrosion properties of ceramics and their electrical properties are mentioned. Recommendations are suggested for using ceramics in different media.

1. INTRODUCTION

Solid materials for construction can be divided to metals in which the metallic bond determines the general properties as opacity, ductility, hardness as well as electrical and thermal conductivity. They are unstable at high temperatures and the oxides are formed. Organic materials which have molecular structure in which covalent bonds exist in the molecule but weak secondary forces exist between the molecules, thus giving their characteristics, soft easily applied, electrical and heat insulation. Raising the temperature causes them to melt and or to oxidize. Ceramics are inorganic non-metallic solids. They are crystalline and or amorphous and are compounds between metals and non-metals. The bond is partly ionic and partly covalent. Accordingly they have high stability, much higher melting temperatures and they are harder and more resistant to chemical alterations. Like organic materials ceramics are usually insulators. At elevated temperatures, with more rapid diffusion, they do conduct ionically (conductivity of metals decreases at elevated temperatures). Due to the absence of free electrons, most ceramic materials are transparent at least in thin sections, and are poor thermal conductors. Properties of compounds such as nitrides and carbides fall somewhat between ceramics and metals since they are partly covalent, partly metallic. They have high thermal conductivity as well as high strength and very high refractoriness. The disadvantage of this group is that they are hard and brittle and will break rather than deform. They resist compression far more better than tension. They show very little bending and creep under load (1, 2, 4 — 6). Main properties of important ceramics are given in Table (1).

Table (1) — Properties of Important Ceramics (3).

Property	Alumina	High voltage porcelain	Low voltage porcelain	Steatite	Zircon
Dielectric constant (60Hz, 25°C)	8-9.5	5.7	5.5-7	5.7-6.5	7.1-9.1
Power factor (X10³, 25°C, 60Hz)	0.5-1.5	8-25	7-20	1.2-2	1.5-36
Tensile strength (kg/cm² x 10³)	0.56-3.5	0.2-0.56	—	0.52-1.05	0.49-1.04
Compressive strength (kg/cm² x 10)	5.6-30	1.75-5.6	1.75-4.2	4.2-30.5	5.6-7
Volume resistivity (ohm-cm, 25°C)	10^{14}-10^{16}	10^{12}-10^{14}	10^{11}-10^{14}	10^{12}-10^{15}	10^{13}-10^{15}
Specific gravity	3.1-3.9	2.35-5.1	2.7-2.4	2.5-2.9	3.1-3.8
Softening temperature °C	1450-2000	1300-1335	1300-1335	1300-1450	1390-1550
Structure limiting temperature °C	1400-1802	1000-1200	1000-1100	1000-1180	1000-1300
Heat conductivity (X10³)	7-50	2-8	3.4-4	5-8	1-15
Water absorption	0.0-0.2	0.0-0.5	0.5-2.7	0.0-0.03	0.0-0.02

2. GLASS

Glass is used not only in chemical laboratories but also in industry in three forms. In bulk, in fairly large pieces of equipment such as pipes, towers, pumps. Also as a coating over cast iron and steel. Thirdly as fibers in insulation, fabrics, tower packing and plastic laminates. It has the advantage of transparency, corrosion resistance and ease of cleaning.

The transparency of glass facilitates inspection of the process operations, while the hardness and smoothness contribute to easy removal of sediments and to cleaning. In some applications the highly insulating electrical properties of glass can be advantageous. Table (2) gives the general properties of commercial glasses. Types of glass are:

2.1 Ordinary soda-lime-silica glass (soft)

As window glass, containers for foodstuffs, medicine, detergents, reagent bottles, tubing, lamps.

Table (2) — General properties of commercial glass (3).

Property	Quartz	Window glass	Electrical glass	Pyrex
Dielectric constant	3.38	7.0	6.6	4.6
Power factor (at 1 mega Hz, 20°C)	0.0002	0.004	0.0016	0.0046
Resistivity (ohm-cm at 25°C)	12	6.5	8.9	8.1
Specific heat (at 25°C)	0.176	0.2000	—	0.185
Coeff. of expansion	$5.5x10^{-7}$	$85x10^{-7}$	$91x10^{-7}$	$32x10^{-7}$
Specific gravity	2.2	2.46	2.86	2.13
Softening point (°C)	1667	730	626	820

2.2 Neutral Glass

Containing higher content of B_20_3 and alumina and lower alkali content.

2.3 Borosilicates (hard glass)

Higher in silica and B_20_3 and lower in alkali. It is used in ovenware, pipelines, sight glasses, valves, laboratory ware, etc. The higher the silica content, the higher is the corrosion resistance to acid media and the higher is the abrasion resistance. Replacing the alkali with B_20_3 decreases the thermal expansion (high thermal shock resistance) and increases the electrical resistivity.

With water at high temperature (in boiling or in autoclave), ion exchange process causes the replacement of Na^+ by H^+. NaOH is thus formed on the surface and attack the silica network. With large volume of water, dilute NaOH is formed and Na^+ ions continue to enter the solution until a layer of silica rich glass develop on the surface. This layer has different optical properties from the main glass. Under high temperature autoclaving, this siliceous layers can be detached as thin flakes.

Acids have slightly greater effect than water. Higher temperature and higher alkalinity has severe effect.

3. VITREOUS SILICA

It consists of pure silica (more than 99.8%) and exists in translucent or transparent forms. It has low coefficient of thermal expansion, low thermal conductivity and excellent insulating properties. It can be safely used up to 1050^{0}C. At higher temperatures it tends to become brittle owing to reversion to crystalline state.

It is completely resistant to all halogens and acids except HF and phosphoric acid. Alkalies react with fused silica. It is also decomposed by metals with higher affinity for oxygen (sodium vapour, Al,...). It is hard and expensive.

4. CLAY PRODUCTS

Clay products vary from bricks and sewer pipes to stoneware and porcelain. They are produced generally from:

a. Clays : which give the plasticity to the mass,
b. Silica : which is non-plastic and controls the drying and firing shrinkages,
c. Feldspar : which acts as a flux.

The porosity can be controlled by the manufacturing technique. High porosity gives a body with low density, strength, elastic modulus, shear modulus, thermal conductivity, high creep rate, slag attack, permeability and spalling resistance.

Pore size is controlled to suit the operating conditions encountered. Such products may be glazed or not. A glaze finish increases the strength and forms a surface which is impermeable with higher corrosion resistance and better electrical properties and can be easily cleaned.

Typical examples for such materials are acid resisting bricks, tiles, absorption and distillation towers, valves, pumps, piping, porous articles for filteration, aeration, diffusion, catalyst carriers and packing materials. To increase the spalling resistance (thermal shock resistance), porosity, thermal conductivity, strength should be maximum and thermal expansion should be minimum.

These products are attacked only by HF and hot concentrated caustic alkalies.

Acid tanks can be lined with acid resisting bricks or tiles cemented with the proper cement. Blue bricks are made from Kaolin and manganese oxide Mn0. The latter is added to increase the vitrification and to achieve minimum porosity.

5. CEMENTS AND CONCRETES

Ordinary portland cement and concrete are cheap, easily fabricated and widely employed where non-acid conditions prevail. With mild acid conditions, concrete can be protected by compounds such as oleic soaps or asphalt.

5.1 Portland Cement

The compounds present in set cement are attacked by water and solutions containing salts and acids, though in most cases the action on an impermeable mass is slow as to be unimportant. Pure water dissolves the lime and part of alumina thus decreasing the strength of mortar or concrete. Portland blast furnace cement is attacked more than ordinary portland cement.

Acidic waters are more aggressive. Sulphates react with free lime and with hydrated calcium aluminte forming the insoluble calcium sulphoaluminte causing expansion and failure of concrete.

Moreover, $MgSO_4$ decomposes hydrated calcium silicate in addition to its attack on the hydrated calcium aluminate. Chlorides form with lime soluble $CaC1_2$ which will cause the concrete mass to be permeable to water and accordingly the reinforced steel oxidized rapidly with the formation of cracks. Accordingly, ordinary portland cement can be used in solutions with pH values above 7. Cements with minimum tricalcium aluminate (high in tetracalcium aluminoferrite) are thus expected to resist sulphates better than normal portland cement.

5.2 High Alumina Cement

They are produced by firing limestone and bauxite. They resist the sulphate attack and can be used in solutions having pH from 5.5-9.

5.3 Supersulphated Cement

It consists of blast furnace slag, calcium sulphate (or small proportion of lime) and portland cement clinker. These cements are the cheapest cements that can resist sulphate solutions and can be used in contact with solutions with pH from 3 to alkaline solutions.

5.4 Acid Resisting Cement

It consists of inert aggregate (quartz, acid resisting bricks) bonded with sodium silicate solution and a setting agent which is sodium silicoflouride or ethylacetate.

It resists all acids except HF and can be used up to 535^{0}C but is attacked easily by water and dilute alkalies.

5.5 Furnace Cement

They are based on condensation of furfural and phenol, phenol and furfuryl alcohol, furfuryl alcohol and furfural, furfural acetone can be used up to 180^{0}C. A filler of carbon or emery dust and asbestos is used. With such a wide range of compositions corrosion resistance varies.

5.6 Phenolic Cement

It is a mixture of powder and liquid resins. The powders are $BaS0_4$, silica, asbestos nd carbon. It is the most resisting cement to the chemical attack and is used for joining bricks in pickling tanks.

5.7 Sulphur Cement

It consists of sand and rubber latex solution. It has low expansion and is suitable in conditions where dilute acid alternates with water or dilute alkalies. It does not resist organic solvents, which attack rubber, or strongly oxidizing acid solutions, which cause ageing of rubber. It is used for joining bricks, tiles and cast iron pipes up to 90^{0}C.

6. Refractories

Refractories are materials with high melting ranges and should not react chemically with the materials in contact with them (solids, liquids or gases) under the operating conditions. They should contain minimum fluxes. They should suffer as well from the external mechanical stresses and the internal physical and chemical changes. A universal refractory that can be used under all operating conditions does not exist and we have to sacrifice the less important properties for a certain use. In the same furnace several types of refractories are used to cover the various requirements. Some bricks conduct the heat very rapidly, others are good for thermal insulating purposes. Some approach diamond in hardness others are light in weight and almost sponge like in formation.

Refractories can be classified according to their nature; acidic, neutral, amphoteric and basic.

Refractories are not wetted by molten metals and they are only wetted by molten oxides, which penetrate by the capillary action, deep into the pores and either react or form low melting composition. The liquid may penetrate between the grains and isolate them from the brick. They are then carried away by the melt. In some cases the liquid phase is concentrated behind the hot face forming a hot pool causing tearing of the hot face. Brick constituents will also diffuse in the melt till the saturation limit is reached. In simple systems the phases produced and the limits of corrosion can be calculated from the phase equilibrium diagrams.

The rate of corrosion will thus depend on porosity, working temperature, viscosity of melt and the velocity of flow. Higher viscosity (i.e. low temperature) and low velocity decrease the slag attack. Accordingly when the attack is excessive cooling of the refractory is essential. With low reaction rates, the resistance of the refractory to the slag may be good and accordingly the prevalent idea that basic refractories must be used with basic slags and acid refractories must be used with acidic slags is not necessary true. For example, magnesite will stand up well under the action of certain highly siliceous slags and silica bricks are known to give good service in lime kilns under highly basic conditions.

Corrosion may occur by gases in the absence of liquids for example C0 precipitates carbon inside the brick at 400-600^{0}C, especially in the presence of iron oxides which act as a catalyst. This deposition causes disintegration of refractories as observed in the upper parts of the blast furnace and in zinc retorts. Also corrosion may occur by solid state reactions in the absence of liquids, chrome magnesite refractories for example, absorb iron oxide forming spinel solid solution with expansion causing bursting of the surface.

7. CONCLUSIONS

1) Ceramics are hard, strong and dense materials. They are completely stable at high temperature applications. They possess excellent dielectric properties. Its electric strength is 24 KV/mm. They are stronger in compression than in tension, moreover, they are weak in impact strength and hence cannot be used as self supporting thin films. Also, they are not affected by moisture and chemical action except with strong acids and alkalies.

2) Glass is highly chemical resistant to most of the corrosive agents except HF. Moreover, it is a good insulating material at low temperature. Dust and moisture do not get settled on glass surfaces.

3) Failure of refractories may occur due to factors other than corrosion such as abrasion, after expansion, or after contraction, thermal spalling and allotropic transformation.

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