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Ceramics as Basic Engineering Materials

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Ceramic products are defined as those made of inorganic, nonmetallic material which are usually subjected to high temperatures during fabrication. This includes a wide range of products, but of more importance to the engineer, it embraces a wide range of unique and useful properties.

Among the unique properties of ceramic materials is refractoriness, that is, resistance to high temperatures. Fig. 1 shows the melting temperatures of some ceramic materials along with those of several metals. The melting temperatures of the basic crystalline phases of most ceramic materials are quite high starting in the range of 3000 F; iron melts at 2895 F. Glasses are ceramic materials also, but they cannot be considered as refractories. This is because they are not compounds but rather behave as supercooled liquids whose viscosity is extremely high at room temperature; thus they have softening ranges rather than melting temperatures.

Melting Temperatures

Ceramic products are being manufactured whose melting temperatures are lower than 3000 F, principally due to a high glass content. Ceramics made of clinoenstatite, titania, silica, mullite, forsterite, alumina, spinel, zircon, beryllia, zirconia, magnesia, and thoria are oxide-type ceramics. All but the first two are used as refractory materials where high-temperature processing is involved; that is, as furnace liners in heat-treating of metals, recovery of metals from their ores, alloying of metals, recovery of petroleum products from crude oil, nuclear applications, and the like. Thoria has a very high melting point, however; it is radioactive. Silicon carbide is used as a refractory and to a large extent as kiln furniture. Boron carbide has a high melting temperature but it is used only in special cases. Other carbides, sulphides, nitrides, and borides have still higher melting temperatures but have only been made experimentally or on a very limited scale because of the rarity of some of the elements involved and the protective atmosphere necessary in using these materials. They are being used experimentally in heat-engine parts such as jets, rockets, and so on.

The highest melting metal is tungsten which melts at approximately 6100 F. Zirconium, tantalum, and hafnium carbides, and graphite have melting temperatures above this with hafnium carbide having the highest melting temperature known of approximately 7520 F.

Ceramic products are generally a mixture of one or more crystalline phases with glass, the latter material varying up to approximately 45 per cent. This glass content affects the refractory properties. Included in Fig. 1 is a graph of the "safe continuous operating temperature" of some of these ceramics. The best glasses can be used continuously only up to approximately 900 F. Steatite and forsterite can be used continuously to 1830 F without distortion when used as technical ware such as high-frequency insulation, or whenever dimensional tolerances in the range of ±1 per cent are prerequisite. However, forsterite, when used as furnace parts, operates successfully up to 3000 F. Normal porcelains have been used up to 2185 F. Zircon, whether used as technical ceramics or as a refractory, operates very well up to 2650 F. Silicon carbide, which is used as furnace parts, stands up very well to approximately 2750 F in air. Silica is used principally as a refractory in open-hearth furnaces where the temperature approaches 3000 F. Mullite refractories are used continuously up to 3200 F.

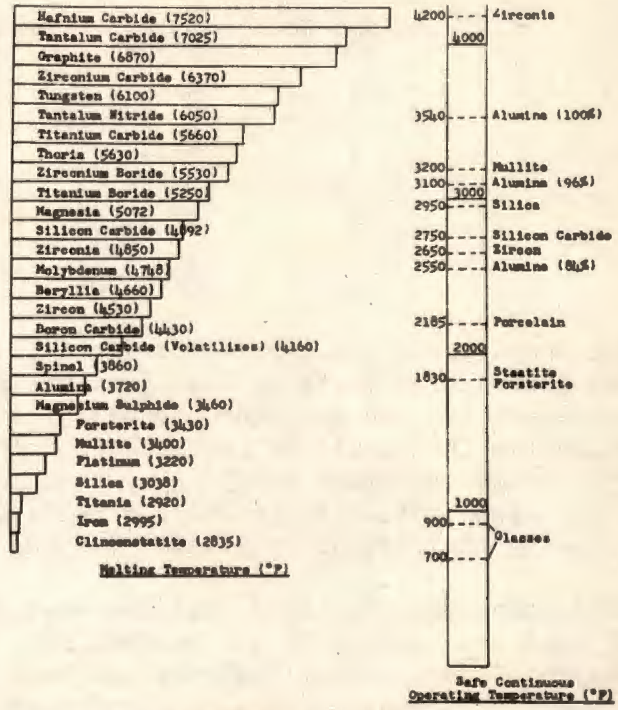

Fig. 1 Thermal properties of ceramic materials and metals

The effect of glass content and/or an additional crystalline phase or phases is illustrated by the safe continuous operating temperatures of several alumina bodies. A body containing 86 per cent alumina can be used continuously up to 2550 F; another containing 96

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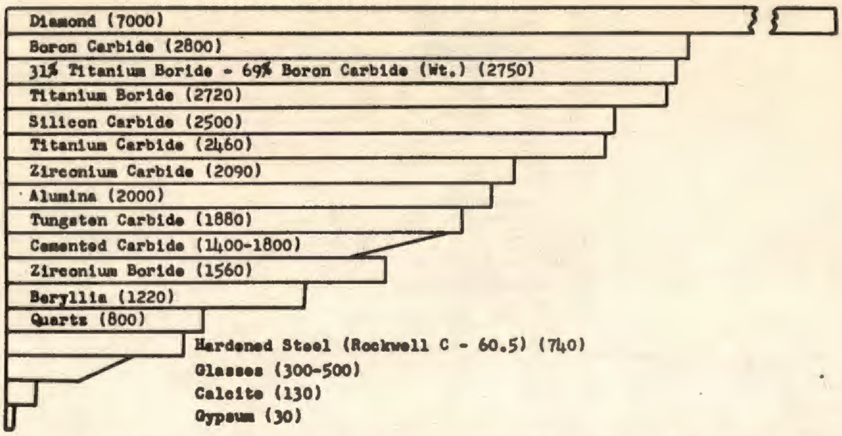

Fig. 2 Hardness (Knoop scale) of ceramic materials ranging from 30 to 7000

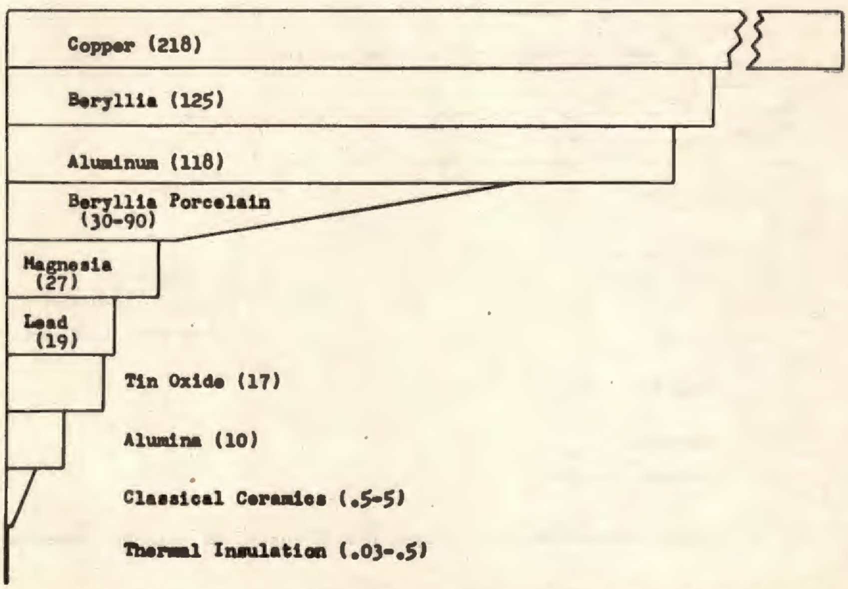

Fig. 3 Thermal conductivity of ceramic products Btu/hr sq ft/(deg F/ft), at 140 deg

per cent, up to 3050 F; while pure recrystallized alumina, that is, containing no glass, can be used continuously up to 3520 F. These are used as furnace parts and technical ceramics of close dimensional tolerance and for high-temperature vacuum applications.

Zirconia provides a very high safe continuous operating temperature (circa 4200 F) and in the fused stabilized form is used as furnace parts.

Alumina and zirconia are applied to metals in thicknesses up to 0.010 in. by the flame-spray process. This type coating shows promise for heat-engine parts, abrasion-resistant coatings, and erosion-resistant parts.

Thus ceramics provide a wide selection of refractory materials for use as furnace parts or as technical ware and the choice depends upon end use and economics.

Hardness

Hardness is another property unique to ceramics covering the range from 30 on the Knoop scale for the mineral gypsum to 7000^{+} for the diamond as shown in Fig. 2. Glasses range from 300 to 500. The hardest metals are hardened steel at Rockwell C 60.5 which is approximately 750 on the Knoop scale. Several ceramic materials fall in this range also but the majority possess greater hardness. The cemented carbides are made of synthetic ceramic materials such as tungsten, titanium, and tantalum carbides whose Knoop hardness numbers range from 1400 to 1800. They are used as tools for machining metals to close dimensional tolerance.

Alumina has a value of 2000 and is used as a grinding and lapping compound, and as the abrading media in grinding wheels for machining steel. A relatively new application is as tool bits for machining metals. This extreme hardness and the fact that this type ceramic can be fabricated to extremely close dimensional tolerance lends itself as wear-resistant parts such as gages, bearings, thread guides, nozzles, and technical ware in general.

Silicon carbide, with a Knoop hardness of 2500, is one of the most important abrasives in terms of lapping and grinding, and as grinding wheels. It lends itself best for fabricating very hard dense materials such as ceramics, including cemented carbides, cast and chilled iron, and nonferrous metals.

Titanium boride has a value of 2720 and boron carbide of 2800; this latter was the hardest synthetic material until quite recently. However, in the past year man has made the first synthetic diamonds. Diamond is the hardest known material. It is marketed in many grain sizes and in many type grinding wheels. Its extreme hardness and durability make this material of economic significance even though the initial cost is quite high.

The property of extreme hardness has made ceramic abrasives actually indispensable in the fabrication of metals and other materials. There are no substitutes for ceramic abrasives.

Thermal Conductivity

Another engineering property of extreme importance is thermal conductivity. Again, ceramic products cover a wide range from near zero up to 125 Btu as shown in Fig. 3. In the very low range of thermal conductivity a variety of thermal-insulating materials are manufactured from mineral products such as asbestos, magnesia, diatomaceous silica, refractory clays, mineral and glass wools, and synthetic fibers; these are used from below room temperature to above 3000 F as drier, oven and furnace liners and backings, pipe covering, and numerous other applications.

Ceramic products in general are characterized by low thermal conductivity and approximately 98 per cent of all products manufactured have thermal-conductivity values no higher than 5 Btu. This is due not only to the property being inherently low but also to the large per cent of pore space or voids which are present in some of these materials. It has been noted in the foregoing that magnesia is an excellent thermal insulator yet Fig. 3 shows that it has a value of 27. The former value is for a very porous material while the latter value is for one containing no more than 1 per cent pore volume. Thus all ceramics possessing thermal-conductivity values above 5 Btu are nonporous materials. Alumina ceramics have thermal-conductivity values up to 10 Btu.

Tin oxide has a value of 17 but has not been used industrially to any extent in ceramic bodies. The metal lead has a value of 19. Magnesia's conductivity as a dense ceramic, as mentioned, is 27 and has been used as electrical insulation in vacuum tubes. Above this range the only ceramic material is beryllia and its value is 125 Btu as compared to aluminum at 118 and copper at 218. By combining beryllia with other ceramic materials a range of porcelains can be made whose thermal conductivity ranges from 90 to 30 Btu. Some sparkplug and high-frequency insulators, where high thermal conductivity is of importance, have been made from beryllia and beryllia porcelains. However, because of the toxic effect of this material, its use has been limited. It is now considered that this material can be used safely when the proper precautions are taken.

Thus ceramic products can be made which cover the wide range of thermal conductivity from values of 0.05 to 125 Btu, which is from the best thermal insulators to conductivities exceeding that of the metal aluminum.

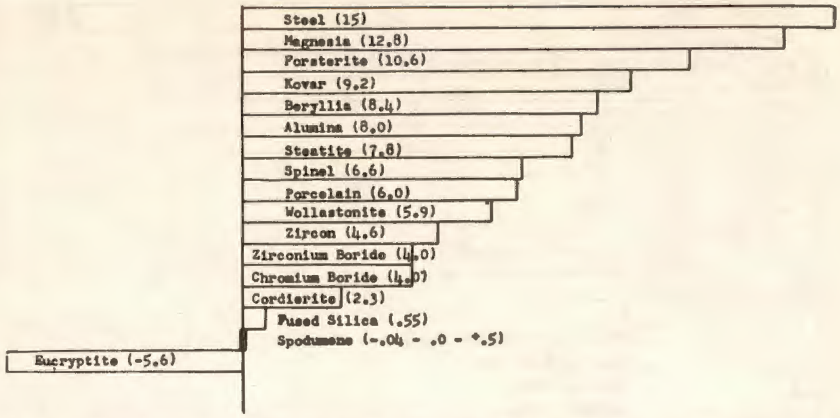

Fig. 4 Coefficient of linear thermal expansion of ceramic materials; room temperature, 700C (1292 F)

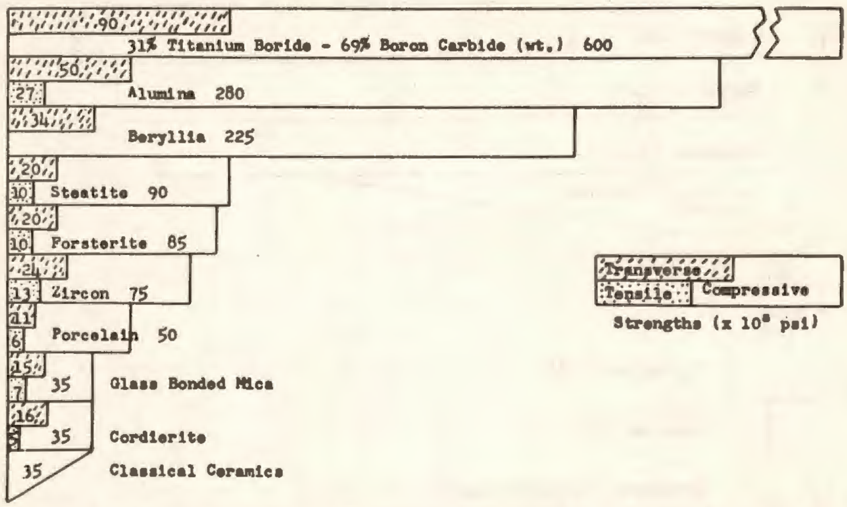

Fig. 5 Tensile, transverse, and compressive strengths of ceramic materials

Thermal Expansion

Ceramic materials are manufactured which cover the range of linear thermal expansion from $0.5\text{–}13 \times 10^{-6}$ in/in/deg C between room temperature and 700 C as shown in Fig. 4. Magnesia has the highest thermal expansion at 12.8. Low-carbon steels have values in the range of 15 over the same temperature range while copper is approximately 17. One of the prime applications of a desired high thermal expansion in ceramics is in glass-to-metal and ceramic-to-metal seals for electron tubes and other vacuum-tight, strong, high-temperature seals. There are two types of seals. The compression type is exemplified by copper and forsterite or alumina, and Kovar and alumina. In this case a metal of higher thermal expansion surrounds the ceramic of lower thermal expansion which, when soldered together, results in a strong vacuum-tight compression seal. The other type is the matched seal in which the thermal expansion of metal and ceramic is approximately the same. Glass-to-Kovar is a glass-to-metal seal of this type. The iron-nickel series of alloys covers a wide range of thermal expansion and a thermal-expansion match can be found for most ceramics; however, only over a limited temperature range.

Invar is a low-expanding material at relatively low temperatures but tends to increase quite rapidly as the temperature is increased. In the realm of ceramics, much lower thermal expansions are possible. In fact, there are two types which actually contract on heating. Both are lithium aluminosilicates. The one type exhibiting the low positive to low negative values (Fig. 4) is the crystalline phase beta-spodumene. It can be made to have no contraction or expansion up to 600 C. Beta-eucryptite is the other crystalline phase and its coefficient of linear thermal expansion is -5.6×10^{-6}. This latter material has not been made in the nonporous state and because of its very high degree of contraction,

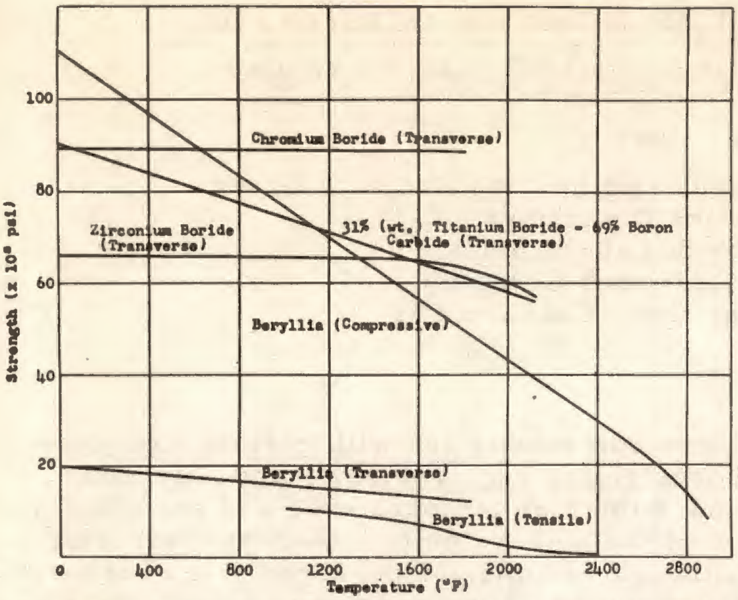

Fig. 6 Strength versus temperature curves of some ceramic materials

has found little use. However, the beta-spodumene is quite important as a refractory material (to 2200 F) of high thermal-shock resistance. Some uses include trays on which dental products are rapidly fired; tubes through which billets are heated to forging temperature by induction heating; and in the firing of certain white wares. It is being used as either zero or low-expanding tubes in dilatometers for determining thermal expansion of ceramics and metals at higher temperatures. It is being evaluated as a base material for precision electrical resistors and capacitors where dimensional variation with temperature is detrimental.

Thermal-shock resistance is relatively high in most porous ceramics because of inherent structure. However, where strong ceramics are desired porosity must be minimized. In dense ceramics the thermal-shock resistance is dependent to a marked degree on thermal expansion; the lower the thermal expansion the higher the thermal-shock resistance. Similar specimens of an alumina ceramic whose coefficient of linear thermal expansion is 8.0, crack when quenched into water at room temperature from 400 F. Beta-spodumene bodies, whose thermal expansion approaches zero, have resisted failure when quenched from 2200 F to water at room temperature.

Thus ceramic products cover the coefficient of linear thermal-expansion range from $+12.8$ to -5.6×10^{-6} in/in/deg C from 25–700 C, and ceramic products are being produced or can be designed to any specific value in this range.

Strength

The compressive strength of ceramic materials covers a very wide range from materials so weak that they can be crushed between the fingers in the case of some heat insulators, to values as high as 600,000 psi for a mixture of 31 per cent (by weight) titanium boride and 69 per cent boron carbide. In general, for more or less conventional ceramics, with tensile strength at unity, the transverse strength is approximately 2 times and the compressive strength varies from 8 to 10 times the tensile strength. One commercial alumina body has a tensile strength of 27,000 psi, its transverse strength is 50,000 psi, while its compressive strength is 290,000 psi. Alumina bodies with compressive strengths as high as 400,000 psi have been reported.

The values given in Fig. 5 are optimum values and these tend to decrease either with a decrease in the basic crystalline phase or with increase in pore volume. As an illustration, alumina ceramics are manufactured as special refractories with compressive strengths of the order of 11,000 psi while that of the completely nonporous material used as wear-resistant parts and electrical insulation has a compressive strength of 290,000 psi. This extremely strong material is being used as extrusion and pressing die parts, precision gages, plungers for reciprocating pumps, mechanical-seal parts, bearing sleeves, liners for pumps and impeller-wear parts, thread guides, and as high-frequency insulation particularly for vacuum-tight ceramic-to-metal seals.

Beryllia is another extremely strong ceramic with a compressive strength of 188,000 psi and transverse strength of 35,000 psi. Steatite, forsterite, and zircon ceramics have compressive-strength values between 75,000 and 90,000 psi. Steatite is the most economical of the group to manufacture. It is used extensively as electrical insulation especially for high-frequency applications and at moderately elevated temperatures because of its high strength, excellent electrical insulating properties, and the ability to fabricate this material to close dimensional tolerance. Porcelain, glass-bonded mica, and cordierite have lower compressive strengths in the range of 35,000 to 50,000 psi. Porcelain, because of its strength, ease of manufacture, and general durability, is used extensively for domestic and technical ceramics.

Fig. 6 shows the effect of temperature on the strength of some ceramic materials. A beryllia ceramic, whose tensile strength is approximately 14,000 psi at room temperature, is still 5000 psi at 1800 F; its transverse strength at room temperature is 20,000 psi and still 11,500 psi at 1800 F; while its compressive strength at the lower temperature is 110,000 psi, 50,000 psi at 1800 F, and 7000 psi at 2912 F. Chromium boride, whose room-temperature transverse strength is 88,000 psi, remains constant to 1700 F. Zirconium boride exhibits the same effect over the same temperature range with a value of 66,000 psi, and at 2200 F this value only drops to 55,000 psi.

The titanium boride-boron carbide material mentioned previously has a transverse strength of 90,000 psi at room temperature and drops steadily to 55,000 psi at 2200 F. It is these high-strength properties at high temperatures that are of extreme interest for high-temperature engines and air frames. Radomes which house radar equipment are being made of ceramic materials because of these properties. One laboratory is experimenting with actual missiles made entirely of ceramic materials, the reason being that as the speed increases, the temperature also increases and it appears that only ceramic materials can withstand the extreme conditions of temperature and pressure encountered.