Science and Technology of Ceramics

3. Advanced Ceramics: Structural Ceramics and Glasses

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In the previous parts, traditional ceramics and some advanced ceramics, namely functional ceramics were discussed to point out the differences between the two categories. The various functions for which ceramics are developed by changing the chemical elements and their ratios in the compound were described. In this part, structural ceramics and advanced glasses will be discussed.

[1] Previous parts
1. Traditional Ceramics, *Resonance*, Vol.4, No.8, 1999.
2. Functional Ceramics, *Resonance*, Vol.4, No.12, 1999.

Structural Ceramics

Some ceramics, because of their high strength, can be used to make structural components. Strength-to-density ratio of structural materials has increased in recent times. It is also important for some applications, that the material used to build the structure is also chemically inert to the working environment. For example, in modern furnaces refractory materials like alumina or mullite bricks and liners, which have high corrosion and oxidation resistance, are used extensively. The processing techniques for producing large size tubes and sheets of such materials have been developed in the last couple of decades. Heating elements for high temperature furnaces are made of refractory ceramics like SiC or super Kanthal ($MoSi_2$).

In automobile and aerospace industries, the emphasis has been on increasing fuel efficiency by decreasing the weight of the engine and increasing the fuel ignition temperature. Some ceramics are ideally suited for this as they can withstand temperatures as high as 1700°C in air without getting oxidized. Also, most structural ceramics have lower densities than the alloys that are currently being used. For this purpose, many ceramics like the nitrides and carbides of silicon and titanium; borides of titanium and zirconium; silicides of molybdenum and titanium; and aluminides[2] of nickel are being studied all over the world. However, there are many problems associated with using ceramics for such applications. The main drawback of these ceramics is that they cannot be machined easily in the usual way because they are hard and brittle. The components have to be made in the required shape and size using difficult and expensive processing techniques. Because of their brittleness, a small defect (like a microcrack or a pore) present will fracture the component catastrophically damaging all other surrounding parts in the machine. In order to improve the mechanical properties of these ceramics other materials are being reinforced into these ceramics. Refractory metals like tungsten or niobium, whiskers[3] and fibers (both short and long) of other structural ceramics like Al_2O_3, Si_3N_4, ZrO_2 or SiC, or particulates of other compatible ceramics are used for reinforcement. Such composites are called ceramic matrix composites or in short CMCs. The CMCs are used mainly in the working temperature range of 800 to 1650 °C. SiC fiber reinforced SiC composite is becoming an important material for aerospace applications. Gas turbine blades have been constructed with Si_3N_4 based composites. Non-aerospace applications of the CMCs include wear resistant parts of nozzles, bearings, wear guides, etc. Cutting tool inserts are being made with silicon carbide whisker reinforced alumina and $TiC\text{-}Si_3N_4/Al_2O_3$ because of their high chemical stability and ability to operate at high cutting speeds. In fact, cutting tool speeds have increased by a factor of 100 since the turn of the century because of the development of these new materials.

[2] Strictly speaking silicides and aluminides are intermetallics. Because of their high temperature stability, they are often considered along with ceramics.

[3] Whiskers are extremely thin (nano-size) and long single crystals.

Then there are metal matrix composites (MMC) where one of the components is a metal. Metals are usually soft and have low wear resistance. It is found that when a ceramic is introduced into the metallic matrix, the mechanical properties improve. The main disadvantage of the MMCs is that they cannot be used at very high temperatures in air as most metals get oxidized at these temperatures.

Carbon fiber reinforced carbon composites (denoted as C-C composites) are becoming extremely popular because of their low density and high strength. They can withstand temperatures in excess of 2000 °C in inert atmospheres. They have high frictional wear resistance and hence are used for making brakes for aeroplanes and racing cars. In fact, the C-C composite brakes save about 800 kgs of weight on a Boeing 747 compared to their metal counterparts and also the plane travels 30% less distance before coming to halt. The main drawback of the C-C composite is that it cannot sustain high temperatures for a long duration of time in air. Hence oxidation protection coatings have to be applied on the surface to increase their durability. All over the world, research is going on to find suitable coating materials for the C-C composites with compatible coefficient of thermal expansion. In the field of sports C-C composites are playing a major role. In the Formula 1 racing cars, the whole structure is normally of this material. Tennis, badminton or squash racquets are made of C-C composites.

The aerospace plane is one which can leave the Earth's atmosphere but can land on a regular runway in an airport. Such planes could drastically cut down trans-continental travel times. However, as an aerospace plane reenters the atmosphere, some of the parts may get heated up to 1800°C. The space shuttle, which is essentially a highly specialized aerospace plane, has its nose-tip and the wing leading edges made of C-C composites coated with SiC which can withstand such high temperatures. Such composites, of course, should also have low density, high strength and be highly oxidation resistant in air.

Glasses and Glass-Ceramics

Advances in glasses were made empirically using common sense to guide experimentation until the 20th century. The application of basic scientific understanding to the improvement of manufacture and to new applications of glass has occurred only in the last few decades. Incorporating elemental and compound ions in them has made much improvement in electrical properties of the traditional glasses. Silica-less new glassy phases are synthesized and studied in great detail. Thus, in addition to traditional insulating glasses there are metallic and semiconducting glasses. Also there are other (silicon-less) oxide and chalcogenide glasses. Glasses are synthesized by rapid solidification processes, electrodeposition, vapour deposition, etc.

In alkali silicate glasses, the electrical conductivity changes with the replacement of silica by alkali ions. The increase is rapid until about 20-30 mole% of alkali ions and beyond that the change is nominal. The relative effect of alkali type on the conductivity is $Na^+ > Li^+ > K^+$. Additions of divalent modifiers to a soda silica glass is found to decrease the electrical conductivity with the relative effect being $Ba^{2+} > Pb^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+} > Zn^{2+} > Be^{2+}$. The most important commercial glasses are based on sodium calcium silicates. Partial substitution of one alkali-metal ion for another in silicate, borosilicate and borate glasses produces large differences in electrical resistance and this effect is called the *mixed alkali effect*. By substituting Al_2O_3 in place of SiO_2 in sodium silicate glasses, it is possible to increase the electrical conductivity. An important group of glasses is the borosilicates that have lower thermal expansion and hence better thermal shock resistance and improved chemical durability. They are mostly used for manufacturing automobile headlamps, cooking ware and laboratory apparatus. Aluminosilicate glasses because of their chemical durability, resistance to devitrification and higher strength are used in making glass-ceramics, fiberglass and seals. Lead glasses, with their high refractive index, are used as optical glass, lamp envelopes, and seals. Fused silica is useful as an optical material because of its high transmission of visible and ultraviolet light. The transmission edge in the ultraviolet range depends on the purity (impurities like Fe, Al, Mg, K, Na, Li, OH, etc. can be present) and stoichiometry of the silica. Many pyrex and lead silica glasses are used as dielectric materials in electrical industries.

Developing semi-conducting glasses became inevitable as the Si, Ge and the III-V semi-conducting compounds no longer satisfied the varied and specific requirements of the technological advances. Examples of glassy semiconductors are $CdAs_2$, $CdGeAs_2$, $CdGeP_2$ and chalcogenide-based As_2S_3, As_2Se_3, As-Te, As-S-Se-Te, As-Tl-S-Se, As-Sb-S-Se systems, etc. Glassy semiconductors are, by and large, *p*-type except the Bi-Ge-X (X= S, Se, Te) system where it is possible to get an *n*-type semiconductor by varying the composition. The conductivity of these materials varies in a wide range [10^{-2} to 10^{-18} $(ohm\text{-}cm)^{-1}$] depending on the composition. The main advantage of glassy semiconductors over crystalline ones is that they have no impurity conductivity and have extremely low carrier mobility. Other desirable features of these materials are high chemical resistance to extremely corrosive media, transparency in the infrared region and the possibility of greatly varying their properties by changing the composition. The main applications are in infrared optics, television engineering, moisture-proof coatings for semi-conducting devices and to construct threshold switches in memory cells.

Another important field where advanced glasses are used is in communication technology. A single glass fiber 0.01mm in diameter can transmit thousands of telephone conversations. Here silica glass is used in the form of a fiber. An optical fiber waveguide is a thin fiber composed of a high refractive index substance surrounded completely by a lower refractive index material. The central part is called the core while the outer part is called cladding. The light that is launched into the high index core is carried along that region by reflecting off at the interface between core and cladding with little attenuation (*Figure* 1). The core material used in many applications is germanium doped silica with the amount of germania decreasing radially

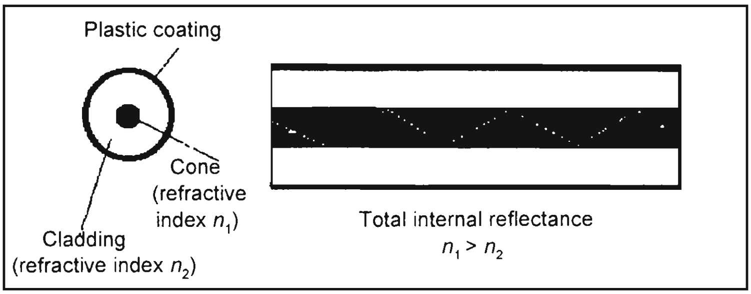

Figure 1. Cross-sectional views of an optical fiber. The velocity of light through a medium is c/n, where c is the velocity of light in air and n is the refractive index of the medium. Thus, the velocity of light in the fiber is very small compared to that in the cladding and hence light that is sent down the fiber will tend to stay within the core.

outward with only silica on the outside acting as cladding. Towards late 1980s erbium doped silica glasses were developed which brought in transmission capacity of the order of thousands of gigabit-kilometer per second (thousands of billions of information bit across a kilometer in one second).

Very high purity glassy silica fibers find application in space shuttles in the form of insulating tiles on parts which are exposed to temperatures in the range of 400–650°C. For temperatures up to about 1250°C the same tiles coated with borosilicate glass and silicon tetraboride are used to reflect off the radiation. There are about 30,000 silica tiles in a space shuttle. No two tiles have the same dimensions and each tile is machined to the right shape and size.

Then there are glass lasers[4]. Laser materials emit coherent light of high intensity by electronic transitions initiated by an external stimulus. Nd^{3+} doped glasses (silicates, phosphates or fluorophosphates) are widely used as laser materials. The important feature of glass lasers is that the composition of the glass host matrix can be varied over large ranges. A typical silicate glass laser host composition, in mole %, is $60SiO_2$: $27.5Li_2O$: 10CaO: $2.5Al_2O_3$ and that of a phosphate glass host being $4Al(PO_3)_3$: $36AlF_3$: $10MgF_2$: $30CaF_2$: $10SrF_2$: $10BaF_2$. It is possible to vary the laser properties systematically by changing the amount and species of network modifying ions. With neodymium ion the wavelength of the output radiation is 1.06 μm whereas with erbium ion it is 1.54 μm.

[4] Laser is an acronym for Light Amplification by Stimulated Emission of Radiation.

Glass-ceramics are polycrystalline solids prepared by the controlled crystallization of glasses. Crystallization is brought about by subjecting glasses to a carefully regulated heat-treatment schedule that results in the nucleation and growth of crystal phases within the glass. Thus, the crystallization process can be arrested at any stage to get the required amount of crystallinity in the glass matrix. In glass-ceramics, the crystalline phases are entirely produced by crystal growth from a homogenous glass phase whereas in other ceramics most of the crystalline material is introduced when the ceramic composition is prepared even though some recrystallization may occur or new crystal types may arise due to solid state reactions. Glass-ceramics are different from glasses because they contain major amounts of crystals while glasses are amorphous or non-crystalline.

The first glass-ceramic was developed in Corning Glass Works, USA. Certain glasses containing photosensitive compounds upon controlled irradiation and heat-treatment were converted to an opaque polycrystalline ceramic. This material had a much higher mechanical strength than the original glass.

Homogenous chemical compositional control in glass-ceramics is good as the process of manufacturing a glass-ceramic involves the preparation of molten glass to start with. The homogeneity of the parent glass along with the controlled crystallization result in ceramic materials with a fine grained uniform microstructure free from porosity. Because of this control of microstructure, advances have been made in the development of machinable glass-ceramics and in the production of bulk and fibrous glass-ceramics having oriented microstructure.

Just as the mechanical properties of glasses can be varied by introducing crystallinity, their electrical properties can also be tuned in a similar way. The onset of crystallization in silicate glasses can bring about large changes in electrical conductivity. For example, the dc-conductivity of Li_2O-SiO_2 and Na_2O-SiO_2 glasses decreases by over two orders of magnitude with crystallisation and this is the manifestation of the presence of a few percent of crystals in the glass. Glass-ceramics are used in and vacuum tube envelopes, telescope mirror blanks, radomes[5] for the aerospace industry and protective coatings for metals.

[5] Radome is a housing or cover for RADAR antenna. The radome material has to be chosen so that it is transparent to the frequency of the transmitting and receiving signal of the antenna.

Conclusion

Thus, starting from clay pots human beings have come a long way in terms of understanding and processing ceramics. Every elemental substitution changes the property of the ceramic and hence a new need of ours is fulfilled. In the era of modern technology over the last few decades, an unbelievable number of new inventions and developments have taken place. Sitting in our living rooms we are able to watch live the events happening around the world or talk to people in far off places. All these have also been made possible by advances in the area of semiconductor materials, which has not been touched upon in this article. It is impossible to cover all different types of materials used by us as the range of materials and the diverse applications that they find in modern technology are too wide. In this series of articles my goal has been to provide a broad view of what is currently happening in the area of modern materials. The endeavor has been to bring out the ingenuity that is required for tailoring new materials for specific applications.

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