Collage of Engineering

Materials Department

Third Class

Lecture (13)

GLASS

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6-3 transport properties:

The transport property of glasses is controlled by the diffusion, or transport of atoms or ions through the vitreous network. The electrical conductivity of almost all inorganic glasses is controlled by the diffusion of the monovalent ions under the influence of an external electrical field. The electrical conductivity of a substance is a result of field induced diffusion of a single ionic species, The electrical conductivity (σ) of the substance is related to the diffusion coefficient (D) of that species via the Nernst-Einstein relation:

$$\sigma = \frac{Z^2 F^2 D c}{f R T}$$

where Z is the ionic charge, F is the faraday constant (C/mol), c is the concentration of the diffusing species in the glass, R is the gas constant, T is the temperature in K, and f is a constant which is experimentally determined and ranges from 0.2 to 1 for glasses. A substance is electrically conductive when mobile free electrons or ions make transport of current possible. The temperature affects the diffusion coefficient, which in turn affects the ionic conductivity of the glass.

Addition of a divalent modifier such as Ca^{+2} to sodium silicate glass decreases the diffusivity of Na^{+} ions. The much less mobile divalent ions occupy interstices in the network and block the diffusion of the more mobile monovalent ions. This effect on diffusivity is at least partially responsible for the improvement in chemical resistance of alkali silicate glasses which occurs when alkaline earth oxides are added to the composition.

6-3-1 ionic exchange

Ion exchange occurs when a glass containing one mobile ion (A) is exposed to a source of a different mobile ion (B). Ions from the glass diffuse out of glass sample, while ions from the source diffuse into the sample. Since these ions have different sizes, their mobility's in the glass are different. The faster ion will tend to outrun the slower ion, which will cause an electric field to develop within the glass sample. This field will act to slow the faster ion and to accelerate the slower ion, until the fluxes of the two ions are identical. Ion exchange can be used to alter the near surface properties of an existing glass. Exchange of alkali ions can be used to strengthen glasses by producing a compressive layer in the near surface region. if exchange is carried out at temperature well below T_g, very little stress relaxation will occur during the exchange process. Furthermore if the ion in the glass is replaced by a larger ion from the external source, the difference in volumes of the two ions will result in a large compressive stress in the exchanged region. This process, which is termed ion exchange strengthening or chemical tempering, can produce very high surface compression in order of 300 to 400 MPa. Most commercial ion exchange strengthening is based on replacement of sodium ions in the glass by potassium ions from a molten salt bath. This choice is based on both economics (the other alkalis are more expensive) and the fact the sodium –potassium pair typically has a very favorable diffusion coefficient.

6-3-2 conductivity in glasses

Most oxide glasses including silicates, borates and most phosphates are ionic conductors, while some phosphate glasses are electronic conductors. Since the current carriers in ionic conducting glasses are ions, the electrical conductivity is closely related to the mobility of these ions. As a result, glasses which contain significant concentration of monovalent ions are poor insulators, while glasses which are free of monovalent ions are excellent insulators. Evan small amount of alkalis have an effect on the glass resistance. for example, at 300ºC a vitreous silica with only 0.04ppm Na^+ has a resistance of about $10^{13}\Omega$ cm, while an Na^+ content of 20ppm causes a decrease in resistance to about $5*10^9\ \Omega$ cm. these results demonstrate how sensitive the effect of slight impurities can be on electrical conductivity. On the other hand, with 0.01% mole Na_2O at the same temperature, borate glasses show high electrical conductivity.

Two effects on the conductivity can be established for alkali silicate glasses: the strength of the bond of the ions in the network, and their size. Thus the k^+ ion is bonded more weakly, but it provided a stronger resistance to diffusion because of its larger radius, while with Li^+ the opposite is true. Consequently, the differences of electrical resistance with equivalent contents become slight. Usually, ρ increases slightly in the sequence Li> Na> K.

Diffusion of an ion which is a primary component of a glass is termed self-diffusion. The results of some measurement done for a set of R_2O-3 SiO_2 glasses, where R is Na, K, Rb, or Cs, reveals that the diffusion coefficient is always greatest for the ion which is the component of the glass. The diffusivity of the impurity ions decreases as the difference between the size of the component ion and the foreign ion increases. The diffusivity of the alkali ions in a sodium silicate glass thus decreases in the order $Na^+ > K^+ > Rb^+ > Cs^+$, whereas that in a cesium silicate decreases in order $Cs^+ > Rb^+ >$Na. this relation between ionic diffusivity and glass composition gives rise to the mixed alkali effect in conductivity.

Glasses containing two or more alkali oxides display the mixed –alkali effect, examination of the diffusion coefficients of sodium and potassium in such a series of glasses reveals that coefficient decreases monotonically as the concentration of the other alkali ion increases. When glasses containing F have a lower conductivity as compared with that of the halide free glasses, caused by a stronger bonding of the alkali ions in the glass structure. On the other hand, the conductivity is raised through the introduction of Cl or Br ions; this is caused by a weaker bonding and a more open structure