

modulus. Although it is reported [15] that annealing can produce transformation from  $\beta$  to  $\alpha$  type, the increase of  $\alpha$ -SiC is hardly observed at 1246h by X-ray diffraction analysis. It is thus considered that growth of new crystallites in the dendritic structure may prevent propagation of cracks along the dendritic structure and cause an increase of the strength. Efforts were made to see why the strength subsequently decreases with longer anneals. Although an increase of crystallite size has been related to a decrease in the strength of SiC [2, 8], it is not possible to explain the present results on this basis, as the mean crystallite size in Table I increases up to 264h and thereafter the size is nearly constant up to 1246h. The density of the sample decreases gradually with annealing time (Table I), probably due to the vapourization of excess Si. The decrease of the strength and Young's modulus may be caused by porosity created by this vapourization [16]. However, further experiments are necessary to test this concept.

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### *The thermal conductivity of stabilized zirconia*

Kingery *et al.* and also Mirkovitch [1, 2] have shown that the thermal conductivity of calcia stabilized zirconia (CSZ) is low and nearly temperature independent, as shown in Fig. 1. This behaviour is not typical of crystalline refractory oxides and resembles the conductivity of a glass [3]. Data for thorium dioxide, which has the same fluorite crystal structure as CSZ is also included in Fig. 1, for purposes of comparison.

CSZ is a defect fluorite material with random substitution of  $Zr^{4+}$  ions by  $Ca^{2+}$  ions on the

cation sub-lattice; charge compensation is effected by an equivalent number of oxygen vacancies on the anion sub-lattice. Both the cation random solid solution and the anion vacancies probably contribute to the phonon scattering process. However, it is suggested that the anion vacancies are more efficient scatterers than the cation solid solution and only the former need be considered in accounting for the thermal conductivity of CSZ.

There is some justification for this assumption in the light of recent work by Schwarz and Walker [4] who observed phonon scattering by lattice vacancies in KCl doped with as little as 200 to 300 ppm of divalent chlorides. Further insight into the

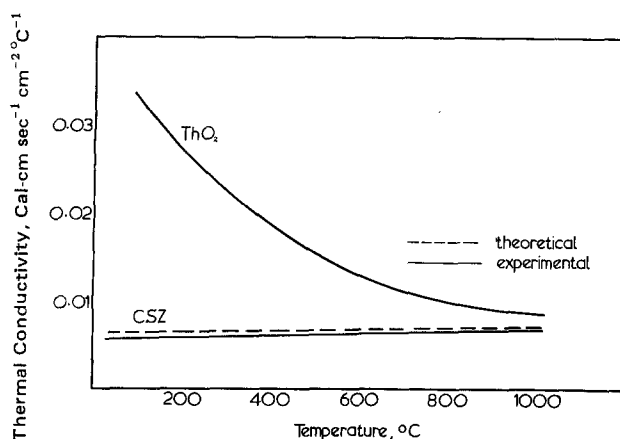


Figure 1 Thermal conductivity of thoria and calcia stabilized zirconia.

structure of CSZ and its relation to phonon scattering was obtained by Keramidias and White [5] who used Raman spectroscopy. The Raman spectra showed only broad diffuse peaks similar to those found in a glass. The authors point out that in solid solutions the Raman spectra remain well defined. It is likely then that the glass-like thermal conductivity of CSZ is primarily due to the anion vacancies which cause a complete breakdown of selection rules in the phonon modes, including the  $k = 0$  selection rule.

The hypothesis can be quantified by considering the well known equation for thermal conductivity in a solid [3]:

$$K = \frac{1}{3} CU\lambda \quad (1)$$

where  $K$  = the thermal conductivity;  $\text{cal-cm sec}^{-1} \text{cm}^{-2} \text{°C}^{-1}$ ,  $C$  = the heat capacity/unit volume;  $0.659 \text{ cal mol}^{-1} \text{°C}^{-1} \text{cm}^{-3}$  for CSZ [6],  $U$  = the velocity of sound;  $5.22 \times 10^5 \text{ cm sec}^{-1}$  for CSZ [7], and  $\lambda$  = the phonon mean free path length, cm.

The phonon mean free path length may be estimated in the following way. Consider the primitive cubic oxygen sub-lattice in the defect fluorite structure: it is known that the vacancies are found in pairs on the body diagonals of unit cells in the sub-lattice [8, 9]. At the vacancy levels encountered in CSZ (about 20 mol%) there is such a vacancy pair for about every  $2\frac{1}{2}$  cells. This implies that the longest free path for a phonon is only approximately a cell body diagonal. The lattice parameter of a typical CSZ composition is about  $5.13 \text{ \AA}$  [10]. Then the body diagonal length

amounts to  $5.13 \times \sqrt{3} \text{ \AA} = 4.45 \times 10^{-5} \text{ cm}$ . When the appropriate values are substituted into Equation 1, the thermal conductivity equals  $5.1 \times 10^{-3} \text{ cal-cm sec}^{-1} \text{cm}^{-2} \text{°C}^{-1}$  at  $100^\circ \text{C}$  — in fair agreement with the experimental value of  $4.7 \times 10^{-3} \text{ cal-cm sec}^{-1} \text{cm}^{-2} \text{°C}^{-1}$ .

The data in Fig. 1 show there is a small increase in the conductivity of CSZ as the temperature increases. The experimental temperature coefficient of the conductivity is about  $8 \times 10^{-7}$  conductivity units/ $^\circ \text{C}$ . The temperature effect is calculated as follows. The total differential of Equation 1 is:

$$\Delta K = \frac{1}{3} [U\lambda\Delta C + C\lambda\Delta U + CU\Delta\lambda] \quad (2)$$

where the differentials are replaced by the small incremental values which occur in the variables during heating through  $1000^\circ \text{C}$ . Upon insertion of the appropriate values in Equation 2 the temperature coefficient of the conductivity is calculated to be about  $5 \times 10^{-7}$  conductivity units/ $^\circ \text{C}$  — in fair agreement with the experimental value, as shown in Fig. 1.

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### *The bulk modulus of solvated elastin*

The great flexibility of rubber is due to the development of large shear strains at stresses so low that volumetric strains are insignificant. It is in this sense that the term incompressible is frequently applied to rubbers. In the discussion of the mode of deformation of elastin in tissues, in particular the aorta, it has been assumed that elastin deforms as a rubber with insignificant volumetric strain [1, 2]. There is, however, powerful evidence both theoretical and experimental which contradicts this apparently reasonable view. Elastin is deformed in the body in the diluted state. If a diluted rubber is deformed in the presence of diluent then the bulk modulus is extremely low. That elastin immersed in diluent does increase in volume when stressed under tensile load is in accord with a correct interpretation [3, 4] of the thermomechanical experiments of Weiss-Fogh and Anderson [5].

The reason for the difference between the bulk modulus of dry and diluted rubber is as follows. In the dry case, the volume can comply with the hydrostatic stress only by moving polymer molecules on average closer (or further) apart. The forces opposing this are extremely high which leads to negligible volumetric strains. However, if the rubber contains diluent and is immersed in diluent then it may comply with an imposed hydrostatic tension by absorbing (or desorbing) diluent. For example, when natural rubber is swollen with petroleum ether and is then stretched while immersed in petroleum ether from 150% of its initial unstretched length to 250% the swollen volume increases by 17% [6]. The essential difference between dry and swollen rubbers is well documented [7-9].

From this premise it follows that an elastin fibre subjected to hydrostatic tension in a diluent will exhibit appreciable volumetric strain. The

relaxation time for the attainment of volume equilibrium after the imposition of a hydrostatic tension will depend on the permeability of diluent in elastin and on the thickness of the fibre. If the hydrostatic stress is oscillatory then diluent will pass in and out of the elastin at a rate which will depend on the relative magnitude of the volumetric relaxation time and the period of the imposed oscillation. An elastin fibre, according to our hypothesis, will act as a sponge accepting and rejecting diluent from neighbouring tissues when acted upon by an oscillatory hydrostatic tension.

It seems likely that the bulk modulus of smooth muscle deformed in the presence of diluent will also be low. In this case the stress-induced diffusion process across an elastin-smooth muscle composite layer will depend on the mechanical properties of the two components, and on their geometry and spatial arrangement. The stress-induced chemical flux generated along a concentration gradient by an oscillatory stress may well be considerably larger than the flux due to normal diffusion processes [10].

What then of the evidence [1, 2] supporting the assumption of incompressibility? It must be stated firmly that in view of the quoted evidence on diluted elastomers [3, 4, 6-9] any observation supporting incompressibility must be considered anomalous. For instance, in the experiments of Lawton [11] no volume increase was observed when a strip of canine aorta was stretched immersed in saline solution. This experiment may be rejected since the dilatometer used by Lawton measured the aggregate volume of both the aortic strip and the saline reservoir in which it was immersed. Any increase in volume of the strip would be caused by saline passing into the strip from the reservoir. The observed change in volume would, therefore, be zero whether the strip increased in volume on stretching or not [12].

The consequence of our hypothesis on, for