Effect of Current-Blackening on the Elastic Constants of Yttria-Stabilised Zirconia

The passage of current through yttria-stabilised zirconia in reducing atmospheres produces visual blackening and leads to an increased friability of the material which restricts its use as a refractory electrode [1, 2]. To assess the effect of current passage on the elastic properties of the material, ultrasound wave velocities have been measured in single crystal, 8 mol % yttria-stabilised zirconia before and after blackening by current passage.

For elastic wave propagation in the [110] direction of a cubic material three modes can be excited with velocities (v) and particle displacements (q) as follows:

$$\rho v^2_{1} = (C_{11} + C_{12} + 2C_{44})/2\ ; \quad q \text{ along } [110], \text{ longitudinal}$$

$$\rho v^2_{s001} = C_{44}\ ; \quad q \text{ along } [001], \text{ shear}$$

$$\rho v^2_{s1\bar{1}0} = (C_{11} - C_{12})/2\ ; \quad q \text{ along } [1\bar{1}0], \text{ shear}$$

Measurements of the variation of ultrasonic wave transit times with temperature were made by the pulse superposition technique [3] in a conventional cryostat system. Pulse superposition allows an accurate estimation of the variation of the transit time (Δ) with temperature since the ratio

$$\frac{\Delta(0^\circ\text{C})}{\Delta(T)} = \frac{prf(T)}{prf(0^\circ\text{C})}$$

(where $prf(T)$ denotes the repetition frequency of the pulsed rf oscillator required to give superposition of successive echoes at a temperature T) is essentially independent of the properties of the seal and transducer [3].

A crystal, oriented by the symmetry of X-ray back-reflection Laue photographs to $\pm\frac{1}{2}^\circ$, was cut with a diamond wheel and polished to yield a sample 10 × 8 × 4.7 mm thick with faces (parallel to within 3×10^{-5} radians) perpendicular to the [110] axis and edges parallel to the [1$\bar{1}$0] and [001] axes. Quartz X- and Y- cut transducers, 5 mm in diameter, were used to generate the ultrasound at a carrier frequency of 15 MHz. "Nonaq" stop-cock grease formed a satisfactory transducer-to-specimen seal from about 283 to 77 K. To excite each of the shear modes, the vibration direction (x-axis) of a Y-cut transducer was very carefully aligned in turn parallel to each of the requisite particle displacement directions. After measurements had been made on the crystal in the as-grown state, it was blackened by current passage in dry argon at 2.5 A/cm^2 and 800°C for 10 min; this treatment was sufficient to produce marked visual blackening without causing fragmentation.

In the as-grown state the velocities at 0°C calculated from the ultrasonic data are:

$$v_1 = 7.05,\ v_{s001} = 3.05,\ v_{s1\bar{1}0} = 5.02$$

(Units 10^5 cm/sec, accuracy, ±1 %)

Comparison with the data reported previously [4] shows that in the earlier work the modes designated fast and slow were incorrectly identified and must be interchanged. This also applies to the data given for 12 mol % yttria-stabilised zirconia. When this alteration is made, the velocities from the previous and present work agree to within the experimental error of ±1 %. The corrected values of the elastic constants, using the measured density of 5.99 g/cm^{-3}, are listed in table I. From these the lattice energy per mole U_0 has been recalculated, assuming ionic binding, from [4]

$$U_0 = \frac{\alpha^2 e^2 N A_{\delta_0}}{\delta_0}\left(1 - \frac{1}{n}\right)$$

Here δ_0 is the cube root of the molecular volume, A_{δ_0} is the Madelung constant (7.33058 for the fluorite lattice) and α is the largest common factor in the valencies of the ions (2 in the present instance). The repulsive exponent n can be obtained directly from the bulk modulus by

$$n = 1 + \frac{9\delta_0{}^4 K}{\alpha^2 e^2 A_{\delta_0}}$$

TABLE I Elastic constant data for 8 mol % yttria-stabilised zirconia. (As-grown single crystal material.)

Elastic-stiffness constants Units 10^{12} dyn cm^{-2}		Elastic-compliance constants Units 10^{-13} cm^2 dyn^{-1}	
C_{11}	3.94	s_{11}	2.78
C_{12}	0.91	s_{12}	−0.52
C_{44}	0.56	s_{44}	18.0
Bulk modulus, K Units 10^{12} dyn cm^{-2}		Anisotropy ratio	
$\frac{C_{11} + 2C_{12}}{3} = 1.9$		$\frac{2C_{44}}{(C_{11} - C_{12})} = 0.37$	
Cauchy relation $\frac{C_{12}}{C_{44}} = 1.6$			

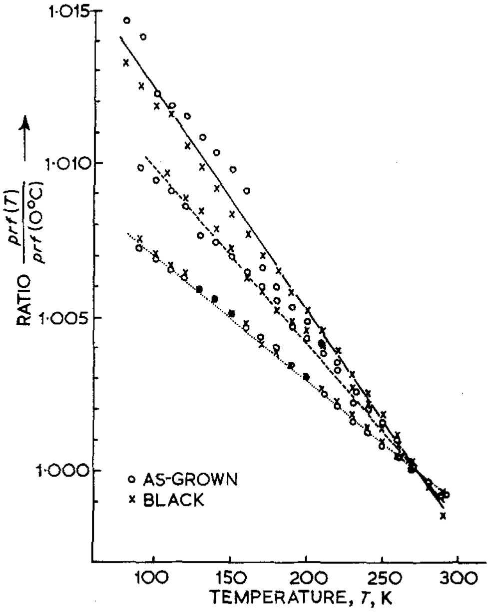

Figure 1 Comparison of temperature dependencies in as-grown and current-blackened 8 mol % YSZ single crystals. Key: open circles, as-grown; crosses, blackened Full line, shear mode with q along [001]. Chain line, shear mode with q along [1$\bar{1}$0]. Dotted line, longitudinal mode.

and is 12.0 for this solid solution. The Madelung attractive energy U_M has been calculated as -2945 kcal/mol and the repulsive energy U_n as 245 kcal/mol. Thus the total binding energy U_0 ($= U_M + U_n$) is -2700 kcal/mol. The elastic stiffness constants were also used to estimate the isotropic Young's modulus; the value obtained (2.1×10^{12} dyn cm^{-2}) can be compared with that (1.5×10^{12} dyn cm^{-2}) for polycrystalline sintered non-stabilised zirconia [5].

A comparison of results before and after blackening is made in fig. 1. It can be seen that the temperature dependencies are substantially the same. Within the experimental error the velocities are unaltered; the elastic constants in the as-grown and blackened states, and thus the lattice stabilities, are the same. This correlates with X-ray evidence [1] that the lattice parameter remains unaltered after blackening at low current densities. In the blackened crystal there was a marked deterioration of echo quality and some intermediate echoes also appeared: the blackened crystal shows the characteristics expected in an inhomogeneous material.

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The Effect of Oxygen Pressure on the Liquid Silver-Alumina Interface

The effect of dissolved oxygen on the surface tension of molten silver has been studied by Eremenko and Naidich [1] who measured the dimensional change of a sessile drop of the metal supported on a ceramic substrate. The liquid-vapour surface tension (γ_{lv}) was calculated by the method of Bashforth and Adams [2]. Under vacuum, this surface tension is about 910 dyn cm^{-1} [1, 3], but with increasing oxygen solubility determined by increasing oxygen pressure, it decreases sharply and the drop spreads. At 10^{-3} atm, the surface tension is about 650 dyn cm^{-1}, but with further increase in oxygen pressures up to ~ 0.1 atm, it is reported to reach a roughly constant value of 600 dyn cm^{-1}.

Our studies by the above method indicate that there is still a detectable spreading of the drop with increasing pressure at oxygen pressures much greater than those above. Owing to changes in refractive index, and optical interference by gas turbulence, the results are assessed qualitatively.

The horizontal pressure vessel used was similar to that employed for previous work on the silver-oxygen system [4]. The furnace was wound with Nichrome and the bore of the furnace tube was 1.7 cm. The sapphire platform which supported the silver drop (wt 0.47 g) and which was mounted in the constant temperature