

Letters

The Effect of Measuring Frequency on the Electrical Conductivity of Thoria Based Oxides at High Temperature

Recently there have been many measurements of the electrical conductivity of refractory oxides at high temperature. The reason for the stimulation of interest was the possible uses of these oxides for electrodes and insulators in magnetohydrodynamic power generators and for electrolytes in high temperature fuel cells. The oxides of group IVA such as zirconia, hafnia and thoria have received particular attention.

Most of the previous work has involved conductivity measurements using a bridge circuit operating at one particular frequency and measurements have been made over a range of temperatures in atmospheres of varying oxygen partial pressure. For example, high temperature measurements on undoped thoria have been made by Hund and Mezger [1] at 1000 Hz, by Subbarao *et al* [2] at 1000 Hz, by Volchenkova and Pal'guev [3] at 3000 Hz and by Lasker and Rapp [4] at 1592 Hz, the effect of frequency being ignored by all these workers. Steele and Alcock [5] claim that their results were independent of frequency at frequencies above 1000 Hz. However, whatever the mechanism of conductivity, whether it is ionic, electronic, or a mixture of both, it would be surprising if somewhere within the range of temperatures investigated, 400 to 1500°C, there were not some evidence of polarisation, and hence an effect of frequency on the conductivity. In fact Danforth and Bodine [6], in the only investigation of the electrical properties of single crystal thoria, reported that there were long term polarisation effects, and Rudolph [7] used four terminal measurements at frequencies from 5 to 100 Hz to "overcome polarisation effects", but no further details are given.

As part of an extensive investigation by the authors into the effects of frequency on the high temperature electrical conductivity of oxides based on thoria, the conductivity of undoped polycrystalline thoria was measured at temperatures from 450 to 1000°C at frequencies from 30 to 1000 Hz using two terminal measurements on sintered disc specimens. The discs were painted with platinum paste, fired at 800°C and placed between platinum foil electrodes. The measure-

ments were made with a standard Wayne Kerr B221 bridge, which normally operates at a fixed frequency of 1592 Hz, but an additional signal generator (Wayne Kerr S121) and waveform analyser (Wayne Kerr A321) enabled a frequency range of 30 Hz to 20 KHz to be used.

The results of the conductivity measurements on undoped thoria in air are shown in fig. 1 plotted as logarithm of conductivity (σ) versus the inverse of absolute temperature at each frequency. The effect of frequency is apparent and is particularly significant at the lower temperatures. Similar frequency effects have been obtained with thoria doped with additions of up to 5 mole % calcia. Measurements have been made at temperatures from 450 to 1450°C at oxygen partial pressures ranging from air (0.21 atm.) to that produced by wet forming gas (10^{-11} atm. at 1450°C to 10^{-32} atm. at 450°C).

The slope of the graph of $\log \sigma$ versus $1/T$ in any given atmosphere is clearly dependent upon the frequency used. This frequency dependence can be explained in terms of electrode and grain boundary polarisation mechanisms [8] and Bauerle [9], investigating the conductivity of zirconia doped with yttria, has found a similar frequency dependence.

However, frequently the variation of conductivity with temperature is represented by an equation of the form $\sigma = A \exp(-q/kT)$, where A is a constant, q is the "activation energy", k is

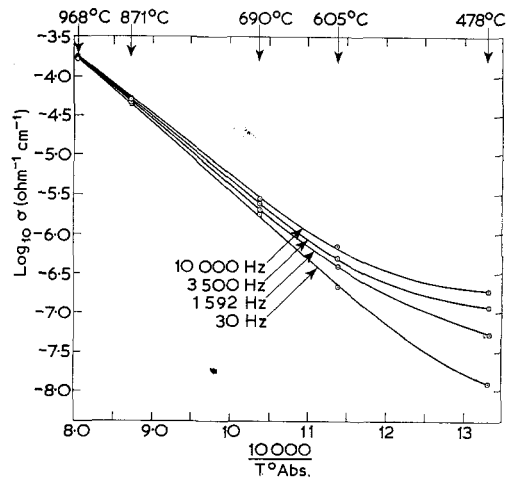


Figure 1 The effect of frequency on the electrical conductivity of undoped thoria in air at various temperatures.

Boltzmanns constant and T is the temperature in °Absolute. A measure of the "activation energy" can be obtained from the gradient of a plot of $\log \sigma$ versus $1/T$, as in fig. 1. It is apparent that these measured values of "activation energy" are dependent upon frequency and attempts to use such measurements, obtained from results at any single frequency, for a determination of conductivity mechanisms must be treated with extreme caution.

References

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Prolonged Sintering of a High-Permeability Ni-Fe-Cu-Mo Alloy Made by Powder Metallurgy

We have shown recently [1] that the initial permeability of 77 Ni-14Fe-5Cu-4Mo wt % alloy sheet prepared from powder metallurgy compacts can be significantly increased by extending the time of sintering (at 1300°C) considerably beyond that normally used. Conventional sintering times (≈ 5 h) lead to short-range copper concentration gradients in the compact; such gradients are not completely removed by subsequent cold-rolling and annealing, so that the alloy sheet is slightly inhomogeneous. Prolonged sintering leads to a reduction in the degree of inhomogeneity in the alloy compact through the elimination of the concentration gradients.

Previous work [1, 2] investigated sintering times in the range 1 to 156 h. The purpose of this letter is to report some new data which show the effect, on the initial permeability, of sintering for times in the range 100 to 1000 h. The alloy compacts were prepared and heat-treated in a similar way to that described previously [2]. The alloy sheet (nominally 50 μm thick) was annealed at 1050°C for 6 h in pure dry hydrogen, followed by furnace-cooling; the furnace-cooling rate in the important range, 400 to 500°C, was 90°C/h which is the optimum cooling rate for this alloy [3].

The new results are shown in fig. 1. Unexpectedly, the initial permeability decreases for

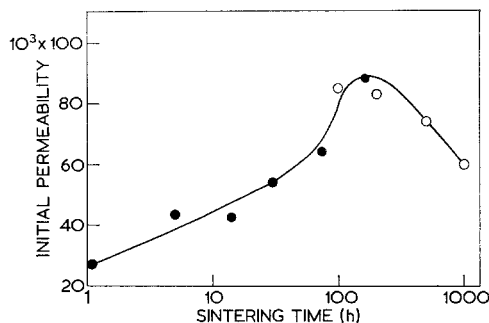


Figure 1 The variation of initial permeability with sintering time for 50 μm alloy sheet cold rolled from sintered compacts and annealed at 1050°C for 6 h. ● previous work [1]; ○ this work.

sintering times greater than 200 h. On the basis of the previous work one of two effects was expected: either (a) there would be no change in initial permeability (showing that the concentration gradients had been eliminated) or (b) there would be an increase in initial permeability (showing that elimination of concentration gradients was incomplete).

It was subsequently found that prolonged sintering leads to a loss of copper from the compact; for example, after 1000 h sintering the copper content of the alloy sheet was 4.1 wt %. Such a small change in alloy composition would