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The Electrical Resistivity of Some Castable Zirconias

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The variation of electrical resistivity with temperature has been measured for four castable zirconias: 6.0 mole % calcia-stabilised, 8.5 mole % yttria-stabilised, and 25 and 50 mole % ceria-stabilised zirconia. The calcia- and yttria-stabilised castables need to be sintered at over 2000° K to develop their electrical conductivity fully, but that of the ceria-stabilised castables is independent of sintering temperature, and is similar to that of normally prepared ceramic. The castables are discussed with particular reference to their possible application as MHD electrode materials.

1. Introduction

A castable zirconia is a size-graded powder of stabilised zirconia, which, after being mixed with a liquid binder, cast in a mould and heated to about 500° K, gives reasonable unfired strength. Shrinkage of less than $\frac{1}{2}$% occurs on sintering commercially available material, so that quite complicated shapes can be made easily and accurately, although the final porosity is generally greater than 20%. The liquid binder is basically a zirconium compound which, when heated slightly, dissociates, giving a thin layer of zirconia around each grain. This provides increased grain contact and strength compared with a normal unsintered ceramic.

The present interest in castable zirconia arose because its use offered a simple way of making zirconia electrodes for magnetohydrodynamic power generation (MHD). In MHD a hot combustion gas flows through a transverse magnetic field and electrodes extract current in a direction approximately normal to both the gas flow and the field. The stringent requirements for refractory MHD electrodes have previously been described by Meadowcroft [1]. Many otherwise suitable refractory materials do not have low enough electrical resistivity, which must not be greater than 0.1 to 1.0 ohm m, the limit depending somewhat on the electrode design. Zirconia-based materials have been considered for electrodes but their resistivity is low enough only at elevated temperatures, a fact which has meant that methods have had to be devised to make electrical contact with the zirconia at high temperatures. By using contacts of suitable metal alloys, or platinum, electrode materials can be considered which have a low enough resistivity only above 1500° K.

Pure zirconia has a destructive phase transition at about 1300° K, and to stabilise it against this transition an oxide is added, usually calcia or yttria, which will form a cubic solid solution with the zirconia. Calcium and yttrium have lower valencies than zirconium, and oxygen vacancies are produced to give charge balance, which means that electrical conduction in the materials is almost completely by oxygen ions. (Paidassi and Caillat [2] have recently reviewed the properties of stabilised zirconia.)

Transport by oxygen ions is not ideal for MHD electrodes [1] because it causes oxidation of the metal contacts, and reduction of the ceramic itself. Therefore consideration has been given to zirconia-based materials with an appreciable electronic transport number (the fraction of current carried by electrons and holes) Ceria-zirconia compositions have received the most attention: 25 mole % ceria-zirconia has an electronic transport number between 0.47 (at 1300°K and 1 to 10^{-1} bar* oxygen) and 0.81 (at 1700° K and 10^{-2} to 10^{-3} bar oxygen) [3] and for 50 mole % ceria-zirconia an electronic transport number exceeding 0.90 has been determined [4, 5].

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*1 bar = 1 standard atmosphere.

Using a castable for MHD electrodes would make construction far easier in view of the very large number of electrodes which would be needed in a commercial generator. Construction would be even simpler if the strength and electrical conductivity of the unsintered castable were adequate for use without pre-sintering. However, it seemed likely that the resistivity of a castable would differ from that of a normally prepared ceramic, especially if the former was not pre-sintered. Such information was not available, and therefore this paper reports measurements made on the variation of electrical resistivity with temperature for various castable zirconias which have been considered as possible MHD electrode materials.

2. Experimental Results

Four-probe DC resistivity measurements were made using bar shaped samples which had a cross-section of approximately 1 sq cm and were about 3 cm long. Platinum paste electrodes were used, around which platinum wires were wrapped. Measurements were made between room temperature and 1800° K, and, by using oxygen/argon mixtures, in oxygen partial pressures between 1 and 10^{-3} bar. Four materials, which were obtained commercially, were examined: 1. 6 mole % calcia-stabilised zirconia; 2. 8.5 mole % yttria-stabilised zirconia; 3. 25 mole % ceria-stabilised zirconia; 4. 50 mole % ceria-stabilised zirconia.

For each castable material the variation of resistivity with temperature was measured: (i) without previous sintering; (ii) after sintering at 1800° K in oxygen; (iii) after sintering at about 2300° K in a propane-oxygen fired furnace. Further it was instructive to compare these results with those for ceramic samples prepared by more usual techniques; e.g. cold-pressing and sintering.

The results for each material are shown in figs. 1 to 4, and are discussed below individually.

2.1. Calcia-stabilised Zirconia

It can be seen from fig. 1 that the resistivity of zirconia castable, stabilised with 6 mole % calcia, decreased markedly as the sintering temperature increased, so that for electrical applications pre-sintering is definitely necessary. At temperatures below 1400° K the resistivity of the previously unsintered sample increased with time, and above 1400° K decreased with time, the changes being of the order of 20% and taking about 2h to reach equilibrium. The resistivity of the castable, when sintered at 2300° K, is very like that of 6 mole % calcia-stabilised rod obtained from the same manufacturer: the difference can partly be attributed to the different porosities, about 25% for the castable and about 10% for the rod.

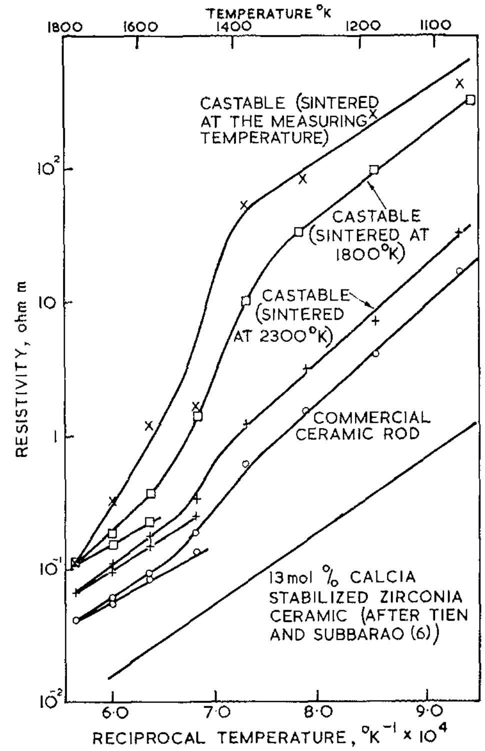

Figure 1 The resistivity of calcia-stabilised zirconia.

The sharp drop in resistivity at about 1400° K, which is evident in fig. 1, is characteristic of pure zirconia. This is probably because 6 mole % calcia does not fully stabilise zirconia, and because for the previously unsintered sample and the sample sintered at 1800° K, there must still have been free zirconia around each grain. The castable material and the ceramic rod are supplied with a low proportion of stabilising oxide to give better mechanical properties and reduced expansion coefficient. However, as both have a much higher resistivity than 13 mole % calcia-zirconia which is fully stabilised and is the composition with the lowest resistivity [6], this composition would be preferable for electrical applications.

2.2. Yttria-stabilised Zirconia

Yttria is expensive, so that yttria-stabilised

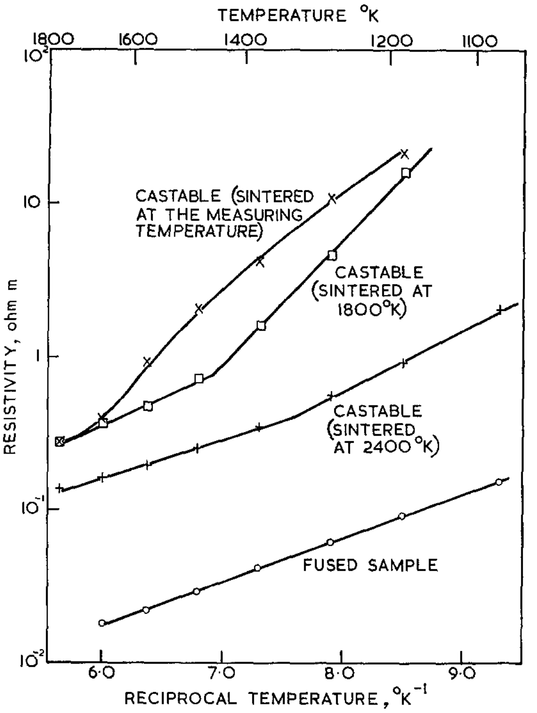

Figure 2 The resistivity of 8.5 mole % yttria-stabilised zirconia.

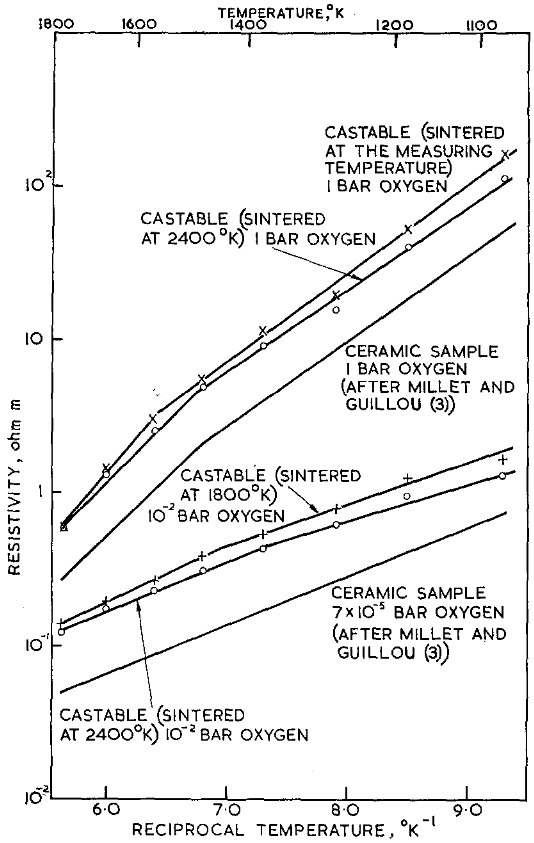

Figure 3 The resistivity of 25 mole % ceria-stabilised zirconia.

zirconia costs about £20 per kg, whereas calcia-stabilised castable costs only about £1 per kg. Yttria-zirconia has a lower resistivity which varies less with temperature, but, like calcia-zirconia, it is almost completely ionic [7]. Fig. 2 shows that, as with calcia-stabilised castable, sintering at 2400° K was needed to markedly decrease the resistivity, especially at the lower temperatures; this was presumably because yttria had to diffuse into the grain-boundaries.

The fused sample measured was of the same material that was used to produce the castable powder; and as porosity is unlikely to cause an order of magnitude increase in resistivity, the main reason for the higher resistivity of this castable must be grain-boundary resistance. This would occur if the yttria content of the grain-boundaries were not the same as in the bulk material [7]. As with calcia-zirconia castable, for electrical applications this castable definitely needs to be pre-sintered.

2.3. 25 mole % Ceria-stabilised Zirconia

Fig. 3 shows that there are two major differences between this material and the previous two castables: the sintering temperature does not appreciably affect its resistivity, whereas the oxygen partial pressure affects it markedly. The latter occurs because the electronic conductivity is defect controlled, and this accounts for between 50 and 80% of the transport in the material [3]. Further discussion of this behaviour is given in the next section on 50 mole % ceria-stabilised zirconia. The results of Guillou and Millet [3] are also reproduced in fig. 3 and show reasonable agreement with the castable measurements. With reference to the MHD application, the oxygen partial pressure in a duct is about 10^{-2} bar [1], so that it should be feasible to have the temperature of the zirconia-metal contact down to 1200° K.

2.4. 50 mole % Ceria-stabilised Zirconia

By comparing fig. 4 with figs. 1 to 3 it is evident that the resistivity of 50 mole % ceria-zirconia is much lower in a partial pressure of oxygen of 10^{-3} bar, than is that of any of the above zirconia compositions (note the compressed

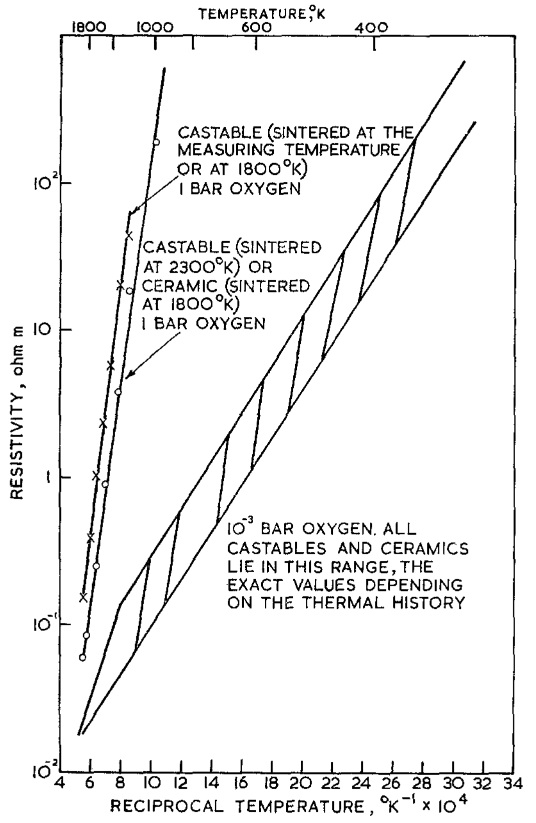

Figure 4 The resistivity of 50 mole % ceria-stabilised zirconia.

temperature scale in fig. 4). The temperature of the zirconia-metal contact in an MHD electrode could be as low as 700° K with this material. As with 25 mole % ceria-zirconia, sintering did not appreciably affect the resistivity of the castable.

It has been found that the changes in the resistivity of 50 mole % ceria-zirconia could be easily induced at 600° K by altering the oxygen partial pressure [8], so it may be deduced that ionic movement is able to occur at this temperature. This could explain why the resistivity of ceria-zirconia castable was not dependent on temperature; whereas, in calcia- and yttria-stabilised zirconia, the present results suggest that grain-boundary diffusion of calcium and yttrium developing the ionic conductivity, occurs mainly above 1800° K.

The high electronic conductivity is caused by the existence of cerium Ce^{3+} and Ce^{4+} ions, conduction occurring between these valency states when both are present. Therefore, with CeO_2–ZrO_2, reducing the oxygen partial pressure increases the Ce^{3+} concentration and conductivity. Unfortunately, at the other extreme, samples of $Ce_2Zr_2O_7$ (formed in a reducing atmosphere) have been known to disintegrate when exposed to an oxidising atmosphere at high temperature, because of the oxidation of the cerium [1]. Samples of 50 mole % CeO_2–ZrO_2 initially sintered in air, have not shown this limitation in reduced oxygen partial pressures; but, as is indicated in fig. 4, the resistivity is then not completely reproducible. The actual values obtained depend on heating rate, for equilibration is very slow and takes several hours even at 1800° K. Guillou and Millet [9] have also found this effect, and consider that there is a slow ordering of the different valency states.

One final effect which was observed with ceria-zirconia castable was the volatilisation of appreciable amounts of ceria, which then condensed on cooler parts of the apparatus. However, this evaporation did not affect the resistivity of the castable, because this varies slowly with ceria concentration in the region of 50 mole % ceria [4].

3. Conclusions

Of these materials, 50 mole % ceria-zirconia has shown the most promise for possible use as an MHD electrode. Its resistivity is the same whether it is used in the form of sintered or unsintered castable or as a normally prepared ceramic: in the atmosphere of an MHD duct its resistivity would enable the ceramic-metal contact to be as low as 700°K. However, whether the castable material would be suitable as a long term MHD electrode would depend on its resistance to corrosion, because the porosity of the material would exacerbate any corrosive attack by the potassium compounds used to seed the flame.

The ionically conducting castables need to be pre-sintered to reduce their resistivity. For electrical applications yttria-stabilised castable could be used down to somewhat lower temperatures than calcia-zirconia castable but the latter is by far the cheaper.

In brief, castables have a high porosity and generally need pre-sintering at high temperature to develop reasonable properties. Their main advantage is the ease with which they can be fabricated into complicated shapes.

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References

1. D. B. MEADOWCROFT, *Energy Conv.* **8** (1968) 185.
2. J. PAIDASSI and R. CAILLAT, *Rev. Int. Hautes Temper. et Refract.* **5** (1968) 27.
3. J. MILLET and M. GUILLOU, *J. Chim. Phys.* **64** (1967) 1726.
4. M. ASQUIEDGE, N. BUSSON, M. GUILLOU, M. JACQUIN, A. LECANTE, J. MILLET, S. PALOUS, and M. PITHON, *Rev. Int. Hautes Temper. et Refract.* **6** (1969) 35.
5. F. G. HICKS, private communication (1968).
6. T. Y. TIEN and E. C. SUBBARAO, *J. Chem. Phys.* **39** (1963) 1041.
7. D. W. STRICKLER and W. G. CARLSON, *J. Amer. Ceram. Soc.* **47** (1964) 122.
8. R. A. CHAPMAN, D. B. MEADOWCROFT, and A. J. WALKDEN, to be published (1969).
9. M. GUILLOU and J. MILLET, private communication (1968).

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