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Phase Relationships of the System ZrO_2 + CaO + P_2O_5 at 1673 K and the Electrical Conductivity of Calcia-stabilized Zirconia Containing Phosphorus Pentoxide

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INTRODUCTION

By employing an electrochemical technique incorporating a zirconia-based solid electrolyte, the activities of P_2O_5 in molten fluxes used for the external dephosphorization of blast furnace hot metal have successfully been measured by the present authors /1, 2/. During these studies it became necessary to know the phase relationships of the $ZrO_2 + CaO + P_2O_5$ system, which have not been investigated, although the binary systems $CaO + P_2O_5$ /3/ and $ZrO_2 + CaO$ /4/ have been studied. The present study is aimed at establishing the phase relations in the system $ZrO_2 + CaO + P_2O_5$ at 1673K. Electrical conductivity measurements were also made with ZrO_2 + 14.6 mol% CaO + 3 mol% P_2O_5.

PHASE RELATIONS IN THE SYSTEM $ZrO_2 + CaO + P_2O_5$

The details of the experimental procedure have been reported elsewhere /5/. Three starting materials for the preparation of the specimens were ZrO_2, $CaCO_3$ and $(NH_4)_2HPO_4$ of high purity. The starting materials were mixed in a mortar to yield requisite bulk compositions and cold-pressed at 1000 kg/cm^2 in a steel die to form pellets of 20 mm diameter and 5 to 10 mm thickness. The resulting pellets were heated at 1673K in air for a period of over 48 hours, cooled, and subsequently submitted for X-ray diffraction analysis for phase determinations.

The experimental results at 1673K are summarized in Table 1, and the phase relationships for the system $ZrO_2 + CaO + P_2O_5$ were established from the data in this table. The 1673K isothermal section is shown in Fig. 1, taking binary systems into account. The numerals in this figure correspond to the sample numbers given in Table 1. Within the composition ranges investigated, no melting of the specimens occurred. The limits of the cubic solid solution in the binary system $ZrO_2 + CaO$ were taken from Garvie /4/ who viewed the cubic field as extending from 15 to 20 mol% CaO at 1673K. The boundaries reported for the two-phase region containing tetragonal ZrO_2 and cubic $CaO \cdot 4ZrO_2$ solid solution also vary considerably /6-8/. Therefore, since the exact value is of little interest to the present investigation, an arbitrary range was assumed.

Calcia-stabilized zirconia is a predominantly ionic conductor because of the presence of a large number of oxygen vacancies. The P_{O_2} independence of the total conductivity and numerous excellent correlations of galvanic cell voltages to known Gibbs energy data have served as evidence that electrical conduction in this material is primarily due to the migration of oxygen ions. The ionic conduction domain of stabilized zirconia in the oxygen potential – temperature space is well delineated /9/. The effect of P_2O_5 on the ionic conductivity of calcia-stabilized zirconia has not been investigated.

From Fig. 1, it is apparent that phosphorus pentoxide, if contained in calcia-stabilized zirconia at relatively small concentrations, will be present as $3CaO \cdot P_2O_5$. With respect to the application of a zirconia-based electrolyte to in-situ determinations of phosphorus in molten metals, attention should be focused on the three-phase region of tetragonal ZrO_2 + cubic $CaO \cdot 4ZrO_2(ss) + 3CaO \cdot P_2O_5$. Consider partially stabilized zirconia containing 14.6 mol% CaO and 3 mol% P_2O_5. This composition corresponds to the solid circle shown in Fig. 1. In such a three-phase region, the activities of components, CaO, ZrO_2 and P_2O_5, are fixed at any given temperature. Hence, if such electrolytes were in contact with liquid metal containing phosphorus, then one can expect the equilibrium:

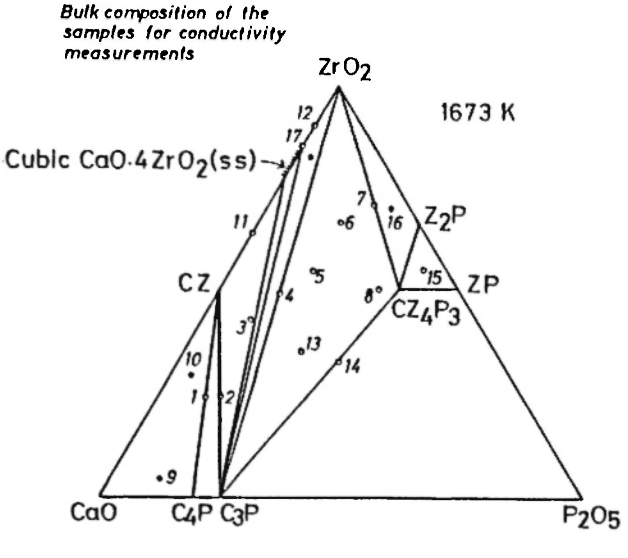

Fig. 1. Secretion of the system $ZrO_2 + CaO + P_2O_5$ at 1673 K. CZ = $CaO \cdot ZrO_2$, Z_2P = $2ZrO_2 \cdot P_2O_5$, ZP = $ZrO_2 \cdot P_2O_5$, CZ = $CaO \cdot ZrO_2$, C_4P = $4CaO \cdot P_2O_5$, C_3P = $3CaO \cdot P_2O_5$, CZ_4P_3 = $CaO \cdot 4ZrO_2 \cdot 3P_2O_5$.

TABLE 1
Experimental Results at 1673 K

Sample No.	Phases present after treatment	Bulk composition X_{ZrO_2}	X_{CaO}	$X_{P_2O_5}$
1	C_4P + CZ	0.250	0.650	0.100
2	C_3P + CZ	0.250	0.625	0.125
3	C_3P + CZ + CZ_4	0.445	0.444	0.111
4	C_3P + Z	0.500	0.375	0.125
5	C_3P + Z + CZ_4P_3	0.555	0.271	0.179
6	Z + CZ_4P_3 + C_3P	0.666	0.167	0.167
7	Z + CZ_4P_3	0.714	0.072	0.214
8	Z + C_4P + CZ_4P_3	0.500	0.167	0.333
9	C + C_4P + CZ	0.300	0.650	0.050
10	C + C_4P + CZ	0.300	0.650	0.050
11	CZ + CZ_4	0.650	0.350	
12	CZ_4 + Z	0.900	0.100	
13	C_3P + Z + CZ_4P_3	0.350	0.400	0.250
14	CZ_4P_3 + C_3P	0.334	0.333	0.333
15	Z_2P + ZP + CZ_4P_3	0.550	0.050	0.400
16	Z + Z_2P + CZ_4P_3	0.700	0.050	0.250
17	CZ_4	0.850	0.150	

Z, ZrO_2 (monoclinic);
ZP, $ZrO_2 \cdot P_2O_5$;
CZ, $CaO \cdot ZrO_2$;
C, $CaCO_3$
C_4P, $4CaO \cdot P_2O_5$;
CZ_4, cubic ZrO_2–CaO solid solution
Z_2P, $2ZrO_2 \cdot P_2O_5$
C_3P, $3CaO \cdot P_2O_5$;
CZ_4P_3, $CaO \cdot 4ZrO_2 \cdot 3P_2O_5$

$$2P\,(\text{in metal}) + 5O\,(\text{in metal}) = P_2O_5\,(\text{in electrolyte}) \qquad (1)$$

It is apparent from this equilibrium that a measure of oxygen potentials corresponds to a knowledge of phosphorus activities in liquid metal. For the application of such a three-phase zirconia electrolyte, reference may be made to a paper by Iwase /10/. In the second series of experiments, electrical conductivities of ZrO_2 + 14.6 mol% CaO + 3 mol% P_2O_5 were determined.

ELECTRICAL CONDUCTIVITY

A schematic representation of the experimental apparatus is shown in Fig. 2. The samples used for these measurements were in the form of pellets with a diameter of 20 mm and a thickness of 7 to 10 mm. A SiC resistance furnace was equipped with a mullite reaction tube, the inside of which was flushed with a stream of argon or Ar + O_2 gas mixtures. The purification chain for argon consisted of silica-gel, magnesium perchlorate, phosphorus pentoxide and magnesium chips. The samples were maintained in compression by means of spring-loaded platinum electrode assemblies which gave optimum contact through the deposited platinum thin films on the samples. The ac conductivity measurements were performed using an impedance bridge with a frequency of 1000 Hz under controlled oxygen partial pressures. Two-probe

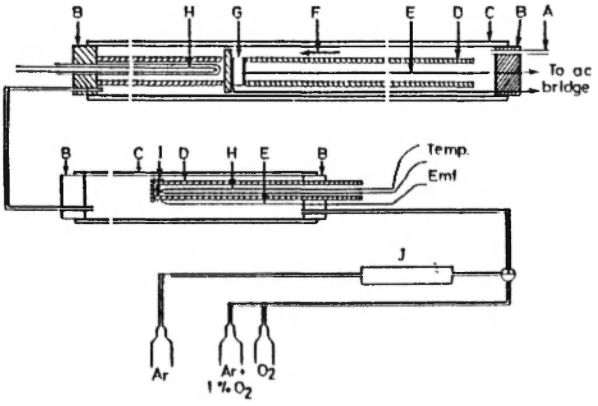

Fig. 2. Experimental apparatus used for conductivity measurements. A, Gas outlet; B, Rubber stopper; C, Mullite reaction tube; D, Spring-loaded alumina tube; E, Platinum wire; F, Spring; G, Specimen, H, Pt-PtRh13 thermocouple; I, Platinum gauze; J, Magnesium chips.

conductivity measurements were employed. The oxygen partial pressures in the gas phase were monitored in-situ by using an oxygen probe of Pt / air / $ZrO_2(CaO)$ / Ar (+ O_2) / Pt. The details of the oxygen probe used have been described elsewhere /11/. By controlling the temperature of the magnesium chips within the gas purification train, which was located up stream from the SiC resistance furnace, the oxygen partial pressures in argon were adjusted to 10^{-5} to 10^{-15} atm. By using the available electrical conductivity data for platinum, the resistance of platinum leads was found to be negligible.

The experimental results obtained at $P_{O_2} = 1$ atm are shown in Figure 3. As a check on the two-probe technique employed in this study, the electrical conductivity of ZrO_2 + 15 mol% CaO was also measured, and the results were in very good agreement with the literature values reported by Dixon *et al.* /12/. From Figure 3, the effect of $3CaO \cdot P_2O_5$ is evident; the addition of P_2O_5 to CSZ results in a decrease in total conductivity over the whole temperature range.

The present results for ZrO_2 + 14.6 mol% CaO + 3 mol% P_2O_5 show hysteresis in the Arrhenius plots during the heating and cooling cycles; Figure 3. The conductivity measurements during the heating and cooling cycles followed different paths for each cycle. This hysteresis was related to the monoclinic-tetragonal phase transformation.

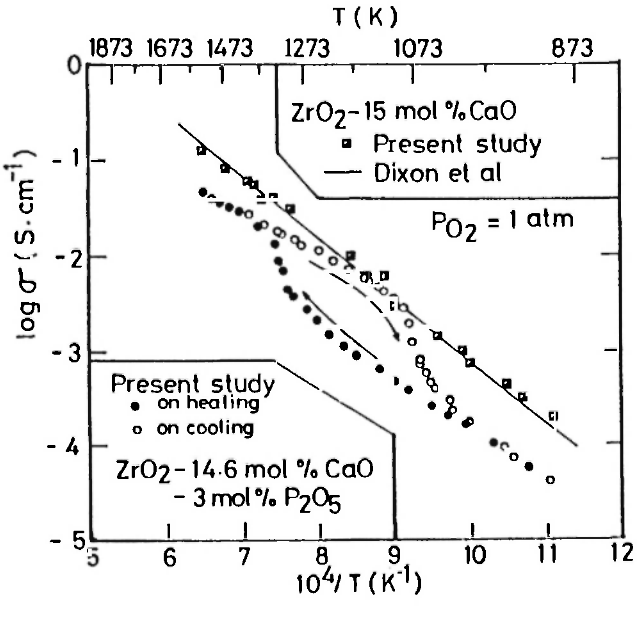

Fig. 3. Electrical conductivity as a function of temperature at an oxygen partial pressure of 1 atm.

Figure 4 shows the effect of oxygen partial pressure on the total conductivity at 1623K; at this temperature hysteresis was not observed. As shown in this figure, total conductivity is substantially independent of oxygen potential, although a slight increase was observed at $P_{O_2} > 10^{-5}$ atm., corresponding to a relatively small portion of electronic conduction. These results indicate that the electrical conduction of the material ZrO_2 + 14.6 mol% CaO + 3 mol% P_2O_5 is essentially due to the transport of oxygen anions. Hence, it appears feasible that the three-phase electrolyte could be used as the electrolyte of solid state galvanic sensors for monitoring phosphorus in blast furnace hot metal.

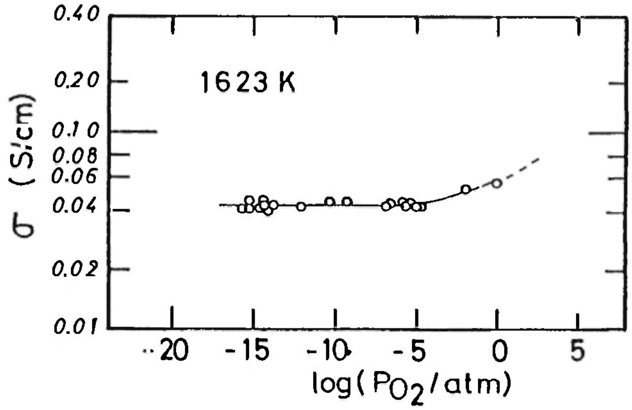

Fig. 4. Electrical conductivity as a function of oxygen partial pressures at 1623K.

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