ELECTRODE POLARIZATION STUDIES
IN HOT CORROSION SYSTEMS

Progress Report
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ABSTRACT

A cell suitable for polarizing metals and alloys in molten sodium salts under controlled atmosphere at one atmosphere pressure and 1000°C has been constructed and operated. The cell comprises a standard three electrode configuration, with a reference electrode contained in a defect zirconia crucible, reversible to oxide ion. Kinetic atmosphere control on H_2 , CO, and H_2S is maintained, thus fixing all compositional parameters in the gas/liquid two-phase system. This system has been modelled thermodynamically, yielding complete solution for gas phase composition as a function of external control parameters. Analysis of the liquid phase is in progress.

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SCOPE OF INVESTIGATION

As per contractual agreement, "The scope . . . shall consist of polarization experiments on metals and alloys in sulfur-bearing molten salts under reducing atmospheres. Parallel metallographic analyses will also be performed."

SIGNIFICANT RESULTS

Progress has been along two discrete, but complementary, routes: 1) The construction of an electrochemical cell to permit controlled polarization studies at or near 1000°C on metals and alloys immersed in molten salts under controlled atmospheres, and 2) The establishment of a model system resembling that within a coal gasifier and the delineation of the equilibrium compositions of the gas and liquid phases of this system. Results to date and projected to the contract expiration date are outlined below.

Polarization Cell

A polarization cell has been designed and constructed as shown in Figure 1. It is contained in a mullite retort in a vertical glow-bar furnace powered by a solid state supply permitting virtually constant temperature control within 1°C. The molten salt electrolyte is contained in a recrystallized alumina crucible, in turn supported by a framework suspended from the top of the retort. This framework and the associated radiation shields were initially fabricated of type 304 stainless steel; however, the scaling which ensued during operation of the cell contaminated the electrolyte, although structural integrity was maintained. Alumina and/or Inconel 600 have been found suitable for use in those areas immediately adjacent to the cell where contact with the electrolyte is probable.

Fig. 1 Polarization cell for use at 1000°C , 1 atm., under controlled atmosphere. (Thermocouple well and gas inlet and outlet not shown)

Polarization is accomplished with three electrodes: the working electrode or specimen under study, a counter electrode whose function is to pass current to the working electrode, and a reference electrode with respect to which the potential of the working electrode is measured. External electronics, i.e., a potentiostat, provides a means to establish any desired working electrode potential via an impressed current. A Wenking Type 68TS3 potentiostat with a Type SMP 69 motor potentiometer permitting automatic potential sweep is used with this cell; cell current and potential are directly recorded via appropriate intermediate circuitry. The working electrode and platinum counter electrode are cemented to alumina support tubes through which platinum leads, clamped to the electrodes, are fed. The reference electrode consists of a platinum electrode immersed in the cell electrolyte contained in a crucible of zirconia - 8% yttria, known to be reversible to oxide ion. These electrodes pass through seals in the water-cooled lid.

In view of the propensity of such systems to experience atmospheric contamination through leakage and internal out-gassing, dynamic atmosphere control is employed. As will be noted in the following section, composition control can be exerted in a simplified gasifier model through specification of three partial pressures in the presence of a sodium salt, e.g., P_{H_2} , P_{CO} , and P_{H_2S} , together with Na_2CO_3 . Provided that other gases making up the equilibrium mixture are present in only small quantities in comparison to the three controlled gases, these pressures can be established in a kinetic system through fixing appropriate flow rate ratios and venting the effluent gas at a fixed pressure. This capability is incorporated into the cell, with the initial intent of operating at a total pressure of one atmosphere. In view of the toxic nature of the gases employed the effluent gas

will be burned in a tube furnace and passed through aqueous NaOH prior to venting to the laboratory exhaust duct system.

Model Calculations

The environment within any coal gasification system is both complex and non-equilibrium; any attempt to model it, either experimentally or through thermodynamic analysis, is, at best, an approximation. As a starting point for this study we have presumed the existence of a simple reducing gas containing H_2 and CO and, therefore, H_2O and CO_2 . Sulfur is presumed present, potentially as S_2 , H_2S , SO_2 and SO_3 . In this first model solid carbon is not included, thus CH_4 and other hydrocarbon gases are omitted. Nitrogen has also been omitted, simply on the basis that its effect on the ensuing equilibria is postulated to be less severe than that of the other gases named. The gas mixture is considered to be in equilibrium with a molten sodium salt, comprised thus of Na_2CO_3 , Na_2O , Na_2S , Na_2SO_4 , and NaOH.

Eight independent chemical equilibria can be construed between these thirteen constituents comprising the system, reducing the number of independent constituents to five. Two phases being present, the phase rule indicates the existence of five degrees of freedom. Most logically, these are temperature, pressure, and three compositional parameters, for example, P_{H_2} , P_{CO} , and P_{H_2S} . Calculations on this model to date have used these parameters, with $T = 1300^\circ K$ (above the melting point of all salts in the system, thus greatly simplifying calculations), $P = 1$ and 10 atm., and partial pressures of H_2 , CO, and H_2S varying from the total pressure, P , to $10^{-10}P$. Thermodynamic data for this analysis are available in standard reference works. Fortunately, the gas phase equilibria, totalling four expressions, together with a fifth expression for total pressure, can be solved independently of the liquid

phase, somewhat simplifying the analytical work. Nonetheless, the system cannot be solved in closed form, necessitating regressive procedures.

Solution of the equilibrium relations for the gas phase is complete; summary diagrams are shown in the Appendix. These figures are not in final form, but will be improved with respect to format of presentation, emphasis on compositional ranges of pragmatic interest, and simplification where warranted. Typical behavior of the liquid phase is shown in Figure 2 for the case where the system pressure is 10 atmospheres. These diagrams are essentially sections through a "phase diagram" in which the three compositional parameters are represented by orthogonal axes. The "phase regions" indicate the dominant anionic species at each point. Detailed treatment of the liquid phase is in progress.

COMPLIANCE WITH CONTRACT REQUIREMENTS

The work reported herein is in compliance with the requirements of Contract No. E(11-1)-2960.

PRINCIPAL INVESTIGATOR

The principal investigator, Owen F. Devereux, devoted 100% of his time during June - July, 1976 and 10% of his time during September, 1976 - January, 1977, to this project. His effort during February - May, 1977 will remain at 10%.

BIBLIOGRAPHY

None to date.

FIGURE 2

Dominant anions vs. P_{H_2S} and P_{CO} for constant P_{H_2} at $P=10$ atm.

Stable system cannot exist in shaded regions under $P=10$ atm. restriction.

APPENDIX

TABLE of CONTENTS

TOTAL PRESSURE	COMPONENT	INDEPENDANT VARIABLES	FIGURE #
1 atm.	H ₂ O	H ₂ , CO, H ₂ S	1a - 1e
	CO ₂		2a - 2e
	SO ₂		3a - 3e
	SO ₃		4a - 4e
	S ₂	H ₂ , H ₂ S	5
10 atm.	H ₂ O	H ₂ , CO, H ₂ S	6a - 6e
	CO ₂		7a - 7e
	SO ₂		8a - 8e
	SO ₃		9a - 9e
	S ₂	H ₂ , H ₂ S	10

FIGURE 1

WATER ISOBARS

TOTAL PRESSURE = 1 atm.

TEMPERATURE = 1300K

FIGURE 1a

FIGURE 1b

FIGURE 1c

FIGURE 1d

FIGURE 1e

FIGURE 2

CARBON DIOXIDE ISOBARS

TOTAL PRESSURE = 1 atm.

TEMPERATURE = 1300K

FIGURE 2a

FIGURE 2b

FIGURE 2c

FIGURE 2d.

FIGURE 2e

FIGURE 3

SULFUR DIOXIDE ISOBARS

TOTAL PRESSURE = 1 atm.

TEMPERATURE = 1300K

FIGURE 3a

FIGURE 3b

FIGURE 3c

FIGURE 3d

FIGURE 3e

FIGURE 4

SULFUR TRIOXIDE ISOBARS

TOTAL PRESSURE = 1 atm.

TEMPERATURE = 1300K

FIGURE 4a

FIGURE 4b

FIGURE 4c

FIGURE 4d

FIGURE 4e

FIGURE 5

SULFER GAS ISOBARS

TOTAL PRESSURE = 1 atm.

TEMPERATURE = 1300K

FIGURE 5

FIGURE 6

WATER ISOBARS

TOTAL PRESSURE = 10 atm.

TEMPERATURE = 1300K

FIGURE 6a

$$P_{H_2S} = 10^{-7}$$

FIGURE 6b

FIGURE 6c

FIGURE 6d

FIGURE 6e

FIGURE 7

CARBON DIOXIDE ISGBARS

TOTAL PRESSURE = 10 atm.

TEMPERATURE = 1300K

FIGURE 7a

FIGURE 7b

FIGURE 7c

FIGURE 7d

FIGURE 7e

FIGURE 8

SULFUR DIOXIDE ISGBARS

TOTAL PRESSURE = 10 atm.

TEMPERATURE = 1300K

FIGURE 8a

FIGURE 8b

FIGURE 8c

FIGURE 8d

FIGURE 8e

FIGURE 9

SULFER TRIOXIDE ISOBARS

TOTAL PRESSURE = 10 atm.

TEMPERATURE = 1300K

FIGURE 9a

FIGURE 9b

FIGURE 9c

FIGURE 9d

FIGURE 9e

FIGURE 10

SULFER GAS ISOBARS

TOTAL PRESSURE = 10 atm.

TEMPERATURE = 1300K

FIGURE 10