

ZIRCONIA SENSOR THEORY

by Thomas H. Lotze

Technical Data

The zirconia carbon sensor is really an oxygen sensor. The primary mechanism for electrical current flow in many ceramic electrolytes is ionic conduction, in this case via oxygen ions. Typical construction, basic theory, opening equations and applications are covered.

INTRODUCTION

The purpose of this paper is to describe the typical zirconia carbon sensor in general terms, and provide a thorough grounding in the mathematical equations governing it's practical use.

COMMERCIAL SENSORS

The basic elements of all commercial carbon sensors are shown in Fig. 1:

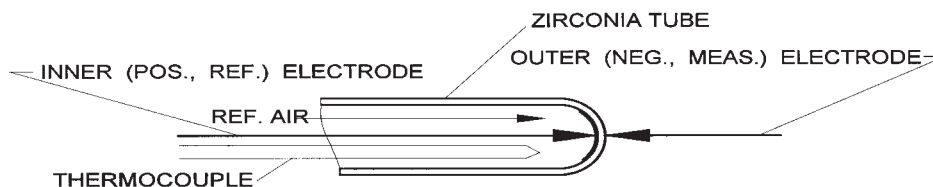


FIG.1

The tubular zirconia sensing element illustrated here is the preferred form for the **SSi Gold Probe™**. Slip cast and fired at exceptionally high temperatures to provide a dense, non-porous body, this component is not prone to develop the leakage paths that are common in probes using a cemented zirconia plug in a tubular alumina body.

The inner, reference electrode, is spring loaded to hold it in intimate contact with the inner zirconia surface. It consists of a specially formed extension of the lead wire that connects it to the probe terminal block. The inner reference components are especially resistant to the normally oxidizing reference atmosphere.

The outer, measuring electrode for most commercial probes is mechanically and electrically part of the alloy protective sheath, and the zirconia substrate is spring loaded to make intimate contact with this electrode. The **SSi** outer electrode, by virtue of premium quality, heat resistant alloy and a proprietary surface treatment, is designed to survive the rigors of the harsh furnace atmosphere.

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While probe manufacturers use a variety of materials and geometries, all properly designed sensors will display precisely the same output when at equilibrium in a furnace atmosphere. Despite this fact, many control instrument manufacturers will provide different algorithms for probes from different manufacturers. This is primarily because manufacturers have derived their algorithms using different sources for data that are not in complete agreement.

PRINCIPLES OF OPERATION

Pure zirconium oxide is a monoclinic crystalline material that transforms reversibly to a tetragonal form at 1832°F with a large change in volume. This makes it unsuitable for normal refractory use. If placed in solid solution, however, with 4% to 12% MgO, CaO or Y₂O₃, it is held in the stable isometric (cubic) form which has no transformation in the range of heat treating atmospheres. By virtue of the addition of these stabilizing oxides, oxygen ion vacancies are established in the crystal lattice. The mobility of O ions is greatly enhanced, and under certain conditions of temperature and composition, the conductivity is entirely due to oxygen ions. This condition coincides with the existence of the pure cubic crystalline phase, and is responsible for the oxygen sensing capability of stabilized zirconia which will be discussed later.

A minimum quantity of the stabilizing oxides will ensure the existence of the pure cubic crystalline phase of zirconia. When this amount is present, the zirconia is said to be fully stabilized. The commercially available zirconia for oxygen sensors will have somewhat less than this minimum amount, resulting in a “partially stabilized” electrolyte, having a better resistance to thermal fracture. The zirconia in **SSI** sensors contains about 6 mole % (10.5 weight %) of Y₂O₃. The cell construction of Fig. 1 demonstrates a characteristic typical of electrolytes having unity transference numbers for an ionic species; there is an electromotive force displayed at its terminals that can be precisely related to the corresponding molecular concentration at the two surfaces. In the case of cubic zirconia, the cell e.m.f. is given by a form of the familiar Nernst equation,

$$E_c = -0.0275 T_R \log_{10}(p_0/p_1) \text{ millivolts} \quad (1)$$

where T_R is the absolute temperature in degrees Rankine ($= ^\circ\text{F} + 459.67$), p_0 and p_1 are the oxygen concentrations at the inner and outer electrodes respectively, stated in any units (usually in atmospheres of partial pressure). Although there are applications where the oxygen present is the only critical parameter, the heat treater is concerned with two other variables he wishes to control; dew point and carbon potential. Fortunately, both parameters can be calculated directly from the oxygen measurement.

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DEW POINT This variable is utilized in control of endothermic generators that supply the basic environment to a heat treating furnace. This environment, commonly called endo or R_x gas, is created in the generator by combining air and a combustible such as natural gas or propane to provide a mixture of about 20% carbon monoxide, 40% hydrogen and 40% nitrogen.

The reversible reaction that expresses the separation into oxygen and hydrogen by water is:



By applying the principals of the law of mass action we can write an expression that accurately describes the composition of the three components in a mixture at equilibrium:

$$K_w = PH_2 \times PO_2^{1/2} / PH_2O \quad (3)$$

where K_w is the temperature dependent equilibrium constant for this reaction and PH_2 , PO_2 and PH_2O are the partial pressures of the corresponding materials, usually stated in atmospheres. This equation dictates that a change of any of the variables causes the others to change as well in order that equilibrium be sustained and the equation remains satisfied. The equilibrium constant is precisely described by the following equation (from Wagman¹):

$$\log_{10} K_w = 2.82 - 23000/T_R \quad (4)$$

The last relationship required to calculate the dew point from the measured variables is²:

$$\log_{10} PH_2O = 6.3979 - 4238.7 / (DP+460) \quad (5)$$

where the dewpoint, DP, is reported in degrees Fahrenheit. Combining equations (2) through (5), we arrive at the **SSz** algorithm for dew point:

$$DP = (4238.7 / (9.55731 - \log_{10} PH_2 + (E_C - 1267.8) / 0.05512 T_R)) - 460 \quad (6)$$

It is important to note here that there are only three specified variables in this algorithm. E_C and T_R are measured directly by the sensor which must include a close coupled thermocouple for precise calculation. The third variable, PH_2 may be measured by other analytical means. More commonly, as in the case of endothermic generators, it is assumed to be approximately 0.4 atmospheres. Because it's value will vary with the control set point, the gauge pressure at the sensor, and other factors such as peak shaving practices by the power company, it is commonly incorporated as part of a correction factor in the control instrument. This factor is set to a value that causes the computed value of dew point to agree with a manually measured value using a device such as the Alnor Dewpointer. The individual correction factor is very stable. Accordingly, heat treaters find that the frequency of manual dew point determination may be reduced significantly.

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CARBON POTENTIAL The carbon potential (%C) of a heat treating atmosphere is defined as “that value of carbon concentration achieved in a coupon of shim stock exposed to the atmosphere until it has reached equilibrium”. The time required for this equilibration will vary with shim thickness and furnace temperature. Table 1 illustrates the approximate effects.

Table 1 Time to equilibrium (minutes)

TEMP	SHIM THICKNESS		
	0.003"	0.005"	0.007"
1550	63	117	173
1600	50	91	136
1650	39	72	107
1700	32	58	86
1750	26	47	70

Corresponding to the reaction (2) for dew point calculations is the following reversible reaction encountered in the furnace atmosphere:



The mass action equilibrium equation for this reaction is:

$$K_{\text{CO}} = a_{\text{C}} \times \text{PO}_2^{1/2} / \text{PCO} \quad (8)$$

where K_{CO} is the temperature dependent equilibrium constant, PO_2 and PCO are the partial pressures of oxygen and carbon monoxide and a_{C} is the carbon activity-- a concentration term similar to the partial pressure. As before, this equilibrium constant is a function of temperature (from Wagman et al)¹:

$$\log_{10} K_{\text{CO}} = 4.5713 + 10638/T_{\text{R}} \quad (9)$$

Finally, the carbon activity a_{C} has been experimentally related to %C (from Collin et al)³:

$$a_{\text{C}} = 1.07 q (10^{3751/T_{\text{R}}})(\text{C}/(1-19.6\text{C})) \quad (10)$$

where q is a function of the alloy being treated, and is calculated as shown in Appendix A. Combining (1), (8), (9) and (10) and rearranging, we derive the **SSI** algorithm relating %C to the measured variables from the sensor:

$$\% \text{C} = 3.792 e^Z / ((324.3q / \text{PCO}) + e^Z) \quad (11)$$

where

$$Z = (E_{\text{C}} - 820.7) / 0.0239 T_{\text{R}}$$

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Note that the value q/PCO is the correction factor, (or a simple function of the correction factor) that is provided in most commercial controllers to make the calculated value of %C agree with shim stock tests.

PRACTICAL CONSIDERATIONS

Properly maintained, the zirconia sensor provides the valuable characteristic of repeatability to the heat treater. Periodic standardization using shim stock tests or dew point tests to establish the appropriate correction factors will ensure repeatability, and hence product quality assurance. Although the purist may frown at the use of such “fudge factors”, the practical considerations overwhelmingly dictate their use. It may be found that the value of the correction factor will vary, at the extremes of temperature and carbon potential. Appropriate values should be determined throughout the operating region, and applied judiciously.

APPENDIX A- CALCULATION OF ALLOY FACTOR “q”

The value of q for carbon steels is close to 1.00. When alloying elements are incorporated in the steel, it is desirable to calculate an additive factor to adjust the value of q , using the formulae in the following table (from Neumann and Person)⁴:

To correct for	add this value to q (= 1.00)
Silicon	$0.15 \%Si + 0.33 o/oSi^2$
Manganese	$0.0365 \%Mn$
Chromium	$-0.13 \%Cr + 0.0055 \%Cr^2$
Nickel	$0.03 \%Ni + 0.00365 \%Ni^2$
Molybdenum	$-0.025 \%Mo - 0.01 o/oMo^2$
Aluminum	$-0.03 \%Al - 0.02 \%Al^2$
Copper	$-0.016 \%Cu - 0.0014 \%Cu^2$
Vanadium	$-0.22 \%V + 0.01 \%V^2$

REFERENCES

1. D.D. Wagman *et al.* J. Res. Burl Standards, 1945, 34, 143.
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4. F. Neumann and B. Person, Hart.-Techn. Mitt., 1968, 23, 296.