PRECISE CONTROL OF PROTECTIVE ATMOSPHERES

Technical Data

The zirconia carbon sensor has been used for nearly three decades to control the carbon potential in many carburizing applications. More recently, the same sensor has been used very effectively in a variety of annealing and special treatment applications.

INTRODUCTION

The utility of the zirconia oxygen sensor is obvious in a carburizing environment. If the carbon monoxide concentration is known, there is a precise empirical relationship between the sensor output and the atmosphere carbon potential. When considering other thermal operations, the sensor millivolt output is preferred because it relates directly (not empirically) to the free oxygen concentration in the surrounding environment. The purpose in an annealing furnace is to achieve the ultimate metallurgical goal without suffering either oxidation or decarburization of the work pieces.

THE TECHNOLOGY

To achieve the goals of any thermal operation, it is desirable to establish an atmosphere low in oxygen. Oxygen can create oxides [rust] in a direct reaction with the work pieces. It also reacts with and removes carbon which is a critical component of the work piece. As is explained in SSi Technical Data Sheet T4401, the Gold Probe TM is an oxygen sensor capable of accuracy better than 4 % of actual value, no matter what the level, extending to extremely low concentrations. This and the defining Nernst relationship are illustrated by Fig. 1.
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EXAMPLE:

IN A FURNACE AT 1700 °F, A SENSOR READS 1150 MV (CORRESPONDING TO 1.0% O₂). WHAT IS THE OXYGEN CONCENTRATION?

SUBSTITUTING IN THE EQUATION, WE FIND THAT THE LOG OF THE FURNACE CONCENTRATION IS -18. THIS CORRESPONDS TO ONE BILLIONTH OF ONE BILLIONTH OF ONE PERCENT.

THE NERNST EQUATION:

\[
E = 0.02756 \left[ T_R \times \log_{10} \left( \frac{\% O_2 \text{ REF}}{\% O_2 \text{ FCE}} \right) \right]
\]

900 °F  1100 °F  1300 °F

1800 °F  1700 °F  1600 °F  1500 °F
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CURRENT PRACTICE

One obvious approach to minimizing oxygen is to flow an inert gas such as nitrogen into the furnace in order to drive out both air and moisture. By itself, unfortunately, this technique is inadequate. Under the best circumstances, oxygen levels below about 10 ppm are not achievable, due to air and moisture in the nitrogen, furnace insulation and the work pieces. Both oxidation and decarburization will inevitably occur. One solution is to add a “getter” to the nitrogen that will selectively react with oxygen and oxygen compounds. One control manufacturer has suggested that some of the lower paraffins such as methane (or natural gas), ethane or propane could be used. Propylene is probably the most “forgiving” hydrocarbon for this purpose, and is currently being used extensively.

A prominent annealing furnace manufacturer has suggested that any of the hydrocarbons mentioned will produce soot when added in sufficient quantities to reduce the oxygen to acceptable levels. Their alternative is a mixture of 92% nitrogen, 5% hydrogen and 3% carbon monoxide, nothing more than a nitrogen diluted endo atmosphere.

Fig. 2 shows the principle reason that the oxygen sensor is useful in control of oxygen levels in annealing furnaces.
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Fig. 2 is a plot of sensor millivolts (which are proportional to the free energy of the reaction) versus temperature. It is useful both in annealing, sintering and decarburizing. Note that if the sensor millivolts are held at a value above the reaction line, the reaction will not proceed as shown because the atmosphere is reducing, and the reaction is an oxidation reaction. For example, if steel is to be decarburized by oxidizing some of the carbon in the metal, and yet simultaneous oxidation of the metal is to be prevented, then at 1800 °F, this could be done at about 1050 mV. Below about 1375 °F, however, it will not be possible.
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to decarburize without simultaneously oxidizing the steel because the carbon line crosses the iron line at this temperature.

While it is desirable to avoid oxidation during thermal treatment, the achievement of adequate control using one of the "getter" gases requires that the sensor millivolts achieved be established at some value higher than the vee formed by the iron reaction at temperatures below 1375 ºF and the carbon reaction above that temperature. The vee will demonstrate the lower limit, but the practical level should be established by evaluation of product quality, getter cost and possible sooting. The appropriate level will be limited by such things as furnace leaks, atmosphere agitation, work porosity, time of treatment, etc.

Although there is a minimum temperature at about 600 0F below which the zirconia oxygen sensor will not reach equilibrium, most data indicate that the sensor performs reasonably well above 1000 0F, and good control can generally be established above that level.

Super Systems has extensive experience in application of the Gold Probe™ to your protective atmosphere system. A typical SSi system will include the following:

- The Gold Probe™,
- A Model 1500 mV control system which includes a JIC enclosure, an AC20 mV controller, a reference air/probe conditioning system, with isolation relays and ring back alarms,
- Accessories such as flowmeters and solenoid valves for additive control and an
- Optional programmable furnace control systems.

Please contact us if you would like some assistance.

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