Carburising Gas

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Carburising Gas Reactions

Technical Bulletin

In the gas carburising process, a low carbon bearing carrier gas is used, which is enriched with a hydrocarbon gas, such as propane or methane (natural gas), to increase and control the carbon availability of the atmosphere. The carrier gas is usually of the Endothermic gas type produced from a sub stoichiometric mixture of a hydrocarbon and air at elevated temperature in the presence of a catalyst. The production of Endothermic gas is usually carried out in an external gas generator.

Alternatively, a nitrogen – Methanol mixture, injected into the furnace can be used to produce a synthetic Endothermic gas. Dependent upon the type of hydrocarbon used and the mixture ratio, the typical composition of the carrier gas is;

15-25% CO, 35-45% H_2, Balance N_2,
plus small quantities of CO_2, H_20, CH_4

The gases CO and CH_4 are carburising, whilst H_2, H_2O and CO_2 are decarburising. In order to control the carbon availability of the atmosphere – the CARBON POTENTIAL, a hydrocarbon gas is used to enrich the carrier gas, by reducing the H_2O (DEWPOINT) according to the reaction:

$CH_4 + H_2O \longrightarrow CO + 3\,H_2$ . . . . (2)

And by reducing the CO_2 according to the reaction:

$CH_4 + CO_2 \longrightarrow 2\,CO + 2\,H_2$ . . . . (3)

as well as allowing the following carburising reaction to take place:

$CH_4 \longrightarrow C_{Fe} + 2\,H_2$ . . . . (4)

in addition to reaction (4) the other main carburising reactions in a CO – CO_2 – H_2 – H_2O – CH_4 atmosphere are:

$CO + H_2 \longleftrightarrow C_{Fe} + H_2O$ . . . . (5)

$2\,CO \longleftrightarrow C_{Fe} + CO_2$ . . . . (6)

Reactions (5) and (6) are considered the main equilibrium reactions for the basic method of carbon transfer into the steel surface. The assumption is that the carburising is taking place as a direct result of the CO content in the atmosphere. However, the Oxygen probe has no way of measuring the %CO. A fixed value has to be introduced into the Carbon potential controller in the form of a Process Factor or CO factor (see below). Furthermore, equilibrium conditions do not exist in a furnace until several hours have passed – the actual %CO will be considerably lower than expected.

It has been shown that reaction (5) is 10-100 times faster than reactions (4) and (6), and it is therefore this that is rate determining.

In most systems, the addition of a hydrocarbon gas such as methane is used for the control of carbon potential. If all the methane was “cracked” using reactions (2) and (3), the atmosphere would remain in equilibrium and predicting carbon potential would be straight-forward. Unfortunately, these reactions occur at very slow rates and only near catalytic surfaces. They are never close to equilibrium.

In an atmosphere with a significant level of free methane, some carburising will be taking place according to reaction (4), but increasing levels unreacted methane will result in the dilution of the %CO. Without measuring and including the effects of free methane in the carbon calculation, the real potential of the atmosphere is not known.

(In the gas reactions described in this Technical Bulletin C_{Fe} is the available carbon, from the atmosphere, for diffusion into the steel surface.)

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Calculation of Carbon Potential using Oxygen probes

The equilibrium composition of the gases is determined by the “water – gas” reaction:

$$H_2 + CO_2 \longleftrightarrow CO + H_2O \tag{7}$$

Combining reactions (5) and (7):

$$2\,CO \longleftrightarrow C_{Fe} + CO_2 \tag{6}$$

By using the thermochemical equilibrium constant for the above reaction the carbon activity of the atmosphere can be calculated:

$$ac = \frac{p\,CO_2}{p\,CO^2}\quad K6 \tag{8}$$

Since K6 is temperature dependent only, it can be seen that the carbon activity can be calculatred from the CO and CO_2 and since the CO is relatively constant, the CO_2 alone can be used.

We have already seen that the Oxyen probe measures the small amount of oxygen in equilibrium with the CO and CO_2 which is according to the following reaction,

$$2\,CO + O_2 \longleftrightarrow 2\,CO_2 \tag{9}$$

Combining reactions (6) and (9), and using the equilibrium constant to calculate carbon activity,

$$ac = \frac{p\,CO}{p\,O_2^{\,0.5}}\quad K10 \tag{10}$$

Hence the oxygen probe can be used to determine the carbon activity of the atmosphere, and the carbon potential can be shown to be a function of carbon activity (ac), temperature and steel composition (q).

Therefore:

$$Cp = f\,(T, V, CO, q) \tag{11}$$

Where

Cp is the Carbon potential (%)	T is the Temperature (K)
V is the Probe voltage (v)	CO is the Carbon Monoxide (%)
q is the Steel alloy factor	

The dependence of carbon potential on the steel composition, can be explained by the fact that in the presence of alloying elements the effective carbon potential of the atmosphere is increased be elements which form more stable carbides than iron, i.e. Cr, Mo, whereas less strong formers, i.e. Ni, Si, decrease the effective carbon potential.

The complex mathematical calculations necessary to determine the Carbon potential of the atmosphere are built into most controllers. Probe voltage (mV) and temperature are input directly into the instrument, whilst the CO and alloy factors are combined as a constant for a given set of load conditions known as the “PROCESS FACTOR” (PF), or CO Factor, where:

$$29\,(PF) + 400 = \frac{945.7}{CO}\,q \tag{12}$$

From the above equation it can be calculated that for a plain carbon steel (q=1) processed in a methane generated Endothermic gas (CO = 20) the Process Factor will be 147. However, practical experience has shown that the process factor, under these conditions can vary between 150 and 250, dependent upon unique furnace conditions. An important aspect when determining the process factor is the Cycle time, since it has been shown that the steel surface does not reach equilibrium with the gas atmosphere until 20 hours have elapsed. Therefore, if the carbon potential is controlled at 0.8%, the steel surface will have only reached 0.7% after 4 hours.

For non-equilibrium atmospheres or when the CO may be constant during a cycle, it is possible to input a CO value from an infra red analyser via the auxiliary input.

For absolute carbon control accuracy the Process Factor can be continuously updated based on the carbon potential calculated from a 3 gas (CO, CO_2, CH_4) ULTRACARB 1000 INFRA RED SYSTEM. This system gives the absolute accuracy of 3 gas carbon calculation with the speed of response of oxygen probe control.

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