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Effect of H_2O Content in Air on the Carburizing Behavior of Charcoal Gas

Y.-C. Chen

Conventionally, charcoal gas is produced by reacting air with hot charcoal. The constituents of such charcoal gas are N_2, CO, and CO_2. Because no H_2 exists in this kind of charcoal gas, its carburizing rate to steels is relatively slow, compared with atmospheres containing CO and H_2. A simple, but effective, method to raise the carburizing rate of the charcoal gas has been found through this study; that is, the air used for generating charcoal gas is humidified with some water vapor before passing through the hot charcoal layer. In this way, the carbon potential and carburizing rate of the charcoal gas can be raised markedly due to the formation of H_2. For example, when the air is humidified with 7.30% H_2O, the carbon potential increases by about three times, and the carburizing rate increases by about four times, compared with the charcoal gas generated from dried air and charcoal.

1. Introduction

Charcoal gas, one of the most popular controlled atmospheres, is generally produced by passing air through a hot charcoal layer. The constituents of the charcoal gas are N_2, CO, and minor amounts of CO_2. In industry, charcoal gas is used as a furnace atmosphere for the bright annealing or carburization of steels.[1]

The carburizing capability of a furnace atmosphere is closely correlated with its chemical composition. According to previous investigations,[2,3] the carburizing rate of an N_2 + CO + H_2 mixture is much more rapid than that of an N_2 + CO mixture. The carburizing rate of the conventional charcoal gas is sluggish because of the absence of H_2. If charcoal gas is generated by reacting an air + H_2O mixture with hot charcoal, then the carburizing rate can be expected to be increased, because H_2 is formed in addition to N_2 and CO. In this study, to understand how the H_2O contents of an air + H_2O mixture influence the carburizing behavior of this modified charcoal gas, a water vapor regulator was used to add some specific amounts of H_2O to air. Then, the air + H_2O mixture was introduced into a charcoal furnace to generate charcoal gas, and steel samples were heated in such charcoal gas. Based on the equilibrium carbon content, weight change, and hardness distribution in the surface layer of the heated samples, the carburizing behavior of the modified charcoal gas was studied and compared with that of the conventional charcoal gas.

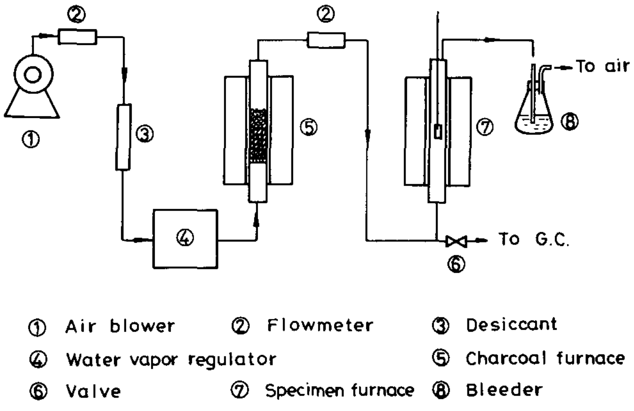

Fig. 1 Experimental apparatus.

2. Experimental Method

To understand the influence of generating conditions of a charcoal gas atmosphere on its carburizing behavior to steels,

Table 1 Experimental Conditions

	Preparation of charcoal gas(a)		Heating of steel		
No.	H_2O content in air, %	Charcoal temperature, °C	Specimen	Temperature, °C	Time, min
1......	7.30	1000	SPCE	900	10 to ~70
	7.30	1000	SPCE	950	10 to ~70
2......	7.30	900	SPCE	900	10 to ~70
	7.30	950	SPCE	900	10 to ~70
	7.30	1000	SPCE	900	10 to ~70
	7.30	1050	SPCE	900	10 to ~70
3......	4.18	900	SPCE	900	10 to ~60
	7.30	900	SPCE	900	10 to ~60
	12.1	900	SPCE	900	10 to ~60
4......	...	1050	SPCE	900	10 to ~60
	4.18	1050	SPCE	900	10 to ~60
	7.30	1050	SPCE	900	10 to ~60
	12.1	1050	SPCE	900	10 to ~60
	...	1050	SPCE	950	10 to ~60
	4.18	1050	SPCE	950	10 to ~60
	7.30	1050	SPCE	950	10 to ~60
	12.1	1050	SPCE	950	10 to ~60
5......	...	1050	Pure iron	900	60
	4.18	1050	Pure iron	900	60
	7.30	1050	Pure iron	900	60
	12.1	1050	Pure iron	900	60

(a) Total flow rate of charcoal gas is about 115 cm^3/min.

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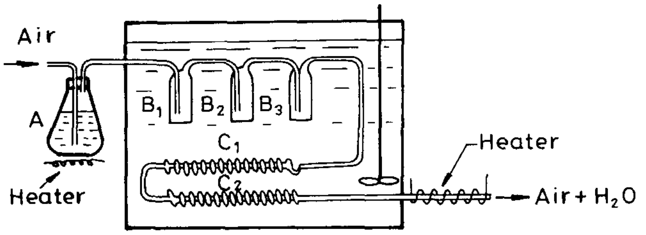

Fig. 2 Details of water vapor regulator.

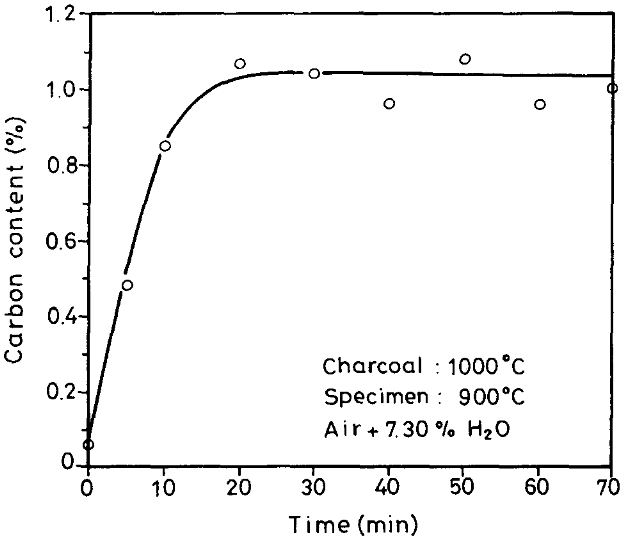

Fig. 3 Relationship between time and carbon content for SPCE heated at 900 °C under the charcoal gas atmosphere generated by reacting an air + H_2O mixture with hot charcoal.

experiments were carried out by using the apparatus shown in Fig. 1, according to the conditions described in Table 1. The air supplied from a blower was passed through a water vapor regulator to be humidified with a specific amount of H_2O. Then, the air + H_2O mixture was introduced into a charcoal furnace to react with hot charcoal and generate charcoal gas. The charcoal gas was led to a specimen furnace, within which steel samples were heated.

The details of the water vapor regulator are shown in Fig. 2. Air was first introduced into the warm water in flask A, which was kept at about 60 °C, and then passed through washing bottles, B_1, B_2, and B_2 and screw-shaped tubes C_1 and C_2 within a water bath of uniform temperature. Because the temperature of the water bath was lower than that of flask A, the supersaturated water vapor in air would condense in washing bottles or screw-shaped tubes. Thus, the outlet air from the water bath contained the saturated water vapor corresponding to the temperature of the water bath. For example, the H_2O contents in air + H_2O mixtures are 4.18, 7.30, and 12.1%, respectively, if the temperature of the water bath is controlled at 30, 40, and 50 °C. To avoid the condensation of water vapor from air + H_2O mixture during transport, the connecting pipe from the water bath to the charcoal furnace was heated with a resistance wire to ensure that the expected amount of H_2O could be completely transported into the charcoal furnace.

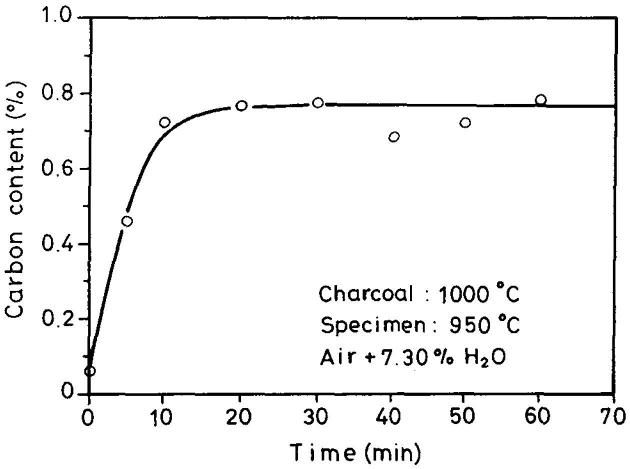

Fig. 4 Relationship between time and carbon content for SPCE heated at 950 °C under the charcoal gas atmosphere generated by reacting air + H_2O mixture with hot charcoal.

Both the charcoal furnace and the specimen furnace were resistance heated furnaces. A ceramic tube, with an inner diameter of 30 mm and a length of 1000 mm, was placed at the center of the charcoal furnace. Inside the tube, pretreated charcoal of 8-16 mesh,[4] with a depth of 200 mm, was filled at the middle part of the charcoal furnace, where the temperature distribution was uniform. The specimen furnace had the same size as the charcoal furnace. A ceramic tube, 1000 mm long by 30 mm ID, was installed at the center of the specimen furnace as a heating chamber for the steel samples. All specimens were suspended at the middle of the furnace for heating.

Steel samples used include two types. One type was an extremely low carbon steel foil, with a thickness of 0.05 mm (JIS-SPCE: 0.057% C, 0.008% Si, 0.28% Mn, 0.023% P, 0.022% S). The specimen had dimensions of 20 by 10 by 0.05 mm. This type of specimen was used to test the equilibrium carbon content of steel (or carbon potential of the charcoal gas) while it was heated in the charcoal gas. Disk-shaped pure iron specimens (0.015% C, 0.005% Si, 0.068% Mn, 0.010% P, 0.008% S) with a thickness of 2 mm and a diameter of 15 mm were also used. This type of specimen was used to test the amount of carbon carburized per unit area (or carburizing rate) and the hardness distribution in the surface layer of the steel after carburizing and quenching.

The composition of the charcoal gas was analyzed by means of a gas chromatograph (Shimazu GC-8A). The constituent gases were separated by a molecular sieve column, with a He carrier at 30 cm^3/min.

3. Results

3.1 *Influence of Steel Temperature on the Carbon Potential of the Modified Charcoal Gas*

To understand the effect of steel temperature on the carbon potential of the charcoal gas obtained by reacting an air + H_2O mixture with hot charcoal, experiments were performed according to Condition 1 in Table 1; that is, SPCE samples were

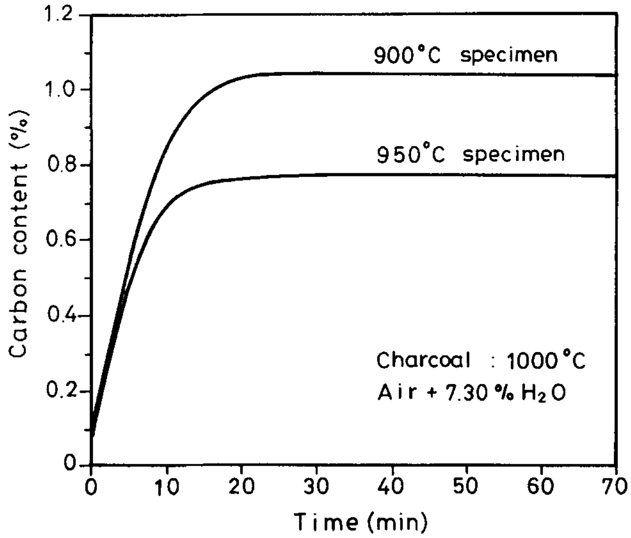

Fig. 5 Comparison of the variations of carbon content with time for SPCE heated at 900 and 950 °C, respectively, under the charcoal gas atmosphere.

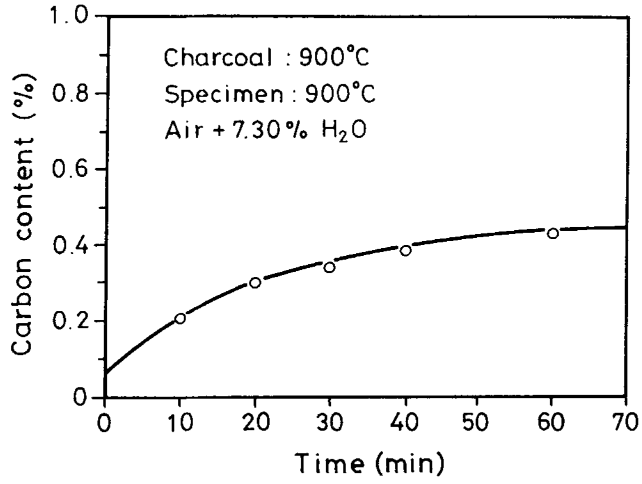

Fig. 6 Relationship between time and carbon content for SPCE heated in the charcoal gas generated at a charcoal temperature of 900 °C.

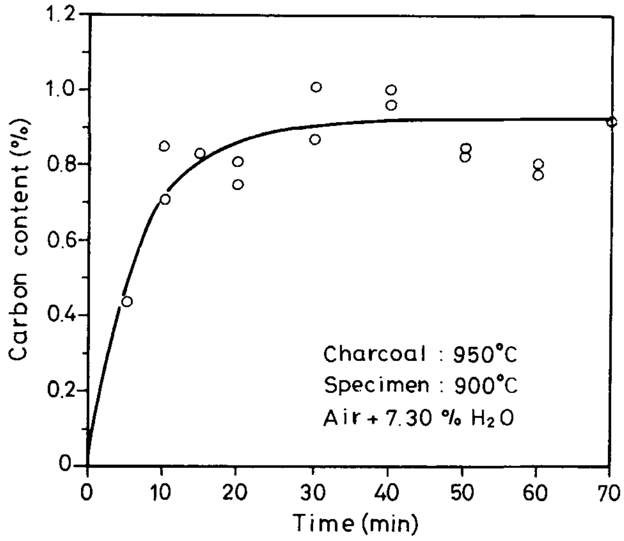

Fig. 7 Relationship between time and carbon content for SPCE heated in the charcoal gas generated at a charcoal temperature of 950 °C.

heated at 900 or 950 °C under the charcoal gas atmosphere generated by passing the air + 7.30% H_2O mixture through a hot charcoal layer at 1000 °C. The relationships between the carbon content of the specimens and heating time are shown in Fig. 3 and 4. From Fig. 3, it is apparent that while heating at 900 °C in the charcoal gas, the carbon content of SPCE increases with increasing heating time. However, the carbon content achieves a steady level in about 20 min and does not change significantly thereafter. This steady carbon level can be regarded as the carbon potential of the charcoal gas. Figure 4 provides the results for SPCE heated at 950 °C. For the convenience of comparison, the curves in Fig. 3 and 4 were plotted together in Fig. 5. From the two curves in Fig. 5, it is apparent that when the charcoal temperature is 1000 °C, the carbon potential of the charcoal gas is 1.05% and 0.77%, respectively, for specimens heated at 900 and 950 °C. In other words, if the temperature of charcoal is kept constant, the higher the heating temperature of specimens, the lower carbon potential of the charcoal gas. This characteristic is similar to that of the conventional charcoal gas.

3.2 *Influence of Charcoal Temperature on the Carbon Potential of the Modified Charcoal Gas*

To understand the effect of charcoal temperature on the carbon potential of the charcoal gas obtained by reacting an air + H_2O mixture with hot charcoal, experiments were conducted according to condition 2 in Table 1; that is, an air + 7.30% H_2O mixture was passed through charcoal layers at 900, 950, 1000, and 1050 °C, respectively, to generate charcoal gas, and SPCE samples were heated at 900 °C in the charcoal gas generated. The relationships between the carbon content of the heated specimens and heating time are shown in Fig. 3, 6, 7, and 8. For the convenience of comparison, the curves in these figures were plotted together in Fig. 9. By comparing the slopes of these curves, it is apparent that the higher the temperature of the charcoal, the steeper the slope of the carburizing curve (namely, the higher the carburizing rate). In addition, the carbon level denoted by the horizontal part of each curve represents the carbon potential of the corresponding charcoal gas. From Fig. 9, it is known that for the charcoal temperature of 900, 950, 1000, and 1050 °C, the carbon potential of the charcoal gas is 0.45, 0.93, 1.05, and 1.18%, respectively. In other words, when the heating temperature of the steel remains constant, both the carburizing rate and the carbon potential of the modified charcoal gas increase with increasing charcoal temperature. This feature is consistent with the conventional charcoal gas.

3.3 *Influence of H_2O Content in Air on the Carburizing Behavior of Charcoal Gas*

To understand the effect of H_2O content in air + H_2O mixtures on the carbon potential and carburizing rate of charcoal

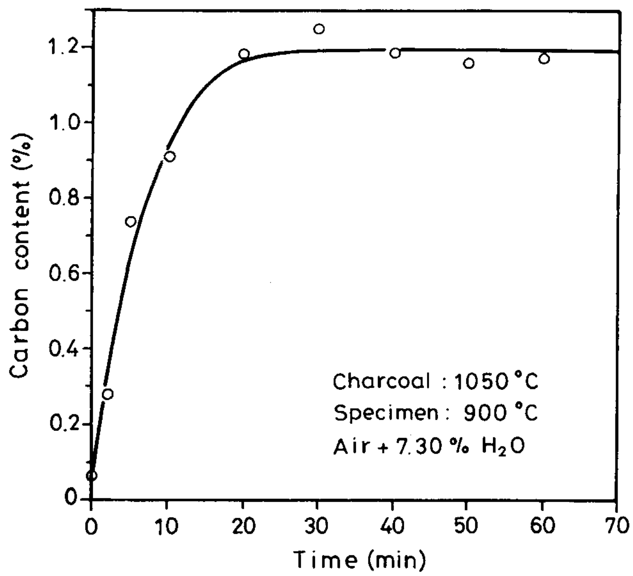

Fig. 8 Relationship between time and carbon content for SPCE heated in the charcoal gas generated at a charcoal temperature of 1050 °C.

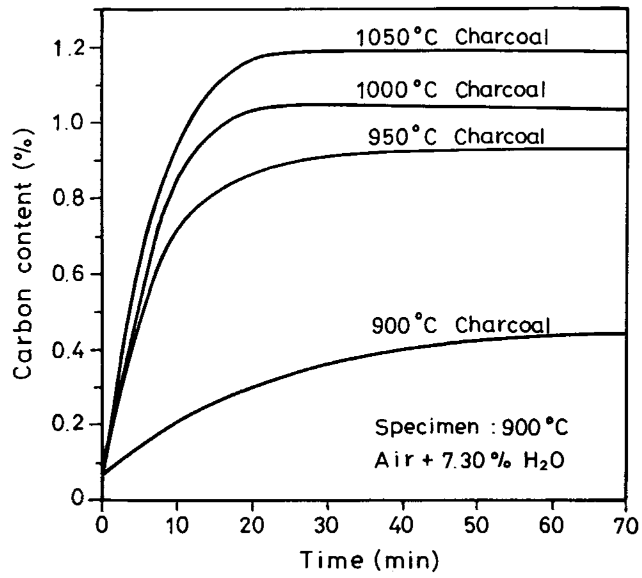

Fig. 9 Comparison of the variations of carbon content with the time for SPCE heated in the charcoal gas generated at various charcoal temperatures.

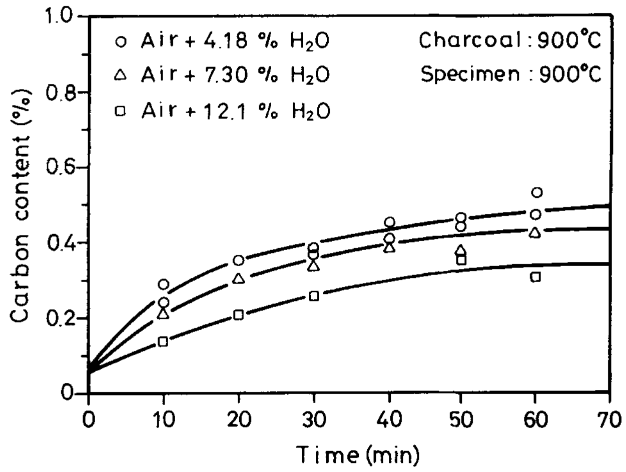

Fig. 10 Relationship between time and carbon content for SPCE heated at 900 °C in the charcoal gas generated by reacting 900 °C charcoal with air + H_2O mixtures containing various amounts of H_2O.

gas, experiments were performed according to condition 3 in Table 1. Air + H_2O mixtures with various H_2O contents (4.18, 7.30, and 12.1%) were passed through a charcoal layer at 900 °C to generate charcoal gas, and SPCE samples were heated in the charcoal gas obtained. The relationship between heating time and the carbon content of the heated specimens is shown in Fig. 10. By comparing the three curves in this diagram, it is known that the curve corresponding to the mixture of air + 4.18% H_2O is uppermost, then the curve for the air + 7.30% H_2O mixture, and the curve for the air + 12.1% H_2O mixture is located lowermost. This indicates that, if the charcoal gas is generated by reacting an air + H_2O mixture with 900 °C charcoal, the higher the H_2O content in the mixture, the weaker the carburizing ability of the charcoal gas obtained.

To see if a similar result could be obtained at a higher charcoal temperature, experiments were performed according to condition 4 in Table 1. Charcoal gases were generated by reacting 1050 °C charcoal with dried air and humidified air containing 4.18, 7.30, and 12.1% water vapor, and SPCE samples were heated under these charcoal gas atmospheres. The relationships between heating time and the carbon content of the heated specimens are shown in Fig. 11. Figure 11(a) shows results for specimens heated at 900 °C. From this diagram, it can be seen that the carburizing rate of the charcoal gas generated from dried air is rather slow and its carbon potential is relatively low (about 0.32%) as well. However, both the carburizing rate and the carbon potential can be raised markedly if some water vapor is added to the air for generating the charcoal gas. Moreover, the more water vapor added, the higher the carbon potential and carburizing rate of the charcoal gas. For example, the carbon potential is 1.07% if the added water vapor is 4.18%, and the carbon potential is 1.18% if the added water vapor is 7.30%. This indicates that, if charcoal gas was produced by reacting air + H_2O mixtures with hot charcoal at 1050 °C, the higher the H_2O content in the mixture, the stronger the carburizing capability of the charcoal gas at 900 °C. To understand if this phenomenon still exists when the heating temperature of the specimens changes, the experiment was repeated at a higher temperature, namely 950 °C. These results are shown in Fig. 11(b). This diagram is similar to Fig. 11(a); that is, the more the H_2O content in the air + H_2O mixture, the stronger the carburizing capability of the charcoal gas generated. The results shown in Fig. 11 are contrary to those of Fig. 10. The inconsistency between these two figures will be explained in the discussion section of this article. On the other hand, by comparing the corresponding curves in Fig. 11(a) and 11(b), it is known that if both the H_2O contents in air + H_2O mixtures and the charcoal temperature remain unchanged, the higher the heating temperature

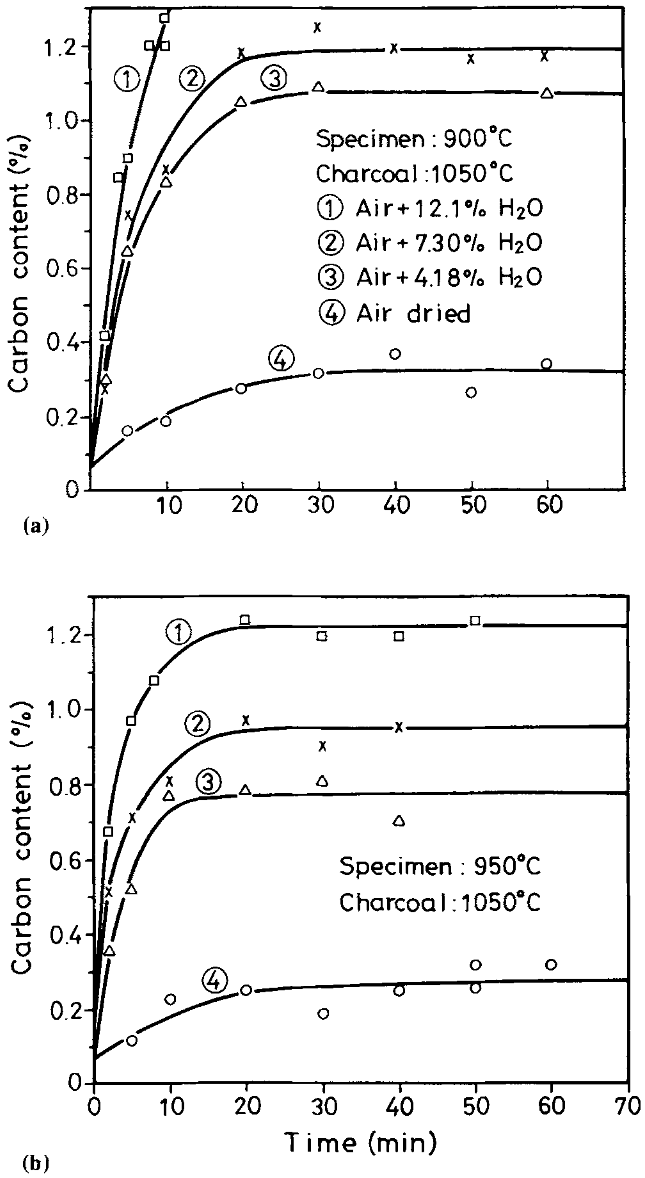

Fig. 11 Relationships between time and carbon content for SPCE heated at (a) 900 °C and (b) 950 °C in the charcoal gas generated by reacting 1050 °C charcoal with air + H_2O mixtures containing various amounts of H_2O.

of the specimens, the lower the carbon potential of the charcoal gas. This result is consistent with that of Fig. 5.

As stated above, Fig. 11 shows that, when the charcoal temperature is high enough (say 1050 °C), the carburizing rate for thin foil of SPCE heated in the charcoal gas increases with increasing H_2O content in the air + H_2O mixtures. However, the steel commonly used for carburization usually possesses a thickness much larger. To determine if the above characteristic exists for steel with greater thicknesses, experiments were carried out according to condition 5 in Table 1; that is, charcoal gas was generated by passing the dried air and the humid air with water vapor contents of 4.18, 7.30, and 12.1% through a hot charcoal layer at 1050 °C, and disk-shaped samples of pure iron, with a thickness of 2 mm, were carburized at 900 °C for 1 hr under the charcoal gas atmosphere. The relationship between the amount of carbon diffused into the pure iron per unit surface area and the H_2O content in air + H_2O mixtures is shown in Fig. 12. The carburizing capability of the charcoal gas made from the dried air was relatively low (the weight gain of specimens was about 0.25 mg/cm^2); however, when small amounts of H_2O were added to the air, the carburizing capability of the charcoal gas was raised markedly. As shown in Fig. 12, when the H_2O contents in air + H_2O mixtures are 4.18, 7.30, and 12.1%, the amounts of diffused carbon achieve 1.03, 1.24, and 1.40 mg/cm^2, respectively. This indicates that small amounts of water vapor in the air can effectively raise the carburizing rate of the charcoal gas generated.

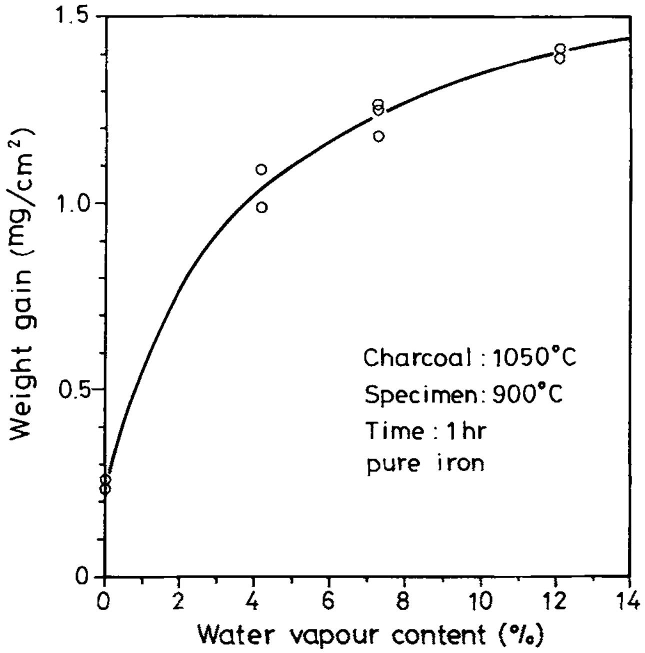

Fig. 12 Relationship between the H_2O content of an air + H_2O mixture and weight gain per unit area due to carburization for pure iron heated at 900 °C for 1 hr in the charcoal gas generated by reacting air + H_2O mixture with 1050 °C charcoal.

3.4 *Influence of H_2O Content in Air on the Hardness Distribution of Steels*

To understand the effect of H_2O content in air + H_2O mixtures on the hardness distribution of steels, pure iron samples were carburized according to condition 5 in Table 1 and followed by water quenching. The hardness distributions in the surface layers of the samples were measured and are shown in Fig. 13. Curve 4 indicates the hardness distribution of the samples carburized in the charcoal gas made from dried air, and curves 1, 2, and 3 represent the hardness distribution of the samples carburized in the charcoal gas made from the humid air with water vapor contents of 12.1, 7.30, and 4.18%, respectively. From the curves in Fig. 13, it is known that when pure

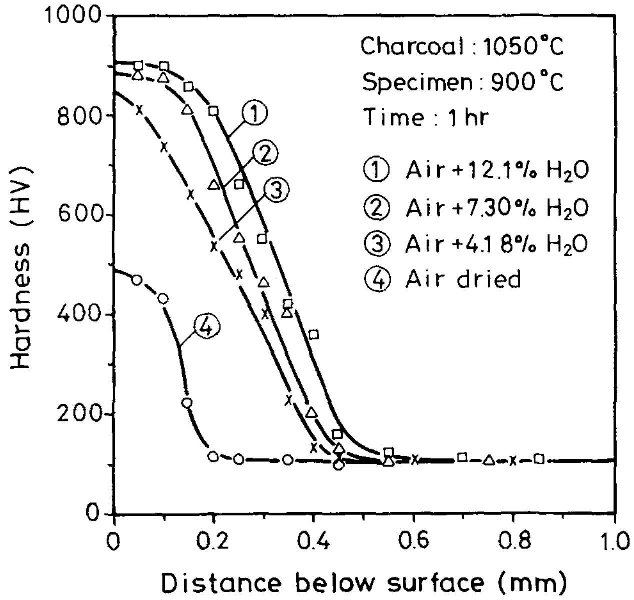

Fig. 13 Comparison of hardness distributions in the surface layer for pure iron carbonized at 900 °C for 1 hr in the charcoal gas generated from air and H_2O mixtures with various H_2O contents and followed by a water quench.

iron was carburized in the charcoal gas made from dried air, the hardness at the surface of the sample was relatively low (less than 500 HV), and the thickness of the hardened case was relatively small (about 0.2 mm). However, when pure iron was carburized in the charcoal gas made from air + H_2O mixtures, both the surface hardness and the hardened depth of the sample were markedly increased. As shown in Fig. 13, the surface hardness can attain to 850 to ~900 HV, and the thickness of the hardened layer can reach 0.5 mm. Based on the above results, it can be concluded that for steels commonly carburized in charcoal gas, the carburizing results can be greatly improved by adding small amounts of water vapor into air during the generation of charcoal gas.

4. Discussion

4.1 *Composition of Charcoal Gas*

Dried air can be regarded as a $N_2 + O_2$ mixture, whereas humid air can be regarded as a $N_2 + O_2 + H_2O$ mixture. Among these constituents, N_2 is inert to hot charcoal, whereas O_2 reacts with hot charcoal to form $CO + CO_2$ mixtures. H_2O reacts with hot charcoal to form $CO + H_2 + CO_2 + H_2O + CH_4$ mixtures. Therefore, the charcoal gas generated by reacting an air + H_2O mixture with hot charcoal is essentially a $N_2 + CO + H_2 + CO_2 + H_2O + CH_4$ mixture, which has a definite equilibrium composition at a given temperature. Consider the case that 1 mol of air (or $0.79\ N_2 + 0.21\ O_2$), mixed with m mol of H_2O, reacts with hot charcoal to form charcoal gas. Assume that the mole numbers of N_2, CO, H_2, CO_2, H_2O, and CH_4 in the charcoal gas are x_1, x_2, x_3, x_4, x_5, and x_6, respectively, after the equilibrium is attained. In other words, the reaction is as follows:

$$(0.79\,N_2 + 0.21\,O_2) + m\,H_2O + y\,C_{(s)} \rightarrow x_1\,N_2 + x_2\,CO + x_3\,H_2 + x_4\,CO_2 + x_5\,H_2O + x_6\,CH_4 \qquad [1]$$

where $C_{(s)}$ stands for the carbon in the charcoal. Reaction 1 has the following relationships for conservation of matter:

Conservation of N atoms: $1.58 = 2x_1$
Conservation of H atoms: $2m = 2x_3 + 2x_5 + 4x_6$
Conservation of O atoms: $0.42 + m = x_2 + 2x_4 + x_5$
Conservation of C atoms: $y = x_2 + x_4 + x_6$ [I]

and the following chemical reactions between the constituent gases and charcoal will reach equilibrium:

$$CO_2 + C_{(s)} \leftrightarrow 2\,CO \qquad [2]$$

$$H_2O + C_{(s)} \leftrightarrow CO + H_2 \qquad [3]$$

$$2H_2 + C_{(s)} \leftrightarrow CH_4 \qquad [4]$$

Therefore, the relationships between partial pressures of the constituent gases and their mole numbers at 1 atm are as follows:

$$K_2 = \frac{P^2_{CO}}{P_{CO_2}} = \frac{(x_2/n_t)^2}{x_4/n_t} = \frac{x_2^2}{x_4\,n_t}$$

$$K_3 = \frac{P_{CO}\,P_{H_2}}{P_{H_2O}} = \frac{(x_2/n_t)(x_3/n_t)}{x_5/n_t} = \frac{x_2\,x_3}{x_5\,n_t}$$

$$K_4 = \frac{P_{CH_4}}{P^2_{H_2}} = \frac{x_6/n_t}{(x_3/n_t)^2} = \frac{x_6\,n_t}{x_3^2} \qquad [II]$$

where K_2, K_3, and K_4 are equilibrium constants for Reactions 2, 3, and 4, respectively. The value of each constant depends on the temperature.[5] n_t represents the total mole number of the constituent gases, namely $n_t = x_1 + x_2 + x_3 + x_4 + x_5 + x_6$. The volume fraction of H_2O in air + H_2O mixture is equivalent to $m/(1 + m)$. If the volume fraction of H_2O is given (namely m is given), and the charcoal temperature is given (namely K_2, K_3, and K_4 are given), then the seven unknowns $x_1, x_2, x_3, x_4, x_5, x_6$, and y can be determined by solving simultaneously the four matter conservation equations in equation group I and the three chemical equilibrium equations in equation group II. In other words, the volume percentages of each constituent gas in the charcoal gas can be obtained.

By using the above method, the equilibrium compositions of the charcoal gas generated by reacting air + 12.1% H_2O mixtures with hot charcoal at 850, 900, and 950 °C were computed and are shown as calculated values in Table 2. From Table 2, it is apparent that the primary reactive constituents for such charcoal gases are CO and H_2, and the contents of CO_2, H_2O, and CH_4 are all pretty low. Besides, the contents of CO and H_2 increase with increasing charcoal temperature, and the contents of CO_2, H_2O, and CH_4 all decrease with increasing charcoal temperature. However, the contents of CO and H_2 are less sen-

Table 2 Comparison between Theoretical and Measured Compositions of the Charcoal Gas Generated by Reacting an Air + 12.1% H_2O Mixture with Hot Charcoal

Charcoal temperature, °C	Composition of the charcoal gas											
	N_2, %		CO, %		H_2, %		CO_2, %		H_2O, %		CH_4, %	
	Calculated	Measured	Calculated	Measured	Calculated	Measured	Calculated	Measured	Calculated	Measured	Calculated	Measured
850	bal	bal	35.96	28.04	9.10	6.00	0.887	2.53	0.240	(a)	0.019	(a)
900	bal	bal	36.77	34.11	9.16	7.50	0.427	0.99	0.132	(a)	0.013	(a)
950	bal	bal	37.15	34.15	9.20	7.75	0.214	0.44	0.076	(a)	0.009	(a)

(a) Too lean to be precisely measured by the gas analyzer.

sitive to the charcoal temperature, whereas the contents of CO_2, H_2O, and CH_4 are more sensitive to the charcoal temperature.

The measured data in Table 2 represent the practically measured compositions of the charcoal gas. The measured data for H_2O and CH_4 are absent from the table because the amounts of H_2O and CH_4 are too low to be precisely detected by the gas analyzer. By comparing the amounts of CO, H_2, and CO_2 at different temperatures, it is known that the varying tendency with temperature for each constituent gas is consistent with that of equilibrium composition. Furthermore, by comparing the equilibrium composition with the measured composition, it is known that the higher the charcoal temperature, the closer the measured composition approaches the equilibrium composition. When the charcoal temperature is relatively low (say 850 °C), the practical content of CO in the charcoal gas is significantly less than the equilibrium content of CO, and the practical content of CO_2 is significantly more than the equilibrium content of CO_2.

4.2 *Carbon Potential of Charcoal Gas*

As stated previously, the charcoal gas generated by reacting an air + H_2O mixture containing a given amount of H_2O with hot charcoal at a given temperature will possess a definite equilibrium composition. Now let's elucidate the relationship between such equilibrium charcoal gas and steels. Assuming that the equilibrium volume fractions of N_2, CO, H_2, CO_2, H_2O, and CH_4 in the charcoal gas generated by reacting an air + H_2O mixture with hot charcoal at T_1 under 1 atm are a_1, a_2, a_3, a_4, a_5, and a_6, respectively, then the mole numbers of N_2, CO, H_2, CO_2, H_2O, and CH_4 in 1 mol of such charcoal gas are a_1, a_2, a_3, a_4, a_5, and a_6, respectively. When the temperature changes, the relative contents for the constituent gases will change and achieve another equilibrium state. Provided that the mole numbers of N_2, CO, H_2, CO_2, H_2O, and CH_4 in the charcoal gas are x_1, x_2, x_3, x_4, x_5, and x_6, respectively, after reaching equilibrium at T_2 and 1 atm, then the total mole number n_t is $n_t = x_1 + x_2 + x_3 + x_4 + x_5 + x_6$ and the partial pressures for the constituent gases are $P_{N_2} = x_1/n_t$, $P_{CO} = x_2/n_t$, $P_{H_2} = x_3/n_t$, $P_{CO_2} = x_4/n_t$, $P_{H_2O} = x_5/n_t$, and $P_{CH_4} = x_6/n_t$, respectively. If steels with a carbon content of C_E can remain at equilibrium with the charcoal gas at T_2; that is, neither carburization nor decarburization occurs, then the carbon potential of the charcoal gas is C_E. The following reactions between the charcoal gas and steels will reach equilibrium:

$$CO_2 + [C] \leftrightarrow 2CO \qquad [5]$$

$$H_2O + [C] \leftrightarrow CO + H_2O \qquad [6]$$

$$2H_2 + [C] \leftrightarrow CH_4 \qquad [7]$$

where [C] stands for the carbon dissolved in austenite. Therefore, the relationships between the carbon content of steels and the partial pressures or mole numbers of the constituent gases are as follows:

$$K_2 = \frac{P_{CO}^2}{P_{CO_2}\,\alpha} = \frac{(x_2/n_t)^2}{(x_4/n_t)\,\alpha} = \frac{x_2^2}{x_4\,n_t\,\alpha}$$

$$K_3 = \frac{P_{CO}\,P_{H_2}}{P_{H_2O}\,\alpha} = \frac{(x_2/n_t)(x_3/n_t)}{(x_5/n_t)\,\alpha} = \frac{x_2 x_3}{x_5\,n_t\,\alpha}$$

$$K_4 = \frac{P_{CH_4}}{P_{H_2}^2} = \frac{x_6/n_t}{(x_3/n_t)^2\,\alpha} = \frac{x_6 n_t}{x_3^2\,\alpha} \qquad [III]$$

where K_2, K_3, and K_4 are equilibrium constants of reactions 5, 6, and 7, respectively, and α represents the saturation degree for the carbon in austenite. In other words, $\alpha = C_E / C_S$, where C_S stands for the saturated carbon content of austenite at T_2. The value of C_S can be found from the Fe-Fe_3C equilibrium diagram.[6] Because the numbers of N, O, H, and C atoms in the charcoal gas remain unchanged at temperatures T_1 and T_2, the following relationships for matter conservation exist:

N atom conservation: $2a_1 = 2x_1$

O atom conservation: $a_2 + 2a_4 + a_5 = x_2 + 2x_4 + x_5$

H atom conservation: $2a_3 + 2a_5 + 4a_6 = 2x_3 + 2x_5 + 4x_6$

C atom conservation: $a_2 + a_4 + a_6 = x_2 + x_4 + x_6$ [IV]

The seven unknowns—$x_1, x_2, x_3, x_4, x_5, x_6$, and α—can be determined by solving simultaneously the three equations for chemical equilibrium in equation group III and the four equations for matter conservation in equation group IV. In other words, the equilibrium composition of the charcoal gas at temperature T_2 and the equilibrium carbon content of the steel heated in the charcoal gas can be solved; that is, the carbon potential of the charcoal gas at T_2 can be determined.

According to the above method, the theoretical carbon potentials at various temperatures for the charcoal gas generated by reacting air + H_2O mixtures with hot charcoal of 900 and

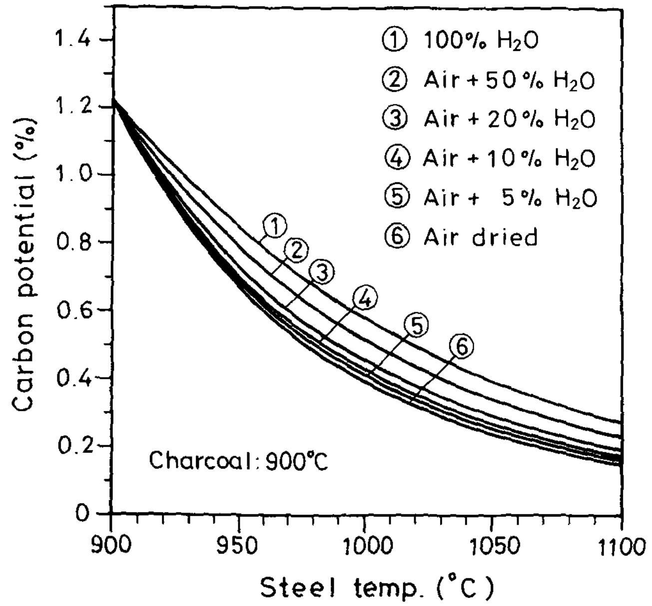

Fig. 14 Theoretical carbon potential at various steel temperatures for the charcoal gas generated by reacting 900 °C charcoal with air + H_2O mixtures containing various amounts of H_2O.

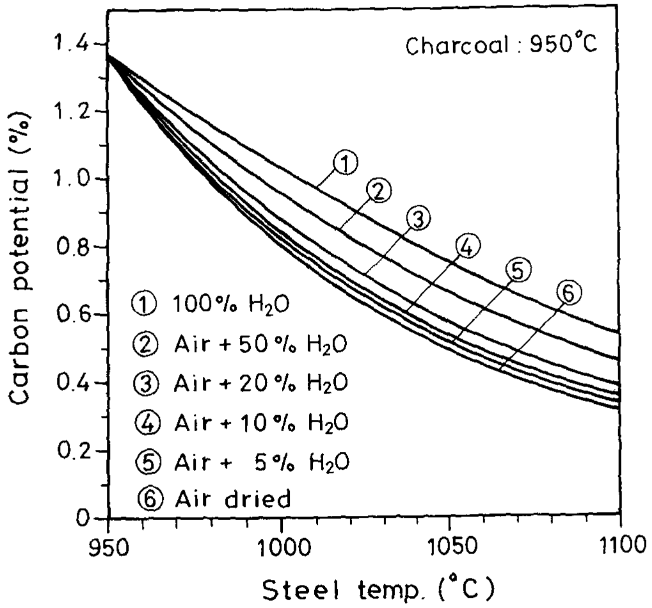

Fig. 15 Theoretical carbon potential at various steel temperatures for the charcoal gas generated by reacting 950 °C charcoal with air + H_2O mixtures containing various amounts of H_2O.

950 °C were computed and are shown as a function of temperature in Fig. 14 and 15. Theoretically, the equilibrium carbon content of the steel heated in the charcoal gas with equilibrium composition can reach the maximum carbon content of the saturated austenite corresponding to the heating temperature of the steel if the heating temperature is lower than the charcoal temperature. If the heating temperature of steel is higher than the charcoal temperature, the equilibrium carbon content of the steel is lower than the maximum carbon content of the saturated austenite corresponding to the heating temperature of the steel. From Fig. 14 and 15, it can be seen that if both the charcoal temperature and H_2O content in air + H_2O mixtures remain unchanged, the higher the heating temperature of steel, the lower the carbon potential of the charcoal gas. This characteristic is consistent with the experimental result of Fig. 5. Furthermore, by comparing the curves in the two figures, it is known that the carbon potential of the charcoal gas increases with increasing the H_2O content in air + H_2O mixtures at a constant charcoal temperature. This feature is consistent with the experimental results of Fig. 11, in which the charcoal temperature is relatively high (namely 1050 °C). However, the result of Fig. 10, in which the charcoal temperature is relatively low (namely 900 °C), indicates that the carbon potential of the charcoal gas decreases with increasing the H_2O content in air + H_2O mixtures. This can be reasoned as follows. When the charcoal temperature is relatively high (1050 °C), the practical composition of the charcoal gas is nearly the same as the equilibrium composition even if the H_2O content in air + H_2O mixtures is relatively high because of the rapid reaction rate. Thus, the higher the H_2O content in air + H_2O mixtures, the higher the carbon potential of the charcoal gas (inferred from Fig. 14 and 15). However, when the charcoal temperature is relatively low (900 °C), the practical composition of the charcoal gas is far from the equilibrium composition because of the sluggish reaction rate. In this case, if the H_2O content in air + H_2O mixture is further increased, the CO_2 content in the charcoal gas is raised obviously, and the CO content in the charcoal gas is lowered obviously; consequently, the carbon potential of the charcoal gas decreases.

4.3 *Carburizing Rate of Charcoal Gas*

As stated previously, the conventional charcoal gas, formed by reacting air with hot charcoal, belongs to the atmospheres of the N_2-CO system, and the modified charcoal gas, formed by reacting air + H_2O mixtures with hot charcoal, belongs to the atmospheres of the N_2-CO-H_2 system. According to the previous investigations,[2,3] the carburizing rate to steels for the atmospheres of the N_2-CO-H_2 system is much faster than that for the atmospheres of the N_2-CO system. The primary carburizing reaction in the atmospheres of the N_2-CO system is

$$2CO \rightarrow [C] + CO_2 \qquad [8]$$

and the main carburizing reactions in the atmospheres of the N_2-CO-H_2 system are as follows:

$$2CO \rightarrow [C] + CO_2 \qquad [9]$$

$$CO + H_2 \rightarrow [C] + H_2O \qquad [10]$$

where [C] stands for the carbon diffused into the steel. The rate of Reaction 10 is about five times as much as that of Reaction 8.[3] Therefore, in comparison with the conventional charcoal gas, the carburizing rate of the modified charcoal gas can be raised greatly. This can be proved from Fig. 11, 12, and 13.

4.4 *Consumption of Charcoal*

The conventional method for producing charcoal gas is to pass air through a hot charcoal layer. In this study, it was found that if some water vapor was added to the air before passing through the hot charcoal layer, then both the carbon potential and the carburizing rate of the charcoal gas were raised greatly. However, what about the charcoal consumption? It will be theoretically compared with that of the conventional method as follows. As stated previously, dried air can be regarded as an $N_2 + O_2$ mixture, in which N_2 does not react with hot charcoal, and O_2 will react with hot charcoal to form CO and CO_2. Because the volume fraction of CO_2 in the charcoal gas is generally very low (less than 1%), the main reaction between dried air and hot charcoal can be regarded as:

$$O_2 + 2C \rightarrow 2CO \qquad [11]$$

where C stands for the carbon in the charcoal. Because 1 mol of dried air contains 0.79 mol of N_2 and 0.21 mol of O_2, 1 mol of dried air will react with 0.42 mol of carbon to form 0.42 mol of CO. The unreacted N_2 is 0.79 mol. In other words, 1 mol of dried air will react with 0.42 mol of carbon to generate 1.21 mol of charcoal gas; 0.42 mol of carbon weighs 5.04 g and the volume of 1.21 mol of charcoal gas at room temperature and 1 atm is about 29.65 liters. Estimated from the above data, 170 g of carbon is needed to generate 1 m^3 of charcoal gas at room temperature under 1 atm by reacting dried air with hot charcoal.

On the other hand, if charcoal gas was generated by reacting air + H_2O mixtures with hot charcoal, the main reactions are as follows:

$$O_2 + 2C \rightarrow 2CO \qquad [12]$$

$$H_2O + C \rightarrow CO + H_2 \qquad [13]$$

That is, O_2 will react with charcoal to generate CO, whereas H_2O will react with carbon to generate CO and H_2. Assuming that the H_2O content in the air + H_2O mixture is 7.30%, then the composition of the mixture is 73.2% N_2 + 19.5% O_2 + 7.30% H_2O. One mol of this mixture will react with 0.39 mol of carbon to form 0.39 mol of CO according to Reaction 12 and will react with 0.073 mol of carbon to generate 0.073 mol of CO and 0.073 mol of H_2 according to Reaction 13. The unreacted N_2 is 0.732 mol. In other words, 1 mol of air + H_2O mixture containing 7.30% H_2O will react with 0.463 mol of carbon to generate 1.268 mol of charcoal gas; 0.463 mol of carbon weighs 5.556 g, and the volume of 1.268 mol of charcoal gas is 31.1 liters. Estimated from the above data, 178.6 g of carbon is required to generate 1 m^3 of charcoal gas at room temperature under 1 atm by reacting hot charcoal with air + H_2O mixtures containing 7.30% H_2O. Compared with the conventional method, the consumption of charcoal increases by 5%; however, the carbon potential of the charcoal gas increases by about 3 times (according to Fig. 11), and the carburizing rate increases by about four times as well (according to Fig. 12).

5. Conclusions

If some H_2O is added to air while producing charcoal gas, then the carbon potential and carburizing rate of the charcoal gas will be raised markedly. For example, if the added H_2O is 7.30%, the carbon potential increases by about three times, and the carburizing rate increases by about four times for the charcoal temperature of 1050 °C and steel heating temperature of 900 °C.

The carbon potential and carburizing rate of the charcoal gas, generated from an air + H_2O mixture and hot charcoal, increases with increasing H_2O content in the mixture if the temperature of charcoal is high enough (*e.g.*, 1050 °C). The carbon potential of the above-mentioned charcoal gas increases with increasing charcoal temperature and/or decreasing the heating temperature of steel. Both the hardness and the thickness of the hardened case of steels carburized in the above charcoal gas are much higher than those carburized in conventional charcoal gas.

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