EFFECTS OF NICKEL AND COPPER ON THE ACTIVITY COEFFICIENT OF CARBON IN γ-IRON

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I. Introduction

It has been already shown that silicon and manganese have decided influences on the activity coefficient of carbon in γ-iron.[1] The purpose of this investigation was to determine the effects of nickel and copper on the activity of carbon in γ-iron. The method employed was essentially the same as that described by Smith[2] on the measurements of the equilibrium of iron-carbon alloys with mixtures of carbon dioxide and carbon monoxide. A study was made of the conditions of equilibrium in the reaction represented by the following chemical equation:

$$C(\text{in } \gamma\text{-iron}) + CO_2 = 2\,CO.$$

It was found that the activity coefficient of carbon in austenite changes as the contents of nickel and copper increase.

II. Experiments

Measurements were made of the carbon contents in γ-iron containing up to 18% nickel and iron-copper alloys containing up to 7% copper, both equilibrated with CO_2—CO atmospheres of known composition at 850°C and 930°C, 900°C and 950°C respectively. The carbon contents of samples were analyzed by the usual combusion method; carbon dioxide solidified by cooling with liquid air was vapourized in the constant volume and then its pressure was measured.

Iron-nickel and iron-copper alloys were prepared by sintering mixtures of known composition of metallic powder in hydrogen flow at 1200°C for 2 to 5 hr. For making the metallic mixture, the solution of the cryohydrate of ferric and nickel or cuprous nitrate was evaporated to dryness and the obtained mixture of oxide and nitrate powders was reduced by hydrogen gas at about 500°C. The crystal of cryohydrate was purified by recrystallizing the crude nitrate three to five times.

The gaseous mixture of constant composition was prepared by the flowing method described by Darken and Gurry.[3] A schematic diagram of the apparatus was shown in Fig. 1. The purified gas of carbon monoxide and carbon dioxide are led through the regulating device W and the flowmeters F_1 and F_2 respectively, and mixed in the chamber M. Carbon monoxide gas generated by the reaction of the pure sulphuric acid on formic acid was purified by passing it through a series of purifiers containing the following substances respectively:

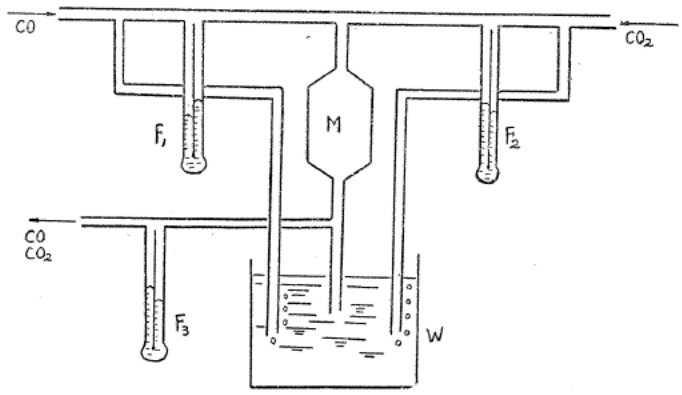


FIG. 1. Apparatus for preparation of CO-CO_2 mixtures of constant composition.

Potassium hydroxide, pyrogallol, and phosphorous pentaoxide. Carbon dioxide gas was prepared in Kipp's apparatus by the reaction of the pure synthetic hydrochloric acid on the marble washed by hydrochloric acid for several minutes, and the oxygen in gas was removed by passing it through the copper gauze heated at about 800°C.

III. Results

The results of measurement were shown in Table 1 and 2, giving the carbon contents of the alloys equilibrated with CO-CO_2 mixtures of several kinds. The effects of nickel and copper on this equilibrium were shown better in Fig. 2, 3, 4 and 5, in which the value of P^2_{CO}/P_{CO_2} for various nickel and copper contents was plotted against the weight percentage of carbon at a constant temperature. The activity a_C of carbon relative to graphite is given by the equation:

$$a_C = P^2_{CO}/P_{CO_2}K,$$

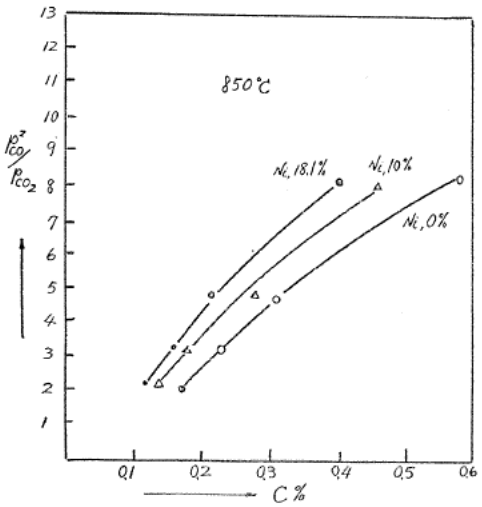
where K is the equilibrium constant for the reaction C(in γ-iron) + CO_2 = 2 CO. Substituting the value of K described by Smith in the above equation, the activity of carbon was obtained as shown in Table 3 and 4. From the tables, it was found that the activity coefficient of carbon in iron increases with increasing nickel content and in contrast with nickel, decreases with copper content.

TABLE 1. Experimental Results on γ-Iron Containing Nickel

P^2_{CO}/P_{CO_2}	C %					
	850°C			930°C		
	Ni 0%	Ni 10%	Ni 18.1%	Ni 0%	Ni 4.9%	Ni 18.1%
1.63	—	—	—	0.06	0.04	0.02
2.25	0.18	0.13	0.12	0.09	0.07	0.03
3.20	0.22	0.17	0.16	0.12	0.10	0.04
4.82	0.30	0.28	0.21	0.16	—	0.07
5.82	—	—	—	0.18	0.16	—
8.10	0.58	0.46	0.40	0.24	0.21	0.12
12.36	—	—	—	0.37	0.31	—

TABLE 2. Experimental Results on γ-Iron Containing Copper

P^2_{CO}/P_{CO_2}	C %					
	900°C			950°C		
	Cu 0%	Cu 3%	Cu 7%	Cu 0%	Cu 3%	Cu 7%
1.63	0.075	0.075	0.090	—	—	—
2.25	0.10	0.11	0.13	0.05	0.05	0.07
3.20	0.14	0.14	0.18	—	—	—
4.82	0.22	0.23	0.27	0.11	0.11	0.13
5.82	0.27	0.28	—	0.13	0.14	0.16
8.10	0.37	0.39	0.44	0.17	0.18	0.23



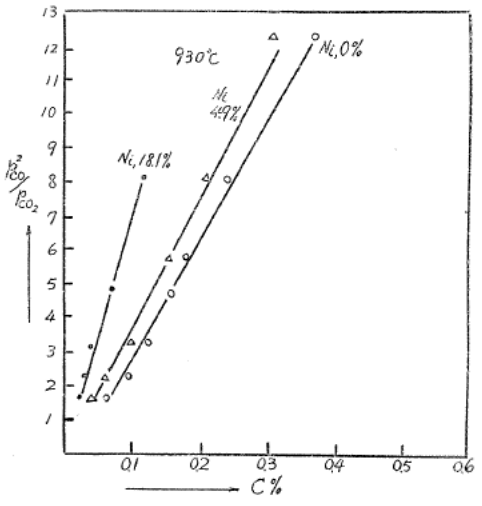
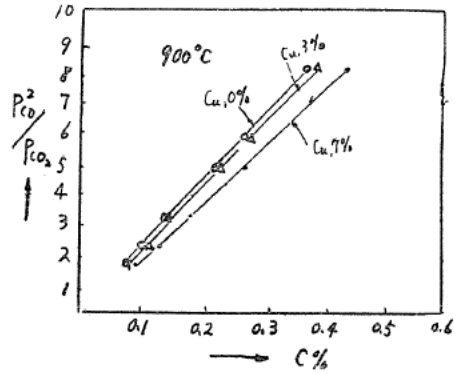


FIG. 2 (*left*). Experimental values of P^2_{CO}/P_{CO_2} as function of carbon content in γ-iron containing nickel (850°C).

FIG. 3 (*right*). Experimental values of P^2_{CO}/P_{CO_2} as function of carbon content in γ-iron containing nickel (930°C).



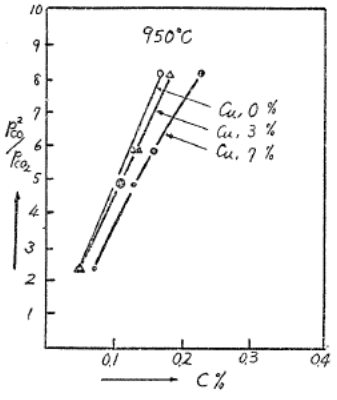


FIG. 4 (*left*). Experimental values of P^2_{CO}/P_{CO_2} as function of carbon content in γ-iron containing copper (900°C).

FIG. 5 (*right*). Experimental values of P^2_{CO}/P_{CO_2} as function of carbon content in γ-iron containing copper (950°C).

TABLE 3. Activity of Carbon in γ-Iron Containing Nickel

850°C				930°C			
ac	C %			*ac*	C %		
	Ni 0%	Ni 10%	Ni 18.1%		Ni 0%	Ni 4.9%	Ni 18.1%
0.136	0.18	0.13	0.12	0.030	0.06	0.04	0.02
0.193	0.22	0.17	0.16	0.041	0.09	0.07	0.03
0.291	0.30	0.28	0.21	0.060	0.12	0.10	0.04
0.490	0.58	0.46	0.40	0 090	0.16	—	0.07
				0.110	0.18	0.16	—
				0.151	0.24	0.21	0.12
				0.230	0.37	0.31	—

TABLE 4. Activity of Carbon in γ-Iron Containing Copper

900°C				950°C			
ac	C %			*ac*	C %		
	Cu 0%	Cu 3%	Cu 7%		Cu 0%	Cu 3%	Cu 7%
0 063	0.10	0.11	0.13	0.031	0.05	0.05	0.07
0.089	0.14	0.14	0.18	0.044			
0.135	0.22	0.23	0.27	0.067	0.11	0.11	0.13
0.163	0.27	0.28		0.081	0.13	0.14	0.16
0.227	0.37	0.39	0.44	0.113	0.17	0.18	0.23

IV. Summary

Effects of nickel and copper on activity coefficient of carbon in γ-iron were studied by means of measurements of the equilibrium values of P^2_{CO}/P_{CO_2} of the reaction C(in γ-iron)+CO_2=2CO in various contents of nickel and copper at 850°, 930°, 900° and 950°C.

From the results obtained, it was found that the activity coefficient of carbon increases with increasing nickel content and in contrast with nickel, decreases with copper content.

References

1) K. Sano: Spring Meeting of Iron Steel Inst. Japan, April 1949.
2) R. P. Smith: J. Amer. Chem. Soc., **68** (1946), 1163.
3) L. S. Darken and R. W. Gurry: J. Amer. Chem. Soc., **67** (1945), 1398.