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Solubility and Diffusivity of Carbon in Metals

INTRODUCTION

The solubility and diffusivity of carbon in metals have been the subject of considerable interest in metallurgy. Recent studies have shown that they are also directly relevant to many catalytic reactions, e.g., metal-catalyzed gas–carbon reactions (*1*, *2*) and filamentous carbon growth on metal catalysts (*3–10*). Many investigations have been made on ferromagnetic metals, of which nickel is of particular interest in the present study. The following discussion is based on nickel but is also pertinent to other metals.

Large discrepancies exist in the literature on the experimental values of solubility and diffusivity of carbon in nickel, and these discrepancies remain unexplained. The reported solubilities vary within approximately a factor of 2, whereas diffusivity data scatter over an order of magnitude. A basic source for the discrepancies lies in the deficiencies of the experimental techniques which have been used to measure these properties; this is especially true for solubility.

There have been two approaches adopted for measuring solubility. The first approach entails decomposing CH_4 or CO on the metal and measuring the amount of carbon in the metal at $a_c = 1$. The respective reactions are $CH_4 \rightarrow C + 2H_2$ or $2CO \rightarrow C + CO_2$. The activity of carbon, a_c, is $a_c = K_pP(CH_4)/P(H_2)^2$ or $a_c = K_pP(CO)^2/P(CO_2)$, respectively, where K_p is equilibrium constant for the pertinent reaction and P is partial pressure. Thus, solubilities are obtained by using ratios of CH_4/H_2 or CO/CO_2 corresponding to $a_c = 1$ (*11–16*). Except Schenck *et al.* (*14*), who used a microbalance to measure the weight gain *in situ*, all others equilibrated the gas/metal system for long periods of time (1–6 days) and subsequently quenched the metal and analyzed its carbon content.

The second approach for solubility measurement is by direct contact of nickel and a graphite powder for a prolonged period of time, followed by annealing, cooling, and analysis for carbon content (*17*, *18*). Polycrystalline nickel foils were used in all cases (in both approaches) except that of Eisenberg and Blakeley (*18*) who used a single crystal. The solubilities obtained by this approach are higher than those obtained by the first approach.

The first approach is based on the assumption that the carbon formed on the surface of nickel is β-graphite, the free energy of formation (ΔG) of which is zero (as the standard state). However, a number of experimental results have shown that a much more carburizing atmosphere than that corresponding to $a_c = 1$ is needed for carbon deposition on Ni (*19*, *20*) and Fe (*21*). Thus the carbon deposit on the surface has a positive ΔG and is less stable than β-graphite. The experimental values of ΔG of carbon on Ni are about +3 kcal/mol at 700 K, decreasing to about +1 kcal/mol at 900 K, as measured by both Dent *et al.* (*19*) and Manning *et al.* (*20*).

There are at least two causes for the positive ΔG of surface carbon. One derives from the structure and bonding of the surface carbon; the surface carbon is bonded to the metal and possibly also with other carbon atoms. In fact, many different forms of carbon on metal surfaces have been identified in terms of their reactivities toward H_2 and O_2 (*22–24*). These carbons are more

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reactive and less stable than β-graphite. Another cause for the positive ΔG pertains to filamentous carbon. Filamentous carbon is formed on polycrystalline metals (especially Ni) with grain sizes less than 0.2–0.5 μm. The filament consists of graphite sheets in a scroll-like structure, and a significant amount of strain energy is associated with this structure (*25, 26*). The ΔG has been shown to increase with decreasing Ni crystallite size (*26*). Still another possible cause for the positive ΔG is associated with an intermediate carbide phase which may exist on the surface of the metal at low temperatures (e.g., near 550°C for Ni; Refs. (*27, 28*)). All these causes can contribute to the positive ΔG. No attempts have been made to resolve these contributions.

The techniques for measuring diffusivity of carbon in metals have been reviewed recently by Bergner (*29*).

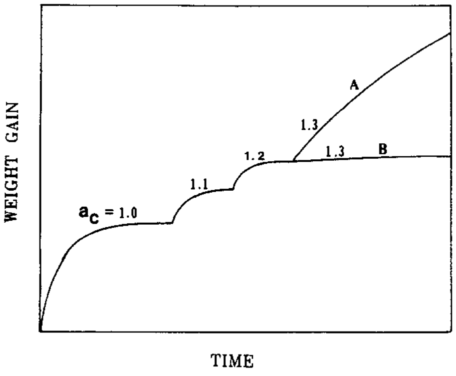

FIG. 1. Weight gain in metal with stepped increases in carbon activity in the gas phase ($a_c = K_pP_{CH_4}/P^2_{H_2}$). Saturation in this example is at a_c = 1.2–1.3. (A) Carbon filament growth on small grains; (B) carbon encapsulated on large grains or single crystals.

PROPOSED TECHNIQUE AND RESULTS

TGA Technique

The proposed technique is a rapid thermogravimetric (TGA) technique which can be used to measure solubility and diffusivity simultaneously. More important, saturation can be guaranteed as the carbon content is monitored *in situ*.

The technique is illustrated via the TGA results shown in Fig. 1. Prior to the experiment, the metal is thoroughly reduced in H_2 at a high temperature, e.g., 750°C for data shown in Fig. 1. This step also helps minimize surface impurities, which at low levels have negligible effects on carbon formation (*26*). A gas mixture of H_2/CH_4 or CO/CO_2 where a_c = 1 is admitted at time zero and the weight gain history is recorded as shown in Fig. 1. As discussed in the preceding section, the saturation of carbon in the metal requires a_c to be greater than unity because of the positive free energy of formation of the surface carbon. In the example shown in Fig. 1, carbon saturation occurs at a_c = 1.2–1.3. Thus stepped weight gains are obtained as the activity of carbon in the gas phase is increased stepwise until saturation is reached. At the saturation point, one of two consequences follow if the carbon activity is further increased. (1) A continual weight gain results from the onset of carbon filament growth. This was observed in our experiments with Ni foils which contained grains less than 0.3 μm in size. This should also occur with supported metals with small sizes. (2) No further weight gain or a continual, miniscule weight gain follows, as the metal is totally encapsulated by carbon which has little catalytic activity for CH_4 or CO decomposition. This was observed in our experiments with Pt and Pd wires as well as Ru powder (which had an irregular flaky shape with sizes in the order of 1 μm). Finer increments in a_c should be used for higher accuracies.

The diffusivity of carbon in the metal can be readily calculated from the weight gain history by matching with the solution of the diffusion equation. An example is shown in Fig. 2. In diffusivity measurement, however, the saturation of carbon is not required; only the equilibrium weight gain is needed. Thus each increment in a_c will yield a diffusivity, and a_c may be well below unity. It is known that the Fickian diffusivity has a strong dependence on concentra-

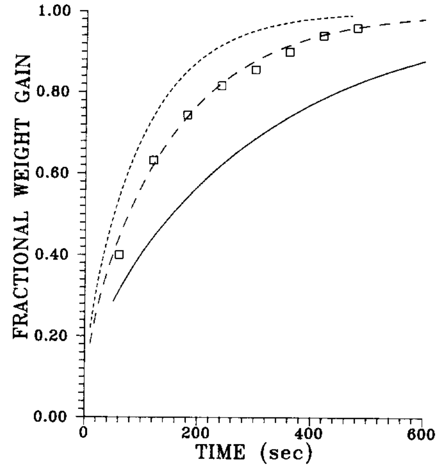

FIG. 2. Diffusivity of carbon in Ni at 750°C by fitting TGA data (squares) to solution of diffusion equation: $D = 2.0 \times 10^{-9}$ cm^2/s (solid line); 4.0×10^{-9} cm^2/s (dashed); 6.0×10^{-9} cm^2/s (dotted).

tion (*30*) because the concentration gradient is used instead of a chemical potential gradient. The concentration dependence can be obtained from the TGA technique.

The free energy of formation of the surface carbon can also be obtained from the technique based on the carbon activity at the saturation point. If more than one type of carbon is formed, such information would pertain to the least active type of carbon.

RESULTS AND DISCUSSION

The H_2/CH_4 system was used in this study. Both gases were supplied by Linde Division with the following stated purities: H_2 UHP grade at 99.999% and CH_4 Custom grade at 99.99%. Four metals were used: Ni foil (0.025 mm thickness, Alfa Products, Puratronic grade), Pt (0.2 mm diameter wire), Pd (0.2 mm diameter wire); both Pt and Pd were from Ernest Fullam, Inc., at a nominal 100% purity, and Ru powder (irregular flaky particles at approx. 1 μm size, 99.997% purity) was from Alfa Products.

As discussed in the Introduction, a number of investigations have been made on the solubility and diffusivity of carbon in Ni. The data on the other three metals studied here are scarce indeed. The solubilities of carbon in Pd and Pt at temperatures above 900°C were measured by Siller *et al.* (*31*), by equilibrating the metal with graphite powder.

The solubility and diffusivity data obtained by using the TGA technique are summarized in Table 1. Nickel was used as the test case for the technique. At 700°C, a carbon activity of 1.4 was needed to reach

TABLE 1

Solubility, ΔG of Surface Carbon (ΔG_c), Solubility Parameters ($\Delta \bar{H}_c$ and $\Delta \bar{S}_c$), and Diffusivity of Carbon in Metal

	T (°C)	Solubility (at%)	$\Delta G_c(a_c)$ (kcal/mol)	$\Delta \bar{H}_c$ (kcal/mol)	$\Delta \bar{S}_c$ (kcal/mol/K)	D (cm^2/s)
Ni	700	0.29	0.78 (1.4)	9.64	-1.69×10^{-3}	4.0×10^{-9}
	750	0.37	0.68 (1.3)			
Pt	700	0.66	0.35 (1.2)	3.86	-6.09×10^{-3}	1.0×10^{-7}
	800	0.79	0.39 (1.2)			1.2×10^{-7}
Ru	700	0.15	0.53 (1.3)	4.17	-8.55×10^{-3}	
	800	0.19	0.39 (1.2)			
	900	0.23	0.42 (1.2)			
Pd[a]	550	0.32	0 (1.0)			5.0×10^{-9}
	600	0.41	0 (1.0)			1.5×10^{-8}
	650	0.55	0 (1.0)			3.5×10^{-8}
	700	0.71	0 (1.0)			6.5×10^{-8}

[a] The "solubility" values for Pd were measured at $a_c = 1$ and were below saturated values.

saturation. The free energy of formation of the surface carbon may be calculated by

$$\Delta G_c = -RT \ln \frac{K_p}{K_p(\beta\text{-graphite})}, \quad (1)$$

where K_p is the actual equilibrium constant

$$K_p = \frac{a_c P_{H_2}^2}{P_{CH_4}} \quad (2)$$

and $K_p(\beta\text{-graphite})$ is the value based on $a_c = 1$ for β-graphite. The value for the free energy of formation of surface carbon at 700°C was 0.78 kcal/mol. The free energy of formation decreased to 0.68 kcal/mol at 750°C. These values were in reasonable agreement with those of Manning *et al.* (*20*). The solubilities in Ni were higher than those reported in the literature where the values corresponding to $a_c = 1$ were taken as the solubilities (*16*). The strong dependence of carbon content in Ni on carbon activity in the gas phase is illustrated by the following for 700°C (in at.%): 0.20 ($a_c = 1$); 0.22 ($a_c = 1.1$); 0.25 ($a_c = 1.2$); 0.27 ($a_c = 1.3$); 0.29 ($a_c = 1.4$). The diffusivity of carbon in Ni was 4.0×10^{-9} cm^2/s (Fig. 2). Typical literature values were 6×10^{-9} cm^2/s (*11*) and 1.7×10^{-9} cm^2/s (*29*). These are in good agreement with our value.

For the case of a dilute solid solution or quasi-regular solution, it can be shown that the temperature dependence of the solubility is (*32*)

$$\frac{C_c}{1 - 2C_c} = \exp\left[-\frac{\Delta \overline{H}_c}{RT}\right] \exp\left[\frac{\Delta \overline{S}_c}{R}\right], \quad (3)$$

where C_c is the solubility in atomic fraction, $\Delta \overline{H}_c$ is the relative partial enthalpy of carbon, and $\Delta \overline{S}_c$ is the relative partial excess entropy. For Pd in which C may prefer tetrahedral sites, $1 - 2\,C_c$ in Eq. (3) would be replaced by $2 - 2\,C_c$. The values for $\Delta \overline{H}_c$ and $\Delta \overline{S}_c$ are also given in Table 1.

The solubilities of carbon in Pt at 700 and 800°C were in excellent agreement with the values extrapolated from those at above 900°C measured by Siller *et al.* (*31*) using the graphite/metal equilibration technique. The temperature dependence of diffusivity of C in Pt appeared to be too low since the activation energy was only 1.6 kcal/mol. The low activation energy indicated that the diffusion was dominated by grain boundary diffusion, which usually becomes dominant at low temperatures.

The available data on Ru and Pd are also included in Table 1. Diffusivity data in Ru were not available due to the irregular shape of the Ru particles. It is interesting to observe the appreciable solubilities of carbon in Ru. Using Eq. (3), the solubility may be extrapolated to the temperature region for methanation and Fischer–Tropsch reactions, e.g., 300°C. The extrapolated solubility at 300°C is 0.35% (atomic) or 4.1×10^{-5} (wt.). At this solubility, a carbon atom can find, on average, the nearest carbon neighbors approximately 14 Ru atoms away. This is not a negligible solubility.

A final comment should be made concerning the solubilities measured by equilibrating the metal with graphite powder (*17, 18, 31*). These solubilities are higher than other published data and, in principle, should be the true solubilities. Although a β-graphite powder was used (in contact with the metal) in the measurement, the solubility should not be regarded as that corresponding to $a_c = 1$. It has been known from the studies on metal catalyst channeling in graphite in gas–carbon reactions that carbon dissolves in metal from the edges of graphite, and the carbon atoms on the basal plane of graphite do not dissolve (*2, 3*). The edge atoms on the graphite layer are unsaturated (with a free sp^2 electron) and are active. The free energy of formation of these edge atoms should be positive and greater than that required for saturation of carbon in metals.

In summary, a rapid and versatile technique is suggested for the simultaneous measurement of solubility and diffusivity of carbon in metals. The technique can also provide information on the free energy of formation of the surface carbon, as well as the concentration dependence of the Fickian diffusivity. Four metals were included in this study. Of particular interest to catalysis is that a significant solubility of carbon in ruthenium has been observed.

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