

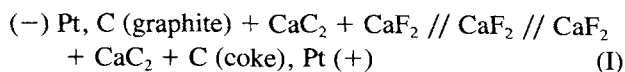
# Communications

## Thermodynamic Stability of Metallurgical Coke Relative to Graphite

K.T. JACOB and S. SEETHARAMAN

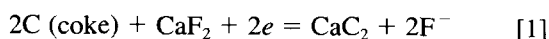
In the thermodynamic analysis of pyrometallurgical processes using coke as a reductant, the data for CO and CO<sub>2</sub> from thermochemical tables,<sup>[1,2,3]</sup> relative to graphite as the standard state for carbon, are used. Since coke is an amorphous form of carbon, its Gibbs energy is expected to be higher than that of graphite. However, there has been no direct measurement of the stability of coke relative to graphite reported in the literature. For an accurate description of the thermodynamics of reactions involving coke, it is necessary to obtain quantitative values for the Gibbs energy difference between coke and graphite as a function of temperature.

This communication reports an experimental determination of the activity of carbon in coke relative to graphite using a solid-state galvanic cell incorporating single-crystal CaF<sub>2</sub> as the solid electrolyte. The electrochemical cell can be represented as the following:

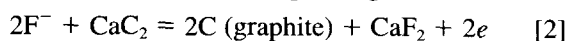


Since CaF<sub>2</sub> and CaC<sub>2</sub> do not have significant mutual solid solubility at the experimental temperatures, their activities at each electrode are unity.

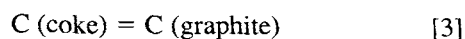
The electrochemical reaction at the right electrode is



At the left electrode, the corresponding reaction is:

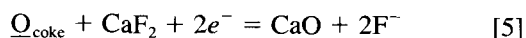
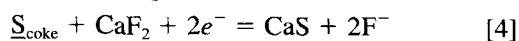


The virtual cell reaction is



for which  $\Delta G_3^0 = -FE$ , where E is the electromotive force (EMF) of the cell in volts and F is the Faraday constant. The electrodes are designed to convert the carbon potential into an equivalent chemical potential of fluorine, which can be measured by the CaF<sub>2</sub> solid electrolyte. At the chemical potentials of fluorine prevailing at the electrodes, CaF<sub>2</sub> is predominantly an ionic conductor.<sup>[4,5,6]</sup>

Since coke contains several impurities, it is possible that the chemical potential of fluorine at the right electrode is influenced by spurious reactions such as<sup>[7,8]</sup>



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Sulfur is present in coke partly in dissolved form and partly as sulfides. The solubility of oxygen in coke is negligible, especially at the low-partial pressures of oxygen prevailing at the electrodes. Most of the oxygen in coke is present as inert inorganic oxides. Therefore, the possibility of Reaction [4] is significantly higher than that of Reaction [5].

The coke used in this study was prepared from high-grade coal, which was washed to remove ash and then subjected to normal coking. When the coke was used for EMF measurements, the volatile matter released at high temperature was found to interfere with the measurement. The EMF decreased with time at constant temperature probably due to the transport of material between the electrodes *via* the gas phase. The removal of volatile matter from the coke was therefore attempted. The coke was heated under vacuum (~10 Pa) at 1273 K for ~12 ks. The ultimate analysis of the coke after vacuum treatment gave the following contents: carbon, 95.2 pct; hydrogen, 0.4 pct; oxygen, 0.6 pct; nitrogen, 0.3 pct; sulphur, 0.4 pct; and ash, 2.9 pct by weight. Coke contains plane polyaromatic units. There are molecular orientation domains, with local parallel orientation, distributed in an amorphous matrix. The average size of these domains determined by transmission electron microscopy was ~10 nm. The use of vacuum-degassed coke resulted in reproducible and constant EMF at each temperature. To check for the possible effect of the sulfur content of coke on EMF, a batch of coke after degassing was treated with carbon disulfide. This treatment reduced the sulfur content from 0.4 to 0.23 pct.

The apparatus used in this study was similar to that described earlier.<sup>[9]</sup> The cell was operated under flowing prepurified argon gas. To prevent the oxidation of CaC<sub>2</sub>, residual oxygen, moisture and oxides of carbon had to be removed from the argon stream. The high-purity argon gas (99.99 pct pure) was passed over Cu<sub>2</sub>O at 873 K to convert residual CO to CO<sub>2</sub>. The CO<sub>2</sub> was then absorbed by passing over NaOH. The gas was then dried by silica gel, magnesium perchlorate, and phosphorus pentoxide. The residual O<sub>2</sub> was removed by passing the gas through columns of copper at 700 K and titanium at 1173 K. In addition to the purification of argon before admission to the EMF apparatus, it was necessary to have internal getters for oxygen inside the enclosure housing the cell. Titanium foils were placed in the path of the argon gas near the electrode. Internal getters remove oxygen from gas species that desorb at high temperature from ceramic components used in the cell assembly.

The electrodes were prepared by mixing fine powders of graphite or coke with CaC<sub>2</sub> and CaF<sub>2</sub> in equimolar ratio. The mixture was compacted and sintered at 1250 K under prepurified argon in the presence of internal getters for oxygen. The electrodes were spring-loaded on either side of a single crystal of CaF<sub>2</sub>. A platinum mesh placed on each electrode was connected to separate platinum leads. The EMF of a symmetric cell with electrodes containing graphite on each side was measured initially as a function of temperature to check for possible thermal gradient across the electrolyte. The cell registered an EMF ±0.3 mV without any systematic trends.

The reversible EMF of cell (I) was measured as a

function of temperature from 955 to 1245 K using a high-impedance ( $>10^{12} \Omega$ ) digital voltmeter. The reversibility was established by microcoulometric titration in both directions. A small current ( $\sim 50 \mu\text{A}$ ) was passed through the cell for  $\sim 300$  seconds and the open circuit EMF was subsequently monitored as a function of time. The EMF returned to the steady value before each titration. The EMF was reproducible on temperature cycling and was independent of the flow rate of argon gas over the cell in the range  $1.5$  to  $4 \text{ mL s}^{-1}$ . The cell registered a steady EMF in  $\sim 6$  ks after the attainment of thermal equilibrium at 1245 K. The response was slower at lower temperatures,  $\sim 20$  ks being required to obtain a constant EMF at 955 K. To check for the possible influence of Reactions [4] and [5] on cell EMF, 5 mole pct of CaS or CaO was added to the right electrode in separate experiments.

At the end of each experiment, the cell was cooled and the electrodes were examined by optical microscopy and X-ray diffraction. No change was observed in the phase composition of the electrodes during the EMF measurement. There was no significant change in the mass of the electrodes during the high-temperature exposure. The volatilization of calcium from  $\text{CaC}_2$  does not appear to be significant under the present experimental conditions.

The EMF of cell (I) is plotted as a function of temperature in Figure 1. The numbers and letters on the figure indicate the sequence of measurement. Within the experimental error ( $\pm 3 \text{ mV}$ ), the EMF is a linear function of temperature. Measurements using coke containing a larger amount of impurities (0.7 pct S) gave an EMF that agreed within  $\pm 5 \text{ mV}$ . Measurements using coke treated with carbon disulfide also gave values lying in this scatter band. Thus, variation in sulfur content between 0.23 and 0.7 pct did not affect the EMF significantly. When 5 mole pct CaO was added intentionally to the right electrode, the EMF was unaffected. Calcium oxide at the electrode thus appears to behave as an inert constituent. The addition of 5 mole pct CaS resulted in EMFs that were not reproducible on temperature cycling. The EMF was always 30 to 80 mV higher than those obtained without the addition of CaS. When the

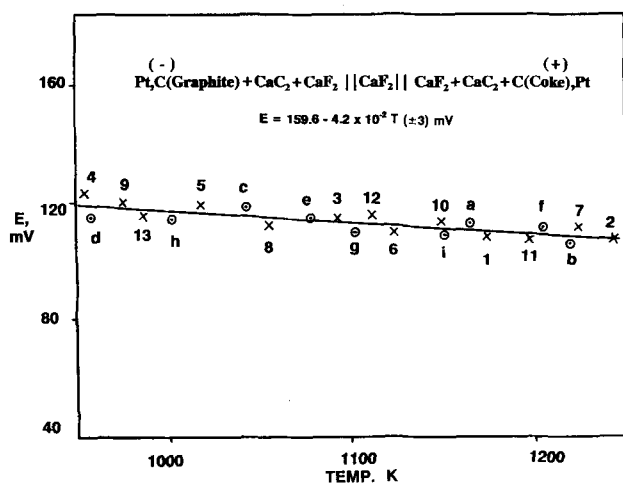


Fig. 1—Temperature dependence of the reversible EMF of cell (I). the numbers and letters on the figure indicate the sequence of measurement.

amount of CaS added to the electrode was less than  $\sim 2$  mole pct, the EMF was unaffected. It may, therefore, be concluded that Reaction [4] interferes with this measurement of carbon potential only when a substantial quantity of CaS is present at the electrode. The least-mean-squares analysis of the EMF gives the expression

$$E = 159.6 - 4.2 \times 10^{-2} T (\pm 3 \text{ mV}) \quad [6]$$

The standard Gibbs energy change for Reaction [3] calculated from the EMF is

$$\Delta G_3^\circ = -15,400 + 4.05 T (\pm 300) \text{ J mol}^{-1} \quad [7]$$

The average value for the enthalpy of coke is  $15.4 (\pm 1.5) \text{ kJ mol}^{-1}$  more positive than that for graphite in the temperature range of measurement. Consequently, the enthalpy change accompanying the combustion of coke will be more negative by the same amount. Direct-combustion calorimetric measurements on coke indicate that the enthalpy of coke is higher than that of graphite by 7.3 to  $14.7 \text{ kJ mol}^{-1}$ .<sup>[10,11,12]</sup> The accuracy of this technique is poor since the values are obtained as relatively small differences between large enthalpies of combustion of coke and graphite in oxygen. The entropy of coke is on the average  $4.1 (\pm 1.4) \text{ J K}^{-1} \text{ mol}^{-1}$  higher than that of graphite. The higher enthalpy and entropy of coke relative to graphite is compatible with the amorphous structure of coke.

The chemical potential of carbon in coke, diamond, and graphite are compared in Figure 2. Graphite is taken as the standard state for carbon. The data for diamond are taken from the compilation of Barin and Knacke.<sup>[3]</sup> The figure indicates that diamond cannot be formed from coke at very high temperatures. This is congruous with observations on changes in the structure of coke during graphitization.

The large negative Gibbs energy accompanying the hypothetical transformation of coke to graphite suggests

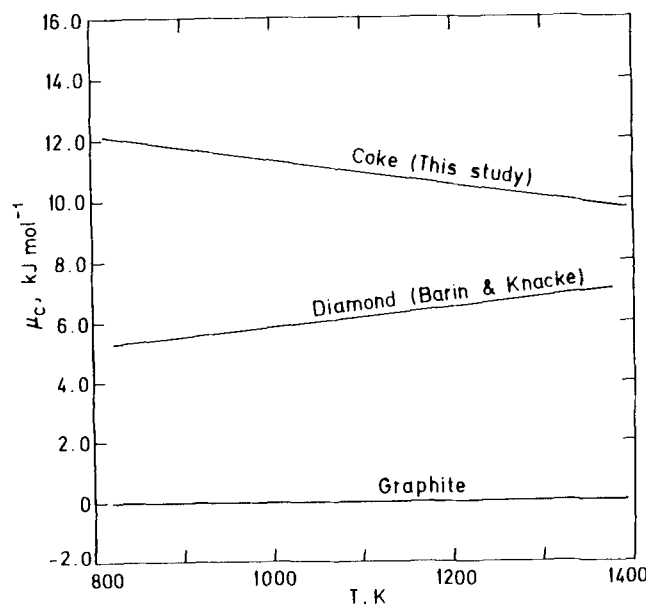
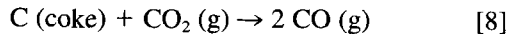


Fig. 2—Comparison of the chemical potentials carbon in coke, diamond, and graphite.

that the equilibrium constants for many reactions of interest in pyrometallurgy need correction. The most important of these reactions is the Boudouard reaction described in the following:



At 1000 K, the result obtained in this investigation indicates that the correct equilibrium constant should be higher by a factor of 3.9 compared with the value calculated from the data given in standard tables<sup>[1,2,3]</sup> relative to graphite as the standard state of carbon. Similarly, a correction for the enthalpy difference between metallurgical coke and graphite should be included in enthalpy balance calculations.

The results obtained in this study indicate a significantly higher solubility of coke compared to graphite in iron. However, metals are known to catalyze graphitization and the surface of coke in contact with the metal is likely to have a graphitelike structure. Thus, the theoretical difference in solubility may not be measurable in practice.

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## Thermodynamic Estimation of $\Delta H_f^\circ$ for $\text{CaGa}_2$ Intermetallic

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Ca-Ga salt scrub (SS) alloys are used in the recovery of actinide metals from spent chloride salts generated in

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pyrochemical processing of actinides.<sup>[1]</sup> The Ca-Ga alloys, in appropriate stoichiometries, are added to the molten process waste salts comprising calcium chloride and actinide oxides/chlorides to obtain an actinide-20 at pct gallium alloy, based on the following reactions:



The combined actinide content of the waste salt, in the form of oxides/chlorides, is in the range of 0.08 to 0.14 moles/mole of calcium chloride. The actinide metal must be recovered from the process salt in order to recycle or discard it. It is evident from Reactions [1] and [2] that calcium serves as the reductant while gallium alloys with the actinide to lower its activity and drive the reactions to the right. Because of the significantly different physical properties of these elements—*i.e.*, Ca and Ga—there are considerable handling problems in adding these elements separately; *e.g.*, melting points of calcium and gallium are 1118 and 302.8 K, respectively. Therefore, a considerable advantage can be gained from both the materials handling and the reaction kinetics points of view by producing an SS alloy of Ca-Ga in the required stoichiometries to achieve maximum recovery of the actinide.

Combustion synthesis is one of the methods available for the production of SS alloys. The formation of the  $\text{CaGa}_2$  intermetallic by the simultaneous combustion mode has been attempted.<sup>[2]</sup> The combustion product is sintered with calcium to produce the required stoichiometries. The Ca-Ga phase diagram is given in Figure 1, in which the  $\text{Ca}_6\text{Ga}$  and  $\text{Ca}_8\text{Ga}$  stoichiometries are indicated.<sup>[3]</sup> The  $\text{Ca}_6\text{Ga}$  and  $\text{Ca}_8\text{Ga}$  SS alloys have hypoeutectic calcium-rich compositions which contain calcium and the  $\text{Ca}_{28}\text{Ga}_{11}$  intermetallic.<sup>[3]</sup>

Combustion synthesis reactions<sup>[2,4-6]</sup> are characterized by their low energy requirement due to the effective utilization of the exothermic reaction heat,  $\Delta H_f^\circ$ . The reaction is initiated at a temperature which is known as the ignition temperature,  $T_{ig}$ . High-capacity operations are possible. The limitations of combustion synthesis reactions are that the maximum reaction heat is obtained for the composition corresponding to the highest melting point intermetallic, in this case  $\text{CaGa}_2$ , containing 77 wt pct Ga, and that a fine particle size of the constituent powders is needed to increase the surface contact area between the reactant powders. The combustion synthesis reaction proceeds by a propagating mode when the powder reactants are ignited locally (*e.g.*, with a high-resistance tungsten wire), followed by a propagating wave rapidly passing through the compact. However, the heat of reaction must be significantly high for the propagating mode to be viable.<sup>[2]</sup> Bulk or simultaneous combustion reactions occur when the reactant powder compact is heated rapidly (*e.g.*, in a furnace) until the synthesis reaction occurs simultaneously throughout the whole sample. The synthesis occurs at the ignition temperature, and the final product temperature, known as the combustion temperature,  $T_c$ , depends on the amount of the exothermic heat release and the efficiency of the system to retain the heat. The possibility of a successful application of the combustion synthesis technique and the choice of