Thermodynamic Investigations of $\text{Cr}_3\text{C}_2$ and Reassessment of the Cr-C System

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The Gibbs energies of formation for $\text{Cr}_3\text{C}_2$, $\Delta_fG_{\text{Cr}_3\text{C}_2}^o$, have been obtained from electromotive force (EMF) measurements, in the temperature range 950 to 1150 K, using the following galvanic cells with CaF$_2$ single crystals as the electrolyte:

\[
\text{Cr, CrF}_2 | \text{CaF}_2 | \text{CrF}_2, \text{Cr}_3\text{C}_2, \text{C} \quad (950 \text{ to } 1150 \text{ K})
\]

Extreme precautions were taken during the experimental measurements to avoid errors. The reliability and reproducibility of the values were confirmed by careful repetition of several of the experiments. The following equation has been obtained by a linear analysis of the EMF results as a function of temperature:

\[
\Delta_fG_{\text{Cr}_3\text{C}_2}^o(\pm 1600) = -58,857 - 22.344T \text{ (J mol}^{-1}) \quad (950 \text{ to } 1150 \text{ K})
\]

The generated values are compared with those reported in the literature.

The values of the enthalpy of formation were evaluated by using a third-law analysis, and an average value of $\Delta_fH^o_{298} = -71.7 \text{ kJ mol}^{-1}$ was obtained. The ground-state energy of the hypothetic end-member compound $\text{Cr}_3\text{C}$ in the bcc structure at 0 K was calculated by using the \textit{ab initio} method. The experimental results obtained, as well as the results from the \textit{ab initio} calculations, were employed in a reassessment of the Cr-C system using the CALPHAD approach. A new set of parameters for the bcc phase was evaluated using first-principles calculations.

I. INTRODUCTION

CHROMIUM carbides are of considerable scientific and technical importance because of their extensive applications in the cutting tool and in the heat-resistant steel industries. A precise knowledge of their thermodynamic properties is essential for the understanding, as well as the prediction of, their chemical behavior in various environments. The chromium-carbon system contains three stable intermediate phases, \textit{i.e.}, $\text{Cr}_2\text{C}_6$, $\text{Cr}_7\text{C}_3$, and $\text{Cr}_3\text{C}_2$.\textsuperscript{[1,2]} The carbides are all nonstoichiometric compounds with very narrow homogeneity ranges below 1200 K.\textsuperscript{[3]}

Numerous experimental investigations have over the years been published on the high-temperature thermodynamic properties of the chromium carbides.\textsuperscript{[4–15]} The available experimental data for the Gibbs energy of formation of the chromium carbides, however, are quite scattered.\textsuperscript{[15]} Among the many previous measurements, there have been six determinations of the Gibbs energy of formation of $\text{Cr}_3\text{C}_2$ by the use of the galvanic cell technique (four of them using CaF$_2$ as the electrolyte). It is especially surprising to find that the disagreement among the data generated by the galvanic cell technique is still quite large. The possible reasons for the large scattering of the electromotive force (EMF) results have already been discussed in the respective investigations.\textsuperscript{[11–15]}

As a preliminary study on the thermodynamic properties of the Fe-Cr-C transition metal carbides, the Gibbs energies of formation of $\text{Cr}_3\text{C}_2$ were determined in the present study by use of the EMF technique. A CaF$_2$ single crystal was used as an electrolyte, and extreme precautions were taken to avoid experimental errors. Based on the new experimental information obtained, as well as the results from the \textit{ab initio} calculations preformed by the present authors, the Cr-C binary system was reassessed by using Thermo-Calc software.\textsuperscript{[16]}

II. EXPERIMENTAL

A. The Cell Arrangement and Reaction

The galvanic cell used in the present study can be represented by the following schemes:

\[
\text{(-)} \text{Pt, Cr + CrF}_2 // \text{CaF}_2 // \text{CrF}_2 + \text{Cr}_3\text{C}_2
\]

\[+ \text{graphite, Pt (+)} \] \textit{[1]}

The individual electrode reactions can be written as follows:

\[
3\text{Cr} + 6\text{F}^- = 3\text{CrF}_2 + 6\text{e}^- \quad \text{(left)} \] \textit{[2]}

\[
3\text{CrF}_2 + 2\text{C} + 6\text{e}^- = \text{Cr}_3\text{C}_2 + 6\text{F}^- \quad \text{(right)} \] \textit{[3]}

\[
3\text{Cr} + 2\text{C} = \text{Cr}_3\text{C}_2 \quad \text{(overall)} \] \textit{[4]}

The molar Gibbs free energy change of Reaction [4] is given by the Nernst equation:

\[
\Delta_fG^o = -6FE = \Delta_fG_{\text{Cr}_3\text{C}_2}^o \] \textit{[5]}

where $6$ denotes the number of electrons participating in the separate electrode reactions, $F$ is the Faraday constant, and $E$ is the electromotive force of the cell.
B. Raw Materials and Electrode Preparation

Chromium carbide (CrC₂) powder (99.5 pct pure; 325 mesh; supplied by Alfa Aesar, Germany) and graphite (99.999 pct pure; supplied by Sigma-Aldrich, Sweden) were used to prepare the two-phase Cr₃C₂-C alloys. The amount of carbon in the Cr-C alloy was adjusted to 18.0 wt pct. The weighed mixtures were compacted into an alumina crucible and sintered in an atmosphere of purified argon at 1273 K for 3 days under a stream of purified argon. (The argon purification system is described in detail in Section C.) The prepared alloys were cooled in the furnace, crushed, and ground to powders before being examined by X-ray diffraction (XRD). The existence of the phases Cr₃C₂ and graphite were confirmed by an X-ray diffractometer (PHILIPS* XRD-PW-1830) with Cu Kα, radiation (35 kV, 20 A).

The working electrodes were then prepared by mixing the powders with CrF₂ powder (97 pct pure; supplied by Sigma-Aldrich) in a weight ratio of 4:1. The prepared mixtures were pressed into discs with a diameter of 16 mm and a thickness of 3 mm (3 to 4 g). The prepared discs were placed in boron nitride crucibles and dried under vacuum (1.0 Pa) at 423 K for 12 hours. The discs were then sintered in an atmosphere of argon at 1173 K for 4 hours before being mounted in the galvanic cell. The reference electrodes were prepared in a similar manner; i.e., chromium powder (99.95 pct pure; supplied by Alfa Aesar) was mixed with CrF₂ powder in a mass ratio of 4:1 to prepare the reference electrode. It is important to point out that due to the hygroscopic nature of the fluoride electrode components, all of the preceding operations were carried out in a glove box in purified argon. Calcium fluoride single crystals (Alfa Aesar, optical disk, 22 mm in diameter and 4 mm in thickness, polished both sides) were used as the electrolytes.

C. The Gas Cleaning System and Oxygen Probe

The chromium metal, as well as its carbides and fluorides, is very sensitive to oxidation and moisture. In other words, it was extremely essential to control the partial pressure of oxygen, as well as the humidity of the argon gas, during the synthesis and during the EMF measurements. Based on the relationship reported in the literature for the Gibbs energy of formation of Cr₂O₃,

\[
\Delta G_{\text{Cr}_2\text{O}_3}^0 = 1.5RT \ln \left( \frac{P_{O_2}}{P^0} \right) = -1,012,411 + 215.37T \text{ (J·mol}^{-1}) \text{ (300 to 1300 K)}
\]

where \( P_{O_2} \) is the partial pressure of oxygen and \( P^0 \) is defined as 101.325 Pa, the equilibrium oxygen partial pressure is 2.44 × 10⁻²⁵ Pa at 950 K and 6.95 × 10⁻¹⁹ Pa at 1150 K. Thermodynamically, the partial pressure of oxygen in the argon atmosphere should be very low in order to prevent the oxidation of chromium. The partial pressure of oxygen in the argon gas used in the present study (99.9999 pct pure; supplied by AGA Gas, Stockholm, Sweden) was only 5 × 10⁻¹⁰ Pa. In other words, additional purification of the argon gas would be needed to fulfill the experimental requirement.

To further lower the oxygen partial pressure of the argon gas, a gas purification train was used. A detailed description of the purification system used in the present study was presented previously. Briefly, in the gas purification train the argon gas was passed through two columns of silica gel, one column of ascarite, and one column of magnesium perchlorate to remove traces of H₂O and CO₂. The residual O₂ in the gas was removed by first passing the gas through a column of copper turnings at 873 K and, later, through two columns of magnesium chips at 773 K. The oxygen partial pressure in the gas stream was monitored throughout the experiment by passing the exhaust from the main furnace (containing the cell arrangement) through an oxygen probe. The oxygen probe employed consisted of a ZrO₂-7.5 mol pct CaO electrolyte tube with a slow stream of dry air as the reference electrode. By periodically renewing the copper turnings and the magnesium chips in the columns, the oxygen partial pressure in the argon gas stream could be maintained at a value less than 10⁻¹⁷ Pa (critical value). It is important to point out that the value registered by the oxygen probe was not the exact value of the oxygen partial pressure in the exhaust. The reason for this was that the measured value was in the electronic conduction region of the electrolyte. The real value, however, was likely to have been less than this critical value.

In addition to purifying the argon gas, it was also found necessary to have an internal getter for oxygen inside the enclosure housing of the cell. Titanium sponge, placed in the path of the argon gas stream near the electrode, served as the internal oxygen getter. This further helped to remove the oxygen desorbed at high-temperature from the ceramic components used in the cell assembly. The electrodes were examined after the EMF measurements and found to be free from oxidation.

D. Cell Assembly and Operation

The galvanic cell assembly used for the EMF measurements was similar to that described earlier by the present authors (Figure 1). Briefly, a single-crystal CaF₂ electrolyte was kept sandwiched between the two electrodes in an open cell arrangement. The cell was placed in a vertically mounted alumina reaction tube inside a resistance furnace. The samples were positioned in the even temperature zone (±0.5 K over a length of 6 cm) of the furnace. The cell EMF was measured, to an accuracy of ±0.01 mV, by a digital millivoltmeter (KEITHLEY 199 system DMM scanner, OH, USA). It is important to point out that in the present cell assembly, tungsten foils were used as transitional electrical contacts between the electrodes and the platinum foils.

Control of the humidity was a critical factor in the present study. Because of this, the electrode preparations, as well as the preparation of the cell assembly, were carried out in a glove box in an atmosphere of purified argon gas. Furthermore, the reaction tube of the furnace was dried in vacuum before use. It was established that the presence of moisture in the reaction tube, or in any of the cell components, resulted in a chemical reaction between the electrodes and the electrolyte. The reactions led to erratic cell behavior, which in turn led to breakdown of the cell. In those cases where moisture was present during the heating process, a thin blue layer was formed at the interface between the reference electrodes and the CaF₂ electrolyte. The original reference electrode material, as well as the contaminated material (with the blue layer), was analyzed by XRD (Figure 2). As can be seen from Figure 2, the main phases in the original reference electrode material were Cr and CrF₂.