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THERMODYNAMIC ANALYSIS IN THE PRODUCTION OF CHROMIUM CARBIDE FROM THE REDUCTION OF CHROMIUM OXIDE WITH METHANE-CONTAINING GAS

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Abstract:

Thermodynamic calculation is done to determine whether the reactions will proceed or not. The more negative values of the Gibbs free energies would indicate that the reactions are going to proceed. The study aimed to determine the thermodynamic feasibility of using methane as a reductant for chromium oxide. It was thermodynamically proven that methane-containing gas is viable and highly suitable. Also, methane is cheaper and abundant thus, the cost of production in the Ferrochromium industry would be lessened eventually. Thermodynamic calculations further revealed that methane-containing gas was feasible in reducing Cr_2O_3 to chromium carbides based on the Gibbs free energies. Methane gas gave negative values of the Gibbs energies in all chromium carbides. It was observed that it was lower compared with the carbothermal and H_2 reductions.

Keywords — **Computational thermodynamics, Gibbs free energy, ferrochromium, methane-containing gas, reductant**

1.INTRODUCTION

The cost of production in the industry of Ferrochromium is very high. It is said that 39.5% of the energy is used for heating of raw materials and 47% is used on reduction reactions of iron and chromium oxides [1]. The smelting of chromite ores uses high electric power. Innovative processes should be realized to reduce the energy requirement and as much as possible look for the cheapest energy source that would reduce the electric power required for the smelting process.The reduction reaction of $Cr_2O_3$by methane containing gas is said to be thermodynamically feasible at alower temperature [2]. Reference [3] added that Chromium and Iron Oxides occurring in the ore in the form of spinelare reduced by methane-containing gas.

The aim of this paper was to study the thermodynamic feasibility of using methane as a reductant for chromium oxide present in chromite ore to produce chromium carbide. Other reductants were also studied in this paper to identify the highly suitable reductant to beused. It was thermodynamically proven that methane-containing gas was worthwhile and reasonable due to its cheapness and abundance. Using the cheapest reductant in lieu of Hydrogen, and reducing the use of Carbon that is carcinogenic and harmful not just to the community but to the environment as well would be a welcome development.

2. METHODS

In modeling smelting and reduction, the computational thermodynamics is one of the convenient ways to better understand and explore

the processes used and the effects of changing process variables. Computational thermodynamics is a very effective educational tool for gaining an understanding of the reduction processes.

In this work, computational thermodynamics had been used to examine the major reactions occurring in the reduction of chromium oxide and to show the effect of various process variables on the recovery of chromium carbide. The standard Gibbs free energies for every chemical reaction during the reduction process were evaluated and modeled using Microsoft Excel 2010. Carbon, Hydrogen, Carbon Monoxide and Methane were compared and evaluated if they were capable of reducing chromium oxide to form chromium carbide.

3. RESULTS AND DISCUSSIONS

3.1 Chromium Oxide Decomposition

The decomposition of Chromium Oxide depends on the Oxygen partial pressure in the gas phase. A plot on the calculated decomposition temperature of Chromium Oxide at different Oxygen partial pressures is presented in Figure 1. The standard Gibbs free energies are taken from Knacke et al [4]. The decomposition of Chromium Oxide is represented by the reaction
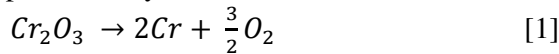
$$Cr_2O_3 \rightarrow 2Cr + \frac{3}{2}O_2 \qquad [1]$$
$$\Delta G^0 = 265,330 - 59.11T, \left[\frac{cal}{gmol}\right] \qquad [2]$$

Equation [2] reveals that the decomposition temperature of chromium oxide (Cr_2O_3) is around $4,216°C$ at atmospheric pressure. This means that to produce chromium or chromium carbides a reducing agent is needed.

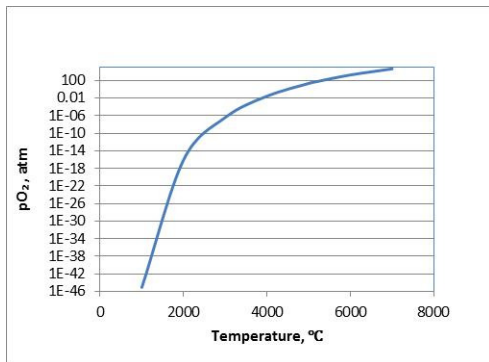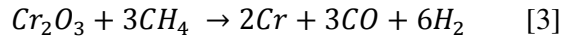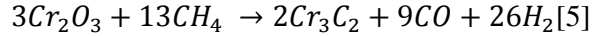Fig.1 Calculated decomposition temperature of Cr_2O_3 at different oxygen partial pressures

3.2 Chromium Oxide Reduction

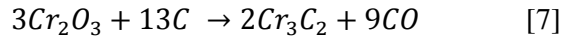The reduction of Chromium Oxide with methane produces Chromium metal or Chromium Carbide according to the reactions

$$Cr_2O_3 + 3CH_4 \rightarrow 2Cr + 3CO + 6H_2 \qquad [3]$$
$$\Delta G^0 = 248,590 - 199.7T \qquad [4]$$
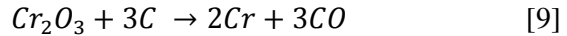$$3Cr_2O_3 + 13CH_4 \rightarrow 2Cr_3C_2 + 9CO + 26H_2 \qquad [5]$$
$$\Delta G^0 = 795,010 - 717T \qquad [6]$$

It is observed that at standard conditions, Equation [5] proceeds spontaneously at temperatures above 836°C. On the other hand, Equation [7] which is a carbothermal reduction proceeds at a temperature above 1,111°C. Reduction by methane (CH_4) is compared with carbothermal, CO and H_2 reductions. It is seen that using CO is only effective at lower temperatures but at higher temperatures, using CH_4 as reductant is favorable. This is shown in Figure 2 and supported by the following reactions:
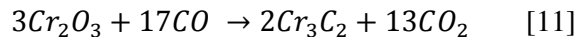
Reactions with Carbon:
$$3Cr_2O_3 + 13C \rightarrow 2Cr_3C_2 + 9CO \qquad [7]$$
$$\Delta G^0 = 512,130 - 369.94T \qquad [8]$$
$$Cr_2O_3 + 3C \rightarrow 2Cr + 3CO \qquad [9]$$
$$\Delta G^0 = 183,310 - 120.5T \qquad [10]$$

Reactions with Carbon Monoxide:
$$3Cr_2O_3 + 17CO \rightarrow 2Cr_3C_2 + 13CO_2 \qquad [11]$$
$$\Delta G^0 = -5400 - 535.96T \qquad [12]$$
$$Cr_2O_3 + 3CO \rightarrow 2Cr + 3CO_2 \qquad [13]$$
$$\Delta G^0 = 63880 - 120.89T \qquad [14]$$
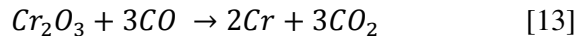
Reaction with Hydrogen:
$$Cr_2O_3 + 3H_2 \rightarrow 2Cr + 3H_2O \qquad [15]$$
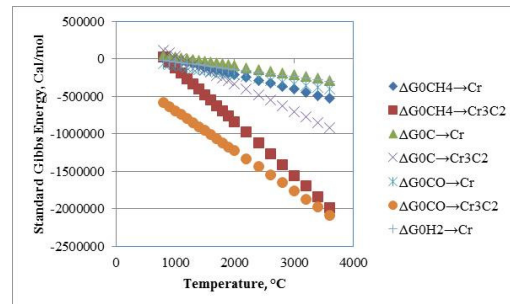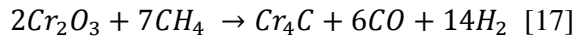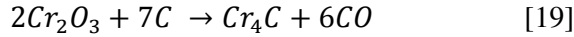$$\Delta G^0 = 87,880 - 99.05T \qquad [16]$$
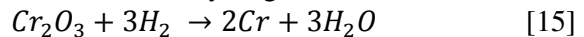
Fig. 2 Gibbs free energies for Cr_2O_3 reduction with C, CO, H_2 and CH_4 producing Cr_3C_2 and Cr

Chromium Oxide (Cr_2O_3) reduction by methane gas may also yield Cr_4C, $Cr_{23}C_6$ and Cr_7C_3 aside from Cr_3C_2. Tomoyuki et al. [5] reported that the XRD of their isothermal experiment of the carbothermic reduction of chromium oxide revealed that Cr_3C_2, Cr_7C_3, $Cr_{23}C_6$ and Cr were formed as the reaction products at 1673 K.
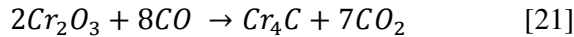
The reduction of chromium oxide to Cr_4C may proceed in accordance with the following reactions:

$$2Cr_2O_3 + 7CH_4 \rightarrow Cr_4C + 6CO + 14H_2 \quad [17]$$
$$\Delta G^0 = 495{,}940 - 428.6T \quad [18]$$
$$2Cr_2O_3 + 7C \rightarrow Cr_4C + 6CO \quad [19]$$
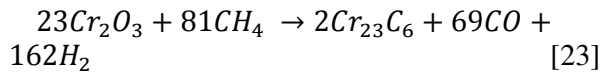$$\Delta G^0 = 343{,}620 - 243.8T \quad [20]$$
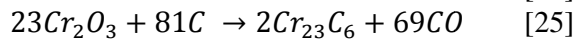$$2Cr_2O_3 + 8CO \rightarrow Cr_4C + 7CO_2 \quad [21]$$
$$\Delta G^0 = 64950 - 275.71T \quad [22]$$

On the other hand, chromium oxide reduction produces $Cr_{23}C_6$ via the following reactions:
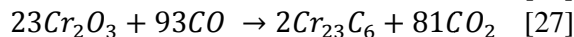
$$23Cr_2O_3 + 81CH_4 \rightarrow 2Cr_{23}C_6 + 69CO + 162H_2 \quad [23]$$
$$\Delta G^0 = 5830690 - 4946.9T \quad [24]$$
$$23Cr_2O_3 + 81C \rightarrow 2Cr_{23}C_6 + 69CO \quad [25]$$
$$\Delta G^0 = 4068130 - 2808.5T \quad [26]$$
$$23Cr_2O_3 + 93CO \rightarrow 2Cr_{23}C_6 + 81CO_2 \quad [27]$$
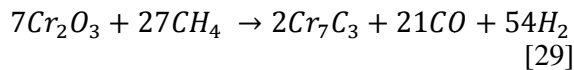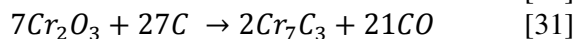$$\Delta G^0 = 843520 - 3313.56T \quad [28]$$

The reactions involved in the reduction of chromium oxide to Cr_7C_3 are as follows:
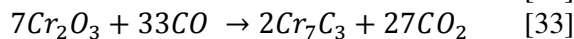
$$7Cr_2O_3 + 27CH_4 \rightarrow 2Cr_7C_3 + 21CO + 54H_2 \quad [29]$$
$$\Delta G^0 = 1797290 - 1574.1T \quad [30]$$
$$7Cr_2O_3 + 27C \rightarrow 2Cr_7C_3 + 21CO \quad [31]$$
$$\Delta G^0 = 1209770 - 861.3T \quad [32]$$
$$7Cr_2O_3 + 33CO \rightarrow 2Cr_7C_3 + 27CO_2 \quad [33]$$
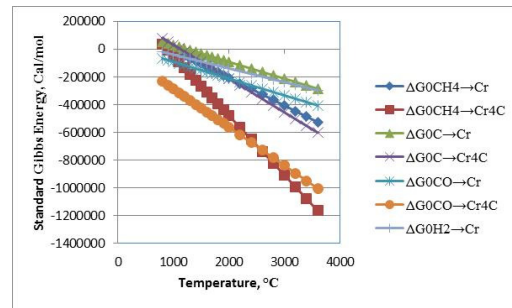$$\Delta G^0 = 134900 - 1111.58T \quad [34]$$

Fig. 3 Gibbs free energies for Cr_2O_3 reduction with C, CO, H_2 and CH_4 producing Cr_4C and Cr
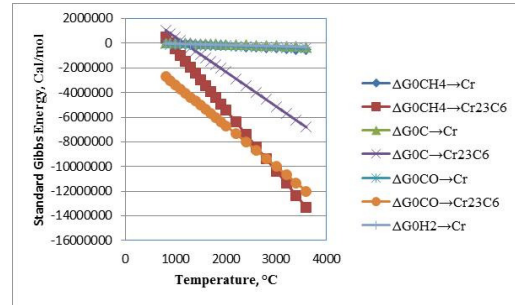
Fig. 4 Gibbs free energies for Cr_2O_3 reduction with C, CO, H_2 and CH_4 producing $Cr_{23}C_6$ and Cr
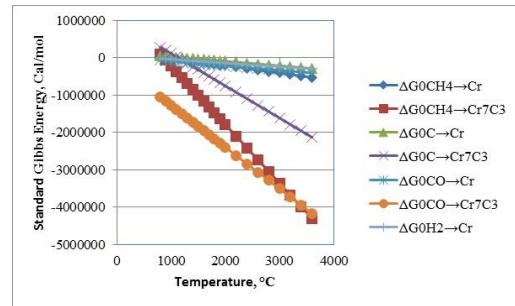
Fig. 5 Gibbs free energies for Cr_2O_3 reduction with C, CO, H_2 and CH_4 producing Cr_7C_3 and Cr

Figures 2 to 5 compare the reductions of chromium oxide by methane gas with carbothermal, CO and H_2 reductions. The CH_4 reductant resulted to more negative values of the Gibbs free energies compared to the carbothermal and H_2 reductants especially at higher temperatures. The reduction of chromium oxide occurs at higher temperatures and is not possible with carbon monoxide [6].

The reduction of Cr_2O_3 to Cr_3C_2, Cr_4C, $Cr_{23}C_6$, and Cr_7C_3 can proceed even at very low CH_4 partial pressures. This is evident thru the calculation of the equilibrium gas composition in the reduction of

chromium oxide by CH_4. This is shown in Figure 6 below. The plot shows the reduction of Cr_2O_3 to Cr_3C_2 by methane-containing gas.Hydrogen concentration is held constant at 60 vol%.

It is observed that as the concentration of carbon monoxide increases the concentration of methane also increases. However, when the temperature is increased the concentration of methane decreases to form Cr_3C_2 . When the temperature reaches to 800 °C, the Cr_2O_3 phase disappears, concomitant with a complete transformation to the Cr_3C_{2-x} phase [7]. Increasing further the carburization temperature to 850°C, leads to the formation of the stable Cr_3C_2 phase along with a small amount of Cr_3C_{2-x} metastable phase [8].
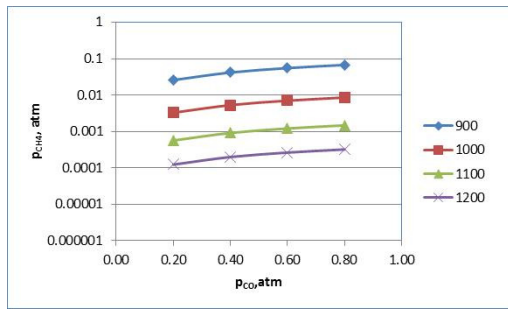

Fig. 6 Equilibrium gas composition of Cr_2O_3 reduction by methane at different temperatures

The values of the partial pressure of oxygen and carbon activity define the condensed phases that are stable during the reduction process. The thermodynamic stability diagram for Cr-O-C system is presented in Figure 7. This is constructed using Equations [1], [2] and the data that can be extracted from the following equations:
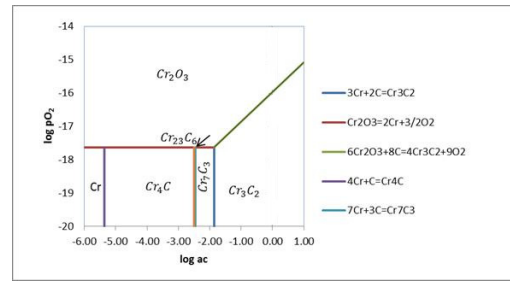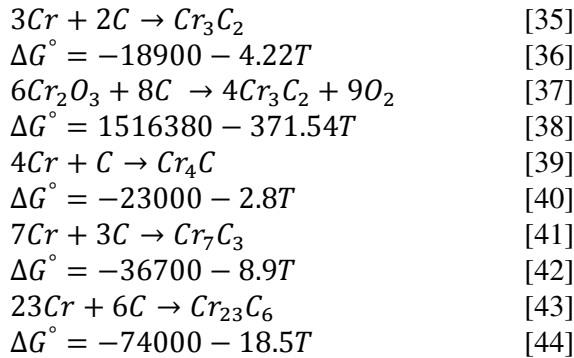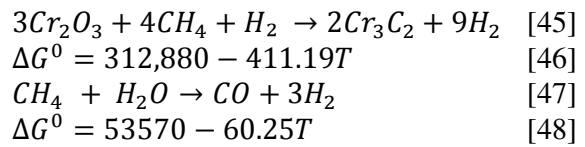
$$3Cr + 2C \rightarrow Cr_3C_2 \qquad [35]$$
$$\Delta G^{\circ} = -18900 - 4.22T \qquad [36]$$
$$6Cr_2O_3 + 8C \rightarrow 4Cr_3C_2 + 9O_2 \qquad [37]$$
$$\Delta G^{\circ} = 1516380 - 371.54T \qquad [38]$$
$$4Cr + C \rightarrow Cr_4C \qquad [39]$$
$$\Delta G^{\circ} = -23000 - 2.8T \qquad [40]$$
$$7Cr + 3C \rightarrow Cr_7C_3 \qquad [41]$$
$$\Delta G^{\circ} = -36700 - 8.9T \qquad [42]$$
$$23Cr + 6C \rightarrow Cr_{23}C_6 \qquad [43]$$
$$\Delta G^{\circ} = -74000 - 18.5T \qquad [44]$$

Fig. 7 Thermodynamic stability diagram of Cr-O-C system at 1200℃

There are three forms of chromium carbides (Cr_3C_2, Cr_7C_3 and $Cr_{23}C_6$) with different atomic ratios of carbon to chromium element. Of these carbides, Cr_3C_2 has a good set of properties of high strength, very good coverage resistance, low density, and good chemical stability. Cr_3C_2 is harder than steel and softer than tungsten carbides [9]. Based on the themodynamic stability diagram (Figure 7), Cr_3C_2 is more stable occupying a bigger area followed by Cr_7C_3 and $Cr_{23}C_6$ occupies the smallest area. Cr_4C and Cr are unstable.

3.3 Steam Reforming of Methane

The formation of Cr_3C_2 as shown in Equation [5] commences in stages with H_2O formation followed by the reaction of methane with water vapor. At standard condition, steam reforming of methane starts at 615℃. The reactions are represented by the following equations:

$$3Cr_2O_3 + 4CH_4 + H_2 \rightarrow 2Cr_3C_2 + 9H_2 \quad [45]$$
$$\Delta G^0 = 312,880 - 411.19T \qquad [46]$$
$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad [47]$$
$$\Delta G^0 = 53570 - 60.25T \qquad [48]$$

The equilibrium constant for the reaction is

$$k = \frac{(P_{CO})(P_{H_2})^3}{(P_{CH_4})P_{H_2O})} \qquad [49]$$

The equilibrium partial pressure of water vapor can be plotted against the partial pressure of carbon monoxide at different temperatures if the vol% of CH_4 and H_2 are assumed constant at 20 and 60
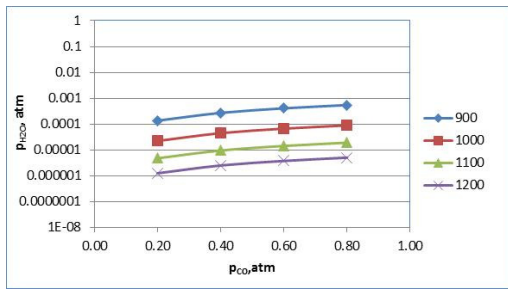
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vol % , respectively [10]. It is shown in Figure 8 below.

Figure 8 Calculated equilibrium partial pressure of water vapor in the steam reforming of CH_4 at different temperatures. CH_4 and H_2 are constant at 20 and 60 vol%, respectively.

Chromium carbides are processed with a high temperature by an electric furnace. It requires so much energy to produce these products. Economic considerations should be considered by the investors when venturing this kind of business. Researchers put so much effort to find ways and means to solve if not minimize this problem. The key factor in the reduction process is high carbon activity in the reducing gas [11].

This can be remedied by pre-reduction of the chromite ores that contain chromium oxides before feeding it to the electric furnace. Efficiency in the production is achieved by lowering the reduction temperature, changing the equilibrium conditions and increasing the reduction rate [1]. Methane containing gas is superior to solid carbonaceous materials with regard to its thermodynamic considerations. This is validated by the work of Khoshandam et al. [9]. They reported that solid chromium carbide (Cr_3C_2) was formed as the reaction product between methane and chromium oxide and it could be produced at a temperature as low as 870^0C, at least 140^0C below the temperature quoted for other conventional methods with carbon (or CO formed in situ) as the reducing agent. Thermodynamic considerations also reveal that aside from methane, carbon monoxide is also a good reductant. However, Niemela et al. [6] revealed that the reduction of chromium oxide occurs at higher temperatures in which carbon monoxide cannot accomplish.

Moreover, carbon monoxide is tasteless, colorless and odorless gas which is very poisonous when breathing because it displaces oxygen in the haemoglobin of the blood and its ability to bind in haemoglobin is 200 to 250 times greater than that of air [6]. Thus, using carbon monoxide is risky and life- threatening.

On the other hand, methane is a main ingredient in natural gas. It is a very powerful greenhouse gas since it traps more heat than carbon dioxide. It can be produced out of the trash from landfills. It is not just economical if methane is used as a reductant but also helps the implementation of the three R's which is reduce, reuse and recycle. Trash cannot be recycled and reused but during decomposition it produces methane. Capturing methane before it gets into the atmosphere helps in reducing the effects of climate change [12].

Therefore, using methane as a reductant would not only be economical but also helps the environment especially in reducing the effects of climate change and the depletion of the ozone layer.

4. CONCLUSIONS

Pre-reduction of chromium oxide that led to the production of chromium carbides started from the adsorption of methane molecules on the oxide surface thereby releasing hydrogen atoms that produce adsorbed active carbon species which have high reducing capacity. Thus, the high carbon activity of the reducing gas was the primal factor in the reduction of chromium oxide.

The chromium carbide produced from chromium oxide in chromite ore was used so that no solid carbon would be added as reductant during the subsequent smelting processes. Solid carbon from coal is harmful to human health.

Thermodynamic calculations revealed that methane-containing gas was feasible in reducing Cr_2O_3 to chromium carbides based on the Gibbs energies. Methane gas gave negative values of the Gibbs energies in all chromium carbides. It was further observed that it was lower compared with the carbothermal and H_2 reductions. This idea would benefit the processing industry of chromite ores in the country.

ACKNOWLEDGMENT

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