THERMODYNAMIC ANALYSIS OF CHROME REDUCTION WITH ALUMINUM AND SILICON

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ABSTRACT

The work is aimed at the search of substitute for ferrochrome silicon in low-carbon ferrochrome production. Thermodynamic aspects of iron and chrome reduction with complex silicon-aluminum alloy were studied in the work. Reference data were used for analysis of thermodynamic parameters of corresponding reactions. Calculations were made for the temperature range from 298K to liquid state with consideration of phase transformations of reagents. Provisional results of the research indicate the possibility of silicon-aluminum alloy application in low-carbon ferrochrome production.

1 INTRODUCTION

Producers of low-carbon ferrochrome are actively searching for alternative kinds of metallic reductants[1]. The interest in new reductants is caused by expensiveness of traditional materials, low quality of reserves and decreasing performance characteristics of ferrochrome smelting. One of possible solutions of the problem is application of complex aluminum-silicon reductants for the production of ferrochrome.

2 THERMODYNAMICS

The principles of low-carbon ferrochrome smelting are based on maximal chrome reduction from ore (slag melt) and maximal efficiency of a reductant.

Thermal reduction of chrome generally comprises the following reactions:

$$Cr_2O_{3(solid)} + 3/2Si_{(solid)} = 2Cr_{(solid)} + 3/2SiO_{2(solid)}, \tag{1}$$

$$Cr_2O_{3(solid)} + 2Al_{(solid)} = 2Cr_{(solid)} + Al_2O_{3(solid)}. \tag{2}$$

In fact, the reduction process includes multiple interactions with formation of intermediate and end compounds. Due to the lack of reliable thermodynamic data for such compounds, only approximate evaluation of reaction's completeness is possible.

Thermodynamic calculations of reactions (1) and (2) were made using the following constants of reagents: enthalpy ($\Delta_f H_{298}^0, \Delta H_{product}$), entropy ($S_{298}^0$, $\Delta S_{product}$) and heat capacity (C_p) equations factors with consideration of phase transformations[2, 3].

Standard values of above functions are usually needed to calculate the thermodynamic parameters at high temperature. The following relations are known from the literature [4, 5]:

$$\Delta_r H_{298}^0 = (\Delta_f H_{298}^0)_{\text{product}} - (\Delta_f H_{298}^0)_{\text{reagent}}, \tag{3}$$

$$\Delta_r S^0_{298} = (S^0_{298})_{\text{product}} - (S^0_{298})_{\text{reagent}}, \qquad (4)$$

$$\Delta_r G^0_{298} = \Delta_r H^0_{298} - T\Delta_r S^0_{298}, \qquad (5)$$

$$\Delta C^0_{p298} = (\sum C^0_{p298})_{\text{product}} - (\sum C^0_{p298})_{\text{reagent}} \qquad (6)$$

The values of thermodynamic functions for the reactions (1) and (2) in the standard conditions are:

$\Delta_r H^0_{298(1)}$ = -216440,00 J/mole; $\Delta_r S^0_{298(1)}$ = 0,00 J/mole·K; (7)
$\Delta_r G^0_{298(1)}$ = -216440,00 J/mole; $\Delta C^0_{p298(1)}$ = -35,76 J/mole·K;
$\Delta_r H^0_{298(2)}$ = -525640,00 J/mole; $\Delta_r S^0_{298(2)}$ = -39,76 J/mole·K; (8)
$\Delta_r G^0_{298(2)}$ = -513791,52 J/mole; $\Delta C^0_{p298(2)}$ = -42,65 J/mole·K.

In order to simplify the calculations of the dependence of Gibbs energy from temperature we applied the formula based on Uhlich third approximation. It involves the equations of heat capacity dependence on temperature represented by empirical power series or polynomials. The final form of the equation is given below[4, 5]:

$$\Delta G^0_T = \Delta H^0_T - T\Delta S^0_T = \Delta a \cdot T + \tfrac{1}{2} \cdot \Delta b \cdot T^2 - \Delta c \cdot T^{-1} + X - T(\Delta a \cdot \ln T + \Delta b \cdot T - \tfrac{1}{2}\,\Delta c \cdot T^{-2} + Y) =$$
$$= X + (\Delta a - Y) \cdot T - \Delta a \cdot T \cdot \ln T - \tfrac{1}{2} \cdot \Delta b \cdot T^2 - \tfrac{1}{2} \cdot \Delta c \cdot T^{-2}. \qquad (9)$$

The variables “X” and “Y” were found through the formulas [4, 5]:

$$X = \Delta_r H^0_T - \Delta a \cdot 298 - \tfrac{1}{2} \cdot \Delta b \cdot 298^2 + \Delta c \cdot 298^{-1} \qquad (10)$$
$$Y = \Delta_r S^0_{298} - \Delta a \cdot \ln 298 - \Delta b \cdot 298 + \tfrac{1}{2} \cdot \Delta c \cdot 298^{-2} \qquad (11)$$

The temperature range studied for both reactions (1 and 2) was 298-3000 K, where main oxidation-reduction reactions take place. The range covers all temperature interval of phase transformation of chrome ore and reductant (silicon or alumina-silicon).

There are 8 and 7 temperature intervals respectively for the reactions (1) and (2). The intervals correspond to phase transformations of initial substances and end products.

The diagram and equations of temperature dependence of Gibbs energy for the reaction (1) are represented in the figure 1 and table 1.

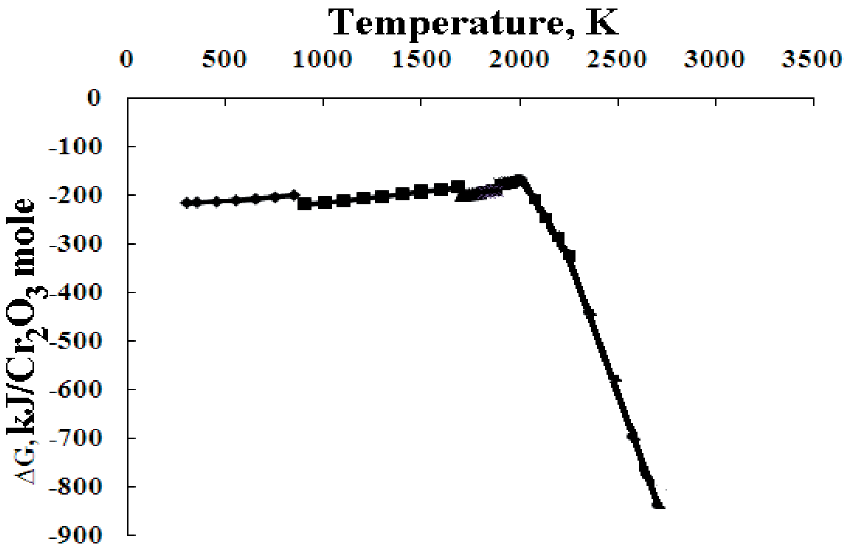

Figure 1: Temperature dependence of Gibbs energy (1)

Table 1: Equations of temperature dependence of Gibbs energy (1)

№	Equation, J/Cr_2O_3 mole	Temp. interval of phase transformations, K
1.	$\Delta G_T = -226601 + 29{,}858T$	ΔT = 298,15-846
2.	$\Delta G_T = -258942 + 43{,}585T$	ΔT = 846-1688
3.	$\Delta G_T = -274956 + 44{,}653T$	ΔT = 1688-1800
4.	$\Delta G_T = -278294 + 46{,}504T$	ΔT = 1800-1883
5.	$\Delta G_T = -280871 + 54{,}434T$	ΔT = 1883-1953
6.	$\Delta G_T = -280172 + 55{,}118T$	ΔT = 1953-2000
7.	$\Delta G_T = -270230 - 13{,}161T$	ΔT = 2000-2173
8.	$\Delta G_T = -274674 - 191{,}01T$	ΔT = 2173-2963

As seen from the figure 1, phase transformations in the range of 846-2000 K have weak influence on reaction (1), promoting the formation of reaction products. Further phase transitions at a temperature above 2000 K intensify the reaction promoting its complete progress.

The results of thermodynamic calculation of reaction (2) are represented in the figure 2 and table 2.

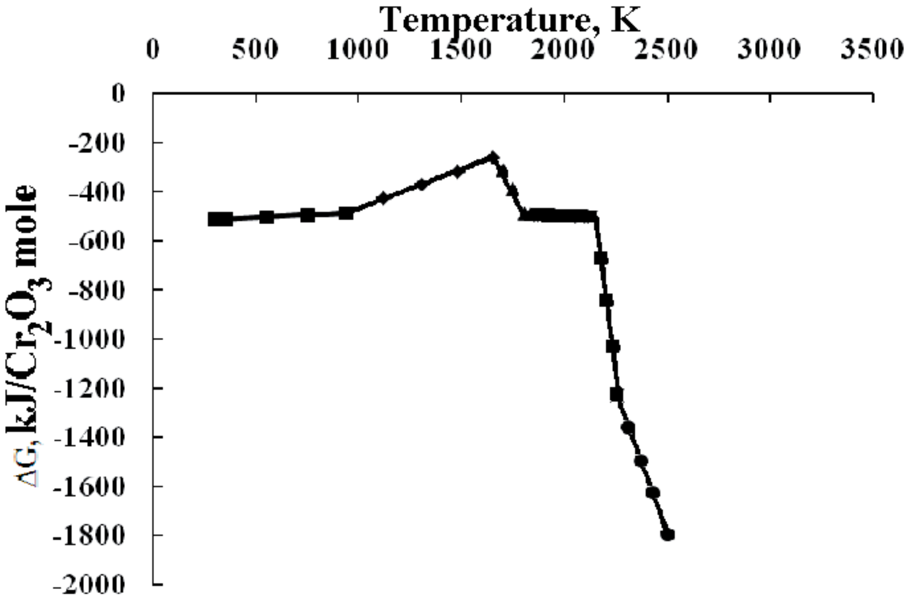

Figure 2: Temperature dependence of Gibbs energy (2)

Table 2: Equations of temperature dependence of Gibbs energy (2)

№	**Equation, J/Cr_2O_3 mole**	**Temp. interval of phase transformations, K**
1.	ΔG_T = -524257 + 40,478T	ΔT = 298,15-933
2.	ΔG_T = -525906 + 161,180T	ΔT = 933-1650
3.	ΔG_T = -467389 – 15,107T	ΔT = 1650-1800
4.	ΔG_T = -445485 – 26,965T	ΔT = 1800-2126
5.	ΔG_T = -421735 – 371,57T	ΔT = 2126-2173
6.	ΔG_T = -395200 – 561,43T	ΔT = 2173-2500
7.	ΔG_T = -471551 – 240,75T	ΔT = 2500-3000

Estimated values and the dependence diagram represented in the figure 2 show that phase transitions in the intervals 298,15-933 K, 933-1650 K and 1650-2126 K do not exert strong influence on reaction progress. Further phase transitions at 2126-2500 K cause abrupt increase in negative value of Gibbs energy which would promote intensive and complete progress of the reaction (2).

According to the calculations, the process of metallothermic reduction of chrome has an explicit exothermal nature. Silicon and aluminum used as chrome reductants have negative values of Gibbs energy in all temperature intervals studied in the present work. It confirms the probability of reaction progress toward the formation of reaction products. The results of thermodynamic evaluation of reactions (1) and (2) indicate the positive influence of combined effect of silicon and aluminum on reduction processes in low-carbon ferrochrome smelting. The calculations of Gibbs energy variation in the range of 298-3000 K confirm the suitability of complex silicon-aluminum alloys for low-carbon ferrochrome production.

3 REFERENCES

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