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Use of a Mathematical Model GPRO to Describe Complex Gas - Metal Reactions

Uporaba matematičnega modela GPRO pri opisovanju kompleksnih reakcij med plinsko in kovinsko fazo

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The knowledge of the thermodynamics in complexe systems consists of gases and metal shoud be valuable for the control of industrial processes. The Gibbs energy minimization model has been implemented in the software program GPRO and associated with a powerfull reliable database. This computer package can perform computation of the equilibrium composition in very complex chemical and metallurgical systems. Some examples in this paper illustrate the simplicity of the computation and use of the program in the field of typically metallurgical applications which have been traditionally assigned to specialists.
Key words: Equilibrium reactions, active gas-atmospheres, decarburisation of non-oriented electrical steels

Poznavanje termodinamičnih odnosov v kompleksnih sistemih plin - kovina ima lahko izreden pomen za kontrolo industrijskih procesov. Gibbsov model o minimizaciji energije je implementiran v programsko opremo GPRO, ki mu služi kot osnova močna baza verificiranih termodinamičnih podatkov. Programska oprema omogoča izračunavanja ravnotežnih sestav v zelo kompleksnih kemijskih in metalurških sistemih. Navedeni primeri v tem članku ilustrirajo enostavnost izračunavanj in način uporabe programa na področju metalurških aplikacij, ki jih večinoma izvajajo strokovnjaki na tem področju.
Ključne besede: Ravnotežne reakcije, aktivne plinske atmosfere, razogljičenje neorientirane elektro pločevine.

Introduction

The application of thermodynamics to a system gas/solid enables to calculate the composition at equilibrium and the direction and extent of change which can take place under specified conditions. In this paper an attempt is made to demonstrate the use of a personal computer software program as an elegant and sensitive method for numerous metallurgical applications especially for analysis of gas-metal systems.

It is expected, that user of this method will be in good position to go more deeply into learning thermodynamic correlations.

Principles of the Gibbs method

In the fields of heat treatment of metals as annealling, carburizing, steel decarburizing, nitrocarburizing and many other operations, the metallurgist is concerned not with pure gases but with mixtures of various components (gases and solids) which form the atmosphere in the furnace.

Description of used method for the complex equilibrium conditions

Several excellent software programs for general studing and calculating of equilibria reactions by high temperatures have been developed in the last two decades (e.g. SOLGASMIX, THERMOCALC, FACT, CHEMSAGE ...)[2,3].

However, most of them are designed and written in complex form requiring very strong computer units, few others are intented simply as a tool to be applied for the purposes of solving real problems.

Therefore, it seemed worthwhile to develop a program which will take some midway path between these two computer program designs. The new software program, called GPRO is based on the method of free energy minimization and extended to systems containing numerous gaseous and condensed phases mainly in accordance with SOLGASMIX-principles[5-8].

Thermodynamical approaches to the Gibbs-method

The advantage of Gibbs method energy minimization is based on his simplicity for description of chemical reactions in complex systems and its ability to facilitate determination of the effect of a change in the external influences on the equilibrium state. In the GPRO software program the user needs only to specify the type, the components present in the system and the conditions (for example: temperature and chemical composition of the system) for the calculation.

The program will perform automatically the equilibrium thermodynamic computions typically associated with complex

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chemical equilibria from a defined database.

With the aid of the GPRO-program, a user is able to perform most of the following operations:

- The energy for pre-heating the initial mixture from the initial temperature T_o to the reaction temperature T,
- The heat of reaction,
- The computation of the complex chemical equilibria in gaseous mixtures and activity of solid compounds,
- Displaying and printing data of compounds and solutions at any temperatures and compositions.

Associated databases for the thermodynamic equilibrium computations

From many excellent standard treatises on thermodynamics it is known, that without reliable thermodynamic data most of the equations are ineffective and numerical answers will be wrong.GPRO software program is based on use of both formula for calculations of the standard Gibbs energies of the formation of the phase:

1. in the form:

$$\Delta G_T^\circ = \frac{A}{T} + B + CT + DT^2 + ET^3 + FT\ln T \qquad (a)$$

2. over the enthalpy ΔH_T° entropy ΔS_T° and heat capacity $C_p(T)$:

$$\Delta G_T^\circ = \Delta H_{298}^\circ + \int_{To}^{T} C_p(T)\,dT - TS_{298}^\circ - T\int_{To}^{T}\frac{C_p(T)}{T}\,dT \qquad (b)$$

$C_p(T) = A + BT + CT^2 + DT^{-2}$

Both methods used from the database involve a search for a minimum value of the free energy G of a system and give equivalent results. However the second method considering the enthalpy H, entropy S and heat capacity Cp has more advantages by combining heat and equilibrium calculation. Typical example is the determination of the adiabatic flame temperature, where enthalpy of reaction serves as the criterion of the heat balance.

Exploiting the GPRO-program for heat and standard free enthalpy calculations

Traditionally the concept of heat enthalpy and standard free enthalpy as a state function are introduced by considering the behaviour and properties of many chemical and metallurgical reactions.

Since the equilibrium state has been obtained, the heat generation or the total heat of process can be computed, using the thermodynamical functions .E.g. the energy necessary for preheating the initial mixture from the initial temperature T to the reaction temperature T, H - H_o, (taking into the account the transition values within the actual temperature interval T - T_o added to the heat of reaction - H_o), gives the H_o - total total heat of the system.

Example No.1

Statement of the problem

A mixture of Fe, (O_2), SiO_2 present in the molar ration 2 : 1 : 1 is adiabatically heated from 298 K to 1173 K. Calculate H_o - H_{298} and G_o for the reaction:

$$2\langle Fe\rangle + (O_2) + \langle SiO_2\rangle = \langle Fe_2SiO_4\rangle \qquad (1)$$

where:

<> = solid, () = gas

Compare the obtained results with results from literature for the Gibbs free energy of the fayalite formation[3]:

$$\Delta G_T^\circ = -555504 + 135{,}23T\,(J.mol^{-1})\,(900...1478K) \qquad (2)$$

$$\Delta G_T^\circ = -505263 + 101{,}32T\,(J.mol^{-1})\,(1478...1508K) \qquad (3)$$

Since the end temperature is higher then 1773 K all transition and latent heats of the reactants and products must be considered:

1. $Fe(\alpha \rightarrow \beta) = 1033K, \Delta H^\circ_{\alpha\rightarrow\beta} = 5024\,(J.mol^{-1})$.
2. $Fe(\beta \rightarrow \gamma) = 1183K, \Delta H^\circ_{\beta\rightarrow\gamma} = 921\,(J.mol^{-1})$.
3. $Fe(\gamma \rightarrow \delta) = 1674K, \Delta H^\circ_{\gamma\rightarrow\delta} = 879\,(J.mol^{-1})$.
4. $Fe(T_m) = 1809K, \Delta H^\circ_{Tm} = 13860\,(J.mol^{-1})$.
5. $Fe_2SiO_4\,(T_m = 1493K), \Delta H^\circ_m = 9210\,(J.mol^{-1})$.

Solution :

Fig. 1 shows a plot of G_o versus T for the reaction (1). There is a change of the entalpy due to melting Fe_2SiO_4 at T = 1492 K and calculated values for G_o over Cp - expression and from a formels (2) and (3).

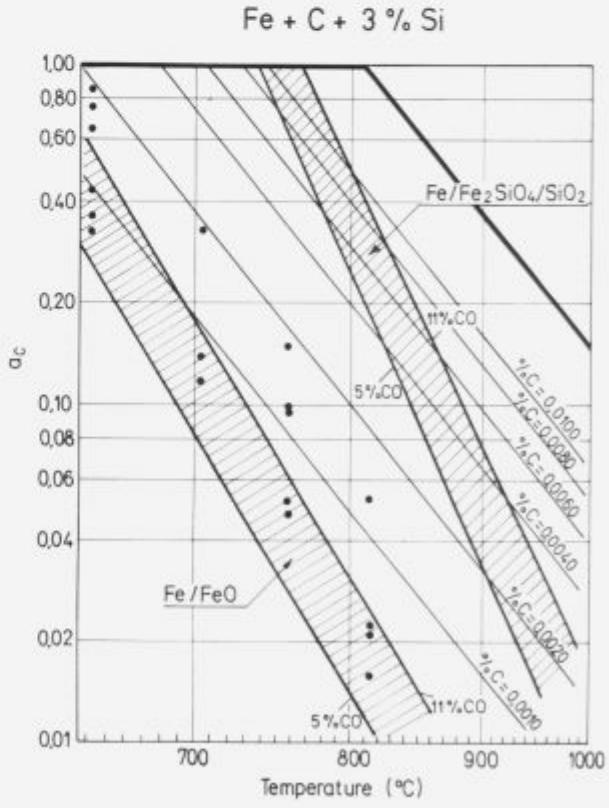

Figure 1: Plot of thermodynamical data for Fe_2SiO_4 as a function of temperature calculated with GPRO-program. (Model) and (Lit.) using data from Richardson and Jeffes[3]

Slika 1: Diagram termodinamičnih podatkov za Fe_2SiO_4 kot funkcija temperature izračunano s programom GPRO.

Exploiting the GPRO-program for complex equilibria calculations

In this chapter, some examples of work performed in our laboratory on the application of the computer-based model GPRO will be reviewed. The accuracy of the gaseous atmosphere control in steel decarburizing furnaces has been remarkably improved owing to the application of computer control systems and the development of new measuring techniques (for example: oxygen and/or carbon sensors).

Gaseous active atmospheres

There is relatively little emphasis in the literature about use of the thermodynamical models on the field of active atmospheres. Such mixtures containing both gaseous and condensed components (for example: Fe + C + O + H + N are extremly complicated for the numerical calculations). Detailed experimental studies are difficult and also thermodynamical results are mostly presented in the graphical form, which are very useful in research work but of little effectivness in searching solutions for a current practical operation.

To obtain equilibrium compositions in the real gaseous mixtures by high temperatures, taking into account both energy and material balances, development of new approaches are strongly required.

Example No. 2

Statement of the problem

The use of gaseous atmosphere with a well-defined oxygen potential for decarburisation of low carbon iron-silicon steels in the continuous furnace can be simulated by use of thermodynamical model.

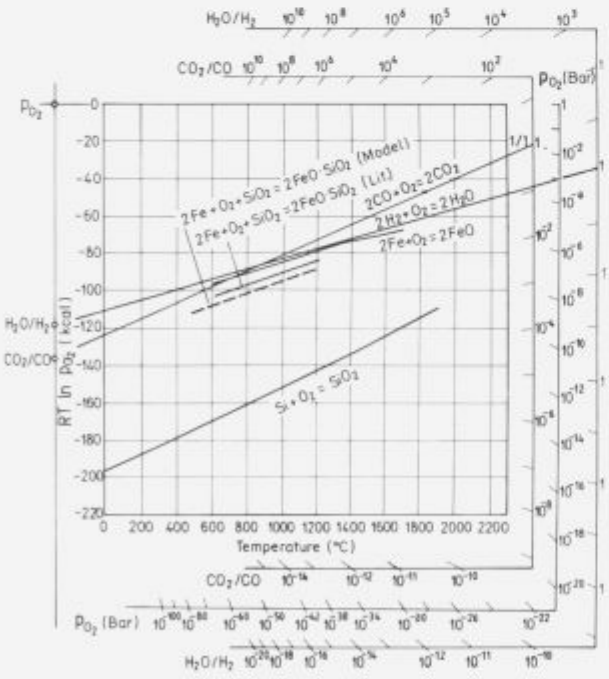

Figure 2: Equilibrium behavior of different oxide phases during the decarburization of Fe-C-Si alloys in active gas atmosphere ($CO + CO_2 + H_2 + H_2O + N_2$)

Slika 2: Ravnotežni odnosi različnih oksidnih faz, ki nastajajo med razogljičenjem jekel Fe-C-Si v aktivni plinski mešanici ($CO + CO_2 + H_2 + H_2O + N_2$)

Equilibrium calculations and practical measurements show that solubility and carbon activity in Fe-C-Si steels depend on the gaseous atmosphere, temperature and steel composition.

The thermodynamic analysis permit on the base of thermodynamical data to predict the equilibrium carbon contents in electrical steels **(Fig. 2)**.

Concluding Remarks

One of the widely known methods for chemical and metallurgical equilibrium calculations by the high temperatures is Gibbs energy minimization method. Based upon these principles and implementing some algorithms from computer program SOLGASMIX, the new user-friendly computer program called GPRO was developed.

GPRO-software program is designed as a system which can perform equilibria thermodynamic computations in systems containing gaseous and stoichiometric and/or non-stoichiometric condensed phases.

The computer program lists options as menu and the user is slowly directed through the program, choosing one option at a time. Before using the level of the main menu, user must create the relevant thermodynamic data file which contains the reliable thermodynamic data as heat capacity, enthalpy, entropy with respect to a chosen references state.

In this paper some typical examples are presented to illustrate the simplicity of the computation in the complex chemical and metallurgical systems at high temperatures for typical industrial applications.

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