

Physical Chemistry

Thermodynamic Analysis of Interaction between the Components In the $\text{Cr}_2\text{O}_3 - \text{SiO}_2 - \text{FeO} - \text{C}$ System

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ABSTRACT. Complete thermodynamic analysis of the system $\text{Cr}_2\text{O}_3\text{-SiO}_2\text{-FeO-C}$ has been carried out for the following structures:



The basic results for all structures are presented in the form of diagrams (dependence of the contents of components at temperature range 800-2000 K). © 2008 Bull. Georg. Natl. Acad. Sci.

Key words: carbide, metallic chromium, chromium silicide.

Chromium-base alloys possess a variety of useful properties and are widely used as alloying additives for the majority of steels and alloys, including those of iron-base. The need of increase of alloyed metal fraction creates a new challenge of improving the quality of industrial chromium ferroalloys. Solution of this problem calls for expansion of theoretical and experimental research dealing with simple and complex chromium-base metallic and oxide systems.

In a number of cases, the conventional technological schemes of chromium-ferroalloys production, do not fit the contemporary level of technological progress, and stand in need of improvement. Therefore development of the physico-chemical base of the carbon-reduction technology of ferroalloy production is a task of primary importance [1].

Since computer-aided complete thermodynamic analysis (CTA) of chemical and phase equilibrium in multi-component systems is widely used in recent years [2,3], it is convenient to apply this approach [2] to chromium ferroalloy systems with a view to predicting their production conditions.

In the present paper the results of the CTA of interaction between the components in the $\text{Cr}_2\text{O}_3\text{-SiO}_2\text{-FeO-C}$ system of near-industrial compositions, are discussed. Data on CTA for the cited system are not known to the authors. Here it should be noted that the CTA used in this study provides an opportunity to judge not only about the equilibrium processes taking place in the system, but also about the mechanism of interaction between the component quently, correct the composition of the final product.

The calculations were conducted using the program ASTRA 4 [2], for atmospheric pressure (101 MPa) and argon medium, with a 50° step in the temperature range 300-2000K.

The initial compositions of starting mixtures were selected on the basis of the following reactions:



During the calculations the following components were taken as the possible condensed ones: C, Cr, Si,

Fe, Cr_2O_3 , SiO_2 , FeO, Fe_2O_3 , Fe_3O_4 , FeCr_2O_4 , $\text{Cr}_2\text{Si}_3\text{O}_9$, FeSiO_3 , SiC, Fe_3C , Cr_3C_2 , Cr_7C_3 , Cr_{23}C_6 , CrSi, CrSi_2 , Cr_3Si , Cr_5Si_3 , FeSi, FeSi_2 , Fe_2Si_5 , Fe_3Si , Fe_5Si_3 and the following as gaseous: Ar, O, O_2 , O_3 , C, C_2 , C_3 , C_4 , C_5 , CO, CO_2 , C_2O , C_3O_2 , Cr, Cr_2 , CrO, CrO_3 , Cr_2O , Cr_2O_2 , Cr_2O_3 , CrC_2 , Si, Si_2 , Si_3 , SiO, SiO_2 , Fe, FeO, FeO_2 .

In the system under consideration the temperature dependence of the processes of interaction between the components (dissociation and reduction in the reactions 1-4) are shown in Fig. 1-4.

For starting mixture 1 (reaction 1), because of interaction between chromium and iron oxides, an iron chromate FeCr_2O_4 is created at comparatively low temperatures, the maximal amount (~63.5 mass.%) of which occurs at about 800K. Increase in temperature causes its decomposition, and at ~1400K the chromate disappears because of the formation of iron and chromium oxides.

The presence of chromium silicate ($\text{Cr}_2\text{Si}_3\text{O}_9$) is detected at ~800K (~11.5 mass.%), and increase in temperature up to ~1400K increases its amount to ~17 mass.%. However, further increase of temperature leads to its decomposition to the respective oxides, and at ~2000K the silicate practically disappears (~1.8 mass.%) from the system.

The chromium oxide Cr_2O_3 is available in the system at ~900K (~1.8 mass. %), and its amount increases when the temperature increases, reaching ~37 mass. %

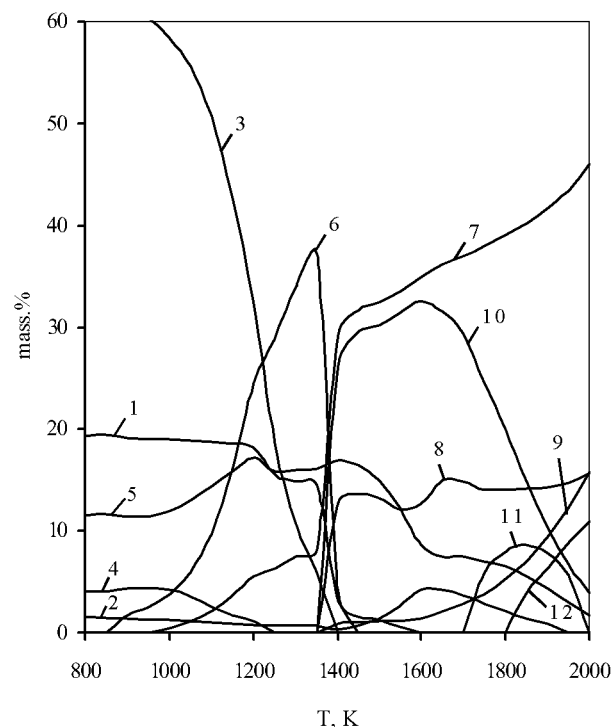


Fig. 1. Content of components versus temperature for reaction 1: 1- C, 2- SiO_2 , 3- FeCr_2O_4 , 4- FeSiO_3 , 5- $\text{Cr}_2\text{Si}_3\text{O}_9$, 6- Cr_2O_3 , 7- CO, 8- Fe, 9- Cr, 10- Cr_3C_2 , 11- Cr_7C_3 , 12- Cr_3Si .

at ~1350K. Then its amount drastically decreases because of its reduction by carbon, and at ~1400K the oxide completely disappears. Starting from this moment, the creation of metallic chromium begins (1 mass %), reaching ~16 mass.% at ~2000K. Precipitation of metallic iron, caused by carbothermic reduction of its oxide, begins at ~1350K, reaching ~16 mass.% at ~2000K.

The chromium oxide Cr_3C_2 is created at temperatures higher than 1400K, reaching maximum amount (~32.5mass.%) at ~1600K. Further, its amount decreases to ~4 mass.% at 2000K because of its participation in the reduction processes and creation of Cr_7C_3 . Another chromium carbide, Cr_7C_3 starts to precipitate at ~1750K; then its amount decreases because of its participation in the reduction processes, completely disappearing at 2000 K.

The chromium silicide Cr_3Si occurs in the system at ~1800K, reaching maximum amount (10.9 mass%) at 2000 K. The amount of carbon decreases noticeably above ~1200K because of the reduction and carbide formation processes, and at ~1600K it is completely utilized. Above ~1350K, precipitation of CO starts in the system, and higher temperatures increase its amount.

Increase of SiO_2 and C content in starting mixture (reactions 2-4), in contrast to reaction 1, causes formation of the following additional compounds in the products of component interaction (Fig. 2-4): In reaction 2 -

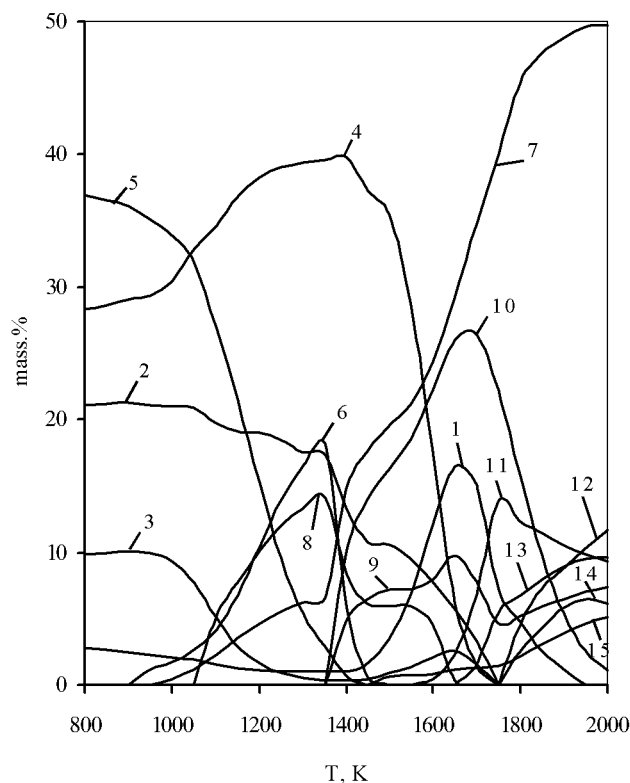


Fig. 2. Content of components versus temperature for reaction 2: 1- SiO_2 , 2- C, 3- FeSiO_3 , 4- $\text{Cr}_2\text{Si}_3\text{O}_9$, 5- FeCr_2O_4 , 6- Cr_2O_3 , 7- CO, 8- Fe_3C , 9- Fe, 10- Cr_3C_2 , 11- FeSi, 12- Cr_5Si_3 , 13- CrSi, 14- Cr_3Si , 15- Cr.

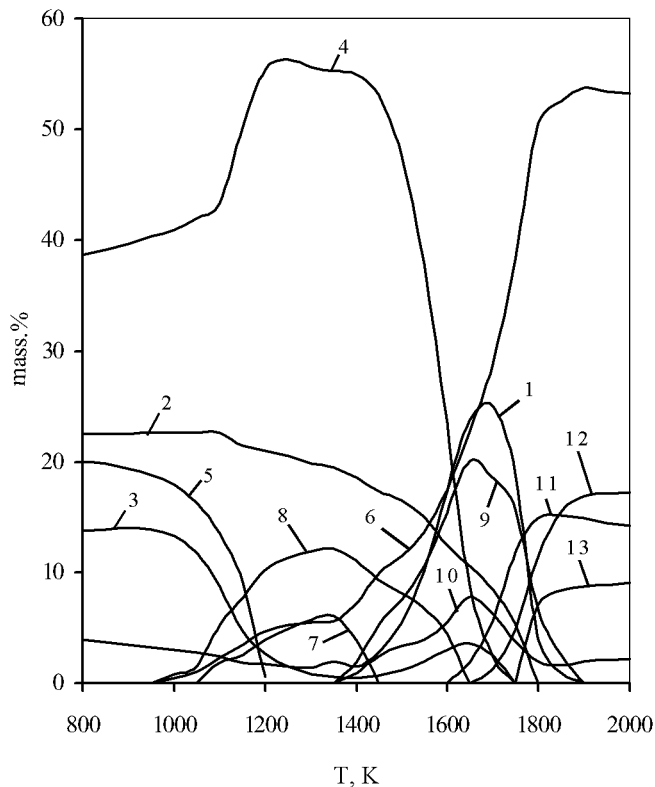


Fig. 3. Content of components versus temperature for reaction 3: 1- SiO₂, 2- C, 3- FeSiO₃, 4- Cr₂Si₃O₉, 5- FeCr₂O₄, 6- CO, 7- Cr₂O₃, 8- Fe₃C, 9- Cr₃C₂, 10- Fe, 11- FeSi, 12- CrSi, 13- Cr₅Si₃.

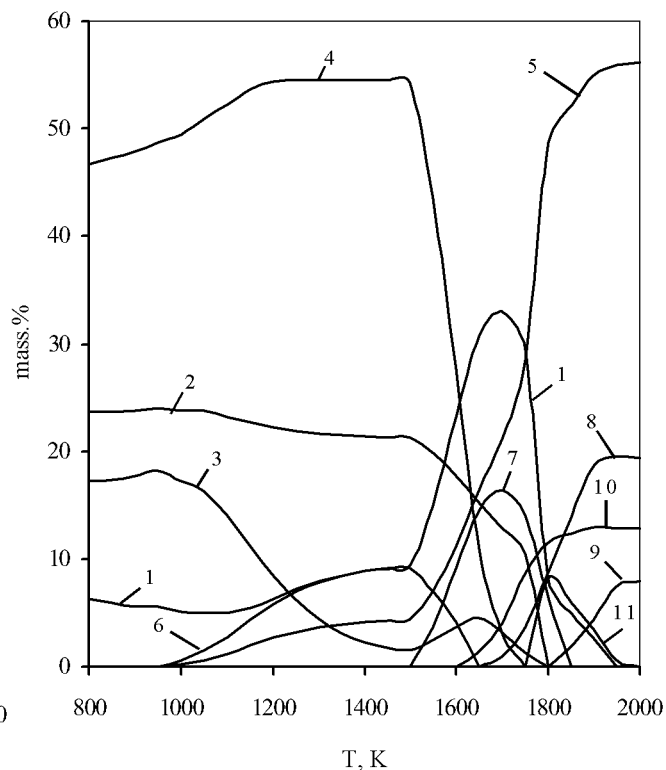


Fig. 4. Content of components versus temperature for reaction 4: 1- SiO₂, 2- C, 3- FeSiO₃, 4- Cr₂Si₃O₉, 5- CO, 6- Fe₃C, 7- Cr₃C₂, 8- CrSi, 9- CrSi₂, 10- FeSi, 11- SiC.

Fe₃C, FeSi, CrSi, Cr₅Si₃; in reaction 3 - Fe₃C, FeSi, CrSi, and in reaction 4 - Fe₃C, FeSi, CrSi, CrSi₂, SiC.

Moreover, the presence of Cr₇C₃ (reaction 2), Cr, Cr₇C₃ (reaction 3) and Cr, Fe, Cr₇C₃, Cr₃Si, FeCr₂O₄ (reaction 4), was not detected.

Iron carbide occurs in the system at ~1100K (reaction 2) and at ~1000K (reactions 3 and 4). Its amount is maximal at 1350K, and decreases to practically zero, at 1650K. In addition to the above components, small amounts of Cr, Si, CrFe₃ and CrSi₂ are precipitated, the respective curves of which are not shown in the diagram. Precipitation of iron silicide (reactions 2-4) takes place at ~1600K, and its amount increases until the temperature reaches ~1750K (reaction 2), and ~1800K

(reactions 3,4).

Chromium silicides, CrSi, Cr₅Si₃ (reaction 2), CrSi (reaction 3), CrSi₂ (reaction 4) and silicon carbide (reaction 4) are formed in the system above ~1600 K. After reaching its maximal value at ~1800 K, the amount of carbide decreases, completely disappearing at 2000 K.

The comparison of Fig. 1 and Figs. 2-4 shows that almost identical reactions take place for the rest of the compounds and elements, taking into account a negligible difference between the quantitative parameters and temperature of the processes. In Table 1 the composition of metallic alloy at 2000 K* for reactions 1-4 is shown (here it is assumed that the elements in the alloy exist in the form of complexes).

Table 1

Reaction	Cr	Si	Fe	C
1	58.3	7.1	33.1	1
2	52.4	20.4	27.0	0.3
3	44.0	30.9	25.0	
4	37.6	41.7	20.7	

ფიზიკური ქიმია

$\text{Cr}_2\text{O}_3 - \text{SiO}_2 - \text{FeO} - \text{C}$ სისტემაში კომპონენტების ურთიერთქმედების თერმოდინამიკური ანალიზი

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ნაშრომში შესრულებულია $\text{Cr}_2\text{O}_3 - \text{SiO}_2 - \text{FeO} - \text{C}$ სისტემის სრული თერმოდინამიკური ანალიზი შემდეგი შედგენილობებისათვის:

1. $\text{Cr}_2\text{O}_3 + 0,5 \text{SiO}_2 + \text{FeO} + 5 \text{C}$;
2. $\text{Cr}_2\text{O}_3 + 1,5 \text{SiO}_2 + \text{FeO} + 7 \text{C}$;
3. $\text{Cr}_2\text{O}_3 + 2,5 \text{SiO}_2 + \text{FeO} + 9 \text{C}$;
4. $\text{Cr}_2\text{O}_3 + 4,0 \text{SiO}_2 + \text{FeO} + 12 \text{C}$;

ანალიზის ძირითადი შედეგები ყველა შედგენილობისათვის წარმოდგენილია დიაგრამების სახით (კომპონენტების შედგენილობის ტემპერატურისაგან დამოკიდებულება 800 - 2000 K ინტერვალში).

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