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*Physical Chemistry*

# Thermodynamic Analysis of Carbothermal Reduction of the Mixture of $Cr_2O_3$ and MnO Oxides

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(Presented by Academy Member Givi Tsintsadze)

**ABSTRACT. Complete thermodynamic analysis of the system Cr-Mn-O-C has been carried out for the following compositions: $Cr_2O_3$ + MnO + 4 C (1), $Cr_2O_3$ + MnO + 5 C (2) and $Cr_2O_3$ + MnO + 6 C (3). The basic results for all compositions are presented as diagrams (dependence of the contents of components on temperature within the range of 800-2000 K).** *© 2011 Bull. Georg. Natl. Acad. Sci.*

***Key words***: carbide, chromium oxide, manganese oxide.

$Cr_2O_3$ and MnO, Cr-Mn alloys possess a series of special properties and are widely used as electrodes which are applied for welding of manganese steel parts. These alloys are characterized by a specific thermal expansion, magnetic susceptibility and nuclear magnetic resonance [1, 2]. Therefore obtaining these alloys by carbothermic reduction of the mixture of $Cr_2O_3$ and MnO oxides is of great interest.

In the present paper we present the results of a complete thermodynamic analysis (CTA) of Cr-Mn-O-C system carried out for the following compositions:

$$Cr_2O_3 + MnO + 4\,C \quad (1)$$

$$Cr_2O_3 + MnO + 5\,C \quad (2)$$

$$Cr_2O_3 + MnO + 6\,C \quad (3)$$

To our knowledge there are no data on the CTA of the above-mentioned system in scientific literature.

The calculations were conducted using the computer program ASTRA 4, described in [3], taking into account the interaction in an inert medium of argon. Reactions were carried out at a total atmospheric pressure in the temperature range 800-2000 K with a 50° step. The following components are taken into account as the possible condensed ones (C, Cr, $Cr_2O_3$, $Cr_3C_2$, $Cr_7C_3$, $Cr_{23}C_6$, Mn, $Mn_3C$, $Mn_7C_3$, $Mn_{23}C_6$, $CrMn_3$, MnO, $MnO_2$, $Mn_2O_3$, $Mn_3O_4$, $MnCr_2O_4$) and the following (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, $CrO_3$, $Cr_2O$, $Cr_2O_2$, $Cr_2O_3$, $CrC_2$, Mn, MnO ) as gaseous agents.

Results of CTA are presented in Figures 1-3.

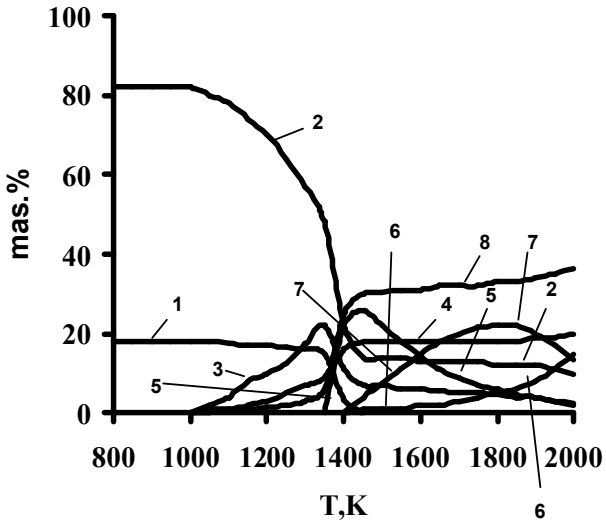


Fig. 1. Dependence of the content of components on the temperature for the composition (1): 1-C; 2-$MnCr_2O_4$; 3-$Cr_2O_3$; 4-$Mn_{23}C_6$; 5-$Cr_3C_2$; 6-Cr; 7-$Cr_7C_3$; 8-CO

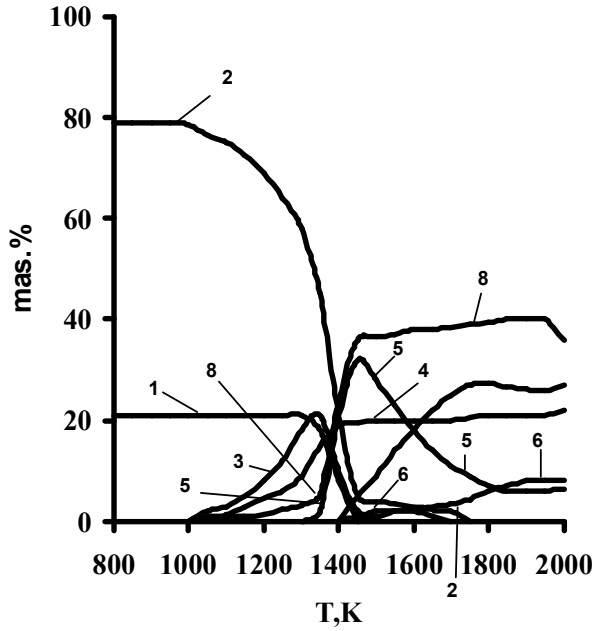


Fig. 2. Dependence of the content of components on the temperature for the composition (2): 1-C; 2-$MnCr_2O_4$; 3-$Cr_2O_3$; 4-$Mn_{23}C_6$; 5-$Cr_3C_2$; 6-Cr; 7-$Cr_7C_3$; 8-CO.

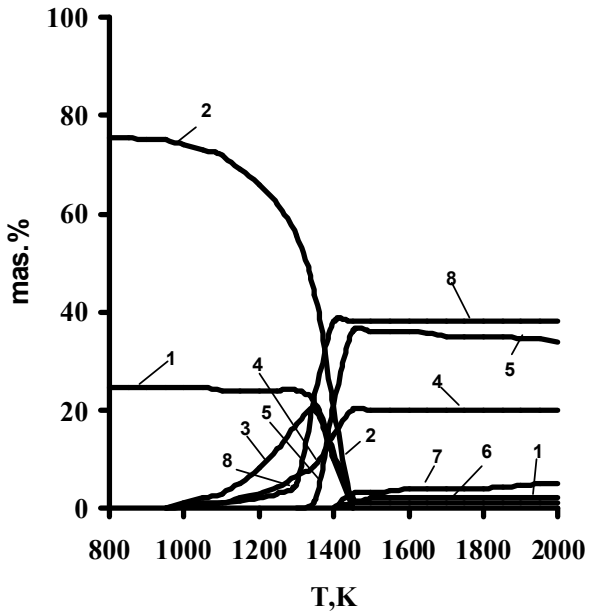


Fig. 3. Dependence of the content of components on the temperature for the composition (3): 1-C; 2-$MnCr_2O_4$; 3-$Cr_2O_3$; 4-$Mn_{23}C_6$; 5-$Cr_3C_2$; 6-Cr; 7-$Cr_7C_3$; 8-CO.

Fig. 1 shows the thermodynamic model of the carbon-thermal reduction of $Cr_2O_3$ and MnO composition in the temperature range 800-2000 K for the first reaction. For this charge mixture manganese chromate ($MnCr_2O_4$) is produced at the expense of interaction between chromium and manganese oxides at relatively low temperatures, the maximum amount of which (~82 mass %) is observed in the 800K area. As the temperature increases from ~1000 K, the decomposition process occurs and sharp decrease in its amount (14 mass % at 1450 K) takes place. Above this temperature the amount of manganese chromate continues to decrease smoothly reaching up to 10 mass % at 2000 K. In the system the release of $Cr_2O_3$ starts from 1050 K and its amount increases, reaching 22 mass % at 1350 K. Above this temperature the amount of $Cr_2O_3$ sharply decreases up to 1450 K, and then gradually decreases to 2000 K to reach 2.5 mass %. Reduction of manganese is observed at ~1000 K with the formation of $Mn_{23}C_6$ and CO in the gaseous phase. The amount of $Mn_{23}C_6$ drastically rises to 1450 K, while it does not change further until the temperature reaches 2000 K (~ 20 mass %). Reduction of Cr with the formation of $Cr_3C_2$ starts at 1350 K and its amount sharply increases up to ~ 1450 K (~ 26 mass %), and further, it drops up to 2000 K temperature and reaches ~ 2.5 mass %. In parallel, changes in the amount of the condensed $Cr_7C_3$ are of the same character to reach a maximum (~ 22 mass %) at ~ 1800 K. Further it decreases and drops to 13.5 mass % at 2000 K. The amount of the condensed carbon does not change up to 1000 K, but decreases above this temperature and completely disappears at ~1450 K. The condensed Cr appears in the system from 1400 K; above this temperature its amount increases, reaching 15 mass % at 2000 K.

The thermodynamic analysis has shown that within the temperature range 800-2000 K reduction of the mixture of oxides in the system was incomplete, which should be explained by the presence of small amounts of carbon.

Fig. 2 presents the results of CTA reaction (2), showing that the process is similar to the reaction (1). In this case, the release of condensed $Cr_2O_3$, $Mn_{23}C_6$ and CO in the gaseous phase in the system starts above 1000 K. The only difference is that the condensed $MnCr_2O_4$ and $Cr_2O_3$ disappear in the system at ~1750 K and ~1700 K respectively. This means that the reduction ends with the restoration of ~1750 K and above this temperature the condensed $Cr_7C_3$, $Mn_{23}C_6$ and Cr, $Cr_3C_2$ are present in the system.

A similar pattern is observed for the reactions (3). The start of the process of reduction with the formation of $Cr_7C_3$, $Mn_{23}C_6$, Cr, $Cr_3C_2$ and changes in the amount of oxides are similar to those for the reactions (2) and (3). The only difference is in the temperatures and amounts of the produced components.

It should be noted that for the reaction (3) reduction is already completed at a temperature of ~1450 K.

The results of thermodynamic analysis have shown that the more the amount of carbon in the initial composition of the charge mixture, the lower is the temperature of the reduction end.

*ფიზიკური ქიმია*

# $Cr_2O_3$ და MnO ოქსიდების ნარევის კარბოთერმული აღდგენის თერმოდინამიკური ანალიზი

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**შესრულებულია Cr-Mn-O-C სისტემის სრული თერმოდინამიკური ანალიზი შემდეგი შედგენილობებისათვის:**

$$Cr_2O_3 + MnO + 4\,C; \quad (1)$$

$$Cr_2O_3 + MnO + 5\,C; \quad (2)$$

$$Cr_2O_3 + MnO + 6\,C. \quad (3)$$

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