Thermochimica Acta, 93 (1985) 477-480
Elsevier Science Publishers B.V., Amsterdam

THERMAL ANALYSES IN THE INVESTIGATION OF NON-STOICHIOMETRIC METAL OXIDES

Stanisława Jasieńska, Jadwiga Orewczyk
University of Mining and Metallurgy,
Cracov Mickiewicza 30 Poland

ABSTRACT

In Fe-O and Mn-O systems there exist non-stoichiometric phases in which the deviation from stoichiometry is limited by temperature and the oxidizing-reducing potential of the gaseous phase in equilibrium with the condensed phase.

Tests on the formation of FeO_x wustite and MnO_x manganosite were carried on by reduction with a gaseous reducer. For the investigation of the reduction process thermal analyses, X-ray diffraction analysis and Cambax X-ray microprobe analysis were applied.

INTRODUCTION

Although in world literature there are available many works on FeO_x wustitute yet the structure of this compound is still not well known because of the serious methodical difficulties hampering the solution of the problem. In the case of non-stoichiometric manganese oxide, MnO_x, the difficulties are due to the limited region of its homogeneity as well as to the sublimation of this compound at temperatures above 1173^{o}K stated in [1]. The prime condition to get veliable results is such a reduction time that would ensure thermodynamic equilibrium stability of the process investigated.

MEASURING METHODS

The reaction of Fe_3O_4 isothermal reduction into FeO_x wustite was carried on in a unit ispecially designed for the purpose where it was possible to introduce the sample into a furnace of 1373^{o}K under $CO+CO_2$ atmosphere a reducing and oxidizing potential calculated from the phase diagram for the Fe-O system [2] and then to cool it rapidly. The quantita examination of the process was carried on in a Matter's thermoanalyser, the results of the thermogravimetric /TG/ and differential thermogravimetric /DTG/ analyses being redorded for the following parameters: TG sensitivity-100/10 mg, DTG sensitivity-5 mg/min.

Proceedings of ICTA 85, Bratislava

The temperature conditions in the cómbined thermal analyses have been adopted to the ones prevailing in the test unit, i.e. preheating rate-100^{o}/min.; T-1373^{o}K; flow rate of the gaseous mixture - 35 l/h; reaction time - hs.

The mangasesite phase, MnO_x, has been got from MnO_2 using CO+ +CO_2 1:1 gaseous mixture as a reducing agent at 1073^{o} and 1273^{o}K. The reduction products were submitted to X-ray diffraction analysis in a DRON-1 X-ray diffractometr as well as to microregion spectral analysis in a MS-46 CAMEC-microprobe.

RESULTS AND DISCUSSION

After Fe_3O_4 reduction at 1373^{o}K FeO_x wustites were obtained where O/Fe = 1.06, 1.09 and 1.11.

The thermogravimetric analysis results are reported in Table I. According to them the deviation from stoichiometry calculated on the basis of TG is in good agreement with the theoreticvalues.

In the case of MnO_2 reduction into manganesite phase the deviation from stoichiometry, O/Mn, /Table II/ calculated on the basis of thermogravimetric analysis is a consequence of reduction and sublimation. The results obtained for O/Mn are lover than those determined from the phase diagram for the Mn-O system [4].

Spectral analyses carried on in a X-ray microprobe on samples got at 1073^{o}K revealed chemical composition inhomogeneity in the grains. Namely, in the grain boundary region MnO has been found whereas inside the grains a pronounced decrement of Mn percentage was observed sometimes, what implies the presence of Mn_3O_4.

In samples got at 1273^{o}K the difference in chemical composition between the grains over the entire surface of the sample is rather small. This is to be understood as a consequence of a faster equilibrium stabilization.

The investigations have proved that the actual deviation from stoichiometry in MnO_x manganesite smaples got in the process of reduction cannot be determined on the basis of thermogravimetric results since these values are burdened with errors in consequence of temperature measurements and the gaseous mixture used as well as due to other effects discussed previously. It should be emphasized however that above 1073^{o}K the sublimation process is mostly accountable for the errors in thermogravimetric analysis. Below this temperature the samples might not be fully reduced because of the very slow stabilization of thermodynamic equilibrium [illegible]. The investigations haw proved that the actual time for thermodynamic equilibrium stabilization is longer than the time determined from thermogravimetric curves.

CONCLUSIONS

On the basis of the investigations it was possible to state that thermogravimetric analysis applied for the examination of the process of reduction into FeO_x wustite phase is quite helpful and its sensivity is adequate.

In the case of reduction into MnO_x manganesite phase the thermogravimetric analysis should be applied jointly with other quantitative methods. Thermogravimetric results are a summarized effect of all the processes taking place with mass variation. Only combined examination methods would allow to understand the partial processes as well as to elucidate the errors burdening the results of the respective methods.

REFERENCES

1. S.Jasieńska, J.Orewczyk, M.Ghodsi, J.Janowski, Zeszyty Naukowe AGH Met. Odlew.8,/1982/23.
2. L.S.Darken,R.W.Gurry, I.Amer.Soc. 67 /1945/ 1398; 68 /1946/798.
3. I.Couzin, A.Duquesonoy, C.R.Acod.Sc.Paris 281 /1975/ C-259.
4. C.Carel IXth International Symposium on the Reactivity of Solids, Cracow Sept /1980/.
5. S.Jasienska, J.Janowski, J.Orewczyk, Proc. 7th Intern. Conf. Electron Microscopy, Haga 24-29.08.1980, 48-9.

Table I

Results of the thermogravimetric analysis of magnetite down to wustite reduction

	Fe_3O_4		FeO_x
O/Fe from the diagram in [2]	Mass theoretic decrement ω	Mass experimental decrement $\overset{\gamma}{\omega}$	Experimetal O/Fe
1.06	5.66	5.74	1.056
1.09	5.05	5.12	1.088
1.11	4.63	4.70	1.107

Table II

Results of the thermogravimetric analysis of MnO_2 down to MnO_x reduction.

Temp. ^0K	O/Mn the from diagram in 4	Mass theoretic decrement %	Mass experimental decrement [%]	Experimental O/Mn	O/Mn from MAR
1073	0,999	18.42	19.14	0.96	1,03
1273	0.998	18.44	19.51	0.94	1.01