Journal of Thermal Analysis and Calorimetry, Vol. 60 (2000) 265–269

MODEL STUDIES OF DOPED IRON OXIDES
Reduction process of magnetite doubly doped with calcium and magnesium

J. Orewczyk

University of Mining and Metallurgy, Faculty of Metallurgy and Materials Science
30-059 Cracow, Mickiewicza 30, Poland

Abstract

The paper presents results of research on the effect of the presence of calcium and magnesium in magnetite structure on its reducibility. These are model studies of the phase which mostly affects reducibility of superfluxed sinter. Examinations were carried out on samples melted and crystallized in a single crystal growing process.

Keywords: doped iron oxides, high basicity sinter

Introduction

Examinations of pure and doped magnetite phase can be considered as model studies of the phase which mostly affects reducibility of blast furnace sinter [1–4]. Magnetite in metallurgical substances is doped with elements present in ores and sintering additions – such as calcium, magnesium, manganese, aluminium. Effects of calcium and magnesium on physicochemical properties of single crystal and polycrystalline magnetite phase were discussed elsewhere [5–8].

Research was conducted on the reduction process of the magnetite doubly doped with calcium and magnesium. Tests were carried out on samples obtained by zone melting and crystallization on a nucleus of a known orientation. As all the samples were treated in the same atmosphere during the same time, the results were not affected by other factors such as grain boundaries, porosity and chemical unhomogeneity.

Experimental

To obtain synthetic doubly doped $Fe_{3-x-y}Ca_xMg_yO_4$ magnetite with $x=y=0, 10$, it was necessary to apply the technique of non-crucible zone melting of a polycrystalline sample in a controlled atmosphere.

Polycrystalline samples were obtained by sintering homogenous mixture of α-Fe_2O_3 with corresponded quantity of oxides of doping elements, in an equilibrium

1418–2874/2000/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

atmosphere with Fe_3O_4 phase. Crystallization of melted polycrystal occurred on a nucleus of a known crystallographic orientation. It happened while leaving the focal zone of an optical system in the Cyberstar single crystal growing apparatus [9].

The reduction course was examined while reducing samples to wustite (p_{CO}/p_{CO_2}=1) and to metallic iron (p_{CO}/p_{CO_2}=4). Thermogravimetric (TG) and derivative thermogravimetric analyses (DTG) were carried out on a Mettler thermoanalyser in the temperature range 20–1200°C, at the gas flow 20 $\mathrm{l\ h^{-1}}$ and heating rate 6°C $\mathrm{min^{-1}}$. Recrystallization of the reduction product was obtained by annealing at 1200°C during 1 h.

To determine the chemical and phase composition of the samples, it was sufficient to apply several complex, complementary research methods such as: classical chemical analysis, X-ray diffraction, optical and scanning electron microscopy and electron probe microanalysis.

Results

Model studies of single crystal and polycrystalline magnetites singly doped with calcium or magnesium allowed us to determine the existence limits of pure doped magnetite phase and the real dopant content [10].

Examinations of doubly calcium and magnesium doped magnetite were conducted only in those cases when the calcium and magnesium contents in the sample were close to their solubility limits.

For calciomagnetite, assumed sample composition was given by the formula: $Fe_{2.88}Ca_{0.12}O_4$. Lattice parameter a of this magnetite was of 8.430±0.005 Å, and the calcium content determined by electron microprobe allowed to settle the formula $Fe_{2.90}Ca_{0.10}O_4$.

In case of magnesium doped magnetite, $Fe_{2.88}Mg_{0.12}O_4$ was its assumed formula while the real one was found to be $Fe_{2.892}Mg_{0.108}O_4$. Lattice parameter of the compound was of 8.393±0.006 Å.

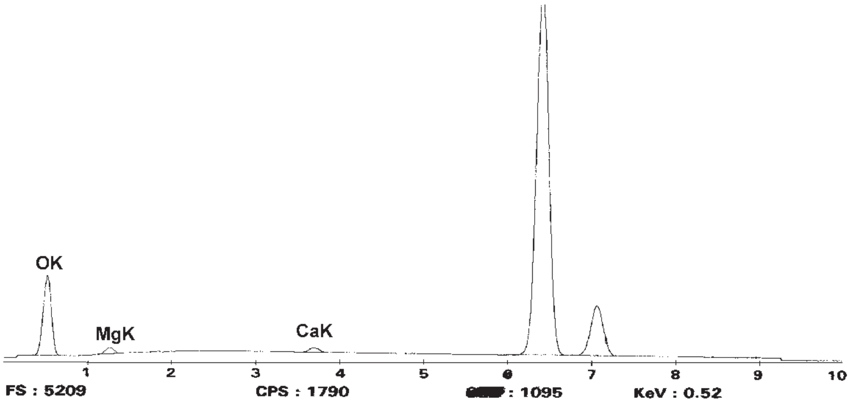

Fig. 1 Spectral analysis of the sample of assumed formula $Fe_{2.8}Ca_{0.1}Mg_{0.1}O_4$

$Fe_{2.8}Ca_{0.1}Mg_{0.1}O_4$ calcium doped magnetite was doubly melted in order to obtain a better homogeneity. The central, most homogenous part of the sample was cut into slices which served to examine reduction process. Results of the spectral analysis of this central part of the sample are shown in Fig. 1.

To determine the effect of crumbling on reduction rate, investigations were carried out on 2 slices, one of which was crumbled.

Samples were subjected to a polythermal reduction in the temperature range 20–1200°C, in a gas mix mixture whose redox potential procured an equilibrium with the wustite phase given by the formula $Fe_{0.92}O$.

In case of the crumbled sample, the TG curve shows that reduction occurs between 580 and 990°C, the maximum reduction rate being observed at 780°C (DTG), and mass loss was of 5.13%. Reduction of the non-crumbled sample was observed in a wider temperature range – up to 1200°C, with a global mass loss of 4.97% (Table 1).

Table 1 Results of the TG analysis of $Fe_{2.8}Ca_{0.1}Mg_{0.1}O_4$

Sample	$p_{CO}/p_{CO_2}=1$		$p_{CO}/p_{CO_2}=4$	
	Temperature/°C	$\frac{m_o-m}{m_o}/\%$	Temperature/°C	$\frac{m_o-m}{m_o}/\%$
Crumbled	580–990	5.13	600–720–1200	18.62
Non-crumbled	580–1200	4.97	600–740–1200	16.59

Figure 2 shows the scanning image of a well crystallized wustite phase where the dopants content measured by electron probe microanalysis, was of 0.32÷0.48% and 0.21÷0.25%, for calcium and magnesium, respectively.

Lattice parameter *a* measured by powder X-ray analysis was 4.302±0.006 Å.

Reduction to metallic iron proceeds with a two-stage mass loss which starts, in both cases, at 600°C.

For the crumbled sample, the rate of mass loss starts to change at 720 and finishes at 820°C. The reduction process lasts until the maximum temperature is reached and does not attain equilibrium with the gaseous phase. The highest mass loss observed up to 1200°C is of 18.62% (Table 1).

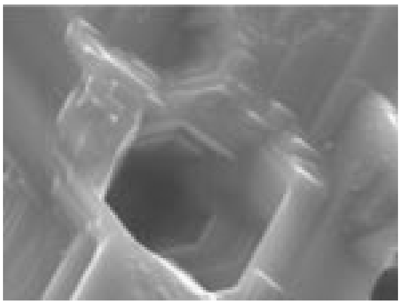

Fig. 2 Reduction of $Fe_{2.8}Ca_{0.1}Mg_{0.1}O_4$ to wustite doubly doped with Ca and Mg. Scanning image of surface of reduction product (8.0 kV)

Reduction of the non-crumbled sample occurs in a similar way, just the rate of mass loss changes at 740°C and the maximum mass loss figures out 16.59%.

The scanning image of the product of reduction in $p_{CO}/p_{CO_2}=4$ atmosphere shows well developed grains of metallic iron – Fig. 3.

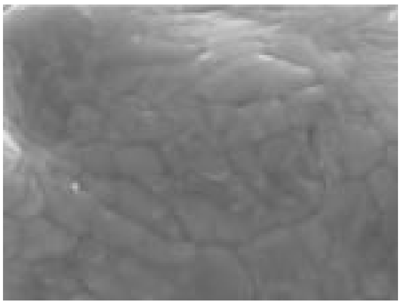

Fig. 3 Scanning image of product of reduction of $Fe_{2.8}Ca_{0.1}Mg_{0.1}O_4$ to metallic iron (8.0 kV)

The analyses by electron microprobe allowed to state that in products of reduction to wustite of $Fe_{2.8}Ca_{0.1}Mg_{0.1}O_4$ slice, magnesium distribution in wustite was rather uniform while calcium segregated at grain boundaries. In case of reduction to metallic iron, a considerable increase of calcium concentration at sample borders was detected.

Discussion

In magnetite doubly doped with calcium and magnesium which was examined, dopants did not cause formation of a multiphase system. X-ray diffraction proved that the only phase present in the samples was magnetite.

Reduction of $Fe_{2.8}Ca_{0.1}Mg_{0.1}O_4$ to wustite phase produces a minimum on TG curve, followed by a stabilization, in both non-crumbled and crumbled forms of the sample. The latter reaches equilibrium state at a lower temperature which can be explained by an easier contact with reducing mix.

Calcium migration towards grain boundaries of wustite can result in surpassing the calcium solubility limit in wustite, and ferrite phases can be formed. Increase in calcium concentration in magnetite as well as in wustite considerably affects the reduction rate. This is not observed in case of magnesium. Different behaviours of elements are related to ionic radii: $r_{Ca^{2+}}=0.99$ Å, $r_{Mg^{2+}}=0.65$ Å, $r_{Fe^{2+}}=0.76$ Å, $r_{Fe^{3+}}=0.64$ Å. The ionic radius of magnesium is comparable with those of iron whereas substituting of iron in magnetite and wustite by calcium leads to an increase of lattice parameter. As both phases are found in metallurgical stuff, the phenomenon is of great importance. While reducing $Fe_{2.8}Ca_{0.1}Mg_{0.1}O_4$ to metallic iron, the two-stage process in both non-crumbled and crumbled samples requires a longer time to reach the equilibrium state with gaseous phase.

Conclusions

Model studies of reduction process were carried out on samples melted and crystallized in a single crystal growing device. This allowed to eliminate effects of such parameters as porosity, polycrystallinity, chemical unhomogeneity on reduction process.

Differences in temperature and time related to corresponding reduction stages in both non-crumbled and crumbled samples are due to gas penetration within the sample.

Calcium migration towards grain boundaries was observed which could result in nucleation of ferrite phases. This phenomenon was not observed in case of magnesium doping.

Results obtained for doubly calcium and magnesium doped magnetite can be applied to real metallurgical systems e.g. ore sinters where this phase co-exists with ferrites and silicate phases. This allows to determine the effect of those phases on the reduction process of metallurgical substances.

References

1 S. Jasieńska, A. Łędzki and J. Orewczyk, Rev. Métall.-CIT, 43 (1996).
2 J. Orewczyk, S. Jasieńska, J. Pacyna, T. Skrzypek and S. Iwanczenko, J. Thermal Anal., 45 (1995) 937.
3 S. Jasieńska, J. Orewczyk, J. Durak and S. Iwanczenko, J. Trace and Microprobe Techniques, 15 (1997) 425.
4 S. Jasieńska, A. Łędzki and J. Orewczyk, 8th Intern. Metall. and Mat. Congr., 6–9 June, Istanbul, Turkiye, 1995, p. 309.
5 J. Orewczyk, Zeszyty Naukowe AGH, Metal. I Odlew., 15 (1989) 235.
6 S. Jasieńska, J. Orewczyk, W. Cieśla and A. Twardowska, Proc.of the 14th ICXOM, Aug. 19–Sep. 2, 1995, Guanzhou, P. R. China, 1995, p. 53.
7 S. M. Dubiel, J. Cieślak, J. Orewczyk and S. Jasieńska, Acta Physica Polonica A., 93 (1998) 547.
8 S. Jasieńska and J. Orewczyk, J. Trace and Microprobe Techniques, 15 (1997) 429.
9 J. Orewczyk, S. Jasieńska, W. Cieśla and J. Durak, J. Thermal Anal., 45 (1995) 97.
10 J. Orewczyk and S. Jasieńska, Polish Journal of Applied Chemistry, 41 (1997) 253.