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STUDIES OF CALCIOMAGNETITE PHASE BY MEANS OF THERMAL ANALYSIS

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Iron oxides doped with calcium occur in such natural metallurgical materials as sinters and lumps for the blast furnace process. In this work the Ca-doped magnetite phase $Fe_{3-y}Ca_yO_4$ with $0<y\leqslant 0.55$ was produced and studied as a pattern phase for investigation of the magnetite phase in sinters.

The synthesis process was studied by means of simultaneous thermal analysis, while the synthesized products were studied by diffraction analysis, scanning and optical microscopy, and spectral analysis in microareas.

The solubility limits for Ca in magnetite were estimated, and an explanation of the shapes of the thermal curves was given.

A precise identification of the oxide phases in blast furnace sinters is very difficult, due to the complex and inhomogeneous chemical composition of the phases.

A possible modification of the blast furnace technology could be reached only if the properties of all the phase components of the sinter are known. Therefore, in this study we first synthesized a sinter with chemical composition close to that of the blast furnace sinter and determined its physico-chemical properties. This enabled us to find a proper investigation technique which could be applied to study some blast furnace sinters.

The magnetite phase doped with calcium was produced and then studied as a pattern phase for the subsequent investigations of the magnetite phase in the blast furnace sinter.

Experimental

The calciomagnetites $Fe_{3-y}Ca_yO_4$ where $0<y\leqslant 0.55$ were produced by annealing and dissociation of Fe_2O_3 with a given amount of $CaCO_3$ at 1603–1623 K in argon atmosphere in equilibrium to Fe_2O_3. The specimens were then homogenized, recrystallized and cooled.

The calciomagnetite phase thus obtained was subjected to some different identification procedures, leading to some complementary conclusions [1, 2]. The

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following methods were applied: X-ray diffraction, optical microscopy, scanning microscopy and spectral analysis in microareas.

The simultaneous analyses were performed with a derivatograph, which permitted observation of the process of formation of calciomagnetite within the temperature interval 293–1373 K. The parameters of the analysis were chosen to correspond to the synthesis conditions. The thermogravimetric analysis TG and DTG determined the mass loss due to the thermal decomposition of $CaCO_3$ to CaO, as well as the transformation of Fe_2O_3 to the magnetite phase. The beginning of the $CaCO_3$ decomposition occurred at 890 K, with maximum rate at 1110 K, followed by a mass loss which was slower in starting at 1230 K. The mass losses taken from the gravimetric curves for the synthesis of the calciomagnetites $Fe_{3-y}Ca_yO_4$ when $y = 0.04$, 0.08 and 0.12 are close to the theoretical ones (within the limit of error). The curves of the simultaneous analysis for the synthesis of the calciomagnetites when $0.16 \leqslant y \leqslant 0.55$ differ substantially from the theoretical ones above 1230 K (Table 1).

The shape of the DTA curve shows an endothermic effect corresponding to the first mass loss, followed by a small endothermic deviation for the lower values of y. At higher values of y, the thermal effects in the higher temperature region are difficult to interpret. The phase composition of the calciomagnetites $Fe_{3-y}Ca_yO_4$ was determined from the diffraction analysis data using a Philips 1050 diffractometer, as well as from the spectral analysis data for microareas using a MS-46 X-ray microanalyser (CAMECA).

Table 1 Results of TG analysis for synthesis of calciomagnetite $Fe_{3-y}Ca_yO_4$

y	0.04	0.08	0.12	0.16	0.20	
$m_{theor.}$, %	4.01	4.68	5.35	6.01	6.67	
$m_{1\,theor.}$, %	0.73	1.46	2.18	2.90	3.61	
$m_{2\,theor.}$, %	3.28	3.22	3.17	3.11	3.06	
$m_{exp.}$, %	3.77	4.44	5.06	4.48	5.03	
$m_{1\,exp.}$, %	0.72	1.44	2.16	2.88	3.58	
$m_{2\,exp.}$, %	3.05	3.00	2.90	1.60	1.45	
y	0.24	0.28	0.32	0.40	0.48	0.55
$m_{theor.}$, %	7.33	7.74	8.61	9.90	11.16	12.26
$m_{1\,theor.}$, %	4.32	4.77	5.72	7.11	8.47	9.66
$m_{2\,theor.}$, %	3.01	2.97	2.89	2.79	2.69	2.60
$m_{exp.}$, %	5.68	5.83	6.70	8.06	9.42	10.49
$m_{1\,exp.}$, %	4.28	4.72	5.68	7.06	8.41	9.59
$m_{2\,exp.}$, %	1.40	1.11	1.02	1.00	1.01	0.90

The X-ray diffraction studies show that at the calcium composition $y = 0.12$ only calciomagnetite is observed. For $0.16 \leqslant y \leqslant 0.55$ the monocalcium ferrite $CaFe_2O_4$ is found, while for y from 0.16 up to 0.28, apart from the ferrite $CaFe_2O_4$, $Ca_2Fe_2O_5$ is observed. The spectral analysis in microareas shows solely the presence of the calciomagnetites for $y = 0.08$. With increase of the Ca dopant, from $y = 0.12$, apart from the calciomagnetite, some monocalcium ferrite grains, $CaFe_2O_4$, are observed. At $y = 0.20$ and $y = 0.28$, bicalcium ferrite, $Ca_2Fe_2O_5$, too is found. The microanalysis data show that above $y = 32$, besides calciomagnetite, the only other compound is the monocalcium ferrite, $CaFe_2O_4$. A comparison of the assumed amount of calcium with the microanalysis results leads to the conclusion that, among the calciomagnetites for y over 0.12, there is a large difference between the theoretical and experimental values of y in $Fe_{3-y}Ca_yO_4$. This fact could be explained by the production of the calcium ferrite phases.

Conclusions

The studies lead to the following conclusions:

— all the methods used give consistent results;

— the synthesized calciomagnetite phase $Fe_{3-y}Ca_yO_4$ up to the calcium content $y = 0.12$ forms a monophase system, while for $0.16 \leqslant y \leqslant 0.55$, apart from the calciomagnetite, the other calcioferrites ($CaFe_2O_4$, $Ca_2Fe_2O_5$) crystallize;

— the TG and DTG analyses of the synthesis of the calciomagnetites $Fe_{3-y}Ca_yO_4$ up to the calcium content $y = 12$ are consistent with the theoretical curves; for $y = 0.16$, the second mass loss effect is lower and proceeds at a lower rate;

— the DTA curves indicate an endothermic effect of the decomposition of $CaCO_3$; at higher temperatures, especially for the synthesis of $Fe_{3-y}Ca_yO_4$ at $y = 0.16$, the effects are very complicated, as the sum of all the processes.

References

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Zusammenfassung — Mit Kalzium versetzte Eisenoxide kommen in natürlichen Metallurgiematerialien wie z. B. Sintererzen und Erzbrocken für die Hochofenverhüttung vor. In vorliegender Arbeit wird die kalziumversetzte Magnetitphase $Fe_{3-y}Ca_yO_4$ mit $0 < y \leqslant 0.55$ hergestellt und als Modellphase

zur Untersuchung von Magnetitsintererzen studiert. Der Syntheseprozeß wurde mittels gleichzeitiger Thermoanalysen, die synthetisierten Produkte durch Diffraktionsanalysen, optischer und Scanningmikroskopie sowie Spektralanalyse im Mikrobereich untersucht. Die Löslichkeitsgrenzen von Kalzium in Magnetit wurden abgeschätzt und eine Erklärung für den Verlauf der thermischen Kurven gegeben.

Резюме — Оксиды железа, легированные кальцием, встречаются в таких естественных металлургических материалах, как шлаки и кусковые отходы доменного процесса. В настоящей работе получена легированная кальцием магнетитовая фаза состава $Fe_{3-y}Ca_yO_4$ с $0 < y \leqslant 0{,}55$ и которая была исследована как фаза родственная магнетитовым шлакам. Процесс получения такой фазы был изучен совмещенными методами термического анализа, а полученные продукты были изучены рентгено-диффракционным анализом, сканирующей и оптической микроскопией, а также спектральным анализом на микроповерхности. Установлены пределы растворимости кальция в магнетите и приведена интерпретация форм термических кривых.