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EFFECT OF THERMAL CONDITIONS ON FORMATION OF MONOCRYSTALLINE CALCIOMAGNETITES

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Abstract

Investigation of pure and calcium doped phase is the model investigation of phase which determine the blast furnace sinter reducibility. The object of examination are mono- and polycrystalline calciomagnetites of large grains dimension $Fe_{3-x}Ca_xO$ where $0.04 \leq x \leq 0.25$. The solubility limit of calcium in magnetite was strictly defined and changes of some physico-chemical properties as well.

Keywords: calciomagnetites, iron oxides, monocrystalline

Introduction

Pure and calcium doped magnetite phases decide the reducibility of a blast furnace sinter. In the paper, model studies of these phases are described [1–5]. They were carried out on both coarse grain polycrystalline samples and monocrystals. The latters have been obtained by a modified Bridgeman method with a vertical temperature gradient. The chemical formula of the examined material is $Fe_{3-x}Ca_xO_4$, where $0.04 \leq x \leq 0.28$. Optical and scanning microscopy observations as well as chemical and phase composition analyses were carried out after each melting. The solubility limit of calcium in magnetite has been found. It results from a considerable difference in ion radii of Ca, Fe^{2+} and Fe^{3+} ($r_{Ca^{3+}}=0.99$ A, $r_{Fe^{2+}}=0.76$ A, $r_{Fe^{3+}}=0.64$ A). As calcium facilitates reduction, this is of extremely important for the reducibility of magnetite.

Experimental

$Fe_{3-x}Ca_xO_4$ $0.04 \leq x \leq 0.28$ samples were obtained by mixing Fe_3O_4 and CaO formerly equilibrated and dried. The mixture were subjected to both mechanical then ultrasonic homogenization. The homogenized powders were formed in a matrix under a pressure of 50 kG/cm^2 (0.049 N/m^2). The obtained samples were 1×1×7 cm cuboids – Fig. 1.

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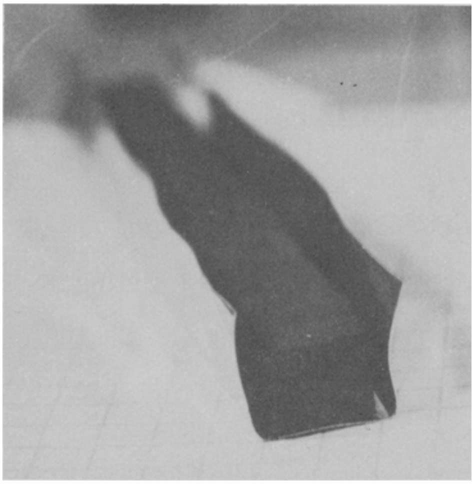

Fig. 1 Polycrystalline sample formed under a pressure

Pressed samples were put on a platinum plate and subjected to a thermochemical treatment. Sintering was carried out in an equilibrium atmosphere with Fe_3O_4 phase at 1100°C during 5 h. After sintering the samples were melted in an 'image furnace' made by CYBERSTAR. The method consists in crystallization of a melted polycrystalline sample on a monocrystalline germ of controlled orientation. The sample material crystallizes from liquid phase while leaving the melting zone situated in the focus of the optical system of the device (Fig. 2).

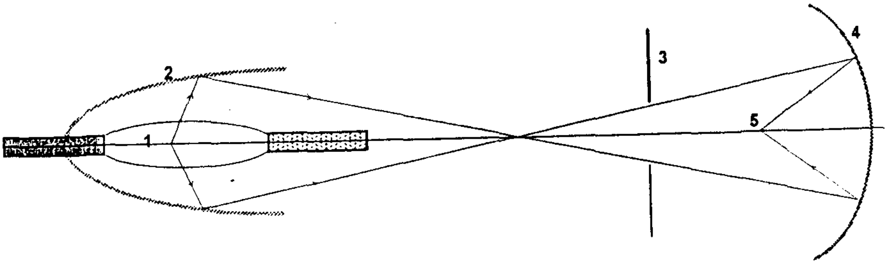

Fig. 2 Optical system of CYBERSTAR equipment. 1. Xenon lampe, 2. elliptic mirror, 3. diaphragm, 4. hyperbolic mirror, 5. optical system focus

Temperature is controlled by the current intensity of the xenon lamp and by the position of a diaphragm. The vertical movement velocity of the germ–melt–polycrystal system was set depending to temperature gradient which determines the growing rate of the monocrystal. The current-counter consisting in opposite rotation directions of the germ and the sample helps homogenizing, removing gas impurities from the melting zone, conserving stable growth conditions – Fig. 3.

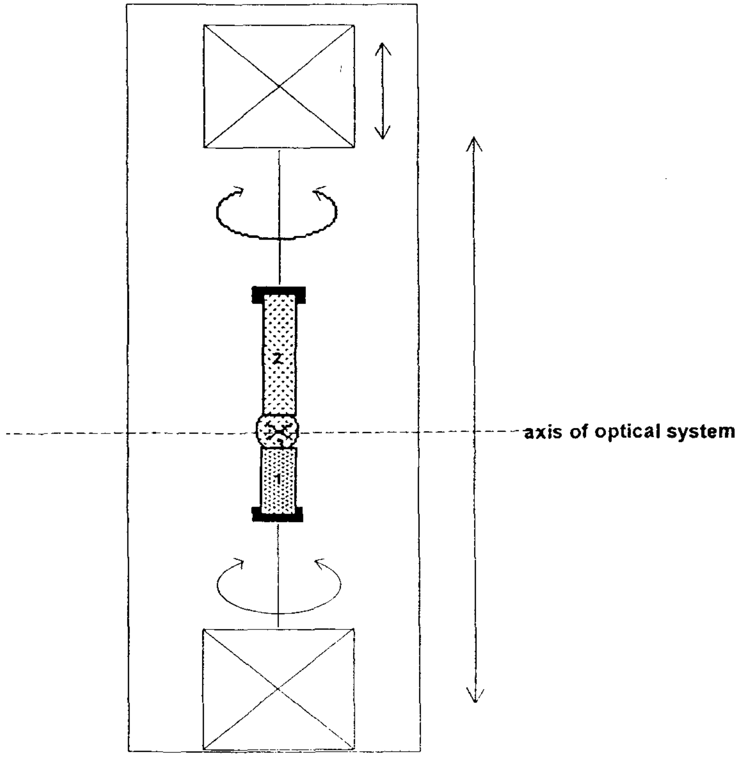

Fig. 3 Vertical shift and rotation system of the germ 1) and the polycrystalline sample 2), 3) melted zone

The method enables also controlling the dimensions of the contact area of liquid sample with the germ – from 'point contact' to 'flowing zone'. This parameter affects also the homogenization of the melt as well as the diameter of the final monocrystal bar.

The parameters of the process are listed in Table 1. Each sample has been melted for several times. After each melting samples were subjected to complex examinations. Chemical composition in microregions was analysed by a MS-46 CAMECA electron probe microanalyser, Fe and CaF_2 were used as standards. Both linear and point analyses were applied, the former along selected cross sections, the latter at different distances from the surface. Phase composition was examined by powder X-ray diffraction method with a HZG-4B diffractometer using Co_{K_α} rays. Optical and scanning microscope observations were made with a JEOL JSM-840 microscope.

Table 1 Parameters of formation monocrystalline using CYBERSTAR equipment

Xenon lampe current	95–110 / A
Diaphragm	8–17 / cm
Vertical speed of the hole system	10–20 / $mm \cdot h^{-1}$
Vertical speed of polycrystalline sample relative to hole system	2–4 / $mm \cdot h^{-1}$
Rotation speed of the germ	+250 / rpm
Rotation speed of the sample	–250 / rpm

Results and discussion

Diameters of the obtained monocrystalline bars vary depending on process parameters, what can be seen in Figs 4 and 5. $Fe_{2.96}Ca_{0.04}O_4$ and $Fe_{2.72}Ca_{0.28}O_4$ monocrystalline bars were cut into slices with a diamond saw, then polished and observed in an optical microscope – Figs 6 and 7. After first melting, non-melted areas were present in samples, which were carried away by the liquid flux. Occluded gases and cavities were also observed at the edges of newly formed crystallographic planes. So, first meltings should be considered as a preparatory step in the production of a monocrystal.

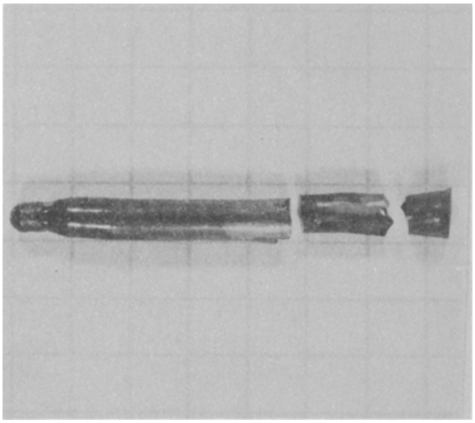

Fig. 4 Melted $Fe_{2.96}Ca_{0.04}O_4$ sample

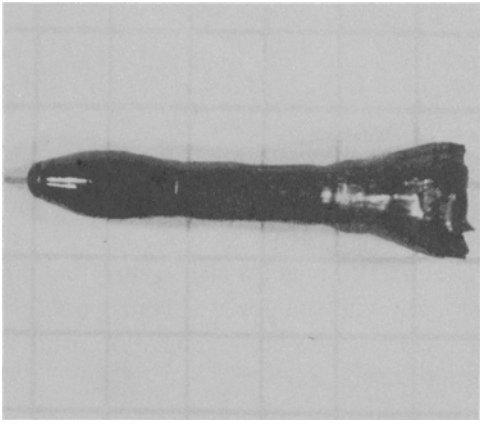

Fig. 5 Melted $Fe_{2.72}Ca_{0.28}O_4$ sample

Calcium is uniformly distributed in $Fe_{2.96}Ca_{0.04}O_4$ magnetite only. In the others (x=0.16 or 0.28), ferrite phases precipitate between calciomagnetite grains. Increase in calcium concentration at the magnetite – ferrite interface means that ferrite phases form at the surface of calciomagnetite grains after the solubility limit of calcium in magnetite has been exceeded. This is confirmed by the results of point microanalysis shown in Table 2.

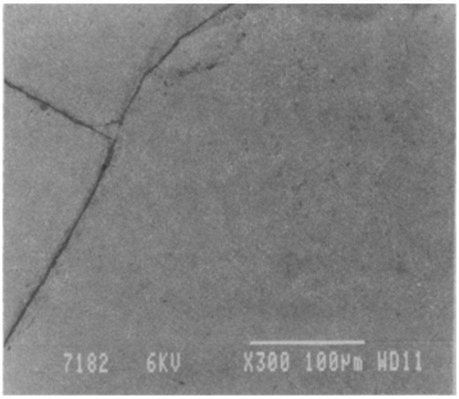

Fig. 6 Scanning image of polished specimen $Fe_{2.96}Ca_{0.04}O_4$ sample

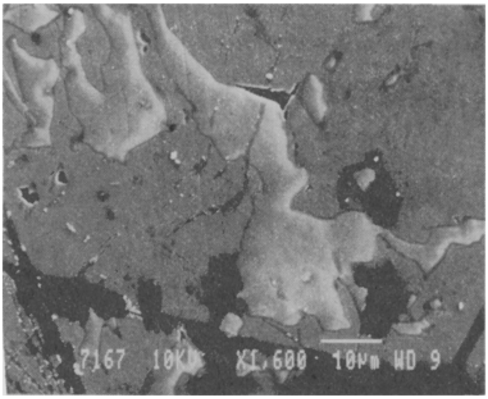

Fig. 7 Scanning image of polished specimen $Fe_{2.72}Ca_{0.28}O_4$ sample

In the $Fe_{2.96}Ca_{0.04}O_4$ sample, a significant difference has been found between calcium content in the middle of the sample and that in outer layers. The calcium concentration was higher in the latter. When calcium concentration was higher than the solubility limit, i.e. in $Fe_{2.84}Ca_{0.16}O_4$ and $Fe_{2.72}Ca_{0.28}O_4$ samples, no homogeneous monocrystalline calciomagnetite phase has been obtained. Instead of this, a layered structure appeared – calciomagnetite in the middle of the sample, calciomagnetite and $CaFe_3O_5$ calcium ferrite at the outer layer. Phase composition of calcium ferrites changes according to initial calcium content in magnetite. In the centre of the $Fe_{2.72}Ca_{0.28}O_4$ sample one can observe calciomagnetite and $Ca_2Fe_2O_5$ ferrite, in the outer layer, besides of calciomagnetite occur $CaFe_2O_4$ and $Ca_2Fe_2O_5$ ferrites. Figure 8 presents ferrite phases precipitations at the calciomagnetite surface in the $Fe_{2.72}Ca_{0.28}O_4$ sample. The existence of observed phases has been confirmed by X-ray powder diffraction.

Table 2 Spectral analysis in microregion of synthetic magnetite

	Inner layer		Outer layer	
	%Fe	%Ca	%Fe	%Ca
$Ca_{0.04}Fe_{2.96}O_4$	68.1–69.2	0.04–0.1	67.2–68.3	0.3–4.1
$Ca_{0.16}Fe_{2.84}O_4$	66.4–68.5	0.5–0.7	67.2–69.5	0.3–0.4
			56.6–57.0	12.2–14.6
$Ca_{0.28}Fe_{2.72}O_4$	66.7–67.1	1.6–1.7	67.6–68.3	2.7–3.3
	36.1–38.2	25.4–26.8	49.7–49.1	16.0–16.6
			36.0–37.4	23.2–24.4

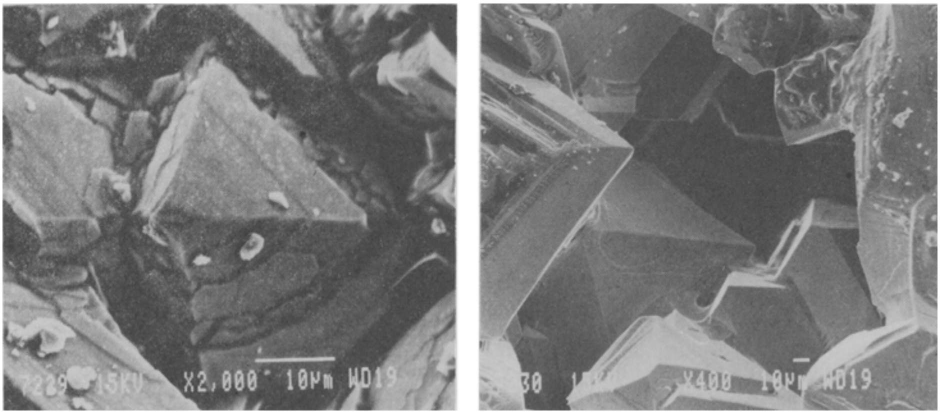

Fig. 8a,b Scanning images of $Fe_{2.72}Ca_{0.28}O_4$ samples

Conclusions

The highest observed calcium concentration in a monophase magnetite ($Ca_{0.04}Fe_{2.96}O_4$) sample is 4.1%. The other samples contain another phases.

Ferrite phases formation occurs while the solubility limit of calcium in magnetite is exceeded. Increase in calcium concentration at calciomagnetite grain boundaries is the first step of formation of these phases. They can also form from oxide substrates contained in the mixture. That is why the results are comparable for given preparation procedures only.

The rotation speed of the germ and the sample should be high enough for the homogenization of the melting zone and low enough for avoid the segregation of the dopants because of the centrifugal force.

It is essential, in monocrystal production processes, to minimize the 'flowing zone' which would decrease the diameter of a sample.

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Zusammenfassung — Die Untersuchung von reinen und mit Calcium versetzten Phasen ist eine Modelluntersuchung einer Phase zur Bestimmung der Sintergutreduzierbarkeit in Gebläseschachtöfen. Die untersuchten Substanzen sind mono- und polykristalline Calciomagnetite großer Kristallkorngröße $Fe_{3-x}Ca_xO$ mit $0.04 \le x \le 0.25$. Die Löslichkeitsgrenze von Calcium in Magnetit wird streng festgelegt, ebenso wie die Änderungen einiger physikalisch-chemischer Eigenschaften.