Contact angles of $Ca_{10}(CrO_4)_7$ melt and transport of chromium into sintered CaO—MgO material

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Behaviour of $Ca_{10}(CrO_4)_7$ melt on solid CaO—MgO pellets has been observed in air atmosphere. On the basis of experiments carried out at 1270°C the dependence of contact angle on the solid body composition was obtained. Distribution of chromium in the solid phase was evaluated by means of an electron probe microanalyzer as a function of distance from the phase boundary and of the exposition time.

Изучалось поведение расплавленного соединения $Ca_{10}(CrO_4)_7$, находящегося на твердой поверхности из смеси окислов CaO—MgO в воздушной атмосфере. На основании экспериментов, проводимых при 1270°С были получены данные по зависимости угла смачивания от состава твердой поверхности, а затем с помощью электронного микроанализатора было оценено распределение хрома в твердой фазе в зависимости от расстояния от границы раздела фаз при разных временах нагревания.

The refractory materials on the basis of dolomite used for lining in oxygen converter [1, 2] can be sintered more effectively when chromium ingredients are added [3, 4]. Advantage of using these ingredients is in formation of liquid phase containing except Ca^{2+}, O^{2-}, and Cr^{3+} ions also chromium in higher valency. The pseudobinary system CaO—Cr_2O_3 is in the range of partial pressure of oxygen similar to air atmosphere sensitive to changes of oxygen content in gaseous phase [5—11]. As might be expected, the atmosphere in technological plant [12, 13] causes reduction of Cr^{6+} and Cr^{5+} [14] to the three-valent form Cr^{3+}. Owing to this process, the initial temperature of melt formation is considerably increased [11].

In discovering the kinetics of sintering process is useful information on contact angles of $Ca_{10}(CrO_4)_7$ melt on solid CaO—MgO bodies and investigation of chromium transport into these materials.

Experimental and results

Observation of contact angles was carried out in air atmosphere at 1270°C. By synthesis described in [15] was prepared $Ca_{10}(CrO_4)_7$, which was pressed to the shape of cubes ($a = 2$ mm, $M \doteq 15$ mg) at about 10 MPa. Tested pellets of 9 mm diameter and 3 mm thickness were produced from a powder mixture with various mass ratio of CaO to MgO by pressing at about 100 MPa and 5 h annealing at 1600°C in air. Real content of CaO and MgO in samples was determined by complexometric titration.

The porosity was calculated by dividing theoretical density and volume gravity estimated by weighing in mercury. The surface of tested pellets was polished by diamond pastes and the last finishing was accomplished by diamond paste with maximum grain diameter 7 μm. Contact angles were determined by the method of laying drop by means of the heating microscope Leitz.

Results of chemical analysis, values of porosity, and measured contact angles are summarized in Table 1.

Table 1

Results of chemical analysis, values of porosity, and contact angles determined at 1270°C

No.	Content of CaO w_{CaO}/mass %	Porosity ε/volume %	Contact angle $\alpha/°$
1	21.5	4.7	8
2	23.3	5.1	8
3	26.4	4.2	9
4	43.8	4.3	15
5	49.2	5.4	19

The chromium transport from liquid to solid phase was detected on the perpendicular cut of quenched pellets by X-ray areal scan using an electron beam microanalyzer JXA 5A (Jeol). The chromium distribution was measured in samples containing 23.3 mass % CaO in width 330 μm and to depth 660 μm. The length of the step was 33 μm. Exposition times varied in the range 5—60 min.

Standards were prepared by addition of a known amount of phase $Ca_{10}(CrO_4)_7$ in powder mixture of calcium and magnesium oxides.

It has been found that the dependence of chromium concentration on the distance from phase boundary may be expressed formally by the relation

$$c = \frac{M_i}{(\pi Dt)^{1/2}} \cdot \exp(-x^2/4Dt) \qquad (1)$$

derived for diffusion from the plane source with reflection at the boundary described in detail in [16].

It is assumed that chromium transport is realized only in perpendicular direction to phase boundary from the plane source (in our case from the liquid phase) inward the solid body.

Value of the ratio

$$\frac{M_{Cr}}{(\pi D)^{1/2}} = (3.106 \times 10^{-4} \pm 0.015 \times 10^{-4}) \ \mathrm{gs^{1/2} m^{-3}}$$

was evaluated from the chromium concentration at the phase boundary c_0 at various times of exposition. The diffusion coefficient and the constant M_i in eqn (1) were calculated by iteration cycle.

$$D = (5.84 \times 10^{-12} \pm 2.01 \times 10^{-12}) \ \mathrm{m^2 s^{-1}}$$

$$M_{Cr} = (1.30 \times 10^{-9} \pm 0.44 \times 10^{-9}) \ \mathrm{gm^{-2}}$$

Discussion

As seen from Table 1, the contact angle increases in the interval 8—19° with increasing content of calcium oxide in the solid phase from 21.5 to 49.2 mass %. Therefore, the reaction surface of materials with higher content of calcium oxide is smaller because the melt does not penetrate into the solid material so well as it does in pellets with lower content of CaO.

On the other hand, higher content of CaO in the solid phase stimulates the formation of liquid phase and consequently the mass transfer is accelerated. As shown by the reaction between $Ca_{10}(CrO_4)_7$ and CaO in solid body

$$6/5Ca_{10}(CrO_4)_7 + 2CaO = 14/5Ca_5(CrO_4)_3 + O_2 \qquad (A)$$

gaseous oxygen is produced in addition to the solid phase $Ca_5(CrO_4)_3$. The presence of oxygen was verified by means of optical microscope. Gaseous bubbles and the presence of $Ca_5(CrO_4)_3$ in products of reaction A cause probably the decrease of velocity of mass transfer inward solid material of calcium and magnesium oxides. This retardation can be explained by formation of an impermeable layer at the phase boundary. The diffusion process run only with that amount of chromium which had been transferred through the phase boundary before the start of reaction A. This is supported also by the comparison of the calculated value of $M_{Cr}(t_0)$ given as a total amount of chromium diffusing in a cylinder of infinite length and unit cross section and the real value of the starting amount related to diffusion cross section. It has been established that the calculated value of $M_{Cr}(t_0)$ is by about ten orders lower than in the case when all amount of chromium takes part in the diffusion process.

With respect to the calculated diffusion coefficient it may be assumed that the dominant transport of chromium is realized by liquid phase at the grain boundary. The amount of liquid phase depends on the content of oxygen in the surrounding atmosphere and when it is lowering, the formation of liquid phase is likely to be suppressed and the diffusion will proceed at the grain boundary. In case of CaO grains the phase $Ca_5(CrO_4)_3$ will originate and in that of MgO a solid solution $Mg_{1-x}Cr_{2x}O$ will be formed.

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