

SINTERING IN THE SYSTEM CaO—MgO WITH AN ADDITION OF Cr₂O₃

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A series of specimens of the system CaO—MgO with Cr₂O₃ additions were prepared chemically; in these specimens, the volume ratios of the main oxides and the amount of liquid phase at the maximum heating temperature were defined. The course of their shrinkage up to 1600 °C was determined dilatometrically, and the final porosity of the material obtained was established. The final porosity of specimens containing Cr₂O₃ additions was found to be always lower than that of specimens without this addition, while its optimum value depended on the volume ratios of the main oxides. By adding Cr₂O₃ uniformly dispersed in the mixture in amounts up to 1% by wt. it is possible to obtain materials containing 50—80 wt. % MgO with a porosity lower than 5%, by firing up to 1600 °C in an oxidation atmosphere.

INTRODUCTION

Development of the production of steel in oxygen converters has brought about a substantial change in the conditions affecting the respective refractories as compared to those acting on refractories during the processing of pig iron and scrap in open-hearth furnaces.

The oxygen converter atmosphere is of reduction character in contrast to the oxidation atmosphere prevailing in open-hearth furnaces [1], thus providing favourable conditions for the stability of the CaCr₂O₄ compound. The firing of clinker in an oxidation atmosphere and its utilization in a reduction atmosphere provided the inspiration for choosing Cr₂O₃ as an addition to the CaO—MgO system. The aim is to assess the possibility of activating the sintering process by the presence of a liquid phase, to improve the chemical resistance and to attain the lowest possible porosity. By choosing correctly the amount of the addition and the atmosphere, it is possible to affect the sintering of the system and the formation of its microstructure, where the following three possible cases can arise: a) at low temperatures there is formed a melt which disappears with increasing temperature, when the amount of Cr₂O₃ added is lower than its equilibrium solubility in CaO and MgO; b) the sintering up to the final temperatures proceeds in the presence of a liquid phase, the refractory phase CaCr₂O₄ being formed only when p_{O_2} has decreased; c) the sintering takes place at lowered p_{O_2} in the absence of the liquid phase. The results being submitted concern the former two cases, as the sintering was carried out in air atmosphere.

The present study of the sintering process is a continuation of work aimed at providing or supplementing principal theoretical knowledge of the system Ca—Mg—Cr—O in particular from the standpoint of phase equilibria in defined atmospheres [2]—[6]. These investigations have shown that 1. no melt is formed up to 1900 °C in the system CaO—MgO—CaCr₂O₄ [2], 2. that calcium chromite

is stable at 1650 °C up to $p_{O_2} \doteq 10^{-8}$ Pa and at 1400 °C up to $p_{O_2} \doteq 10^{-11}$ Pa [3]. 3. that alpha-calcium chromite can be stabilized by the presence of MgO already from 1470 °C upwards (equilibrially) while its conversion to the beta modification is very slow at lower temperatures [4], [5], 4. that the reduction of $Ca_3(CrO_4)_2$ starts at 1050 °C and at $p_{O_2} \doteq 244$ Pa [6].

On the basis of these results it may be assumed that the system CaO—MgO— α - $CaCr_2O_4$ will be stable under the operating conditions of the oxygen converter.

EXPERIMENTAL

Powdered specimens of the system CaO—MgO— Cr_2O_3 were prepared by the method after Marcilly et al. [7], that is by evaporation and thermal decomposition from aqueous solutions containing the required amounts of calcium, magnesium, chromic nitrates or ammonium bichromate and citric acid (of A.R. purity) in amounts of 0.5—I mole per 1 mole of the metals. The particle size of the powders prepared in this way amounted to about 40 nm. A detailed description of the method is presented in [7], [8]. The sintering process was studied on a series of specimens the composition of which was obtained as follows:

a) the content of the compound $Ca_3(CrO_4)_2$ and the volume ratio of MgO_{ss} (solid solution) and CaO were determined, while calculating with the solubility of Cr_2O_3 in MgO at 1500 °C (the phase composition at 20 °C is listed in Table I);

b) the chemical composition of the mixtures was calculated from the known content, volume and density of the individual components, using the density values at room temperature; the density of MgO_{ss} was calculated by the procedure described below;

c) the phase composition of the mixtures at 1600 °C was calculated on the basis of the phase diagram of the system CaO—MgO— $Ca_3(CrO_4)_2$ [8].

The solubility of Cr_2O_3 in CaO—MgO at 1500 °C was taken over from [9]; it was assumed that the solubility at 1600 °C (the final firing temperature of all the specimens) will not be very different. According to [9], the solubility of Cr_2O_3 in CaO is 20-times lower than that in MgO (0.05 wt. % and 1.07 wt. % respectively), so that formation of the CaO solid solution has not been considered in the phase composition calculations. The mutual solubility of CaO and MgO was likewise neglected in the calculations of phase composition and theoretical densities. The latter were calculated on the basis of the additivity rule and on the knowledge of phase composition. The following values were used in the calculation: 3.581 g cm⁻³ for MgO, 3.345 g cm⁻³ for CaO, 3.19 g cm⁻³ for $Ca_3(CrO_4)_2$ (determined by X-ray measurements) and 4.24 g cm⁻³ for α - $CaCr_2O_4$ determined pycnometrically. The density of the MgO— Cr_2O_3 solid solution was calculated on the basis of the schematic reaction



and on that of the constancy of lattice parameters of this type of solid solutions (probably as a result of the similar ionic radii of Mg^{2+} and Cr^{3+}). In the schematic reaction, $(V)_{Mg}''$ signifies a vacancy with a 2- charge in the position of magnesium. The other symbols have similar significances. The calculated density of the "saturated" solid solution [9] of $Mg_{0.9915}Cr_{0.0057}V_{0.0028}O$ is 3.589 g cm⁻³. In the

presence of atmospherical oxygen, an addition of Cr₂O₃ in amounts exceeding that corresponding to the formation of a saturated solid solution, will bind to the low melting phase Ca₃(CrO₄)₂, which dissolves only very small amounts of CaO and MgO above the melting temperature [9] and cannot be obtained without crystallization by current quenching methods. These findings as well as the knowledge of the phase diagram of the system MgO—CaO—Ca₃(CrO₄)₂ [8] justify and permit calculation of the theoretical densities from the calculated phase composition at room temperature, and possibly allow to obtain data on phase composition at high temperature. A series of specimens with a defined phase composition was prepared so as to permit study of the dependence of final porosity on the amount of the addition or melt, and on the volume ratio of the main oxides, while endeavouring to work with specimens showing identical initial porosity.

The powders were compacted into standard pellets (12 mm in diameter, 6 mm in height) by pressing the weighed amounts in a double-acting die. The pellets were heat treated under identical conditions in a Netzsch high-temperature dilatometer in dry air. The rate of heating and cooling was 10 °C min⁻¹, the time of heating at the highest temperature 1600 °C was 30 minutes. The initial and final densities were determined on the basis of the known buoyancy force arising during immersion of the specimen in mercury. The estimated standard deviation of this method is $\sigma = \pm 0.02 \text{ g cm}^{-3}$. The actual porosity was calculated from the ratio of the final and of the theoretical values. The physico-chemical parameters of the specimens are listed in Table I, while graphic plots show the relationship between porosity and Cr₂O₃ concentration (Fig. 1) and melt content (Fig. 2). The dependence of linear shrinkage of four selected specimens on temperature is shown in Fig. 3.

DISCUSSION

The final porosity of specimens treated under identical conditions was always lower when the specimens contained the Cr₂O₃ addition. At the lowest concentrations of the addition the decrease of porosity was approximately linear down to a minimum situated at about 1 wt. % Cr₂O₃ for the various volume ratios of the main oxides. A different behaviour was exhibited by specimens with the volume ratio equal to unity; when the optimum concentration of Cr₂O₃ (0.6—0.8 wt. %) was exceeded, their porosities sharply increased and attained a maximum in the concentration region most favourable for the respective volume ratios of the oxides. This may be explained so that at equal volumes of the main components the addition has different effects on the sintering of CaO and MgO, which is due above all to the difference in their solubility in the melt and in the wetting angle. The non-uniform sintering within the separate intermixed matrixes may bring about increased porosity whereas in the other instances the CaO minority component does not form a continuum, being so to speak carried along in the course of sintering.

Figs. 1 and 2 indicate that there is a certain optimum concentration of the addition which allows formation of an amount of melt useful from the standpoint of the individual stages of the sintering process and which results in attainment of minimum porosity [11]. This state corresponds to a ratio of the liquid and solid phase volumes $V_l/V_s = 2 \times 10^{-3}$ at temperatures higher than the melting temperature of Ca₃(CrO₄)₂. In such instances, the rate of sintering was high and the maximum rate of shrinkage involving rearrangement of particles was situated in the temperature range cor-

Table I
Physico-chemical parameters

Designation	Chemical Composition (wt. %)			Phase Composition 20 °C (wt. %)		
	CaO	MgO	Cr ₂ O ₃	CaO	MgO _{ss}	K
1	48.3	51.7				
2	31.8	68.2				
3	23.8	76.2				
4	18.9	81.1				
5	48.1	51.5	0.4	48.1	51.9	
6	31.7	67.9	0.4	31.7	68.3	
7	23.7	75.9	0.4	23.7	76.3	
8	18.9	80.7	0.4	18.9	81.1	
9	48.1	51.3	0.6	48.0	51.9	0.1
10	31.7	67.5	0.8	31.5	68.3	0.2
11	23.8	75.4	0.8	23.8	76.2	
12	18.9	80.2	0.9	18.9	81.0	0.1
13	48.2	51.0	0.8	48.0	51.6	0.4
14	31.9	67.2	0.9	31.7	67.9	0.4
15	23.9	75.1	1.0	23.7	75.9	0.4
16	19.3	79.7	1.0	19.1	80.5	0.4
17	48.3	50.7	1.0	47.9	51.2	0.9
18	32.2	66.7	1.1	31.7	67.4	0.9
19	24.5	74.3	1.2	24.0	75.1	0.9
20	19.5	79.3	1.2	19.1	80.0	0.9
21	48.5	50.3	1.2	47.8	50.8	1.4
22	32.4	66.3	1.3	31.7	66.9	1.4
23	24.5	74.1	1.4	23.8	74.8	1.4
24	19.8	78.7	1.5	19.2	79.4	1.4
25	48.8	48.6	1.6	47.5	50.0	2.5
26	32.9	65.3	1.8	31.7	65.8	2.5
27	26.0	72.1	1.9	24.7	72.7	2.6
28	20.6	77.5	1.9	19.4	78.2	2.4
29	49.6	47.7	2.7	46.9	48.0	5.1
30	34.3	62.8	2.9	31.7	63.2	5.1
31	26.8	70.2	3.0	24.3	70.6	5.1
32	22.4	74.6	3.0	19.8	75.1	5.1

ss — solid solution, K — Ca₃(CrO₄)₂, L — liquid phase, V_M/V_c — volume ratio of MgO and

responding to the formation of melt (about 1270 °C). This instance corresponds to curve 12 in Fig. 3. The melt is present above the temperature of its formation up to the final firing temperature, so that the first two stages of sintering can take the active part, namely the rearrangement of particles taking place immediately after formation of the liquid phase, and the subsequent stage involving dissolution of the substance at the points of contact of the particles and crystallization at other points, which results in a shortening of distances between the particle centres. Shrinkage of the body is ended by conclusion of this stage, solid contacts are formed and residual porosity is eliminated (approx. 2–3%), so that the process is identical with that taking place in the absence of the liquid phase.

of the specimens being studied

Phase Composition 1600 °C (wt. %)			V_M/V_C	ρ_0 (g cm ⁻³)	ρ_k (g cm ⁻³)	ρ_t (g cm ⁻³)	P (%)
CaO	MgO _{ss}	L					
			1	1.22	3.19	3.467	8.0
			2	1.22	3.17	3.506	9.6
			3	1.24	3.23	3.525	8.4
			4	1.22	3.29	3.536	7.0
48.1	51.9		1	1.23	3.29	3.470	5.2
31.7	68.3		2	1.22	3.26	3.508	7.1
23.7	76.3		3	1.22	3.30	3.527	6.4
18.9	81.1		4	1.23	3.38	3.538	4.5
48.0	51.9	0.1	1	1.22	3.35	3.472	3.5
31.5	68.3	0.2	2	1.25	3.33	3.511	5.2
23.8	76.2		3	1.26	3.41	3.531	3.4
18.8	81.0	0.2	4	1.22	3.48	3.542	1.8
47.9	51.5	0.6	1	1.20	3.36	3.470	3.2
31.6	67.8	0.6	2	1.19	3.36	3.510	4.3
23.6	75.8	0.6	3	1.23	3.42	3.530	3.1
19.0	80.4	0.6	4	1.21	3.45	3.541	2.6
47.6	51.1	1.3	1	1.28	3.19	3.468	8.0
31.4	67.3	1.3	2	1.25	3.37	3.508	3.9
23.7	75.0	1.3	2.9	1.25	3.43	3.527	2.8
18.7	80.0	1.3	3.9	1.24	3.42	3.539	3.4
47.2	50.7	2.1	1	1.26	3.19	3.467	8.0
31.2	66.7	2.1	2	1.28	3.36	3.506	4.2
23.3	74.6	2.1	2.9	1.27	3.38	3.525	4.1
18.6	79.3	2.1	3.9	1.27	3.37	3.357	4.7
46.9	49.8	3.3	1	1.26	3.23	3.463	6.7
30.1	65.6	3.3	1.9	1.25	3.31	3.502	5.5
24.0	72.5	3.5	2.7	1.25	3.35	3.518	4.8
18.7	78.1	3.2	3.8	1.23	3.37	3.532	4.6
45.4	47.6	7.0	1	1.26	3.30	3.454	4.6
30.3	62.8	6.9	1.9	1.19	3.28	3.491	6.0
22.8	70.2	7.0	2.7	1.21	3.32	3.509	5.4
18.4	74.7	6.9	3.5	1.24	3.40	3.520	3.4

CaO, ρ_0 — initial density, ρ_k — final density, ρ_t — theoretical density, P — actual porosity

The curve 28 in Fig. 3 corresponds to a sample with a higher content of the liquid phase ($V_l/V_s = 4 \times 10^{-2}$). The force acting between two particles joined with a liquid phase wetting the particles is known to consist of two components and to be a result of surface tension and capillary pressure of the liquid phase [12]. Its size depends on the wetting angle, the volume of the liquid phase situated between the particles, and the geometry of the particles, while being constant for a given volume of the liquid phase. At a certain volume of the liquid phase (so-called critical) the attractive effect of the force is zero or negative when the amount of the liquid phase exceeds the critical amount [13]. The larger amount of liquid phase in the case of specimen 28 compared to specimen 12 resulted in the decrease of the attractive

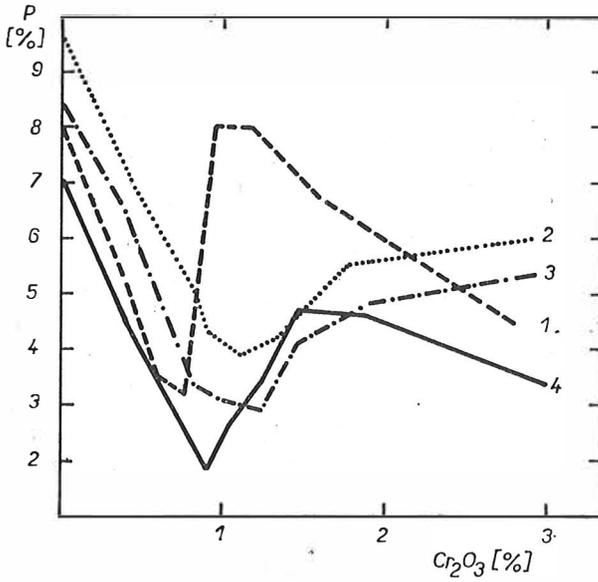


Fig. 1. Actual porosity (P) vs. concentration of Cr_2O_3 (wt. %); 1 — $V_M/V_C = 1$, 2 — $V_M/V_C = 2$
3 — $V_M/V_C = 3$, 4 — $V_M/V_C = 4$.

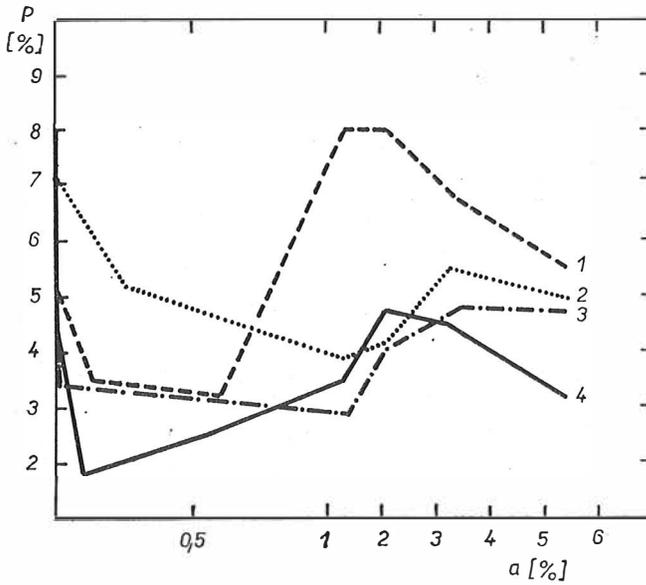


Fig. 2. Actual porosity (P) vs. the content of liquid phase a (wt. %); 1 — $V_M/V_C = 1$, 2 — $V_M/V_C = 2$
3 — $V_M/V_C = 3$, 4 — $V_M/V_C = 4$.

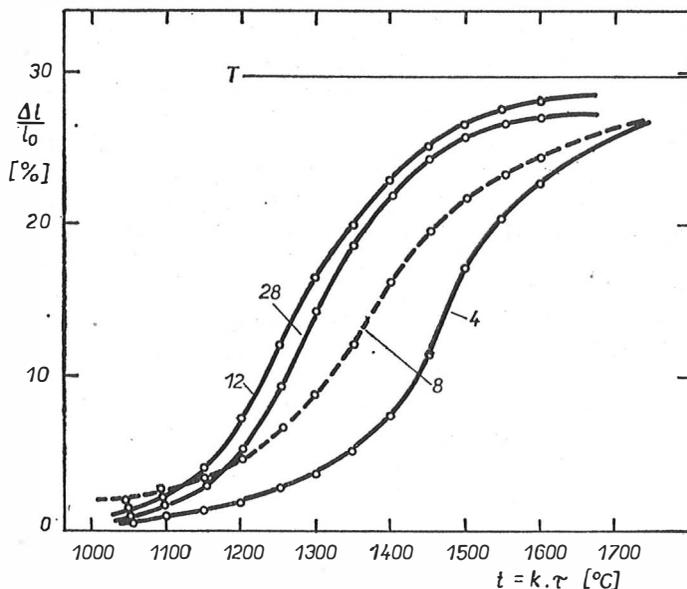


Fig. 3. Linear shrinkage vs. temperature; the designation of curves corresponds to the designation of specimens in Table I; k — $10^\circ\text{C min}^{-1}$, τ — time (min), T — shrinkage corresponding to zero porosity.

forces which are active not only in the particle rearrangement stage, but also increase the chemical potential or solubility of the substance in the region of contact between the particles. As favourable can be considered those instances which can be characterized by the presence of adequate, generally very small amounts of liquid phase required for the formation of the maximum attractive force. Larger amounts of the liquid phase cause a decrease of these forces, the body will shrink less and more slowly, even though by the same mechanism. The initial denser packing of particles resulting from their rearrangement will have a favourable effect on the entire subsequent sintering process as shown by the comparison of curves 12 and 28 in Fig. 3. The final porosity of specimen 12 is lower (similarly to other cases) despite the fact that both specimens have been tempered for 30 minutes at the maximum temperature. On attaining 1600°C , the porosity remained virtually unchanged throughout the isothermal heating, which is indicative of the formation of strong grain boundaries; the melt (situated mostly in pores) was found to be present in specimen 28 only.

When the sample contains an amount of admixture lower than that corresponding to the formation of a saturated solid solution at the maximum heating temperature (specimen 8), a small amount of the liquid phase will probably be formed only temporarily. With increasing temperature, the Cr^{3+} will dissolve in CaO and MgO in a quasi-equilibrium way owing to the high degree of dispersity and to the general homogeneity; however, at the temperature corresponding to the formation of the liquid phase it is assumed that the solubility of Cr^{3+} in both oxides is lower than would correspond to the amount added. The solubility at lower temperatures (up to 1300°C) is unknown. The solubility increases with temperature while the amount of liquid phase decreases.

At higher temperatures the specimens sinter in the absence of the liquid phase. In contrast to specimens 12 and 28, the shrinkage proceeds even when the maximum temperature has been attained (Fig. 3); there is an obvious similarity of the relationships 8 and 4, while curve 4 illustrates shrinkage of a specimen free from the addition. The maximum shrinkage rate (differentiation of curves in Fig. 3 in terms of time) of samples 12 and 28 corresponds to the temperature at which the liquid phase is formed, and in the case of the addition-free specimen, the maximum is shifted towards the higher temperature. It is assumed that the lowest concentration of the chromic oxide addition affects favourably the surface diffusion and that along the grain boundaries in the initial and intermediate stage of sintering, as indicated by a comparison of curves 4 and 8 in Fig. 3.

Despite the attainment of the suitably low final porosity even by heat treatment by linear temperature increase (the study has been aimed at assessing the effect of the addition on the sintering process), further work will be aimed at optimizing the firing process by controlling the sintering rate on the basis of the known shrinkage rate values in terms of temperature and time.

CONCLUSION

A uniformly distributed addition of Cr_2O_3 has a positive effect on the rate of sintering of finely dispersed mixtures of the system $\text{CaO}-\text{MgO}$. The final porosities of synthetic specimens containing Cr_2O_3 additions were always lower than those without this addition. The optimum amount of the addition depends on the composition of the mixture of the main oxides. By adding Cr_2O_3 in amounts of up to 1 wt. % to the mixture of $\text{CaO}-\text{MgO}$ oxides prepared chemically in the concentration region of 50–80 wt. % MgO , it is possible to obtain materials with a porosity lower than 5 % by firing at temperatures up to 1600 °C in an oxidation atmosphere. The lowest porosity was obtained when the amount of melt did not exceed 1 wt. %.

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SLINOVANIE V SÚSTAVE CaO—MgO S PRÍSAĐOU Cr₂O₃

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Metódou odparovania a termického rozkladu z vodných roztokov sa pripravili práškové zmesi sústavy CaO—MgO s prísadou Cr₂O₃ s definovaným fázovým zložením pri konečnej teplote záhrevu tak, aby bolo možné sledovať priebeh slinovania a konečné pórovitosti v závislosti od množstva prísady resp. taveniny a pomeru objemov hlavných oxidov vychádzajúc z výliskov s približne rovnakou počiatočnou pórovitosťou. Priebeh slinovania sa sledoval pomocou dilatometra do teploty 1 600 °C, získané výsledky sa uvádzajú v tabuľke I, vybrané závislosti sú graficky znázornené na obr. 1—3.

Zistilo sa, že rovnomerne rozdelená prísada Cr₂O₃ vplyva pozitívne na rýchlosť slinovania jemne disperzných zmesi sústavy CaO—MgO. Konečné pórovitosti syntetických vzoriek s prísadou oxidu chromitého boli vždy nižšie ako bez prísady, pričom jej optimálne množstvo je závislé od zloženia zmesi základných oxidov. Prísadou Cr₂O₃ v množstve do 1% hm. k zmesi oxidov CaO—MgO, pripravených chemickou cestou v koncentračnej oblasti 50—80% hm. možno získať výpalom do teplôt 1600 °C v oxidačnej atmosfére materiálu s pórovitosťou pod 5%.

Obr. 1. Závislosť skutočnej pórovitosti (P) od koncentrácie Cr₂O₃ [% hmot.]; 1 — $V_M/V_C = 1$, 2 — $V_M/V_C = 2$, 3 — $V_M/V_C = 3$, 4 — $V_M/V_C = 4$.

Obr. 2. Závislosť skutočnej pórovitosti (P) od obsahu taveniny a [% hmot.]; 1 — $V_M/V_C = 1$, 2 — $V_M/V_C = 2$, 3 — $V_M/V_C = 3$, 4 — $V_M/V_C = 4$.

Obr. 3. Závislosť lineárneho zmrštenia od teploty; označenie kriviek zodpovedá označeniu vzoriek v tab. 1, $k = 10^\circ\text{C} \cdot \text{min}^{-1}$; τ — čas (min.), T — zmrštenie zodpovedajúce nulovej pórovitosti.

СПЕКАНИЕ В СИСТЕМЕ CaO—MgO С ДОБАВКОЙ Cr₂O₃

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Методом испарения и термического распада из водных растворов приготовили порошковые смеси системы CaO—MgO с добавкой Cr₂O₃ с определенным фазовым составом при окончательной температуре нагрева таким образом, чтобы можно было исследовать ход спекания и окончательные пористости в зависимости от количества добавки или расплава и отношения объемов основных окислов, уходящих из пресс-изделий с приблизительно одинаковой начальной пористостью. Ход спекания исследовали с помощью dilatometra до температуры 1600 °C. Полученные результаты приводятся в таблице I, подобранные зависимости графически изображаются на рис. 1—3.

Было установлено, что равномерно распределенная добавка Cr₂O₃ оказывает положительное влияние на скорость спекания тонко дисперсионных смесей системы CaO—MgO. Окончательная пористость синтетических образцов с добавкой окиси хрома была всегда ниже, чем без добавки, причем оптимальное количество зависит от состава смеси основных окислов. Добавляя Cr₂O₃ в количестве до 1% по весу к смеси окислов CaO—MgO, приготовленных химическим путем в концентрационной области 50—80% по весу, можно получать обжигом до температур 1600 °C в окислительной среде материалы с пористостью ниже 5%.

Рис. 1. Зависимость действительной пористости (P) от концентрации Cr₂O₃ % по весу; 1 — $V_M/V_C = 1$; 2 — $V_M/V_C = 2$; 3 — $V_M/V_C = 3$; 4 — $V_M/V_C = 4$.

Рис. 2. Зависимость действительной пористости (P) от содержания расплава a [% по весу]; 1 — $V_M/V_C = 1$; 2 — $V_M/V_C = 2$; 3 — $V_M/V_C = 3$; 4 — $V_M/V_C = 4$.

Рис. 3. Зависимость линейной усадки от температуры; обозначение кривых отвечает обозначению образцов в табл. I, $k = 10^\circ\text{C} \cdot \text{мин}^{-1}$, τ — время (мин), T — усадка, соответствующая нулевой пористости.