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THE EFFECT OF ADDITIONS OF CHROMIUM OXIDES ON THE SINTERING OF CaO

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The study deals with the effect of chromium oxides (0.01 — 1.3. wt %. Cr_2O_3*) on the sintering of CaO in air atmosphere at 900—1200 °C. The samples were prepared from precursors obtained by thermal decomposition of evaporation residues of homogeneous aqueous solutions of calcium nitrate, chromic nitrate and citric acid of A. R. purity. The sintering of* CaO *is substantially accelerated by the addition of chromium oxides. The intensification of the process is due above all to the presence of the liquid phase at the boundaries of* CaO *grains. The sintering rate is also positively affected by the dissolution of* Cr^{3+} *in* CaO. *The rapid course of the process in the subsolidus region of the* CaO—Cr_2O_3 *pseudobinary system is probably related to intermediate formation of a non-equilibrium melt.*

INTRODUCTION

The studies dealing with the effect of additions on the sintering of CaO belong for the most part to the field of applied research and are related to the development of CaO-based refractory ceramics. Their results have been surveyed e.g. in [1], [2]. The sintering of compositions in the system CaO—TiO_2 was studied by Loshkarev [3] who established a positive effect of several percent of TiO_2 on the rate of sintering of CaO. In an oxidation atmosphere, additions of Al_2O_3, Fe_2O_3 and Cr_2O_3 form melts with CaO already at relatively low temperatures so that their effect on solid phase sintering of CaO (resulting from affecting the defect structure) has not so far been evaluated. Reactions of CaO in mixtures with chromic oxide are complicated by partial oxidation of Cr_2O_3. The arising ternary phase 9 CaO . 4 CrO_3 . Cr_2O_3 ("9.4.1") exhibits a low melting temperature (about 1240 °C) and co-exists with CaO as well as with MgO [4]. Nadachowski [1] mentions the possibility of filling the pores in sintered CaO with eutectic melt CaO — "9.4.1" for which a melting temperature of 1170 °C is reported. The present work had the aim of studying the effect of chrome oxides on the sintering of CaO.

EXPERIMENTAL

The CaO samples containing additions of chromium oxides were prepared by the wet process using the method according to [13], namely by mixing aqueous solutions of $Ca(NO_3)_2$. 4 H_2O A. R. (Lachema, N. C., Brno), $Cr(NO_3)_3$. 9 H_2O C. P. (Soyuzchimexport, U.S.S.R.) and citric acid $C_6H_8O_7$. H_2O A. R. (Lachema, N. C., Brno) in amounts of 0.5 M per 1 M of the metals. The solutions were evaporated to dryness and the decomposition of the precursor was concluded by heating in air atmosphere at a rate of 200 °C/hr up to 900 °C with a 30-minute delay at this temperature. The CaO powder free from additions was analysed spectrally and the result is listed in Table I.

The powders were compacted in a double-acting cylindrical mould 12 mm in diameter under a pressure of 100 MPa into pellets 1—2 mm in height. The apparent density of the pellets was in the range of 1.3—1.6 g/cm³. The pellets were prepared directly before the measurement.

The course of sintering in the 900—1050 °C temperature range was measured by Chevenard type dilatometer. The specimens were heated up to the respective temperature at a rate of 20 °C/min (gradual heating). At the higher temperatures the shrinkage was measured in a Leitz high-temperature microscope. The changes in the specimen length were measured continuously with an accuracy of 0.01 mm. Before measurement the specimens were kept for 15 minutes in the cooler furnace zone at 800 °C and then were pushed into the furnace center heated up to the required temperature. The shrinkage measurement was started within about 10 seconds after pushing in the specimen. Another series of isothermal measurements in the Chevenard dilatometer was effected in a similar way at 800—1050 °C (abrupt heating).

Table I

The content of impurities in the precusor CaO

Concentration, %	
0.1—0.5	Mg, Al
0.05—0.1	Si
0.01—0.05	Cr
0.001—0.005	Fe, Cu

The specimen length was measured with a micrometer before and after the experiment. The specimen volume was determined by measuring the weight of mercury displaced by the specimen. Adapted single-pan balance was used for determining the buoyancy due to submersion of the specimen in mercury which equals the weight of the displaced mercury. The apparent density was then calculated according to the relationship

$$\varrho = \frac{m}{m_{\mathrm{Hg}}} \varrho_{\mathrm{Hg}} \qquad [\mathrm{g\ cm^{-3}}],$$

where

ϱ is apparent density of the sample [g cm^{-3}],

m is weight of the specimen [g],

m_{Hg} is the weight of mercury displaced by the specimen [g],

$\varrho_{\mathrm{Hg}} = 13.55$ g cm^{-3} is the density of mercury at 25 °C.

On the basis of final apparent density of the specimens measured at room temperature and on that of instantaneous specimen length value read from the shrinkage curve the apparent specimen density at time τ was calculated using the formula

$$\varrho_\tau = \varrho_k \left(\frac{l_k}{l_k + \dfrac{\Delta l^T}{1 + \alpha \, \Delta T}} \right)^3,$$

where

ϱ_τ is apparent density of the specimen at time τ at room temperature,

ϱ_k is the final apparent density of specimen at room temperature,
Δl^T is the difference between the final specimen length and its length at time τ read from the shrinkage curve,
l_k is the final specimen length at room temperature ascribed to the last point on the shrinkage curve,
α is the mean temperature coefficient of linear expansion — 13×10^{-6} K^{-1}.

The time dependence of apparent density of the specimens in the course of sintering at 1200 °C is plotted in Fig. 1. Fig. 2 shows the plot of apparent density in the 60th minute of heating in terms of the amount of chromium added expressed in wt % of Cr_2O_3. The course of sintering is rendered considerably more intensive already by very small additions of chromium oxides.

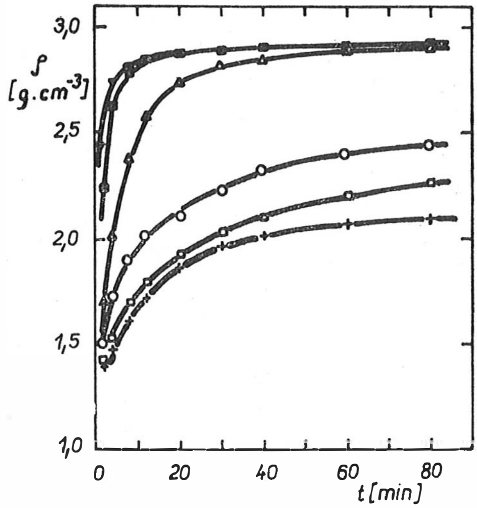

Fig. 1. Apparent density of specimens in the course of sintering at 1200 °C in terms of time; addition of Cr_2O_3 *in wt %* + — ○, □ — *0.013,* ○ — *0.04,* △ — *0.09,* ■ — *0.27,* ▼ — *0.64.*

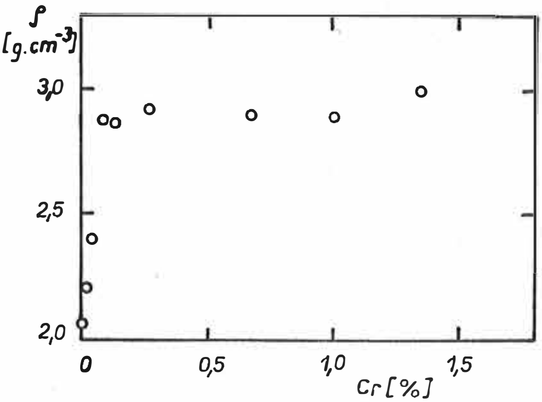

Fig. 2. Apparent density of pellets in the 60th minute of firing in terms of the amount of chromium added expressed in wt % *of* Cr_2O_3.

The solubility of chromium oxides in CaO was also determined. A pellet with an addition of 0.4 % Cr_2O_3 fired at 1200 °C and quenched rapidly was dissolved in ethylene glycol and since the chromium dissolved in CaO passes into solution, the solubility of chromium oxides in CaO was determined by weighing the insoluble residue (a phase of "9.4.1" composition); the result amounted to about 0.2 wt % expressed as Cr_2O_3.

Observation of the specimens in reflected light and under a binocular lens revealed remarkable changes in the localization of the addition. In the precursor powders and in the pellets before the heating the admixture was dispersed quite homogeneously as indicated by uniform light-green colour. Heating up of the specimens resulted in agglomeration of the phase containing the chromium oxides. This phenomenon was established in specimens containing additions of Cr_2O_3 in excess of 0.2 wt %, and was becoming more intensive with prolonged time of heating. The co-existing phase was observed to be forced off the boundaries of CaO grains into the pores and free surfaces.

Table II lists the data on apparent density of pellets sintered with a delay of 60 minutes at 1015 °C either following abrupt heating or in the course of gradual heating up to this temperature.

Table II

Apparent density of CaO with Cr_2O_3 addition after 60 minutes at 1015°C in terms of the way of heating

Cr_2O_3 addition [%]	Gradual heating [20 °C/min.] [g cm^{-3}]	Abrupt heating up [approx. 200 °C/min.] [g cm^{-3}]
0.1	2.66	1.35
0.4	2.85	2.18
1.32	2.85	2.04

In the case of abrupt heating the specimens attained a considerably lower apparent density than those heated up to the sintering temperature at a rate of 20 °C/min. Fig. 3 shows a plot of apparent density of a pellet containing CaO + 0.27 % Cr_2O_3 in terms of time at various temperatures. Shrinkage obviously takes place already at temperatures from 900 °C upwards.

DISCUSSION

The significant effect of small additions of chromium oxides on the rate of sintering of CaO, which starts at temperatures of only about 900 °C may be understood from the point of view of reactions taking place in the system in the course of heating as well as from that of the defective structure of CaO.

According to the studies of equilibrium behaviour of the system Ca—Cr—O [4] the following phase changes take place in the CaO-rich region in dependence on temperature and composition of the ambient atmosphere: In air atmosphere of normal humidity calcium chromate is present up to 800 °C, between 800—900 °C under the same conditions there exists the $Ca_5(CrO_4)_3OH$ phase and in the range of 900—1170 °C CaO co-exists with the phase $Ca_3(CrO_4)_2$ (the so-called "9.4.1"). The following reactions take therefore place in the system in question at temperatures above 900 °C:

$$2\,Ca_5(CrO_4)_3OH \rightarrow CaO + 3\,Ca_3(CrO_4)_2 + H_2O.$$

Above 1170 °C (eutectic temperature of CaO—$Ca_3(CrO_4)_2$) there appears a melt the composition of which is very close to that of phase "9.4.1". The lowest melting temperature established so far in the pseudobinary system CaO—Cr_2O_3 corresponds to an eutectic between "9.4.1" and $CaCr_2O_4$, and is situated at 1022 °C [5].

Insofar as a equilibrium behaviour of the system Ca—Cr—O is considered, no melt can arise in the specimens in question at temperature below 1170 °C.

However, in the present experiments the stability region of the individual co-existing phases was passed through at a relatively high rate so that these phases may have been present in the system simultaneously. It is by no means impossible that their mutual interaction brings about intermediate formation of an inequilibrial melt, unsaturated with calcium oxide, which has a favourable effect on sintering while this property is not exhibited by the melt of epuilibrium composition. This assumption is supported by a comparison between the changes in the rate of shrinkage in terms of the rate of heating in the range of 800—1000 °C (Table II) and the changes observed in the localization of the admixture. In the stage of reaction between the melt and calcium oxide their mutual interfacial tension is decreasing. As a result of this the melt is located at the grain boundaries and promotes the course of shrinking [6]. The high rate of the sintering process at a relatively low temperature (Fig. 3) which resembles the sintering of MgO with a LiF admixture also indicates the presence of a melt.

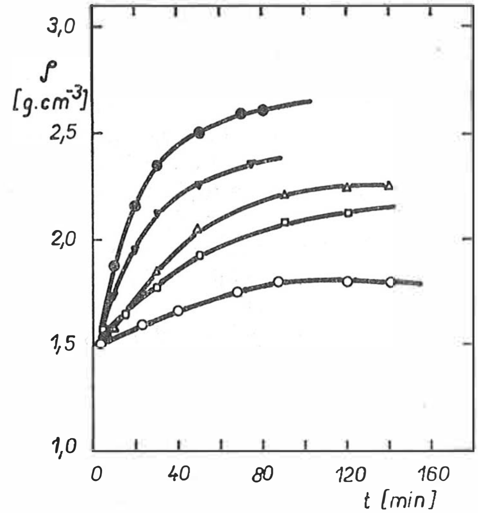

Fig. 3. Apparent density of pellets CaO + 0.27 % Cr_2O_3 *vs. time during sintering at various temperatures; abrupt heating;* ○ — *900 °C,* □ — *930 °C,* △ — *960 °C,* ▼ — *980 °C,* ● — *1015 °C.*

The reactions in the system in question may likewise be affected by the impurities present in the specimens. Apart from the impurities determined by spectroanalysis

(Tab. I) the content of about 0.1 % Na is typical. The impurities are only partially soluble in CaO and some of them, which are situated at the grain boundaries of CaO, react with the admixture. In this way the composition and properties of the phase co-existing with CaO is also subject to changes.

The high rate of sintering of specimens containing Cr_2O_3 in excess of 0.09 % at 1200 °C (Fig. 1) within the first minutes of the isotherm may be explained by the rearrangement of particles in the presence of the liquid phase [7]. This stage is concluded comparatively early, while the further shrinkage takes place by the mechanism of dissolution and precipitation from melt. The solubility of CaO at the points of higher curvature is higher than that of other points of the boundary between solid particles and the melt, thus facilitating the transfer of material from the contact area through the liquid phase to other points. However, the powder reactivity is simultaneously decreasing as a result of the rounding off of surfaces due to dissolution and reprecipitation from liquid phase. The joint effect of these phenomena is a slowing down of the shrinkage in the presence of a larger amount of liquid phase following the initial rapid shrinkage. The relatively high final porosities of the specimens (Figs. 1, 2) are probably caused by the formation of pores during rapid liberation of H_2O vapours according to the reaction mechanism in the course of heating up to 1200 °C.

The theory of sintering of ionic compounds indicates that the rate of sintering by the bulk diffusion mechanism is determined by the diffusion of the slower ion [8], [9], [10]. As shown in the studies by Gauthier et al. [11] and De Keyser et al. [12], Ca^{2+} is the slower ion in calcium oxide and its diffusion is the limiting process of mass transport in CaO. These results are in a certain disagreement with the conception of ions as hard spheres ($r_{Ca^{2+}} = 0.99 \times 10^{-10}$ m; $r_{O^{2-}} = 1.32 \times 10^{-10}$ m); however, they are probably related to the polarizability of the ions.

When assuming that the trivalent chromium ion dissolving in the CaO structure forms one half of cation vacancy, then such an addition should activate the sintering process by vacancy controlled bulk diffusion. However, the situation is complicated by the presence of impurities dissolved in the CaO structure. These impurities likewise affect the diffusion processes and obscure the effect of chromium oxide addition. For instance, when 0.55 % Na_2O was added to the mixture of CaO + 0.67 % Cr_2O_3 the resulting specimen exhibited no shrinkage at all at 1200 °C. On the other hand other impurities present may have taken part in the activation of sintering of our specimens.

SUMMARY

Additions of chromium oxides were found to have a positive effect on the sintering of CaO within the temperature range of 900—1200 °C. The sintering process is already activated by minimum additions of chromium oxides (0.04 %). The sintering activation is due to the effect of melt which probably changes its composition and properties in the course of the process. Dissolution of the Cr^{3+} ions in the CaO structure accelerates the diffusion of Ca^{2+}, thus promoting the sintering.

References

[1] Nadachowski F.: Ceramurgia Inter. *2*, 551 (1976).
[2] Popilskij R. J.: Ogneupory [11], 37 (1972).

[3] Loshkarev B. A.: Ogneupory 127 (1951).
[4] Pánek Z., Kanclíř E.: Silikáty *19*, 113 (1976).
[5] Ford W. F., Rees W. J.: Trans. Brit. Ceram. Soc. *47*, 207 (1948).
[6] Reynen P.: Erzmetall *28*, 54 (1975).
[7] Petzow G., Huppmann W. J.: Ztsch. f. Metallk. *67*, 579 (1976).
[8] Readey D. W.: J. Appl. Phys. *37*, 2309 (1966).
[9] Readey D. W.: J. Am. Ceram. Soc. *49*, 366 (1966).
[10] Reijnen P. J. L.: *Problems of Nonstoichiometry*, (ed. A. Rabenau), p. 219. Amsterdam, North-Holland.
[11] Gauthier M., Duclot M., Hammou A., Deportes C.: J. Sol. State Chem. *9*, 15 (1974).
[12] De Keyser W. L., Wollast R., Duvigneaud P. H.: J. Mat. Sci. *4*, 989 (1969).
[13] Marcilly Ch., Courty Ph., Delmon B.: J. Am. Ceram. Soc. *53*, 56 (1970).

VPLYV PRÍDAVKU KYSLIČNÍKOV CHRÓMU NA SPEKANIE CaO

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V práci sa zisťoval vplyv prísad kysličníkov chrómu (0,01 — 1,3 % hm. v prepočte na Cr_2O_3) na spekanie CaO vo vzdušnej atmosfére pri 900—1200 °C. Vzorky sa pripravili termickým rozkladom odparkov homogénnych vodných roztokov obsahujúcich dusičnan vápenatý, dusičnan chromitý a kyselinu citrónovú čistoty p. a. Získané prášky sa lisovali tlakom 100 MPa na tablety s objemovou hmotnosťou 1,3 — 1,60 gcm^{-3} a izotermicky sa meralo ich zmrštenie v zahrievacom mikroskope alebo v dilatometri.

Rýchlosť zmršťovania CaO sa prídavkom kysličníkov chrómu výrazne zvyšuje (obr. 1, 2) a po 80 min záhreve pri 1200 °C dosiahli vzorky s prísadou > 0,09 % hm. Cr_2O_3 pórovitosť ~ 10 %. Aktivovanie spekania je spôsobené hlavne prítomnosťou kvapalnej fázy na hraniciach zŕn CaO. Intenzívny priebeh procesu sa zaznamenal (obr. 3) tiež v subsolidusovej oblasti pseudobinárnej sústavy CaO—Cr_2O_3 (pod 1170 °C), čo pravdepodobne súvisí s prechodnou tvorbou nerovnovážnej taveniny v priebehu záhrevu. Tento názor podporujú tiež pozorované zmeny v lokalizácii prísady a závislosť objemovej hmotnosti, ktorú dosahujú vzorky po 60 min izotermického záhrevu pri 1015 °C, od režimu teplotného vzostupu v rozmedzí 800—1000 °C (tab. II). Súčasťou taveniny môžu byť tiež nečistoty prítomné vo vzorkách (tab. I).

Spekanie môže byť pozitívne ovplyvňované tiež zmenami v defektnej štruktúre CaO, keďže vstupom Cr^{3+} sa vytvárajú katiónové vakancie a tým sa urýchľuje difúzia iónu Ca^{2+}, ktorý limituje rýchlosť pri objemovej difúzii CaO.

Obr. 1. Objemová hmotnosť vzoriek počas spekania pri 1200 °C v závislosti od času. Prídavok Cr_2O_3 *% hm.:* + — 0, ☐ — 0,013, ○ — 0,04, △ — 0,09, ■ — 0,27, ▲ — 0,64.

Obr. 2. Objemová hmotnosť tabliet v 60. minúte výpalu v závislosti od množstva pridaného chrómu, prepočítaného na hmotnostné percentá Cr_2O_3.

Obr. 3. Závislosť objemovej hmotnosti tabliet CaO + 0,27 % Cr_2O_3 *od času počas spekania pri rôznych teplotách; náhly ohrev;* ○ — *900 °C,* ☐ — *930 °C,* △ — *960 °C,* ▼ — *980 °C,* ● — *1015 °C.*

ВЛИЯНИЕ ДОБАВКИ ОКИСЛОВ ХРОМА НА СПЕКАНИЕ CaO

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В предлагаемой работе определяется влияние добавок окислов хрома (0,01—1,3 % по весу в пересчете на Cr_2O_3) на спекание CaO в атмосфере воздуха при температуре 900—1200 °C. Образцы приготовили термическим разложением сухих остатков гомогенных водных растворов, содержащих нитрат кальция, нитрат хрома и лимонную кислоту д. а. Полученные порошки прессовали под давлением 100 MPa в таблетки удельного веса 1,30—1,60 гсм$^{-3}$ и изотермически измеряли их усадку в нагревающем микроскопе или дилатометре.

Скорость усадки CaO с добавкой окислов хрома резко повышается (рис. 1,2) и после 80-тиминутного нагрева при температуре 1200 °C получали образцы с добавкой $> 0,09$ % по весу Cr_2O_3, пористость ~10 %. Активирование спекания вызывается главным образом присутствием жидкой фазы на границах зерен CaO. Интенсивный ход процесса также установили (рис. 3) в области субсолидус псевдобинарной системы CaO—Cr_2O_3 (ниже 1170 °C), что правдеподобно связано с переходным образованием неравновесного расплава во время нагрева. Такое мнение поддерживается также наблюдаемыми изменениями в размещении добавки и зависимостью объемного веса, которого достигают образцы после 60 минут изотермического нагрева при температуре 1015 °C, от режима подъема температуры в пределах 800—1000 °C (табл. II). Составной частью расплава могут быть также загрязнения, присутствующие в образцах (табл. I).

На спекание могут положительное влияние оказывать также изменения в дефектной структуре CaO, когда при входе Cr^{3+} образуются катионные вакансии, а в результате того ускоряется диффузия иона Ca^{2+}, лимитирующего скорость при объемной диффузии CaO.

Рис. 1. Зависимость объемного веса образцов от времени спекания при температуре 1200 °C в зависимости от времени. Добавка Cr_2O_3 *% по весу; + — 0, □ — 0,013, ○ — 0,04, △ — 0,09, ■ — 0,27, ▼ — 0,64.*

Рис. 2. Объемный вес таблеток в 60-ой минуте обжига в зависимости от количества добавляемого хрома при пересчете на % по весу Cr_2O_3.

Рис. 3. Зависимость объемного веса таблеток CaO + *0,27 %* Cr_2O_3 *от времени во время спекания при разных температурах; резкий нагрев; ○ — 900 °C, □ — 930 °C, △ — 960 °C, ▼ — 980 °C, ● — 1015 °C.*