

PROPERTIES OF CaO SINTERED WITH ADDITION OF ACTIVE ALUMINA

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This work provides research and evaluation of the influence of active gama alumina addition on green and sintered CaO material properties, microstructures and mineralogical phase formation. Experimental results have shown the possibility to prepare more stable CaO with excellent properties by energy saving one-stage burning process of natural ground limestone with small addition of γ -Al₂O₃ (1 wt. %) at up to 1550°C for two hours. The additive caused increasing of the sintered density but especially significant decreasing of apparent porosity of CaO. X-ray diffraction and energy dispersive X-ray fluorescence analysis confirmed mainly the presence of 3CaO·Al₂O₃ on the grain boundaries. Formation of other phases during sintering, more specifically 12CaO·7Al₂O₃ and CaO·6Al₂O₃ with lower tendency to hydration was also proved.

INTRODUCTION

The production of calcium oxide by using limestone CaCO₃ is one of the oldest chemical processes performed in the world. Abundance of limestone in the Earth crust (4 wt. %) and its relatively simple transformation to CaO caused wide exploitation of this material in the past as well as in the present. The consumption of lime has rapidly increased during last decade. In 2002 the world total production represented around 120 mil. tonnes in comparison with 2012 when the total production of lime worldwide was about 340 mil. tonnes. The annual production in the EU is estimated at around 12 percent of world production [1-3].

The most important application of CaO in metallurgy results from its ability to create compounds with silicates. Iron and steel industries are significant consumers of CaO (around 45 percent). Processing of each tonne of iron consumes around 80 kg of CaO [4]. Besides utilisation in iron and steel industry, it is used in cement, glass, fillers, stone blocks, pulp&paper, chemicals and plastics production, water and flue gas processing, environmental applications etc. Only one use disappears, i.e. „limelight“. Before electric light era the lime was used as a source of very bright light used for example on theatre stage.

However, attempts for utilising CaO chemical stability at high temperatures and its refractoriness started at the end of the 19th century. Just then the burnt CaO was used probably for the first time for lining Bessemer converter in order to desulphurise and dephosphorise pig iron [5].

At present the successful application of high refractory CaO material with melting point of ~ 2600°C not only in steel industry could bring certain solution to lack of high quality raw material. Its application as refractory material is advantageous because of its high thermodynamic stability especially in presence of carbon at high temperatures. Low vapour pressure of CaO at high temperatures enables to use it in secondary metallurgy operations of steel as processes VOD (Vacuum Oxygen Decarburisation) and AOD (Argon Oxygen Decarburisation). The low price and availability of good quality natural CaCO₃ raw material is undisputed lucrative aspect, too.

From the quality of steel point of view, the ability of CaO to bind non-metallic inclusions from molten steel and ability for desulphurisation and dephosphorisation of molten steel is especially advantageous. It was shown that the content of aluminium in CaO or in molten steel is useful in deoxidation process of steel due to enhancing effect of total deoxidation in the presence of molten

calcium aluminate. Presented works discuss character and mechanism of inclusion formation in aluminium killed steel after calcium processing in more details [6-8]. Aluminium addition to molten steel causes decreasing of oxygen activities in molten steel and the rate of oxygen reduction by each per cent of Al was estimated at more than 0.05. Higher ratio of CaO/Al₂O₃ in the slag could result in less oxygen activity of molten steel [9].

Research in the field of preparation of CaO refractory material and experiences with its application outlined that the main problem is vicious hydration resistance of CaO. In this respect, the dominating driving force for development of such refractory bodies appears finding the suitable preparation method in order to obtain CaO product with the highest density and hydration or corrosion resistance. Furthermore, the solution is also to find some special application where the lower hydration resistance would not be a great barrier. The CaO refractory could serve for example as a nozzle or active refractory lining assuring high quality of steel at the same time. Another possible application for the CaO refractory could be offered also by cement industry. Although, the industrial applications of lime as the refractory material are still quite rare, some attempts are known of. CaO was used for example as a converter lining in Poland in the '80s [10], in continuous casting of steel in Liuzhou Iron & Steel Co. (China) in 1994 [11] and for liquid steel filtration and steel vacuum processing (AOD and VOD) in Japan [12]. On the other hand, some slow increase in consumption of CaO refractory bodies can be seen from CaO application trend in 2003 [13].

As it was said, the main problem is limited lifetime of CaO refractory due to atmospheric moisture attacking. This makes difficulties mainly during storage period of sintered product. Such kind of refractory needs special storage conditions. Various hydration inhibitors or methods for protection of CaO burned bodies have been studied. For instance, immersing of individual bodies in kerosene and packaging in polyethylene bags, mixing with carbon or other additives were tested. Results concerning the type and amount of additives differ from each other. On the other hand, few additives, e.g. Fe₂O₃, Ca(OH)₂ and Al₂O₃ have been selected as prospective ones from density and hydration resistance point of view. Additives based on MgO, ZnO, ZrO₂, SnO₂, NiO, Cr₂O₃, V₂O₅, MnO, CoO, Ca(PO₃)₂ showed no or minor effectivity in hydration prevention [14]. The natural inclination of CaO to hydration even on air is possible to suppress not only by decreasing the open porosity but also by structure and/or product surface make-up. An optimal from the hydration resistance point of view seems to be preparation of molten CaO. However, the high price of molten CaO pushes the research forward to look for other 'cheaper' alternatives for CaO refractory protection. The latest patent activities bring also other perspectives of lime-based refractory clinker with Al₂O₃ addition. Authors presented refractory composition with

improved insulating character and penetration resistance of liner in contact with molten aluminium during aluminium manufacturing and transporting process [15].

The preparation of more stable CaO refractory material from limestone with addition of γ -Al₂O₃ by one-stage burning process was studied in this work. The main aim was to study and evaluate the influence of active additive on CaO properties, microstructure and phase formation after sintering process in order to show possible perspective of preparation the CaO refractories with better properties and higher hydration resistance.

EXPERIMENTAL

Experiments were aimed to preparation of CaO refractory by one-stage burning process using ground natural limestone from Gombasek-site (Slovakia). The chemical composition of input limestone is given in Table 1. From mineralogical point of view, the limestone contains phase calcite, CaCO₃ (JCPDS 5-586). Other potential phases were under the detection limit of used method.

Furthermore, the influence of γ -Al₂O₃ addition on CaO characteristic after one-stage burning process was examined. The gamma modification was chosen due to known „Hedvall effect“, phenomenon which provides higher activity of unstable, low temperature allotropic modification of alumina in contrast to stable substances. Papers where the addition of alumina to CaO was studied do not provide information about the character and modification of Al₂O₃ for experimental study [16-18]. Hereby, unstable γ -modification of Al₂O₃ was chosen because of preference of active status of solid substances during sintering process. It is well known that apparent forms of active status of solid substances are represented by unstable modifications, dispersive and warp substances status, unstable lattice defects, amorphous and vitreous status, presence of small amount of extrinsic components in the lattice, surface defects and

Table 1. Chemical composition of natural limestone Gombasek-site.

Chemical composition	Limestone Gombasek Trias (wt. %)
CaO	52.20
MgO	2.00
SiO ₂	-
Al ₂ O ₃	-
Fe ₂ O ₃	-
LOI (1000°C)	40.00
Decomposition temperature (°C)*	835
Density (g·cm ⁻³)**	2.75

* measured by use of thermal analysis (Derivatograph C MOM, Budapest; heating rate of 10°C·min⁻¹)

** measured by use of AccuPyc 1330 V1.00

physical inhomogeneities. The higher activity of powder is the higher sintering driving force and faster course of sintering [19].

Input sample of limestone in amount of 100 g with granularity in the range of 0.32 - 4 mm was put to the grinding process in laboratory vibration mill (VM 4, Czech Republic) for 5 minutes. Parameters of limestone grinding (charge and time) were chosen on the basis of results of previous works dedicated to optimization of limestone grinding process [20-22].

The ground limestone from Gombasek site and addition of pure powder γ - Al_2O_3 of analytical grade with pycnometric density of $3.25 \text{ g}\cdot\text{cm}^{-3}$ and granularity of 94 % less than $63 \mu\text{m}$ were used for experiments. The aim of experiments was to find out the influence of amount of additive on CaO properties and microstructure after one-stage burning process at 1550°C for 2 hours.

The sample of limestone ground for 5 minutes with grain size of 100 % less than $63 \mu\text{m}$ and surface area of $2.35 \text{ m}^2\cdot\text{g}^{-1}$ (measured by use of ASAP 2010 V4.0 G) was homogenized with individual amounts of additive of 0, 1, 3, 6 wt. %. Then the mixture was uni-axially pressed into the pellets by pressure of 20 MPa using 1 wt. % or 2 wt. % of water as a binder. The parameters of pressing were chosen on the basis of own previous works [23-24]. After pressing, the samples were burned in the laboratory resistance furnace NETZSCH T-417/1 up to 1550°C at the heating rate of $5^\circ\text{C}\cdot\text{min}^{-1}$ and with holding time at maximal temperature of 2 hours followed by cooling with the furnace. After burning process the CaO pellets were tested for bulk density, apparent porosity according to the standard method ISO 5017:2013 (under the vacuum) and volume shrinkage was counted after measuring volume before and after burning. The samples of sintered CaO pellets without any addition and with addition of γ - Al_2O_3 were subjected to morphology and microstructure testing by using electron microscope JEOL JSM - 35 CF, Japan, equipped with EDX analyser (Energy Dispersive X-ray Fluorescence Spectrometry) and optical microscope Neophot 23 (Germany). The XRD qualitative phase analysis using powder diffractometer Phillips Panalytical XpertPro and software HighScore Plus was used for mineralogical analysis of the chosen sample after sintering.

RESULTS AND DISCUSSION

Figure 1 and Figure 2 show the experimental results of the influence of additive to ground limestone on green bulk density of pressed pellets and on bulk density after one-stage burning process up to 1550°C . The effect of additive on apparent porosity and volume shrinkage are presented in Figure 3 and Figure 4, respectively.

From the results in Figure 1 it is obvious that bulk density of green pellets decreases slightly as the consequence of presence of extrinsic particles of γ -modification of Al_2O_3 . The highest relative bulk density of

92.22 % of sintered CaO pellets after burning process was achieved with a mixture containing 99 % CaCO_3 and 1 wt. % γ - Al_2O_3 (Figure 2). The theoretical density of CaO is $3.34 \text{ g}\cdot\text{cm}^{-3}$. The significant decreasing of bulk density of sintered CaO with addition higher than 1 wt. % is possible to explain by rising apparent porosity of such sample. On the other hand, quantitatively similar values of apparent porosity for CaO with higher addition of γ - Al_2O_3 suggest melted surface of these samples during burning process. This causes final creating of the protective layer on the surface of CaO pellets and grains. This layer hinders the penetration of liquid (kerosene) at the measurement of bulk density. These arguments confirm also achieved values of apparent porosity for sintered CaO (Figure 3). The research has shown significant difference between apparent porosity (AP 5.2 %) of pure sintered CaO and CaO/ γ - Al_2O_3 mixture with addition of one per cent (AP 0.2 %). From Figure 3 it is clear that addition does not affect the volume shrinkage markedly. Similar shrinkage as well as apparent (open) porosity values for CaO/ γ - Al_2O_3 mixtures and different values for their bulk densities signify increasing of closed porosity of these samples in dependence on amount of addition.

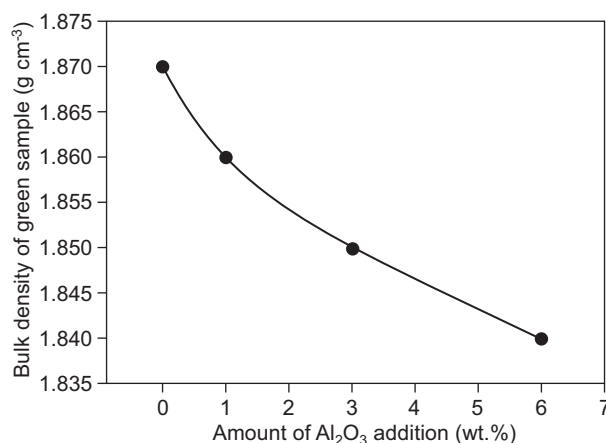


Figure 1. Influence of alumina addition on green bulk density.

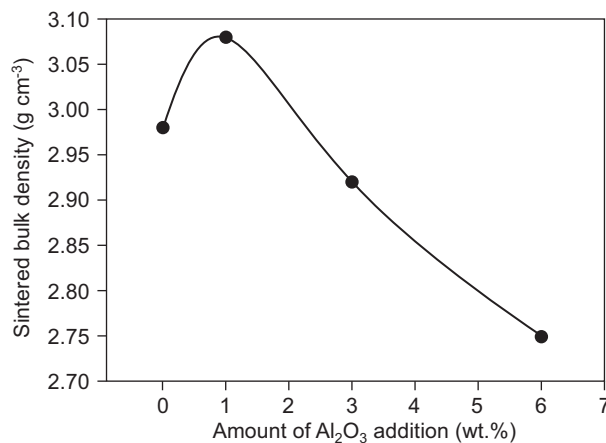


Figure 2. Influence of alumina addition on bulk density of sintered CaO.

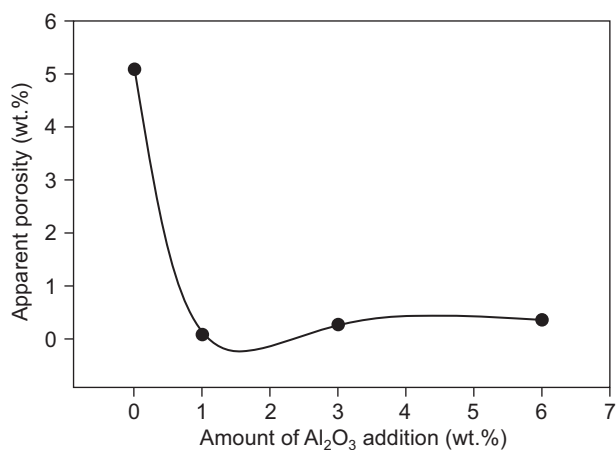


Figure 3. Influence of alumina addition on apparent porosity of CaO.

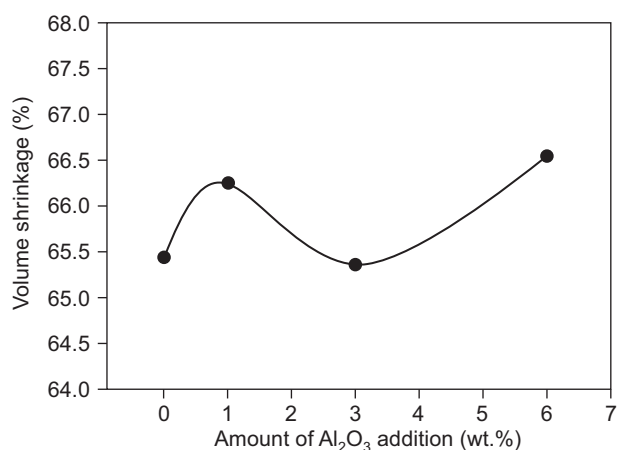


Figure 4. Influence of alumina addition on volume shrinkage of CaO.

Figures 5-7 shows the SEM microstructures of polished section of sintered CaO samples at magnification 50, 100, 300, 330, 500 and 550 times. Moreover, the presence of elements or phases in pure sintered CaO and with maximum γ -Al₂O₃ addition was detected by using spot EDX analysis.

As can be seen in Figure 5, the microstructure of pure CaO sintered sample differs from those with addition, Figures 5b-d. The pure CaO contains many small pores. EDX analysis did not confirm any other composition of visible dark spots compared with light background. There are probably bigger pores on the grain boundaries. The samples with addition have one mutual feature – evident presence of macropores (~ 100 μ m) which dimension is increasing with increasing of addition amount (up to ~ 150 μ m). Moreover, the sample with the highest amount of addition has a tendency of coalescence of macropores.

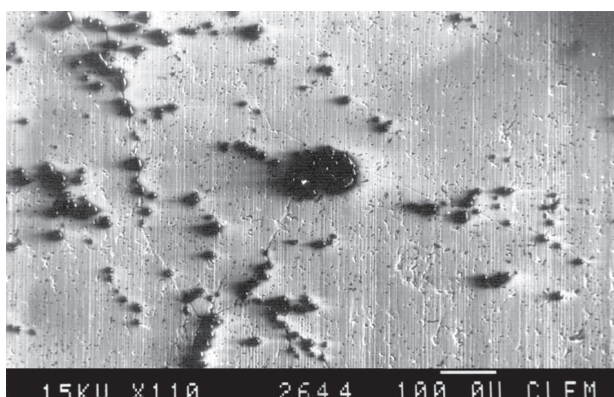
Figure 6 shows the microstructures of the same samples at higher magnification 300 or 330, times respectively. Grain boundaries are visible in the microstructure of the sample with 1 % of addition in

Figure 6b and grains are sintered together without larger amount of liquid phase. The sample microstructure in Figure 6c with addition of 3 % points to visible bright CaO grains and darker phase located on the grain boundaries. This means that sintering was run with a presence of greater amount of liquid phase. Maximum Al₂O₃ addition causes increasing of macropores dimension and their coupling as well. SEM pictures complement assumptions about density and porosity development of sintered CaO. It is obvious that higher amount of γ -Al₂O₃ addition during burning pressed CaCO₃ at 1550°C causes formation of more liquid phase followed by greater amount of macropores, their growing as well as coupling. This phenomenon then proves given values of lower bulk density and higher porosity of sintered CaO samples on Figure 2 and Figure 3.

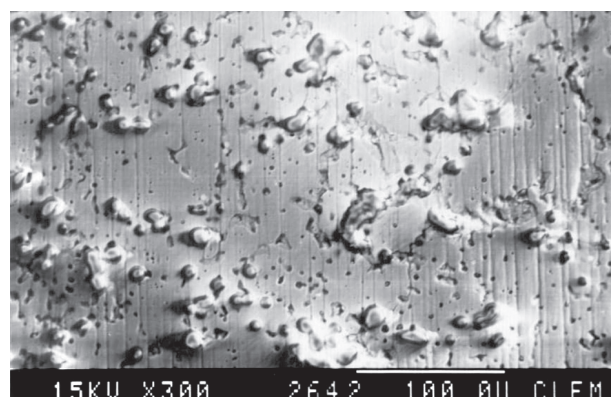
By spot EDX analysis it was found out that inside the grains mainly calcium or, in some cases, small amount of magnesium occurs. Darker phase separated on the grain boundaries in the sample with addition of 3 wt. % and 6 wt. % suggested change in quantitative ratio of CaO to Al₂O₃ phase. The calculation based on EDX results of CaO with 3 wt. % and 6 wt. % γ -Al₂O₃ sample outlined possible compound of 3CaO·Al₂O₃. Figure 7 shows the microstructures of the same studied CaO samples but at greater magnification 500 and 550, respectively.

From Figure 7a it is obvious that pure CaO sample has poor developed structure with great amount of small pores which are present mostly at grain boundaries. In the SEM picture of the sample with 1 wt. % of addition are visible grain boundaries and relatively rare small pores with size of 10 nm distributed inside the grains and on the grain boundaries as well. The amount of pores in the sample with addition of 1 wt. % seems lower than in the sample of pure CaO as can be seen in Figure 7b. An interesting phenomenon is whisker shapes inside the macropores in the sample with 6 wt. % of addition in Figure 7d. However, EDX analysis does not indicate the presence of new specific phase. It is possible that pore's interior contains impurities (fibres) as a consequence of polishing operation or fibres of generated calcium hydroxide from manipulation or etching process of the samples. On the other hand, this phenomenon occurred only in the samples with higher content of addition. Thus, the possible explanation is that new CaO/Al₂O₃ phase crystallized during sintering-cooling operation. However, these presumptions were not confirmed.

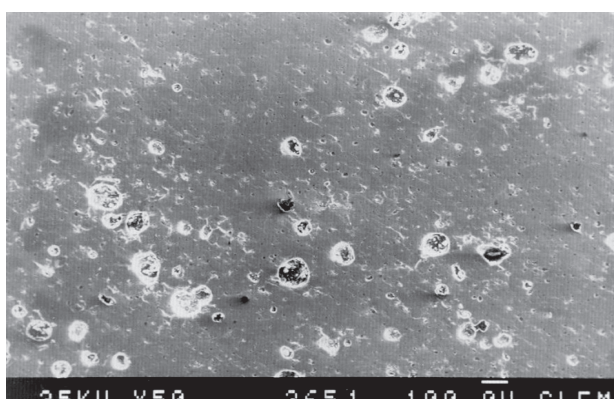
For the comparison, the microstructure of CaO with addition of 1 wt. % γ -Al₂O₃ made by optical microscope Neophot 32 is shown in Figure 8. This material exhibited the highest bulk density after sintering. The sample for optical microscope was etched by use of 2 v/v-% solution of ice acetic acid in methanol. On the grain boundaries it is visible evenly distributed glass phase in adequate amount which ensures better sintering of individual grains also with the protection effect.



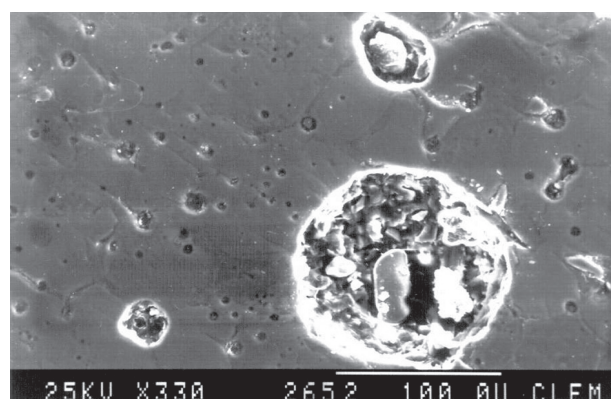
a) CaO without addition



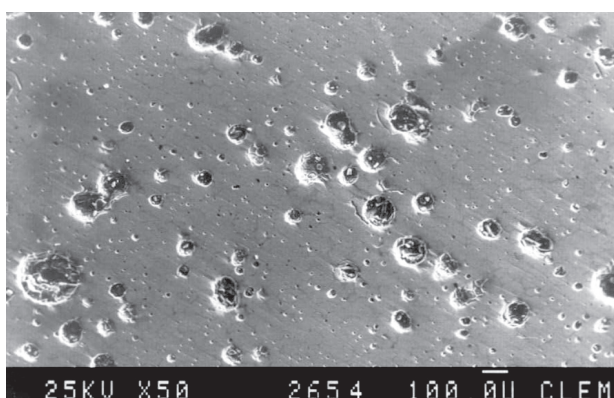
a) CaO without addition



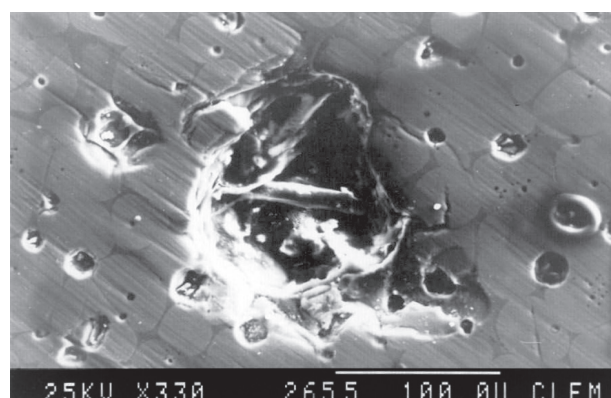
b) 1 wt. % of γ -Al₂O₃



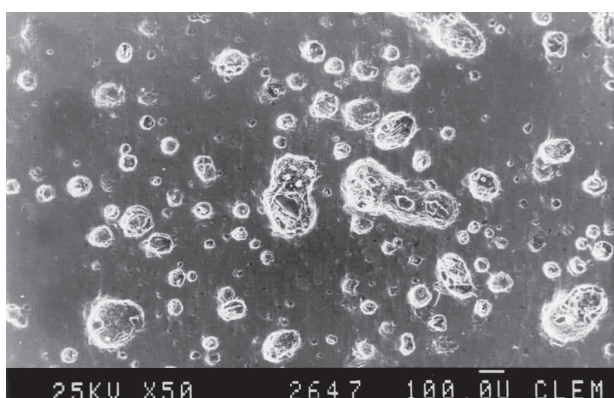
b) 1 wt. % of γ -Al₂O₃



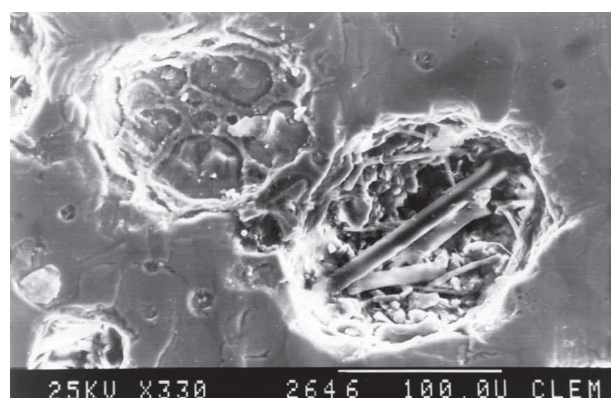
c) 3 wt. % of γ -Al₂O₃



c) 3 wt. % of γ -Al₂O₃



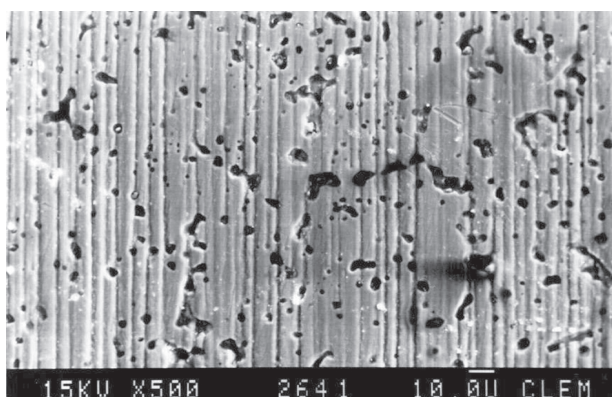
d) 6 wt. % of γ -Al₂O₃



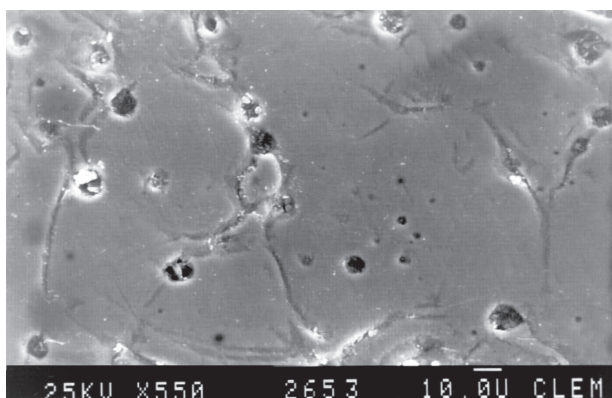
d) 6 wt. % of γ -Al₂O₃

Figure 5. SEM microstructure of CaO and CaO/ γ -Al₂O₃ mixture after burning up to 1550°C (magnification 50, 110×).

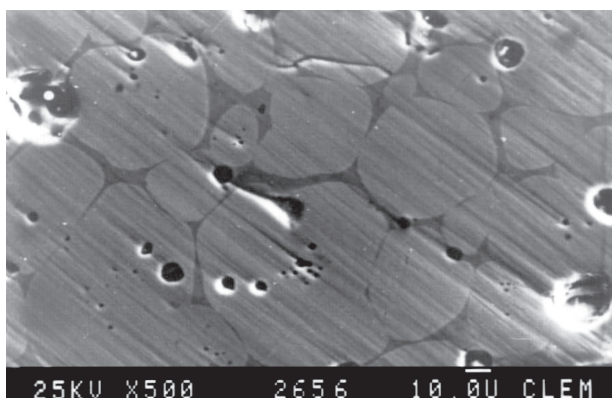
Figure 6. SEM microstructure of CaO and CaO/ γ -Al₂O₃ mixture after burning up to 1550°C (magnification 300, 330×).



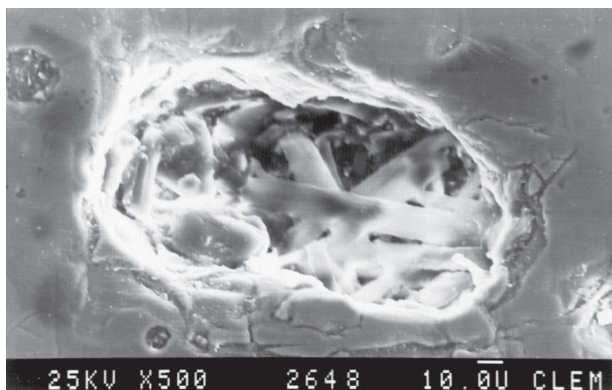
a) CaO without addition



b) 1 wt. % of γ -Al₂O₃



c) 3 wt. % of γ -Al₂O₃



d) 6 wt. % of γ -Al₂O₃

Figure 7. SEM microstructure of CaO and CaO/ γ -Al₂O₃ mixture after burning up to 1550°C.

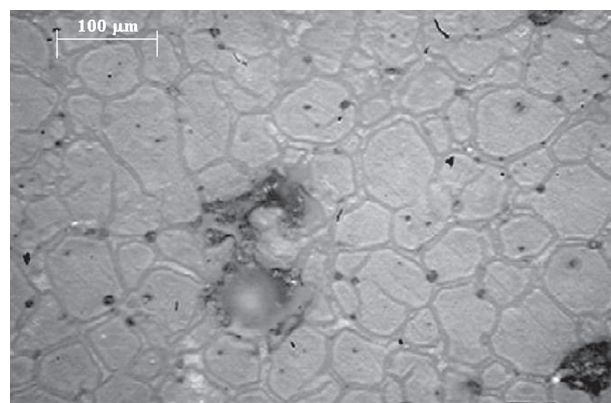


Figure 8. The microstructure of CaO with 1 wt. % of γ -Al₂O₃ addition (magnification 215 \times).

The thermodynamic probability for phase's formation in the system CaO and γ -Al₂O₃ during sintering at 1550°C was studied by using the data from binary phase diagram CaO-Al₂O₃ and by thermodynamic calculations using HSC Chemistry 6.12 [25]. Figure 9 points to the binary phase diagram of system CaO-Al₂O₃ which documents possible phases present at various temperature and concentration conditions and presence of liquid phase as well. From the thermodynamic point of view it is obvious that at the temperature of 1550°C phases such as CaO, 3CaO·Al₂O₃ (C3A), 12CaO·7Al₂O₃ (C12A7), CaO·Al₂O₃ (CA), CaO·2Al₂O₃ (CA2), CaO·6Al₂O₃ (CA6), 2CaO·Al₂O₃ (Ca2A) and other phases could exist in the system in whole concentration range [26]. The thermodynamic data are not available only for 3CaO·5Al₂O₃ (C3A5). In Table 2 there are shown thermodynamic probabilities of selected compounds formation in system CaO-Al₂O₃ according to equations (1-6) at burning temperature 1550°C. On the basis of thermodynamic calculations it is possible to compile the rank of probability of formation following compounds: 12CaO·7Al₂O₃ > CaO·6Al₂O₃ > 3CaO·Al₂O₃ > CaO·2Al₂O₃ > CaO·Al₂O₃ > 2CaO·Al₂O₃. From the binary diagram it is obvious that in the system CaO - Al₂O₃ at the burning temperature of 1550°C liquid phase could form already at 1400°C. On the other hand, depending on reactivity of used additive, it is possible that liquid phase creates in the system at even lower temperature as it is declared thermodynamically. At the same time, this was indicated also by the microstructure observations given in Figures 6, 7 and 8 together with results presented in Figure 2 and Figure 3. It was shown that amount of macropores in CaO structure increases with an amount of additive added. This could be explained by the fact, that at the burning process of ground limestone the gaseous product at around 850°C is evolved. When no addition is added, CO₂(g) can escape from the bulk without special problems (providing that not extreme pressure to green body is applied). In case, the active addition is present, releasing of gas could be partly inhibited due to earlier formation of liquid

phase at the grain boundaries. The gas molecules are then concentrated at the grain boundaries because glass phase works as a “liquid barrier” which do not permit gas to release. The similar phenomenon was observed when the higher pressure to ground CaCO₃ powder at the green bodies’ preparation step was applied. When the higher pressure (more than 20 MPa) was employed, the gas has a problem to release and causes finally decreased sintered bulk density and increased apparent porosity of CaO [24].

Table 2. The thermodynamic propability of selected compounds formation in the system CaO–Al₂O₃ at the temperature of 1550°C.

T (°C)	ΔG (kJ)	log K
1550	3CaO + Al ₂ O ₃ = 3CaO·Al ₂ O ₃ (1) -84.395	2.148
1550	2CaO + Al ₂ O ₃ = 2CaO·Al ₂ O ₃ (2) -16.559	0.474
1550	CaO + Al ₂ O ₃ = CaO·Al ₂ O ₃ (3) -55.178	1.581
1550	12CaO + 7Al ₂ O ₃ = 12CaO·7Al ₂ O ₃ (4) -515.385	14.767
1550	CaO + 2Al ₂ O ₃ = CaO·2Al ₂ O ₃ (5) -74.775	2.143
1550	CaO + 6Al ₂ O ₃ = CaO·6Al ₂ O ₃ (6) -111.876	3.206

In order to identify potential compounds in burned material, the sintered sample of CaO with addition of 3 wt. % of γ-Al₂O₃ was subjected to X-ray diffraction qualitative phase analysis by using Phillips Panalytical

XpertPro (Bragg-Brentano arrangement) with radiation of CoKα. The qualitative phase analysis showed the presence of major phase CaO and minor phase 3CaO·Al₂O₃. Other possible minor phases that could occur are 12CaO·7Al₂O₃, CaO·6Al₂O₃. The qualitative phase analysis of CaO pellets in this work was quite difficult because of the small content of minor phases. The XRD pattern indicates also presence of some part of glass phase in the sample. In the sample also residual non-reacted γ-Al₂O₃ was detected. X-ray diffraction pattern of analysed CaO sample is given in Figure 10.

These observations are in correlation with binary diagram and thermodynamic probability calculations. This system was studied also by Kohatsu et al [27]. By sintering CaO pellets and Al₂O₃ at 1330°C for twenty days they found all the known compounds of the system CaO–Al₂O₃ and quantitatively these compounds were present as follows: C₁₂A₇>>C₃A>CA₂~CA. It was suggested that the reaction in the system is principally carried by Ca-ion diffusion into Al₂O₃. Another authors Weisweiler and Ahmed [28] confirmed also the presence of all known phases by microprobe analysing of formed reaction zone between pressed aluminium oxide powder (Al₂O₃) and natural calcinated CaCO₃ crystal after sintering for forty-eight hours at 1400°C. In the region rich in CaO, phase C₃A and close to Al₂O₃ phase CA6 were found. According to results given in paper [29], the phase C₁₂A₇ could be formed by solid state diffusion according to reaction (Equation 7) at the interface.

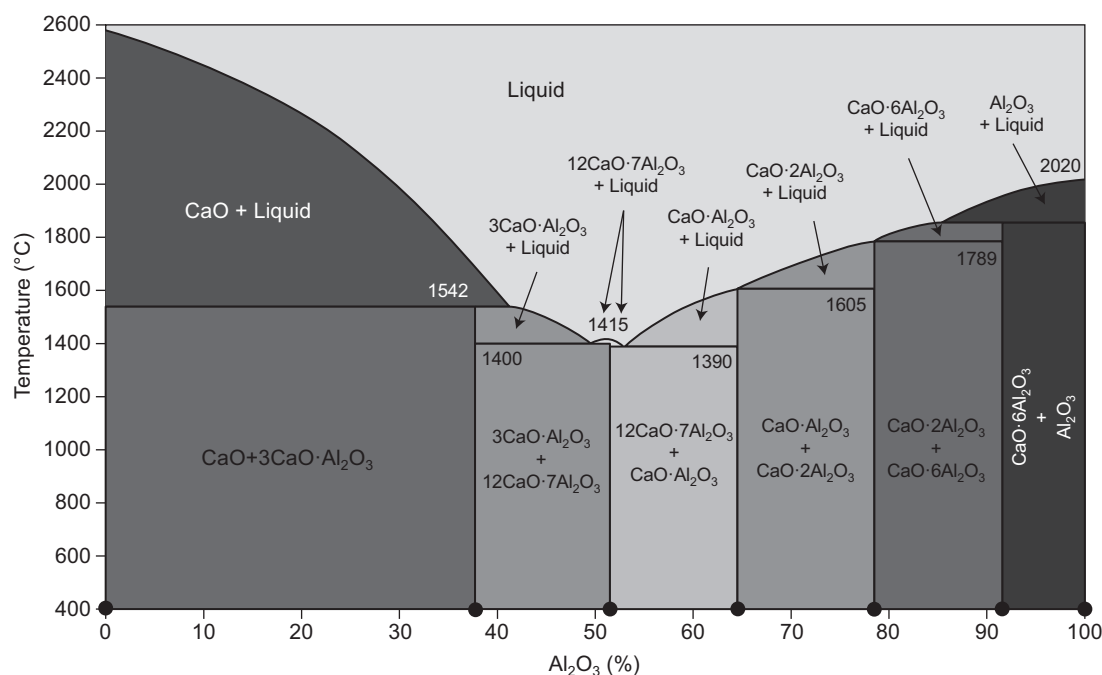
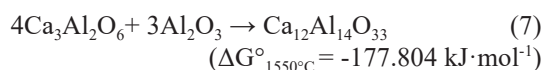


Figure 9. Binary phase diagram of CaO–Al₂O₃ system (with permission of www.wikipedia.org) [27].

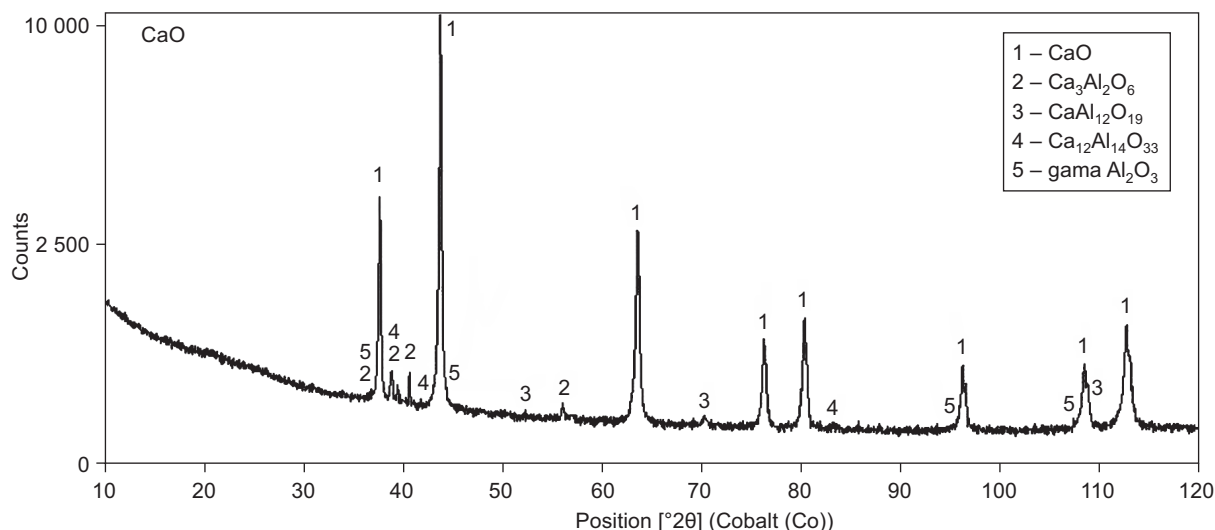
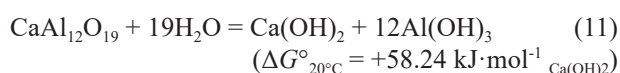
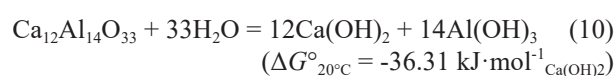
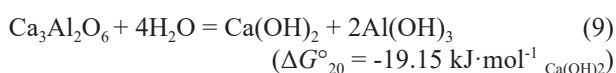


Figure 10. XRD pattern of sintered CaO with addition of 3 wt. % of γ - Al_2O_3 .

At the same time it was confirmed that presence of phase C_{12}A_7 is dependent on water content in the atmosphere during sintering [30]. In the study of steel inclusions' character and slag composition at the Al deoxidation process with CaO containing slag it was shown that the average content of CaO and Al_2O_3 in all inclusions was close to composition of the phase $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ in contrast to those occurred in the slag which were close to composition of the phase $\text{Ca}_3\text{Al}_2\text{O}_6$ [9].

Another significant knowledge is that phase Ca_3A with density of $3.04 \text{ g}\cdot\text{cm}^{-3}$ is mainly formed in experiments realised in this work. This phase is relatively inert and exhibits small reactivity with water what allows to assume the greater stability of CaO bodies in moisture environment. The previous assumption was confirmed by the hydration reactions of CaO and $\text{CaO}/\text{Al}_2\text{O}_3$ materials (equation 8-11) and standard Gibbs energy change of formation of hydrated products. From ΔG° value of equation (11) it can be also seen that phase CA_6 should not react with water under standard atmospheric conditions. The presence of CA_6 phase could then contribute to higher hydration resistance of prepared $\text{CaO}-\text{Al}_2\text{O}_3$ refractory bodies, too. The phase C_6A has at the same time the highest density ($3.38 \text{ g}\cdot\text{cm}^{-3}$) among all phases in the system $\text{CaO}-\text{Al}_2\text{O}_3$.



In the previous works it was shown that sintered CaO samples with bulk density in the range of $2.1 - 2.5 \text{ g}\cdot\text{cm}^{-3}$ without any additives were destroyed after approximately 50 hydration hours. The CaO samples with bulk density of around $3.17 \text{ g}\cdot\text{cm}^{-3}$ exhibit no apparent mass and integrity change even after 250 hydration hours and multiply surface polishing before hydration kinetics measurement [31]. Moreover, from own long-period observations it was shown that CaO prepared by one-stage burning process with addition of γ - Al_2O_3 (1 - 6 wt. %) stored in desiccator is able to resist few years without degradation or visual cracking. On the contrary, samples without additive were destroyed in couple of days or weeks under the same conditions as the previous ones. It is also clear that its bulk density value after burning is the most important for CaO life time.

For further research it will be helpful to study the kinetics and mechanism of hydration process of CaO samples with and without additive. Except for mentioned aspects, it is essential to investigate also corrosion resistance of refractory lime with addition of γ - Al_2O_3 in melts and high-temperature characteristics.

CONCLUSION

The experimental investigation confirms that active additive γ - Al_2O_3 can serve as suitable modifier in the sintering process of CaO in order to increase the bulk density of refractory body. The optimal amount of additive 1 wt. % according to experimental results was defined. After one-stage burning process at 1550°C for two hours CaO bulk density increased from the value of $2.97 \text{ g}\cdot\text{cm}^{-3}$ to $3.08 \text{ g}\cdot\text{cm}^{-3}$. This represents rising of relative densification from 88.92 % to 92.22 %. Further increasing of additive is ineffective due to

increased closed porosity of the sintered sample. These assumptions were confirmed by microstructure observations which showed rising amount and volume of macropores with increasing amount of $\gamma\text{-Al}_2\text{O}_3$ added. Moreover, the quantity of liquid phase at sintering up to 1550°C increased with rising addition amount, too. At the CaO grain boundaries the presence of phase $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ was confirmed by SEM - EDX. Moreover, other phases such as $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$, $\text{CaO}\cdot 6\text{Al}_2\text{O}_3$ were indicated by XRD diffraction qualitative phase analysis. On the contrary, interior of CaO grains consists of pure CaO with some Mg content. The additive caused also significant decreasing of apparent porosity, especially at the amount of 1 wt. % $\gamma\text{-Al}_2\text{O}_3$ which value dropped from 5.2 % to 0.2 %.

By experiments realised in this work the main positive role for the $\gamma\text{-Al}_2\text{O}_3$ addition to CaO in one stage burning process were assigned, i.e.:

- i) increase of the bulk density of material,
- ii) significant decrease of the apparent porosity of material,
- iii) earlier formation of liquid phase in adequate amount for CaO sintering,
- iv) formation of glass phase of suitable composition which causes protecting of grains and surface of refractory body against hydration.

The created glass phase contains compounds which are relatively more resistant to hydration. From thermodynamic calculations it is clear that phase $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ is relatively inert in respect of hydration. Moreover, phase $\text{CaO}\cdot 6\text{Al}_2\text{O}_3$ does not react with water what assures finally a lower hydration activity of CaO refractory body.

From densification and economical point of view it is positive if natural material contains small amount of impurities based on Al_2O_3 . On the other hand, the form and amount of Al_2O_3 will also influence the protection layer formation on grains. Coating character is influenced at least by temperature, sintering procedure, cooling rate of samples and atmosphere in the furnace.

One stage burning process of natural ground limestone mixed together with small amount of active $\gamma\text{-Al}_2\text{O}_3$ additive showed that this economical method is promising for preparing more stable CaO refractory with excellent properties prospective for steel, aluminium, cement or other industrial applications.

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