Available online at www.sciencedirect.com
ScienceDirect
Journal of the European Ceramic Society 27 (2007) 1651–1655
www.elsevier.com/locate/jeurceramsoc

Effect of iron oxide addition on the hydration resistance and bulk density of doloma

H. Aygül Yeprem *
Department of Metallurgical and Materials Engineering, Yildiz Technical University, Davutpasa Campus, Esenler, Istanbul 34210, Turkey

Available online 5 June 2006

Abstract

In this study, pure (with no additives) and mill scale (98.66 wt.% Fe_2O_3 content) added (up to 1.5 wt.%) natural dolomite of Selcuklu-Konya-Turkey fired at 1600–1700 °C for 2–6 h using the one-stage process. The resulting bulk densities and apparent porosities of the sintered doloma are investigated. According to the results of experiments with 15 sintered samples, sintering temperature, soaking time and increase of mill scale amount were found to increase the bulk density and thus decrease the observed apparent porosity.

In hydration resistance tests, it seemed that the same characteristics also increased the resistance. Furthermore, EDX analysis of the dolomas that were sintered at three different temperatures each with 0.5 wt.% mill scale additions and also at 1700 °C/2 h with 0–1 wt.% mill scale additions were performed. Quantities of $Fe^{2+,3+}$ inside the periclase (MgO) were examined. Bulk density of pure doloma (CaO·MgO) was calculated using density values of both pure CaO and MgO given in the literature. The difference between the extrapolated value of the measured densities and bulk density of doloma, which is calculated from literature data without porosity is very close.

Keywords: Dolomite; Refractories; Sintering; MgO; Grain growth

1. Introduction

Dolomite is a refractory raw material with the ideal composition of [Mg, $Ca(CO_3)_2$]. Doloma, produced from the dolomite, consist of a phase mixture of lime (CaO) and periclase (MgO). Doloma is the semi product used to produce dolomite refractory. They have extremely high melting points, as the eutectic for the CaO–MgO binary system occurs at 2370 °C. Doloma is a material that is susceptible to hydration and thus its free lime ratio must be lower than a critical value. A usable doloma should have a bulk density greater than 3 g/cm^3. Varying amounts of other impurities, including SiO_2, Al_2O_3, and Fe_2O_3 are usually present.[1–5] The amounts and types of the accessory oxides may have a large effect on the extent of densification, as it has been established that with these impurities sintering may occur by a liquid phase mechanism. It has been reported that the trivalent oxides, especially Fe_2O_3, enhance the sintering during the commercial manufacturing process.[6] Doloma is one of attractive steelmaking refractories because of its potential cost effectiveness and worldwide abundance.[7]

In liquid phase sintering, there should exist quite thin powders in the environment which should be inversely proportional to the capillary diameter to form capillary pressure which is a driving force of the process. Dihedral angle of the liquid phase should be as small as possible in order for the liquid phase formed to infiltrate into the powder boundaries to form required capillary pressure.[8] When the liquid phase soaks the solid grains, gaps among the grains gains capillary feature and therefore the total capillary pressure increases.[9]

Sintering occurs because the particle boundary energy of the substituted surface is less than surface energy. Grain growth depends on the particle boundary movement.[10] Grain boundary gap expands with the increasing temperature.[11] When grain growth occurs in the ceramics, pores commonly become separated from particle boundary.[10–12] During the sintering of dolomite, it was observed that CaO grains adhered to each other grow faster than MgO grains and as a result greater CaO grains were formed.[13] It was suggested that the reason of this is the bond energy of CaO molecules are lower than MgO molecules and they can move in the crystal structure. CaO activity, as a result of calcination, is the highest after the $CaCO_3$ disaggregation; it reduces when both time and temperature increases.[14,15] Doloma is found to sinter more rapidly and more readily than CaO component.[14] CaO has a perfect thermodynamic stability.

* Tel.: +90 212 449 1778; fax: +90 212 449 1554.
E-mail address: canaygul@gmx.net.

0955-2219/$ – see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2006.05.010

The hydration degree and rate of the sintered CaO depends on the absorption rate of water on the grain boundary surface.[12]

It was seen in the previous studies that Fe_2O_3 is an important addition which increases the sintering ability of the dolomite, because it forms compounds with lime (CaO) which have low melting points and as a result reduces the sintering temperature. It has been mentioned that especially Fe_2O_3 addition smaller than 100 μm diameters affects the sintering ability, because this addition forms compounds which have low melting points such as C_4AF (C = CaO, A = Al_2O_3, F = Fe_2O_3) and C_2F. In addition it increases the resistance against the hydration which is the biggest disadvantage of the dolomite.[1,16–21] Besides, iron oxide addition results in the increase of the density.[16,19,21–23] Sintered dolomite including iron oxide is termed as "dead burnt".[5] Searle and Grimshaw[24] mentioned in their article that in the previous studies of stabilizing dolomite when iron oxide was added it usually formed C_4AF (brownmillerite) and when the effects of this phase at high temperatures were analyzed, liquid phase increased with the increasing temperature. Shi and colleagues[25] mentioned in their studies of $CaCO_3$ that, when the content of Fe_2O_3 is more than 1.7 wt.%, especially in high sintering temperatures, there is no change or little increase in the density.

Although FeO is completely soluble in MgO, it has not been proved that Fe_2O_3 formed solid solution with MgO below 1000 °C. In the normal atmosphere, Fe_2O_3 solubility in MgO has been found to be 10% at 1200 °C and 35% at 1400 °C. While Fe-ions diffuse into periclase grains and forms solid solution, they change the crystal structure and increase the inner crystal energy by developing thin inclusions. This provides the growth of periclase (MgO) grain and facilitates the sintering by increasing the recrystallization ability.[26,27] During the Fe^{2+}/Fe^{3+} changing, high ion density of O^{2-} that provides the electrical stability causes the Fe-compounds to increase the MgO grain growth rate even at very low rates.[28] The structure formed when the iron compounds exist in the periclase is magnesiowustite [(Fe, Mg)(O)].[29] MgO (periclase) development is known to inhibit the hydration in dolomas.[16,30]

Table 1
The chemical composition of the dolomite used in this study (without loss of ignition)

CaO	29.46
SiO_2	0.15
MgO	22.52
Fe_2O_3	0.04
Al_2O_3	0.15

2. Experimental procedure

Average grain size of the dolomite extracted from a dolomite reserve which is local and not used for refractory industry before was found to be 200 μm by taking a thin cross-section in the image analysis LEICA Q 550 CW optical microscope, and it was granulated in the 3–6 mm fraction range after wet chemical analysis. The composition of dolomite is given in Table 1. Natural and 0.5–1.5 wt.% mill scale (98.66 wt.% Fe_2O_3 under 45 μm size) added mixture was produced using distilled water as a binding material.[6] Then they were put into pure magnesite crucibles and dried at 110 °C for 2 h and sintered at a heating speed of 10 °C/min, for 2–6 h in the temperature range of 1600–1700 °C. After that the bulk density and hydration resistance of acquired dolomas were measured. The tests were performed in air in a laboratory furnace with $MoSi_2$ heating elements. Sintering conditions, bulk densities, apparent porosities and hydration resistance results are shown in Table 2. Bulk density and apparent porosity of dolomas were measured by "Archimedes" method using ethyl alcohol media.

The dolomas were mounted in acrylic resin and then ground with SiC from 320 to 1000 grit in the presence of ethyl alcohol. The polishing of the specimen was carried out with 3 μm diamond paste. During the specimen preparation, water was not

Table 2
Variation of bulk density, apparent porosity and hydration degree due to sintering conditions of dolomas

Sintering conditions of dolomas	Bulk density (g/cm^3)[a]	Apparent porosity (%)	Hydration degree (%)[b]
Natural and with iron oxide			(−2500 + 2000) range of sieves
1600 °C/2 h, natural	1.57 ± 0.01	56.04 ± 0.34	Hydrated
1600 °C/2 h, 0.5% iron oxide	1.56 ± 0.01	55.01 ± 0.33	Hydrated
1600 °C/2 h, 1% iron oxide	1.57 ± 0.07	56.57 ± 1.17	Hydrated
1600 °C/2 h, 1.5% iron oxide	1.57 ± 0.01	55.24 ± 0.34	Hydrated
1650 °C/2 h, natural	2.00 ± 0.01	42.92 ± 0.26	Hydrated
1700 °C/2 h, natural	2.10 ± 0.01	36.65 ± 2.23	Hydrated
1600 °C/4 h, 0.5% iron oxide	2.95 ± 0.01	19.71 ± 9.63	1.16
1600 °C/6 h, 0.5% iron oxide	2.95 ± 0.03	8.62 ± 0.63	0.75
1600 °C/6 h, 1.5% iron oxide	3.10 ± 0.10	8.24 ± 3.91	0.09
1650 °C/2 h, 0.5% iron oxide	2.82 ± 0.13	23.01 ± 9.85	1.55
1650 °C/4 h, 0.5% iron oxide	3.02 ± 0.04	13.14 ± 7.38	0.91
1650 °C/4 h, 1.5% iron oxide	3.17 ± 0.12	6.05 ± 3.61	0.26
1650 °C/6 h, 0.5% iron oxide	3.17 ± 0.01	3.72 ± 0.08	0.62
1700 °C/2 h, 0.5% iron oxide	2.83 ± 0.00	15.38 ± 0.22	1.05
1700 °C/2 h, 1% iron oxide	3.13 ± 0.02	2.60 ± 2.49	0.63

[a] Standard deviation estimated for 10 measurements.
[b] In an autoclave under the action of steam at 120 °C, a pressure of 1.5 kg f/cm^2 and time period of 5 h.

used because the lime phase rapidly hydrates, causing cracks in the lime grains of the doloma microstructure. $Fe^{2+,3+}$ amounts were determined in the periclase existing in doloma with three different additions in the range of 0–1 wt.% at 1700 °C/2 h and with addition of 0.5 wt.% mill scale at three different temperatures by using SEM/EDX. About 25–30 microanalysis were done for each sample and each analysis reported in this study is the mean value of three analysis conducted in periclase. EDX analysis are performed by ignoring O_2. Microstructure of some selected dense samples was investigated using a scanning electron microscope Jeol JSM (SEM) of model 5410 LV equipped with an energy dispersive X-ray microanalysis (EDX) unit of system 5480 IXRF.

3. Results and discussion

The effects of mill scale additions and sintering temperatures on bulk density of doloma are shown in Table 2. As it is seen, mill scale addition is not effective at 1600 °C/2 h condition in which sintering occurs partially. However in other groups it is seen that the increase of addition ratio together with time and temperature is effective on the increase of bulk density. The increase in bulk density implies that sintering has occurred; it also shows that sintering temperature has been reduced. It is seen that this increase is higher especially between 0–0.5 wt.% addition and at 1650 °C/2 h sintering. The bulk density increases approximately 41% while passing from non-added sample to the 0.5 wt.% added sample. This increase continues nearly up to 6% between 0.5–1 wt.% addition range, and there is hardly ever an increase between 1 and 1.5 wt.% addition range. It appears that optimum values for mill scale ratio is in the range of 0.5–1 wt.%. It is also seen in previous studies that higher additions above this level does not have much effect on the bulk density.[31]

To compare the doloma with the pure one obtained from pure CaO and MgO, as seen in Fig. 1, the density of all the dolomas is presented. They all give a regression line equation $y = 104.36 - 30.952x$. The bulk density of doloma accepted without pores when $y = 0$ is $B = 3.37$ g/cm^3. The bulk densities of CaO and MgO obtained from the literature[32] are: $B_{MgO} = 3.65$ g/cm^3, $B_{CaO} = 3.32$ g/cm^3. The 40.37 wt.% MgO and 59.63 wt.% CaO values were obtained by taking the mean value of chemical analysis of pure dolomas used in the study at three different temperatures and by equilibrating it to 100%. Bulk density was found to be

$$B = 0.4037 \times 3.65 + 0.5963 \times 3.32 = 3.45\ \text{g/cm}^3 \quad (1)$$

The difference between the bulk density of the doloma calculated from extrapolation ($B = 3.37$ g/cm^3) and the density calculated from individual pure oxide densities ($B = 3.45$ g/cm^3) differs only by 2.3%, which shows an encouraging result.

We can see in Table 2 that mill scale addition secures strength against hydration resistance (except the samples sintered at 1600 °C/2 h condition in which sintering does not occur) after the appropriate temperatures and time at which sintering occurs. In the hydration test of samples with 0.5 and 1.5 wt.% addition and sintered at 1650 °C/4 h, it is seen that the resistance of sample with 1.5 wt.% addition against hydration is approximately 200% higher compared to the sample with 0.5 wt.% addition. A similar situation is observed in the samples under 1600 °C/6 h sintering conditions. However, as it is known that excessive iron oxide addition results in slag erosion[33] and the effect of this increase in iron oxide amount on bulk density – as also seen in the results of the experiments – is not too much, it was not recommended to use mill scale more than 0.5 wt.% in practice. It is seen in Fig. 2 that hydration resistance increases rapidly with the increasing time in the range of 2–4 h sintering periods, and that further increase with time is asymptotic. It can be concluded from data presented in Table 2 that for the hydration resistance increase in sintering time seems to be more effective than the temperature increase.

The microstructures of doloma granules with 0.5 wt.% mill scale addition are given in Fig. 3 for three different temperatures, where grain growth is evident. The changes of iron amount of periclase are given in Fig. 4. Iron amount in the periclase increases when the temperature increases. This increase is significant in the lower temperature range and gets smaller with increasing temperature. Periclase shows grain growth and takes the form of magnesiowustite during the growth with the increase of temperature and also an increase of its inner energy is given with iron diffusion. This iron amount is bound to the iron oxide amount in doloma. The linear increase in the amount of iron

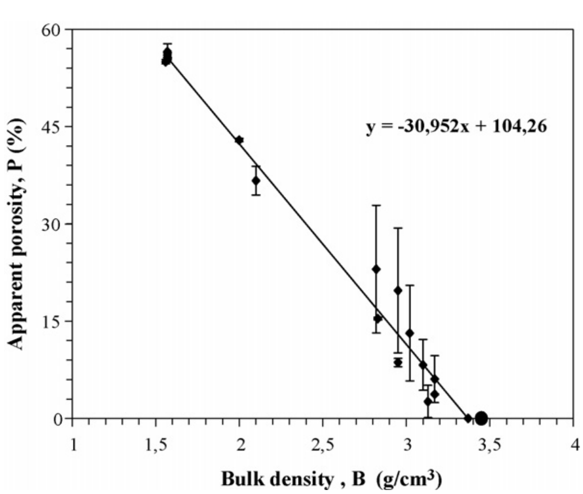

Fig. 1. The relationship of bulk density with apparent porosity.

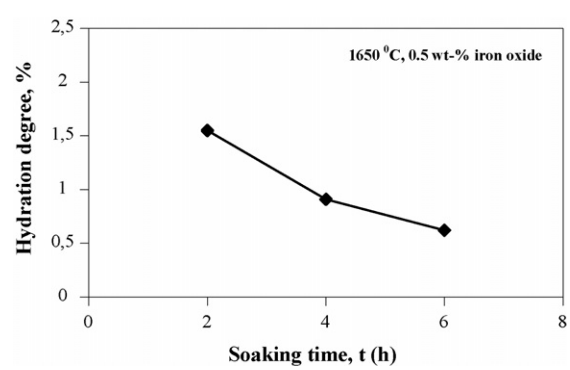

Fig. 2. The relationship of soaking time with hydration degree.

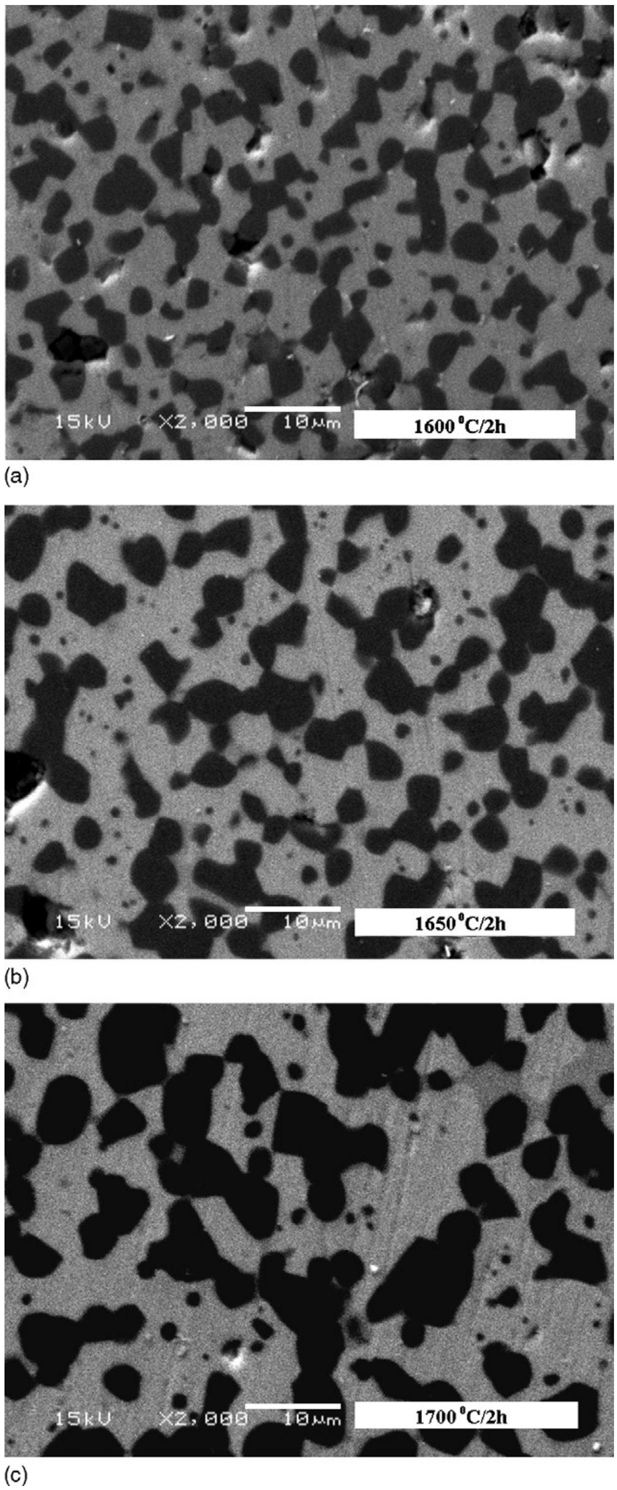

Fig. 3. ((a)–(c)) SEM images of dolomas with the addition of 0.5 wt.% iron oxide at different temperatures (the darkest phase is periclase).

in the periclase together with the mill scale addition increase is seen in Fig. 5. Here it can easily be seen that with increasing addition ratio, periclase, in other words magnesiowustite, takes the iron into its structure at the same proportion with addition ratio. Although the range of 1 and 1.5 wt.% addition is not studied it is thought that the addition ratio could have little effect

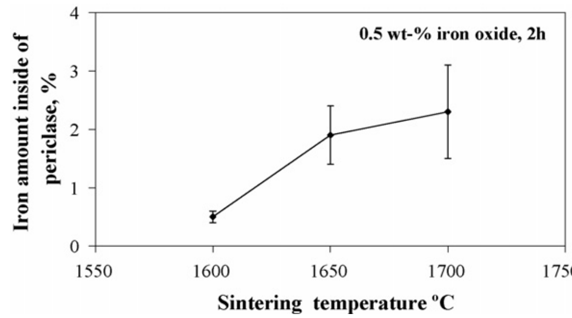

Fig. 4. The relationship between the iron in periclase and temperature.

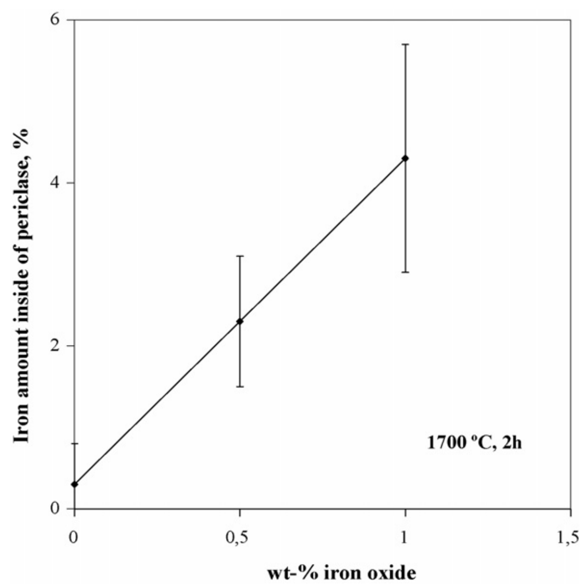

Fig. 5. The relationship between the iron in periclase and amount of mill scale.

on iron content of periclase as the same trend was observed in density values in the same addition range.

4. Conclusions

- It has been seen that the mill scale addition increases the bulk density and provides resistance against hydration.
- After sintering, some iron is also found in the periclase (MgO), so that the phase becomes magnesiowustite [(Mg, Fe)O], which introduces the destabilization of the periclase phase.
- Periclase shows a higher growth tendency with the iron oxide addition.
- It has been found that optimal and economic sintering conditions are 4–6 h at 1650 °C with 0.5 wt.% mill scale additions.
- It has been proved that the average CaO and MgO amounts of dolomas obtained in this study is very close to the value generally given in the literature.
- The results of this study show that dolomite received from Konya-Turkey can be used for refractory brick making.

References

1. Chesters, J. H., *Steelplant Refractories: Testing, Research and Development*. The United State Com, Sheffield, 1963, 167.

2. Trojer, F., *Mineralogie Basissche Feurfest-Produkte*. Springer-Verlag, New York, 1981, p. 42.
3. Anonymous, *Didier Refractory Techniques—Refractory Materials and Their Properties English Handbook*, 1982, p. 41.
4. Routschka, G., *Feuerfeste Werkstoffe*. Vulkan Verlag, Essen, 1987.
5. O'Driscoll, M., Refractory dolomite. *Ind. Miner.*, 1998, **6**, 35–43.
6. Koval, E. J., Messing, G. L. and Bradt, R., Effects of raw material properties and Fe_2O_3 additions on the sintering of dolomites. *Ceram. Bull.*, 1984, **63**, 274–277.
7. Meyer, W., Franchi, A., Buchebner, G. and Willingshofer, M., The use of dolomite-carbon-lined ladles for the production of superclean steels. *Veitsch-Radex Rundschau*, 1998, **2**, 32–44.
8. Huppmann, W. J. and Riegger, H., Modelling of rearrangement processes in liquid phase sintering. *Acta Metall.*, 1975, **23**, 965–971.
9. Kingery, W. D., Bowen, H. K. and Uhlmann, D. R., *Introduction to Ceramics*. John Wiley & Sons, New York, 1976.
10. Pask, J. A., *Grain Boundaries in Sintering, Science of Sintering: New Directions for Materials Processing and Microstructural Control*. Plenum Press, New York, 1989.
11. Nan, L., Sintering of aggregated MgO powders. In *Proceedings of the International Institute for the Science of Sintering (IISS) Symposium*, 1987, pp. 346–351.
12. Bhattacharya, T. K., Ghosh, A. and Das, S. K., Densification of reactive lime from limestone. *Ceram. Int.*, 2001, **27**, 455–459.
13. Yeprem, H. A., Turedi, E. and Karagoz, S., A quantitative-metallographic study of the sintering behaviour of dolomite. *Mater. Char.*, 2003, **52**, 331–340.
14. Oates, J. A. H., *Lime and Limestone Chemistry and Technology*. Wiley-VCH, USA, 1998, p. 150.
15. Boynton, R. S., *Chemistry and Technology of Lime and Limestone*. John Wiley and Sons, New York, 1980.
16. Yeprem, H. A., Characterization of sintering of a local dolomite for production of dolomite refractory, PhD thesis, Yildiz Technical University, Istanbul, Turkey, 2003.
17. Obst, K. H. and Münchberg, W., Mineralogical studies of dolomite as a basic refractory material. *Br. Ceram. Soc.*, 1979, **6**, 225–241.
18. Nishikawa, A., *Technology of Monolithic Refractories*. Plibrico Japan Co., Tokyo, 1984.
19. Schlegel, E., Sintering of dolomite as a function of the raw material properties. *Sprechsaal*, 1987, **120**, 170–176.
20. Paksocimas, C. A., Varela, J. A., Longo, E. and Whittemore, O. J., The influence of Fe_2O_3 on stabilization and sintering of MgO stabilized zirconia. In *Proceedings of the Fifth International Symposium on the Science and Technology of Sintering*. Vancouver, 1991, pp. 23–26.
21. Serry, M. A., Mandour, M. A., Osman, A. M. G. and Girgis, L. G., Low-flux hydration-resistant refractory dolomite grains from Egyptian raw materials. *Interceram*, 1993, **42**, 20–23.
22. Antonov, G. I., Grivakova, Zh. A. and Maslov, A. G., Suitability of Zavadov deposit dolomites for use as raw material. *Refract. Ind. Ceram.*, 1987, 95–100 [translated from Ogneupory].
23. Harabi, A. and Achour, S., A process for sintering of MgO and CaO based ceramics. *J. Mater. Sci. Lett.*, 1999, **18**, 955–957.
24. Searle, A. B. and Grimshaw, R. W., *The Chemistry and Physics of Clays and other Ceramic Materials*. Ernest Benn Limited, London, 1960.
25. Shi. Ying, Y., Messing, G. L. and Bradt, R., Reactive-phase calsintering of calcium-carbonate-derived lime. *Commun. Am. Ceram. Soc.*, 1984, **6**, 109–111.
26. Chaudhury, M. N., Kumar, A. and Bhadra, A. K., Microstructure of sintered natural Indian magnesite with titania additions. *Ceram. Bull.*, 1992, **71**, 345–348.
27. Marechal, P., Thermal shock resistance of electrofused magnesia grains. *Ceram. Bull.*, 1991, **70**, 1780–1782.
28. Green, J., Calcination of precipitated $Mg(OH)_2$ to active MgO in the production of refractory and chemical grade MgO. *J. Mater. Sci.*, 1983, **18**, 637–651.
29. Satyoko, Y. and Lee, W. E., Dissolution of dolomite and doloma in silicate slag. *Br. Ceram. Trans.*, 1999, **98**, 261–265.
30. White, J., *High Temperature Oxides. Part I. Magnesia, Lime and Chrome Refractories*, ed. A. M. Alper. Academic Press, New York, 1970.
31. Şeşen, K., *The Kinetics of Metallurgical Durations*. I.T.U. Faculty of Chemical-Metallurgical Ofset Workshop, Istanbul, 1998.
32. Perry, J. H., *Chemical Engineering Handbook*. McGraw-Hill, New York, 1985.
33. Kappmeyer, K. K., *The Importance of Microstructural Considerations in the Performance of Steel Plant Refractories*, ed. Fulrath and Pask. Robert Krieger Publishing Company, New York, 1966 [chapter 23].