Investigation of Temperature Parameter on the Sinterability of Magnesia

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Abstract: A sintering procedure in constant heraus muffle furnace was carried out at an interval of 1600-1900 ^{o}C for 50 min dwelling time and 5 ^{o}C min^{-1} cooling rate to improve the grain growth of magnesia. The effects of temperature on the grain growth and microstructural examination of samples were investigated by using Scanning Electron Microscopy (SEM). The average grain size was also determined separately by an intercept measurement method. According to the findings, crystal size and bulk density were enhanced significantly as a linear relationship with the increasing temperature. For the samples sintered at 1900 ^{o}C, a maximum average grain growth (~100 μm) has been obtained. In this paper, the effects of temperature on the crystal size and bulk density of the treated magnesia and its marketability were evaluated.

Key words: Sintering, grain size, bulk density, purchasability

Introduction

Grain size, impurities, porosity, sintering temperature and practice shape play an important role in controlling many physical, mechanical and chemical properties of magnesia-based bricks (Kingery, 1984, Itatani, Nomura, Kishioka, Kinoshita, 1986, Rice, 1972). It is known that porosity can alter or eliminate the appearance of grain-size control of strength (Itatani, Nomura, Kishioka, Kinoshita, 1986). As grains grow, grain boundaries sweep past many pores, which are then within the grains not at grain boundaries. This commonly results in an additional regular pore shape, which may well decrease stress concentrations.

The size of the MgO crystals within the magnesia grains is critically an important factor in controlling the resistance to corrosive attack of basic bricks (Aksel, Rand, Riley, Warren, 2002). When the size of the crystals increases, a corresponding decline occurs in crystal surface area and open porosity (Aksel, Rand, Riley, Warren, 2002). Furthermore, as the mean MgO grain size increases, the wear rate as a result of corrosive slag attack decreases (Lee, Rainforth, 1994). Magnesia-based refractories with a large grain size (>100 mm) are used comprehensively where the corrosion resistance is required. On the contrary, a high thermal shock resistance in fused magnesia grain requires a fine crystal size and a compromise may be required in applications where thermal shock resistance is important (Williams, Taylor, Soady, 1990) Critical microstructural factors affecting properties and performance of a brick are basically density, grain size, impurities and CaO/SiO$_2$ ratios (Aksel, Rand, Riley, Warren, 2002).

Currently, researchers focused on the improvement in the resistance of corrosive attack of sintered magnesite with the greatest grain growth. As the grain size increases, the penetration of slag through the grain boundaries can be minimised. The enlargement in grain size leads to a high resistance to fracture and corrosion. To reach the optimum grain size increases the quality and performance of the refractory material, leading to an economical benefit and longer service life for industrial applications in terms of corrosion and thermal shock resistance.

In this study, under optimum test conditions in the literature (Marechal, 1991) such as constant dwelling time (19 min) and the cooling rate (5 ^{o}C min^{-1}), crystal size and bulk density is separately determined according to rising temperature. The role of temperature on the enlargement of grain size and bulk density were also evaluated by SEM analysis. Furthermore, Crystal size and bulk density, which have a pronounced effect on quality and purchasability, are investigated It is considered that this paper will provide a platform to improve understanding of relationships between microstructure and those parameters, affecting grain size of the sintered magnesite significantly.

Experimental procedures

The magnesite concentrate was provided from Kümas Magnesite Mine Inc, Kütahya. The representative sample was crushed and classified into -5 +3 mm particle size. Mineralogical characterization by X-ray diffraction spectrometry evidenced MgO while main additional minerals were Fe_2O_3, SiO_2, CaO and Al_2O_3. Quantitative chemical analysis of the elements by emission spectroscopy technique revealed that MgO content is 48, 53 % [Table 1].

MgO, %	SiO_2, %	CaO, %	Fe_2O_3, %	Al_2O_3, %	LOI*, %
49.56	0.30	1.10	0.30	0,04	48,70

*LOI: loss on ignition **Table 1.** Chemical analysis of magnesite concentrate

A sintering procedure close to industrial situation was performed in the constant heraus muffle furnace at interval 1600-1900^{o}C for 50 min dwelling time and 5^{o}C min^{-1} cooling rate [7]. Sintered samples were placed in polyethylene moulds by a mixture of epoxy resin and hardener. Surfaces of samples were ground using progressively finer SiC papers. The polishing of specimens for SEM was carried out using a “Metcom Forcipol 1V” grinder polisher. Chemical etching was then carried out in a HNO_3 and CH_3OH (3:2) diluted solution at room temperature for ~25 min (Aksel, Kasap, Sesver, 2005). Microstructural examination of the regarding samples was carried out using JEOL JSM-6060 SEM. Grain sizes of polished and chemically etched surfaces were then measured from photographs taken in SEM, using an intersecting grain numbers method (Clinton, Freer, 1987). Similar results were achieved by standard lines mean method (Köknal, Eyüboğlu, Özmen, 2008). Average grain size was determined from intercept measurements on the observed plane, by using the following formula:

$$\bar{D} = (n*l)/(Z*M) \tag{1}$$

where $\bar{D}$ is the average grain size, n number of lines, l intersecting grain numbers and M is the magnification unit, taken over 2000 grains and measured on the plane of polish. Supposing for the grain size variables, in order to identify an average grain size, were that the structure consisted of nontextured, equiaxed grains of ordinary polyhedral shape. All the values calculated for each sample were the average value of ~300 measurements of seven SEM micrographs. According to those values, the improvement in grain growth was investigated for each sample based on the effect of temperature. After sintering, bulk density values were measured using the standard water immersion method (Mendelson, 1969). The rise in sintering temperature to 1900^{o}C for 19 min, using cooling rate of 5 ^{o}C min^{-1}, resulted in maximum grain growth (~100 μm).

Microstructure of sinter magnesia

Sintering process was carried out in the range temperatures of 1900 and 1600 ^{o}C. At 1900 ^{o}C, crystal grains formation ranging from large and coarse to fine have been observed [Fig 1a]. Maximum and minimum crystal sizes have ranged from 20 to 200 μm and average size has also been calculated as approximately 100 μm, utilizing intersection method. At the duration of sintering process, many particles up to 200 μm were formed by the combination of 2 or 3 grains. Though crystal size is differential at 1850 ^{o}C, relatively steady and homogenous distribution is observed. Locked particles, more than one grain, in range of 120 μm have also been seen [Fig 1b]. Crystal forming at 1800 ^{o}C sintering temperature show a more homogenous distribution compared to ones formed at 1850 ^{o}C.

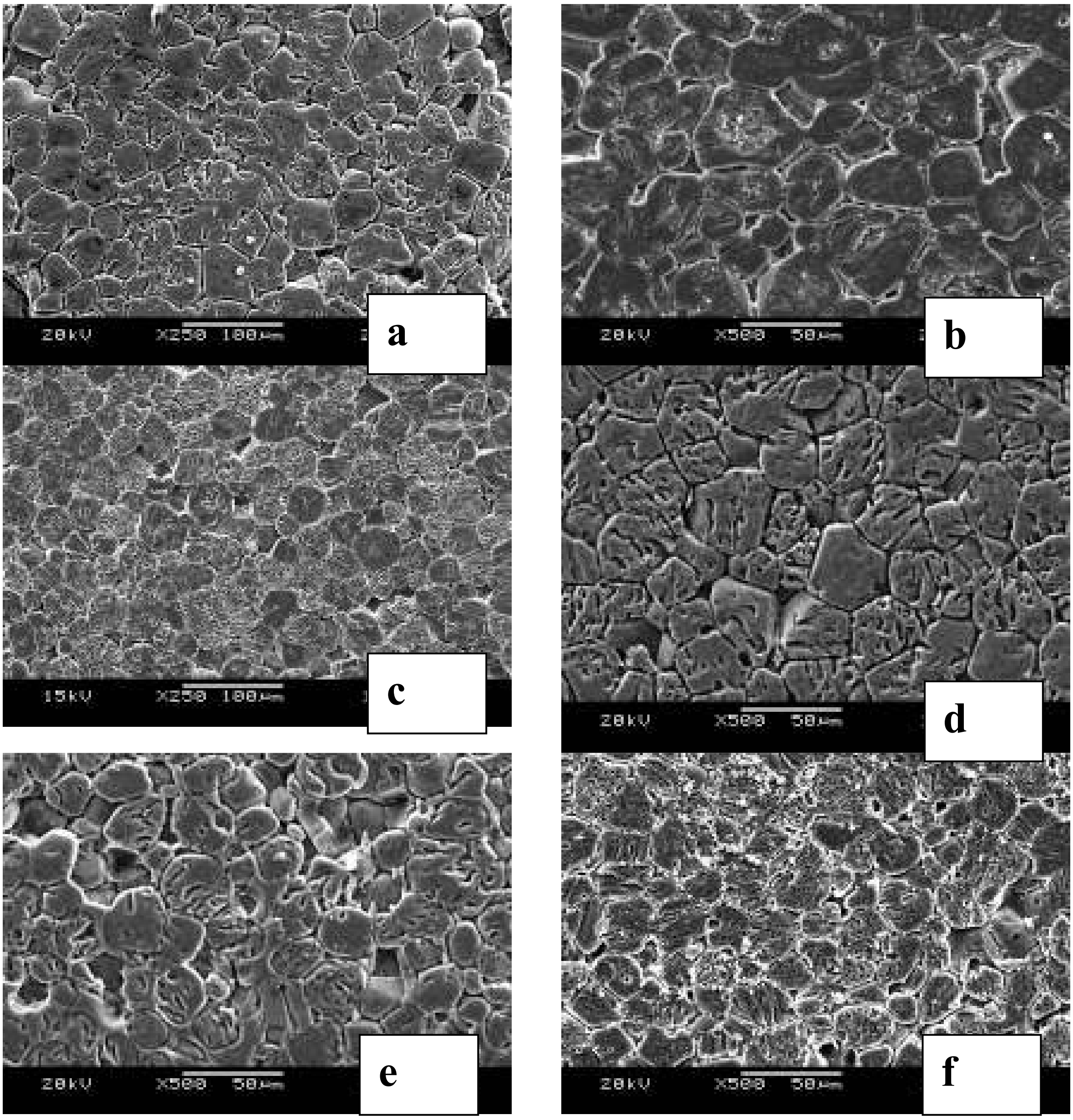

Fig 1. SEM micrographs of sintered magnesia at various temperatures (*a: 1900°C, b: 1850°C, c: 1800°C, d: 1700°C, e: 1650°C, f: 1600°C*)

Associated particles of 120 μm size are also observed at this temperature. Despite the homogenous distribution, there are many finer particles around 17 μm. The average crystal size was calculated as 53 μm [Fig 1c]. At 1700 oC, crystal size varies between 42-25 μm. The average size was calculated as 31 μm. Fewer blocked particles have been observed in this group of tests [Fig 1d]. Maximum and minimum crystal size varies between 35-12 μm at temperature of 1650 oC. The average size was calculated as 23 μm [Fig 1e]. At 1600 oC, sintering temperature maximum, minimum and average crystal sizes were determined as 32, 10 and 17 μm respectively [Fig 1f].

Result and Discussion

It is known that density and crystal contact surface area increase with the increase in the crystal size of sintered magnesia. Refractory materials produced from high quality magnesia have high resistance to acid, moisture and loads at high temperatures (BS 7134, 1989). Product quality is directly affected by crystal size and bulk density, therefore a small increase in those values can be considered as a big step as far as purchasability is concerned. Therefore, crystal size of magnesia, density, MgO and silica content are important parameters. Magnesia-based refractories with a large grain size (>100 mm) are used extensively where the corrosion resistance is required. In contrast, a high thermal shock resistance in fused magnesia grain requires a fine crystal size and a compromise may be required in applications where thermal shock resistance is important.

In this study, the changes in the crystal size and cast density of magnesia as a function of temperature and the effect of these changes on the purchasability of magnesia were investigated. According to the findings of the study, which are in agreement with the literature (Marechal, 1991, Köknal, Eyüboğlu, Özmen, 2008, Mendelson, 1969, Erdoğan, Yıldız, 1995, Hara, Kusunose, Kenmochi, 1986), crystal size and cast density of magnesia increase with temperature [Fig 2]. Under identical cooling conditions (5 °C min^{-1}), the temperature dependent increase in the crystal size is clearly linear.

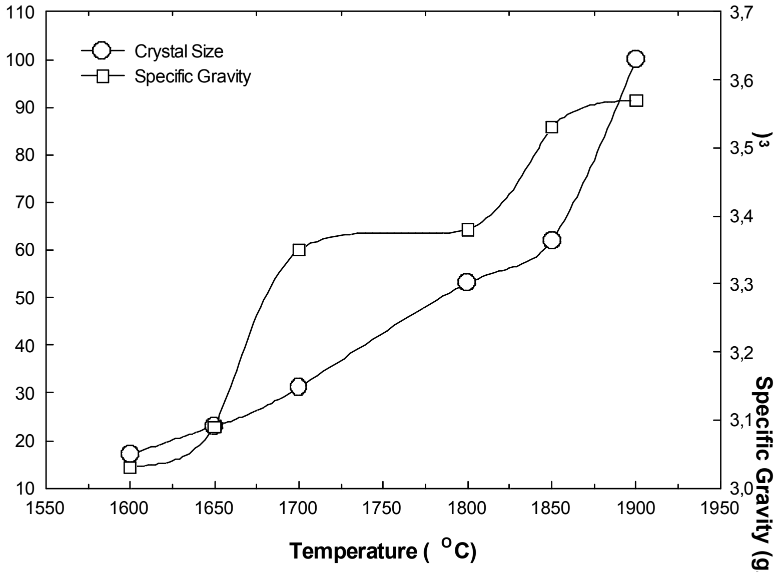

Fig 2. The change in crystal size and density with temperature

The literature shows that density and crystal contact surface area show a parallel increase with crystal size (Köknal, Eyüboğlu, Özmen, 2008). As the particles grow in size, the resulting porosity increase causes an improvement in the resistance of the refractory material to acid and moisture (Kingery, 1984, Itatani, Nomura, Kishioka, Kinoshita, 1986, Rice, 1972). These additional beneficial properties, in turn, raise the saleability of the product. Saleability shows a small improvement with particle size and density; increases with every increase in density, but remains constant after a particle size of 150 microns [Fig 3].

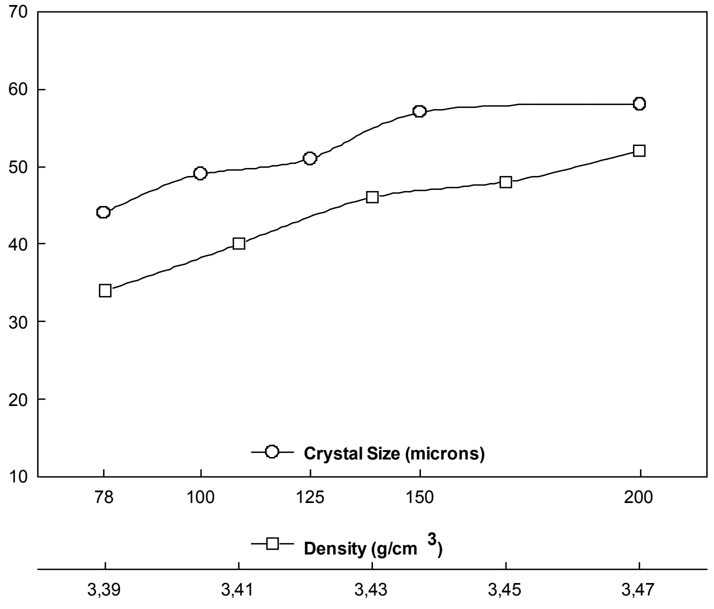

Fig 3. The effect of parameters affecting quality of refractories on purchasability [15]

The quality perception of magnesia has changed with the advances in the refractory materials technology. For example, a magnesia product with a density of 3.36 g/cm^3 was considered high quality; today's specifications expect a density of 3.47 g/cm^3. Considering these facts, it is expected that magnesia products manufactured at temperatures above 1850 ^{o}C should have a strong place in the market.

Conclusion

A high quality sinter magnesia should have a number of specifications such as low B and SiO_2, coarse crystal size, ideal CaO/SiO_2 ratio (~1.86) and high bulk density (>3.40 gcm^{-3}). Magnesia product like this can be easily sold in the market. Under optimum test conditions in the literature such as constant dwelling time (19 min) and the cooling rate (5 ^{o}C min^{-1}), crystal size and bulk density is separately determined according to rising temperature. Saleability of each product is separately evaluated. The results obtained are summarized;

1. The rise in the sintering temperature up to ~1600 ^{o}C improved the densification and gave rise to maximum enhancement in grain size. The values of 17 μm and 3.03 gcm^{-3} at 1600 ^{o}C have risen to 100 μm and 3.57 gcm^{-3} respectively at 1900 ^{o}C.
2. As values of 80 μm, $\geq$3.40 gcm^{-3}, specified for good quality magnesia in the literature, are taken into account 1850 ^{o}C temperature is just about sufficient. At this temperature the bulk density is within the acceptable limits however the crystal size remains below the saleability limit. At lower temperatures (such as 1800 ^{o}C), quality magnesia of required bulk density is obtained. On the other hand needed crystal size can not acquired.
3. At 1900 ^{o}C temperature, saleable quality magnesia (100 μm> 78 μm, 3.57 gcm^{-3}> 3.40 gcm^{-3}) could be obtained
4. According to experiment results, the temperature was subsequently found to be major parameter improving grain growth and specific gravity of magnesite substantially.

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