# Turkey`s Magnesite for Production of Fused Magnesia, Properties and Uses in Refractory Applications

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Magnesite ($MgCO_3$) is natural source for production of caustic calcined, dead burned and fused magnesia. Turkey's magnesite sources have a well-known reputation internationally with high purity, cryptocrystalline structure and suitability for refractory applications.
For high temperature processes, there is a great need for refractory raw materials that can withstand oxidative environment at elevated temperatures. Fused Magnesia (FM) is the most important material for these purposes with melting point 2800 °C and one of the key element of the refractory heat resistant materials especially for steelmaking refractory bricks. Fused magnesia is considered to be one of the best thermal and electrical insulators with high density, high purity and large crystals.
FM is produced by electric arc melting of magnesite or CCM in a traditional Higgins furnace or in tilt-type furnace at >2800 °C. Quality of the electrically fused magnesia is determined by choosing magnesite source, beneficiation processes, arc furnace electrical parameters and sorting. Final product were characterized by using chemical analysis, scanning electron microscope and EDX. Samples from different process parameters were investigated according to their crystal size, bulk density and impurity formation.

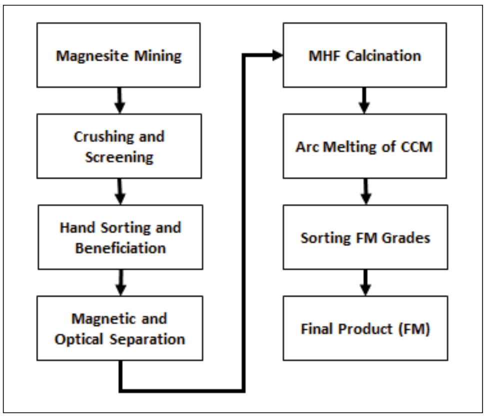


**Fig. 1 Flow diagram of fused magnesia production**

## 1 Introduction

Magnesite ($MgCO_3$) is the main raw material of fused magnesia production. Magnesite resources in the world are mainly in China, North Korea, Russia, Greece, Austria and Turkey. Magnesium carbonate ($MgCO_3$) occurs naturally as the mineral magnesite in two physical forms, macrocrystalline (spathic) and cryptocrystalline (amorphous, compact) [1].

Turkey mostly has cryptocrystalline magnesite reserves. Cryptocrystalline magnesite is generally of higher purity than macrocrystalline magnesite and generally contains less iron oxide but deposits are usually smaller and have a lower yield of ore to waste material, which makes them more expensive to extract. The ore deposits often occur as an alteration product in ultrabasic rocks, typically serpentine (magnesium silicate).

Magnesite processing (Fig. 1) can be divided into crushing, sizing and beneficiation stages. The degree of beneficiation required depends on the quality of the ore and its intended end use. Cryptocrystalline ores may only need crushing, screening, washing and hand-sorting to produce a material suitable for Caustic Calcined Magnesia (CCM), Dead Burned Magnesia (DBM) or Fused Magnesia (FM). After beneficiation, purity level can reach 98 mass-% MgO. Calcination reaction that occurs during heating is the loss of carbon dioxide from magnesite, with the corresponding formation of magnesium oxide, the full decomposition of 1 kg of pure magnesite yields 0,48 kg of magnesium oxide and 0,52 kg of $CO_2$; see reaction (1):

$$MgCO_3 + Heat + MgO + CO_2 \qquad (1)$$

Fused magnesia is an essential material that has been widely used in many industries, such as the chemical industry, metallurgical industry, heating elements industry and aerospace industry [2]. Fused magnesia is considered to be one of the best thermal and electrical insulators with high density, high purity and large crystals. High-purity fused magnesia is mainly pro-

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**Tab. 1** Production temperatures and physical properties of MgO products

| Material | Temp. [C°] | Crystal size [µm] | Porosity [%] | Density [g/cm³] |
|---|---|---|---|---|
| Caustic Calcined | 700–900 | <0,5 | 75 | – |
| Dead Burned | 1600–2000 | >75 | <0,3 | 3,10–3,40 |
| Fused | >2800 | >800 | <0,1 | >3,48 |

**Tab. 2** Two types of CCM materials for fusion experiments

| Material | $SiO_2$ [mass-%] | CaO [mass-%] | $Fe_2O_3$ [mass-%] | $Al_2O_3$ [mass-%] | MgO [mass-%] |
|---|---|---|---|---|---|
| CCM-1 | 0,92 | 1,75 | 0,42 | 0,04 | 96,87 |
| CCM-2 | 1,74 | 2,11 | 0,57 | 0,05 | 95,53 |

**Tab. 3** Chemical and physical properties of fused MgO samples

| | FM-1 (CCM-1 Feed) | | | FM-2 (CCM-2 Feed) | | |
|---|---|---|---|---|---|---|
| Zone | A1 | B1 | C1 | A2 | B2 | C2 |
| $SiO_2$ [mass-%] | 0,58 | 0,42 | 1,62 | 0,96 | 0,57 | 1,86 |
| CaO [mass-%] | 1,44 | 0,85 | 2,12 | 1,93 | 1,18 | 2,25 |
| $Fe_2O_3$ [mass-%] | 0,38 | 0,25 | 0,53 | 0,44 | 0,34 | 0,61 |
| $Al_2O_3$ [mass-%] | 0,02 | 0,01 | 0,05 | 0,02 | 0,02 | 0,06 |
| MgO [mass-%] | 97,58 | 98,47 | 95,68 | 96,65 | 97,89 | 95,22 |
| Density [g/cm³] | 3,50 | 3,52 | 3,41 | 3,49 | 3,52 | 3,39 |
| C/S ratio | 2,48 | 2,02 | 1,31 | 2,01 | 2,07 | 1,21 |

duced by the three phase AC arc furnace (Fig. 2).
Fusion furnaces can be operated on both one-step and two-step processes depending on energy costs and quality. Magnesite is used in the one-step and CCM in the two-step process. FM is characterised by very large periclase crystals of more than 600 µm (compared to 75 µm for DBM) and a density approaching 3,55 g/cm³.
After melting and cooling process, fused magnesia ingot is formed in the furnace [3]. Ingot will be broken into pieces with crushers to desired grain size and the last step in the process is the separation of fused magnesia from the crust material (Fig. 3).

## 2 Experimental procedure

In this investigation, two type of CCM material which is processed from Turkey's magnesite reserves from Kütahya region are fed into fusion furnaces and samples are taken from the melted ingots. Feeding materials' properties are given in the Tab. 2. Fusion furnace secondary voltage was 180 V and secondary current was 7,5 kA. Melting time was 11 h. Specific energy consumption for FM production is 2500–3500 kWh [4]. After 4 d cooling period, ingots are crushed and sized for further investigation.

Sampling was done based on 10 kg for different testing and samples are taken from different zones of ingots. Chemical analysis of each sample was done by X-ray fluorescence (XRF) against appropriate standard at KÜMAŞ Laboratories. Grain bulk density was measured by boiling water method using coarse grains.
For average grain size measurement and distribution of impurities present in fused magnesia, scanning electron microscope and EDX method (ZEISS Supra55VP) was conducted for different fused magnesia samples at Ceramic Research Centre, Eskişehir/TR.

## 3 Results and discussion

Three zones of fused magnesia ingots labelled as A, B, C are used in the experiments (Fig. 4). Sample A is the equiaxial fused magnesia crystals and the most amount of FM material from ingots. Sample B is the columnar crystals which is formed during slow cooling period. Sample C is the semifused/sintered material from ingots.
Chemical analysis and bulk densities of FM samples are given in Tab. 3 referred to feeding CCM-1 and CCM-2 materials. As expected, CCM-1 feed results are better than CCM-2 feed in terms of purity level. As shown in the Tab. 3, ingots are heterogeneous in terms of chemical analysis and all zones have different properties. Samples from A and B zones are the main FM material and its purity is higher than starting materials. The purest zone of ingot is sample B1 and B2 for both experiments due to columnar single crystal forming.

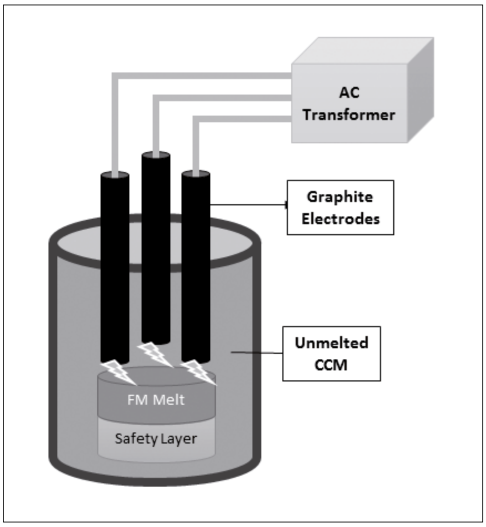

**Fig. 2** Electric arc furnace for production of fused magnesia

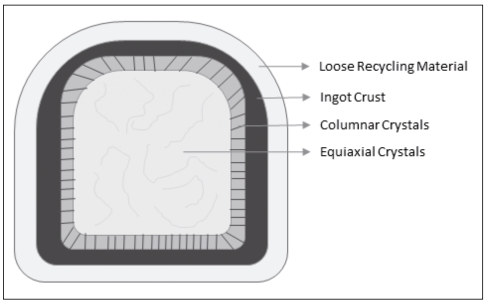

**Fig. 3** Zonal structure of fused MgO ingot

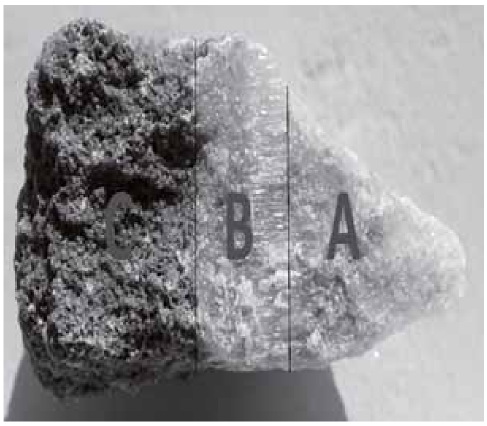

**Fig. 4** Sample labels of different zones from FM ingots

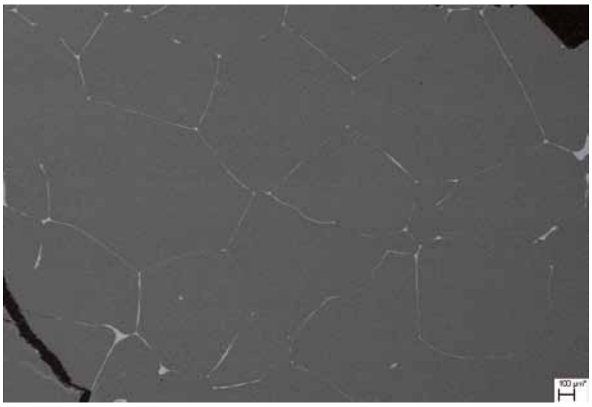

**Fig. 5** SEM image of A1 sample

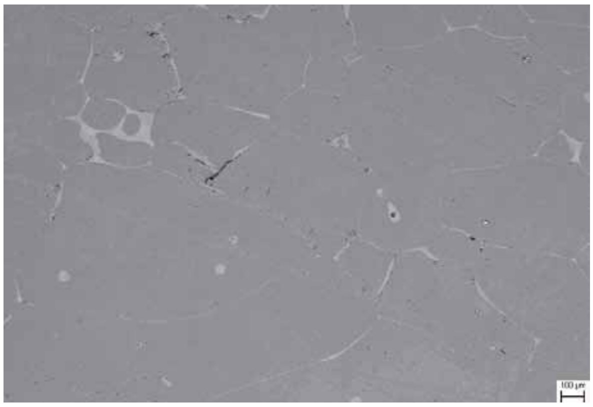

**Fig. 6** SEM image of A2 sample

**Fig. 7** SEM image of B1 sample

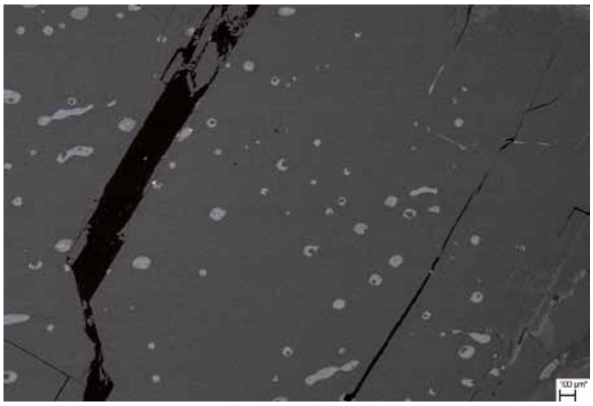

**Fig. 8** SEM image of B2 sample

Sample C has high impurity level compared to feeding material because of the migration of the impurities to the outside of the ingot with thermocapillary transfer mechanism and it occurs by density difference between periclase and silicate phases [5].

Lime/silica ratio is also important indicator of phase formation. C/S ratio for samples A and B are above 2, whereas for samples C this value is below 2 in the results. These test results always indicate that silica present in A and B is expected to exist mostly as $C_2S$ (dicalcium silicate, $T_m$ = 2130 °C) [6]. As shown in the Tab. 4, lower C/S ratio causes the formation of the low melting point phases on the grain boundaries. Samples C have a low C/S ratio and it is expected to formed mostly as CMS (monticellite) and $C_3MS_2$ (merwinite) phases on grain boundaries.

The Bulk Density (BD) of the grains of Samples A1–2 and B1–2 varies from 3,49–3,52 g/cm$^3$. These materials are suitable for steelmaking bricks as raw materials whereas corrosive slags occur. High bulk density indicates low porosity and highly compact material. However, density of samples C varies from 3,39–3,41 g/cm$^3$ and it is comparable with high quality dead burned magnesia.

Periclase crystal size is important for refractory bricks because it reduces surface area and penetrability of corrosive slags into the refractory bricks. For that reason, high quality fused magnesia is essential raw material for high performance magnesia-carbon bricks. These MgO–C bricks are specially used at Basic Oxygen Furnace (BOF) vessels, ladles and Electric Arc Furnace (EAF) slag liners [7].

**Tab. 4** Phases in equilibrium with MgO in the MgO–CaO–$SiO_2$ system

| C/S Weight Ratio | Phase Name | Composition | Melting Temp. [°C] |
|---|---|---|---|
| 0,90–1,40 | Monticellite | CaO · MgO · $SiO_2$ | 1488 |
| 1,40–1,86 | Merwinite | 3CaO · MgO · 2$SiO_2$ | 1576 |
| 1,86–2,80 | Dicalcium Silicate | 2CaO · $SiO_2$ | 2130 |
| >2,80 | Tricalcium Silicate | 3CaO · $SiO_2$ | 1899 |

In the SEM examination, it is found that average crystal size for samples A1, A2, B1, B2, C1 and C2 are >800 µm, >745 µm, >2000 µm, >1800 µm, >410 µm, >375 µm respectively.

As shown in the SEM images (Fig. 5–10), darker areas are the periclase crystals of solid solution with very little amount of iron oxides, lighter areas are mostly calcium silicate impurities on grain boundaries.

Samples from A zone have very thin impurity formation which enhances the refractory properties. A1's grain boundaries examined by EDX method and 61,3 mass-% CaO, 27,7 mass-% $SiO_2$ and 11,0 mass-% MgO was found.

Samples from B zone have very large columnar single crystals with barely visible grain boundaries. B2 sample has some impurity in the centre of crystals. These are stucked in the crystals when solidification stage. These impurities examined by EDX method and 52,4 mass-% CaO,

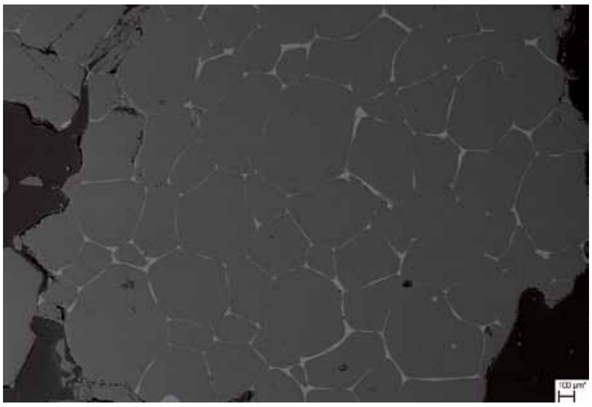

**Fig. 9** SEM image of C1 sample

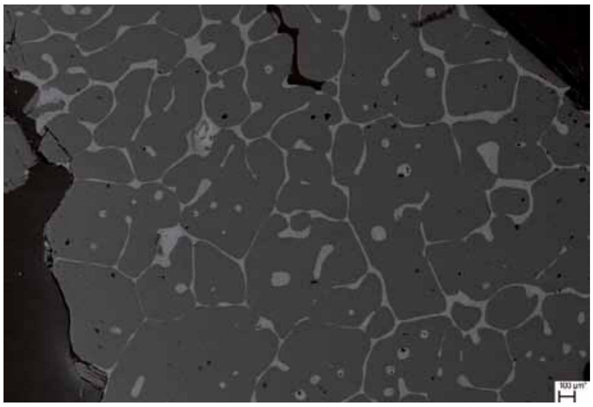

**Fig. 10** SEM image of C2 sample

34,2 mass-% $SiO_2$ and 13,4 mass-% MgO was found.

Samples from C zone have smaller crystals than A and B zones and they have thicker impurity formation on grain boundaries. C2's grain boundaries examined by EDX and 37,3 mass-% CaO, 32,6 mass-% $SiO_2$ and 30,1 mass-% MgO was found. It is expected that impurity phases are mostly monticellite and merwinite and these phases have lower melting points than dicalcium silicate. Samples from A and B zones of ingots have low silica content, high lime/silica ratio, with high density.

## 4 Conclusion

This paper focused on fused magnesia derived from Turkey's cryptocrystalline magnesite reserves. It was shown that the main factors in obtaining high quality fused periclase are the purity of the feed raw materials, determining the high MgO concentration in periclase; occurrence of impurity transfer into the skin of the ingots.

The specification of columnar and center crystals of fused magnesia ingots derived from the present study can give high performance in magnesia-carbon bricks and subsequently longer campaign life for better converter and electric arc furnace hot spots/slag line applications. Crust materials can also be used as medium grade dead burned magnesia for shaped and unshaped magnesia refractories.

## Acknowledgment

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