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Review Article

Review on the elaboration and characterization of ceramics refractories based on magnesite and dolomite

Chaouki Sadik[a,*], Omar Moudden[b], Abdselam El Bouari[a], Iz-Eddine El Amrani[c]

[a] Laboratory of Physical Chemistry of Applied Materials (LPCMA), Department of Chemistry, Faculty of Sciences Ben Msik, University Hassan II, Casablanca, Morocco
[b] Laboratory of Structure and Rehabilitation (LSR), Casablanca, Morocco
[c] Department of Earth Sciences, Geomaterials and Geo-Environment Team (Geo M&E), Scientific Institute, University Mohammed V, Rabat, Morocco

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ABSTRACT

One of the most important elements of furnaces, boilers and other heating units is the structure (lining), usually made of silica–alumina, basic or special refractories. The basic refractories are materials that are increasingly in demand and whose manufacturing involves necessarily the use of MgO and CaO. In this article, the description and characterization of magnesite ($MgCO_3$) and dolomite ($Mg,Ca(CO_3)_2$) and their contribution in industrial ceramics-refractories have been reviewed.

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1. Introduction

Different mixtures of geomaterials (kaolin clay, red clay, marl, andalusite, perlite, pozzolana, schist, silica sand, magnesite, forsterite, etc.), and additives (natural and synthetic) are used for the elaboration of ceramics and refractories [1]. These industrial minerals and rocks are the raw materials of economic value that are not classified as metallic minerals, fossil fuels or precious stones.

Shaped and unshaped basic ceramics-refractories, based on magnesite and dolomite are produced worldwide for lining industrial furnaces, especially primary and secondary steel furnaces [2]. Actually, there are two methods to produce refractory by using dolomite and magnesite as materials, one is fired in rotary or shaft kilns up to dead burning temperatures of 1500–1800 °C, the other is produced by electric smelting furnace with a temperature over 2500 °C, for example burned magnesite (i.e. fused magnesia) and electrocast spine are produced by electric smelting furnace. The behavior of these elaborated materials in high temperature has been investigated through the use of complementary methods of characterization: structural (X-ray diffraction), microstructural (scanning electron microscopy (SEM)), macroscopic (optical and polarized microscope), technological (porosity, water absorption, density, flexural strength, and shrinkage), thermal (DTA, expansion, shock, and conductivity), and chemical (resistance toward acid attack) [2].

* Corresponding author. Tel.: +212 6 45405676.
E-mail addresses: schawki37@gmail.com (C. Sadik), o.moudden@gmail.com (O. Moudden), elbouari@gmail.com (A. El Bouari), izdinelamrani@yahoo.fr (I.-E. El Amrani).

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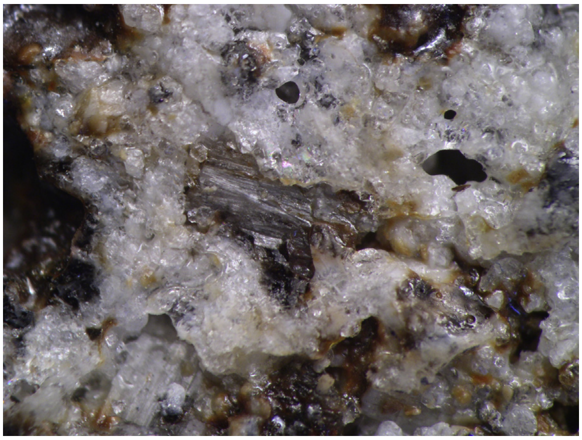

Fig. 1. Schema of the four textural elements of a refractory.

Refractory materials can be divided into several classes: chemical composition (acid, basic and special), method of implementation (shaped and unshaped), method of manufacture (fused and sintered), and porosity content (porous and dense). They are supposed to be resistant to heat and are exposed to different degrees of mechanical stress and strain, corrosion from liquids and gases, and mechanical abrasion at high temperature. The application fields of refractory are multiple and depend on the properties of each type. In fact, the performance of a refractory (good resistance to heat and thermal shock) is directly related to its texture and its richness in refractories minerals such as mullite, corundum, periclase, doloma, spinel and alumina [1]. Generally, every refractory is composed of four major structural elements that are depicted in Fig. 1 as the following; (1) aggregates (mean grain size: 1000–2500 mm) [3,4]; (2) matrix or filler materials smaller than 150 μm; (3) binder, bond, or cement; (4) pores.

The basic refractories are materials that are increasingly in demand and whose manufacture involves necessarily the synthesis of periclase, spinel and doloma. The primary attributes that make magnesia (MgO) an attractive choice are its high melting point (2800 °C) and excellent resistance to attack by iron oxides, alkalis and high lime content of flakes formed at the working temperature of steel melting furnaces [5]. Moreover, it does not suffer from issues of hydration like dolomite and lime, while also being nontoxic. Today, magnesia for refractory production is obtained from three basic sources [2] as the following: (a) natural magnesite, (b) extraction from sea water, and (c) extraction from inland brine. Basic refractories have the attributes of being relatively inexpensive compared to other bricks (special carbon refractories, zircon, zirconia, fused-cast refractory). In addition, they can be used in several applications as the following: coating of laboratory furnaces, refractory supports, thermal insulating, industrial ceramics, concrete, chemical producers and especially in the steel sector.

Several research studies have investigated the use of magnesite and dolomite in building materials and ceramics. The behavior of minerals (quartz, potassium feldspar, sodium feldspar, kaolinite, illite, calcite, dolomite, siderite, pyrite and apatite) in an improved ash fusion test was studied by Reifenstein et al. [6]. Arvanitidis [7] published a paper in 1998 on Northern Greece's industrial minerals. He studied the production and the environmental technology developments. The thermal analysis studies on the decomposition of magnesite and dolomite were studied respectively in 1993 and 1990 by Sheila [8] and Mclntosh et al. [9]. The effect of rate of heating on the decomposition reactions of some raw materials (kaolinite; $CaCO_3$; dolomite; magnesite; and mixes of these) was studied in 1984 by Ibrahim et al. [10]. In 1975, Khalifa et al. [11] studied rapid and quite reliable procedures for analysis of phosphate, quartzite and fluorspar minerals, as well as chromite, chrome–magnesite and magnesite–chrome bricks-basic refractories.

This review is intended to provide a large overview of the current status of this type of basic ceramics-refractories and to provide a summary of recent information concerning the elaboration and the characterization of refractories elaborated from magnesite and dolomite.

2. Materials

Basic refractories are manufactured using forsterite, spinel, cordierite, magnesite and dolomite. They will refer, somewhat arbitrarily, to common crystalline compounds with melting temperatures of at least 2000 °C [5]. In this work, we are interested only with magnesite and dolomite.

Magnesite is a well-known raw material widely used for making magnesia refractories. Magnesite is the mineral name for magnesium carbonate, $MgCO_3$, and was one of the original sources for magnesium oxide used in refractory products. Its theoretical composition is as follows: MgO: 47.7%; CO_2: 52.3%, with traces of Fe; Mn; Ca; Co; N and organic compounds. Magnesite is usually white or yellowish with compact appearance. It does not melt but decomposes at 700 °C. The residual MgO forms at the bottom at 2800 °C. The decomposition of magnesite in an inert N_2 atmosphere can be represented as follows: $MgCO_3 \rightarrow MgO + CO_2$.

Magnesite is delivered in three forms as the following: (1) Brute; (2) Calcined at 850 °C; (3) Dead burned and agglomerated (bricks at 1500–1800 °C). Magnesite occurs in nature in three distinct textures as the following: macrocrystalline rich in MgO (MgO content greater than 43%); microcrystalline with inclusions of dolomite (MgO content is between 39 and 43%); macrocrystalline but containing many impurities and having a MgO content of less than 39% [12].

The different methods used for the enrichment of magnesite are based on techniques such as optical or manual sorting, magnetic separation, gravity and flotation. These operations are used depending on the nature and texture of the mineral accompanying magnesite. Treatments show that the obtained concentrate has a good quality, considering the high content of MgO (exceeding 47%), and has low impurity content. The semi-industrial tests are focused on the manufacture of magnesia and magnesium sulfate from the concentrates obtained from raw magnesite.

Production of caustic magnesia and dead burned magnesia from magnesite Boudkek (north of Morocco) was carried out at 850 °C for the first and between 1650 and 1800 °C for the second. The obtained contents during these operations are as the following for the caustic magnesia: 95% MgO, 3% CaO, 0.3% Fe_2O_3, 0.12% $A1_2O_3$, and 1.2% SiO_2; and as the following for the dead burned magnesia: 96.5% MgO, 1.5% CaO, 0.6% Fe_2O_3, 0.6% $A1_2O_3$ and 0.75% SiO_2 [12].

In order to produce magnesium sulfate from magnesite, Boudkek tests were performed on representative samples whose average chemical composition is as follows: 44.16% MgO, 3.80% CaO, 0.26% Fe_2O_3, 0.35% SiO_2, 1.12% Al_2O_3 and 50.00% LoI. The treatment method is an acid attack allowing the transformation from the magnesium carbonate (magnesite) to sulfate. Three techniques were tested as the following: (1) direct attack on the raw magnesite at room temperature; (2) direct attack with heating; and (3) attack after roasting magnesite. Only the acid attack after magnesite roasting at 700 °C presents advantages, especially a coarse grain size (1 mm), and instant reaction and very high efficiency up to 99%. The obtained magnesium sulfate is of the hydrated kind ($MgSO_4 \cdot 7H_2O$) comparable to the commercial sulfate.

Dolomite is a carbonate sedimentary rock that contains more than 50% of carbonate, half of which is at least in the