Thermochimica Acta xxx (2013) xxx–xxx

Contents lists available at SciVerse ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Influence of time and temperature on ageing and phases synthesis in the $MgO–SiO_2–H_2O$ system

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ARTICLE INFO

Article history:
Available online xxx

Keywords:
Thermal analysis
M–S–H
Refractories
Basic castables
Magnesia
Microsilica

ABSTRACT

The behaviour of the mixture of MgO and SiO_2 with water was studied and analyzed by DTA–TGA–EGA and XRD after ageing for 1, 3, 10, 30 and 180 days at 20 °C. The samples also were aged at 30 °C and 40 °C for 1 and 3 days. Additionally, after 180 days the samples were heated in 500 °C, 700 °C and 900 °C for 24 h. The paste was composed of magnesium oxide and microsilica in 1:1 molar ratio and water in addition of 50% wt. of oxides. The DTA–TGA–EGA curves in the temperature range 20–950 °C were analyzed. The aim of this work was to study the reaction and phase composition in the $MgO–SiO_2–H_2O$ phase system. This system has wide applications in refractory materials, especially in basic castables. The compounds of this system may constitute an innovative bonding phase in a new generation basic castables.

1. Introduction

Fused or dead burned magnesium oxide (MgO) whose mineralogical name is periclase also is known as magnesia. Magnesia is one of the most important raw materials in the refractories industry. Magnesium oxide is popular because of its high refractoriness, which is approximately 2840 °C, and high resistance to basic slags and natural environment [1–3]. Numerous refractory materials are based on magnesia. The most popular ones are shaped magnesium bricks which are in common use in metallurgy of steel and other metals as well as in the cement and lime industry. Basic castables based on MgO are less widespread refractories than the shaped one. The limitation in use of basic castables is the result of hydration of magnesia which is connected with the change in volume. The lack of knowledge about the method of control and potential use of the interaction between water and magnesium oxide (in order to create a useful bonding system) effectively causes the limitation in applying this type of refractory materials [4].

Basic castables based on MgO belong to the unshaped class of refractories, which also include commonly used alumina castables. In the recent years the increasing interest in unshaped refractory materials, especially refractory castables and potentially wide applications of the basic castables, has increased the efforts to develop these materials. The great interest in $MgO–SiO_2–H_2O$ phase system is related to formation of magnesium silicate hydrate gels (M–S–H) which are present in the refractory ramming bodies and concretes as a strong bonding phase.

Many studies were carried out to learn of the mechanism of hydration of magnesium oxide [3,5–7]. Hydration of magnesia is caused by water in the liquid and vapour form or as an environmental moisture, and depends strongly on surface area and temperature. In the literature two main mechanisms can be found, which explain the hydration of magnesia. First of them is the mechanism of shrinking core [3,5,7] and the second one is based on the dissolution and precipitation process of MgO [6]. The shrinking core mechanism refers to the highly reactive magnesia. According to Kitamura et al. who examined polycrystalline magnesia, the hydration process occurs in two steps. Firstly, on the surface, the brucite layer is formed and on the boundaries between single crystals polycrystalline grains are created. Brucite fills pores and free spaces on crystals boundaries and causes tensions inside the grains. In the second step, when tensions are strong enough, they break a grain into several smaller ones, after which the hydration rate increases drastically, parallel with the total surface area [2,3,5,7]. The second mechanism of hydration of MgO consists of stages which are presented as follows.

(I) Magnesium oxide is a donor of the electron for proton from water; the surface is positively charged.

$$MgO_{(S)} + H_2O_{(L)} \rightarrow MgOH^{+}{}_{(surface)} + OH^{-}{}_{(aq)} \qquad (1)$$

(II) The positively charged surface attracts electrostatically negative OH^- ions and adsorbs them.

$$MgOH^{+}{}_{(surface)} + OH^{-}{}_{(aq)} \rightarrow MgOH^{+}\cdot OH^{-}{}_{(surface)} \qquad (2)$$

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http://dx.doi.org/10.1016/j.tca.2013.01.018

Please cite this article in press as: J. Szczerba, et al., Influence of time and temperature on ageing and phases synthesis in the $MgO–SiO_2–H_2O$ system, Thermochim. Acta (2013), http://dx.doi.org/10.1016/j.tca.2013.01.018

Table 1
Specification of the starting materials.

%	SiO_2	MgO	Al_2O_3	CaO	Fe_2O_3	K_2O	Na_2O	TiO_2	Others
Microsilica (Elkem 955U)	96.51	0.31	0.45	0.23	0.24	0.75	0.18	0.02	1.31
MgO (Chempur)	–	95.00	–	1.00	0.05	–	–	–	3.95

(III) Mg^{2+} and OH^- ions are adsorbed on the dissolution surface in the aqueous medium.

$$MgOH^+ \cdot OH^-_{(surface)} \rightarrow Mg^{2+}_{(aq)} + 2OH^-_{(aq)} \quad (3)$$

(IV) Dissolved ions reach supersaturation in the solution and the precipitation of the brucite layer starts on the surface of magnesium oxide. After the formation of the brucite layer the process becomes controlled by water diffusion by the brucite layer [1,2,6].

According to both models of hydration, in order to prevent the hydration of MgO, it is necessary to avoid or inhibit dissolution of magnesia or (and) precipitation of brucite [1,8]. This can be achieved by adsorbing additives on the magnesia surface. In the literature many studies can be found on the compounds which inhibit the hydration process, such calcium chloride, boron acid, citric acid and others [1,9,10]. Among these, one can mention microsilica as a promising compound for this purpose. Microsilica, in the highly alkaline solution (pH 10–12), which is created in the reaction of MgO and water, is partially dissolved and forms silicic acid ($HSiO_3^-$). On the surface of MgO grains, silicic acid in the presence of magnesia can be attracted by $Mg(OH)_2$ and forms a layer. This generates a poorly crystalline phase, called magnesium silicate hydrate (M–S–H), according to the scheme:

$$HSiO_3^- + Mg(OH)_2 + H_2O \rightarrow MgHSiO_4{\bullet}2H_2O \quad (4)$$

The generated phase surrounds grains of magnesia and prevents it from hydration [11].

In the literature there are many studies about the M–S–H phase, both in terms of structure and phase composition as well as its application in refractory castables [12–23]. The MSH phase not only prevents magnesia from hydration but also represents a new binding system in refractory castables. This binding system contributes to the creation of a high quality basic concrete, without any significant losses of characteristic magnesia features. Thanks to the application of microsilica as a retardant of hydration the problem of volumetric expansion is substantially solved. Moreover, by adding microsilica to castables the flow and setting time of concrete can be influenced. Another advantage of microsilica is constituted by high refractoriness of castables with its additive. This is because at about 900 °C and higher microsilica reacts with magnesia and creates forsterite, which is a highly refractory compound with the melting point around 1840 °C.

In this work attention is focused at the application of phases coexisting in the system $MgO–SiO_2–H_2O$ (M–S–H), as a bonding material in refractories. The aim of this study was to evaluate the

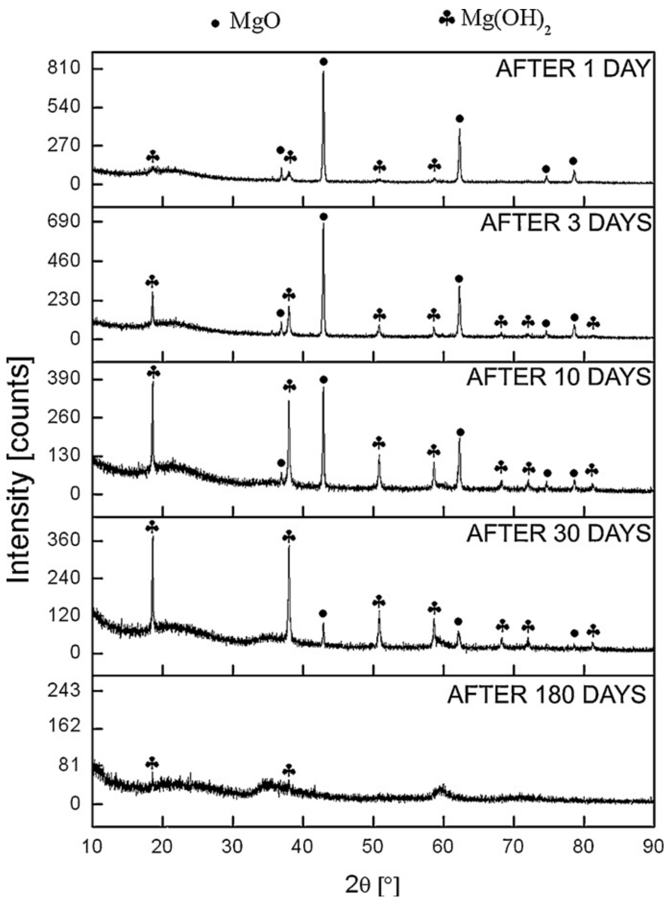

Fig. 1. XRD patterns of the samples ageing up to 180 days at 20 °C.

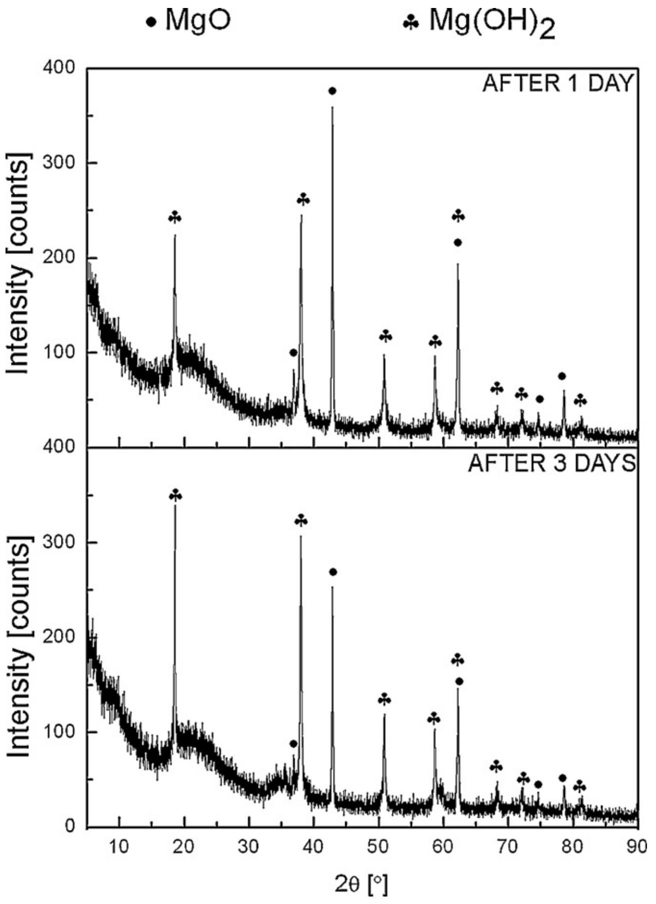

Fig. 2. XRD patterns of the samples ageing up to 3 days at 30 °C.

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