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Original Research Paper

Production of forsterite from serpentine – Effects of magnesium chloride hexahydrate addition

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ABSTRACT

In this paper, forsterite production via reaction sintering technique was presented. Experimental studies consist of three steps. In the first step mixture containing 57.62% serpentine, 42.38% magnesium chloride-water solution was first calcined in a furnace for chloride removal, ground and then shaped using dry pressing technique. In the second step the shaped samples were sintered in the range of 750–1400 °C for 2 h. In the third step firing shrinkage, water absorption and three point bending strength tests and XRD (X-Ray Diffraction) analysis were applied to the sintered samples. XRD analysis showed that forsterite phase formed in all of the sintered samples.

1. Introduction

Serpentine soils cover huge areas in many countries [1,2] and more particularly in Albania (Balkans) [3,4]. These soils are derived from the hydro-thermal alteration of ultrabasic rocks. They are characterized by high levels of Ni (0.5–8 g/kg), Mg and Fe, and high contents of Cr and Co as well [2,3,5]. It could be economically interesting to recover nickel from these soils. Serpentine is known to be produced naturally as a hydrated magnesium silicate which crystallizes in the monoclinic system. This hydrated magnesium silicate has the three principal polymorphic forms: antigorite, chrysotile and lizardite. A large amount of serpentine is produced even in Japan. However, beneficial utilization is limited to some engineering applications such as a flux in iron and steel making and as a filler for road reclamation [6]. The mineral has been utilized as a magnesium resource by applying an acid extraction technique [7–15]. There have been several investigations on the extraction of serpentine to extend the field of application. For example, Raschman [7] explored how calcination of serpentinite can enhance the dissolution rate of magnesium in solutions of three different leaching agents: hydrochloric acid (strong acid), acetic acid (weak acid) and ammonium chloride (hydrolyzing salt). In another study, the mechanochemical effects of hydrated silicates have been investigated. The main purpose of the investigation was to provide information on the mechanochemical effect induced by dry grinding and on the acid extraction of magnesium and silicon from the mechanically activated serpentine [8]. The production of tribofilm from serpentine has been attempted by Yu et al. [16]. They studied the microstructure, micromechanical properties and tribological behaviors of the tribofilm by serpentine ultrafine powders (average size 1 μm) as additives, and aimed to further clarify the mechanisms responsible for the excellent tribological properties of serpentine as additives. In particular, a phenomenological model of the tribofilm generated by serpentine was developed based on the experimental results. However, little research has been made on its use for silica production [17]. Because of its theoretical composition of SiO_2 (34.3%), MgO (44.1%), Fe_2O_3 (6%), Al_2O_3 (0.2%) and CaO (0.45%), serpentine can be a raw material for production of silica after acid treatment. It is well known that acid treatment of minerals results in formation of porous material. Therefore, serpentine treated by acid yields porous, reactive and amorphous silica of high purity, which can then be used for synthesis of silicon carbide (SiC). Cheng and Hsu aimed to treat waste serpentine by acid and the amorphous silica of high reactivity thus obtained is then used for making synthetic SiC at lower temperature [17]. The effects of reductant addition and reaction temperature (1200, 1400, 1450 and 1550 °C) on phase behavior and microstructure of serpentine by in situ carbothermal reduction nitridation (CRN) treatment were studied by Li et al. [18]. Furthermore, the synthesis mechanism of serpentine via CRN route was also analyzed briefly. The production of synthetic

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oxy-fluoride construction material from serpentine, kaolin and calcium fluoride tailings and converting them into useful and value-added construction materials have been investigated by Zhu et al. [19]. In another study, a serpentine mineral was treated in hydrochloric acid solution to obtain amorphous silica with high surface area. The highly porous silica residue was used as a silica source for the synthesis of zeolite ZSM-5 by hydrothermal method [20]. Due to its theoretical composition given above, serpentine is also frequently used to manufacture forsterite-based refractories that contain about 85% of forsterite and 15% magnesioferrite. This type of refractory is made from serpentine, talc or olivine–serpentine using high temperature [21]. When serpentine is used for making forsterite, it needs to be calcinated to release its structural water that results in 12% of volume reduction. From MgO–SiO_2 binary phase diagram and MgO–Al_2O_3–SiO_2 ternary phase diagram [22,23], it was found that refractoriness of serpentine is low. In order to form forsterite by serpentine as a raw material, the ratio of MgO, Al_2O_3 and SiO_2 needs to be controlled under certain optimum fractions. In particular, sufficient amount of magnesite must be added to convert the low-melting metasilicate to the high-melting orthosilicate. The literature is relatively scarce in this field. Carniglia [23] has noted that forsterite based refractories must be kept to the MgO-rich side of the forsterite composition ($\geqslant$58 wt.%) to ensure the MgO–Mg_2SiO_4 eutectic at 1850 °C which governs initial melting. Carniglia and Cheng et al. were investigated the addition of magnesium-based compounds, such as MgO, $MgCO_3$ or $Mg(OH)_2$, for making synthetic forsterite, which involves a potential usage of the serpentine waste in Taiwan [23,24].

The purpose of this research is to seek the effects of magnesium chloride hexahydrate on synthetic forsterite formation, which involves a potential usage of serpentine in Turkey.

2. Experimental procedures

2.1. Materials

The following raw materials were used in the investigation: serpentine was taken from KÜMAŞ (Kütahya/Turkey Magnesite A.Ş). As shown in Fig. 1 and Table. 1, it contains orthochrysotile [46-1445 (Mg, Fe, Ca)$_3$·(Si, Al)$_2$O$_5$·(OH)$_4$], antigorite [44-1447 $Mg_3Si_2O_5$·(OH)$_4$] and quartz (46-1045 SiO_2) phases. The chemical analysis of serpentine and commercial $MgCl_2$·$6H_2O$ (99%, ECeR Ceramic-Turkey) are presented in Table 2.

2.2. Experiments

Test samples based on forsterite composition were prepared by the conventional solid state reactions of powder mixtures.

Table 1
Mineralogical compositions of serpentine (calculated from XRD patterns).

Minerals		wt.%
44-1447 $Mg_3Si_2O_5$·(OH)$_4$	Antigorite	65.14
46-1445 (Mg, Fe, Ca)$_3$(Si_7Al)$_2$O$_5$ (OH)$_4$	Orthochrysotile (Lizardite)	32.68
46-1045 SiO_2	Quartz	2.18

Table 2
Chemical compositions of serpentine, magnesium chloride hexahydrate and mixture.

Chemical composition	Serpentine wt.%	$MgCl_2$·$6H_2O$ –	Mixture[a] wt.%
SiO_2	39.09	–	22.52
MgO	34.73	19.83	28.42
Fe_2O_3	9.21	–	5.31
Al_2O_3	0.64	–	0.37
Cr_2O_3	0.43	–	0.25
CaO	0.40	–	0.23
NiO	0.38	–	0.22
Co_2O_3	0.02	–	0.01
MnO	0.11	–	0.06
F	0.10	–	0.06
Na_2O	0.01	–	0.006
SO_3	0.04	–	0.02
P_2O_5	0.01	–	0.006
K_2O	0.01	–	0.006
ZnO	0.01	–	0.006
LOI	14.77	80.17	42.49

[a] Serpentine 57.62 wt.% and $MgCl_2$·$6H_2O$ 42.38 wt.%.

Serpentine sample was ground to minus 90 μm in a ball mill. Wet blended sample with $MgCl_2$·$6H_2O$ powder in the ratio of 42.38 wt.%, were then dried and heated by a programmable control electric furnace to 500 °C for 1 h in order to release the structural water and Cl. The temperature was slowly increased at a heating rate of 2.5 °C/min until certain temperatures, (i.e. 150, 300 and 500 °C) and soaked for one hour at these temperatures and then cooled to room temperature. Fig. 2 shows the test samples sintered at 900–1400 °C.

Table 3 shows the transformation temperatures and corresponding solubilities of magnesium chloride hydrates. The penta- and hexahydrates can be dehydrated to the tetrahydrate stage almost without decomposition. On dehydration to the dihydrate however, hydrolytic decomposition starts. Dehydration of the dihydrate at 240 °C leads to extensive decomposition forming magnesium oxychlorides or oxide. To obtain anhydrous $MgCl_2$, dihydrate must be dehydrated in an atmosphere of hydrogen chloride [25].

The stoichiometric forsterite batch was dry mixed in a ball mill with alumina balls for 2 h. Green compacts were formed by using

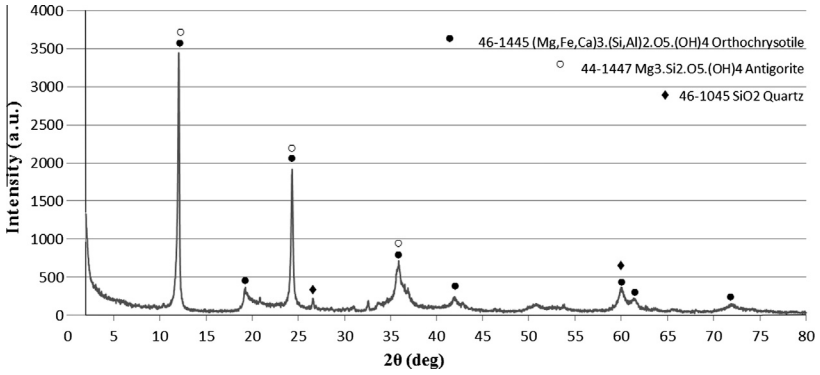

Fig. 1. XRD pattern of the serpentine sample.