RISET
Geologi dan Pertambangan

THE CHARACTERISTICS OF PADAMARANG MAGNESITE UNDER CALCINATION AND HYDROTHERMAL TREATMENT

KARAKTERISTIK MAGNESIT PADAMARANG DENGAN PERLAKUAN KALSINASI DAN HIDROTERMAL

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ABSTRACT Magnesite ($MgCO_3$) is the main source for production of magnesium and its compound. In Indonesia, magnesite is quite rare and can be only found in limited amount in Padamarang Island, Southeast Sulawesi Provence. Thus the properties of magnesite and the reactivity degree of the obtained product are of technological importance. The aim of this work was to analyze the characteristics of Padamarang magnesite under calcination and hydrothermal treatment processes. The processes were carried out at various temperatures with range of 150-900°C for 30 minutes. The solids were characterized with respect to their chemical and physical properties by using scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDX), Fourier-transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD). SEM image indicates that magnesite was formed from thin and flat hexagon sheets. The FTIR and XRD analysis disclose that MgO formed at temperature above 300°C, where as the magnesite sample also lost its mass around 50%. These results demonstrate that Padamarang magnesite decomposes to magnesium oxide and carbon dioxide at high temperature.

Keywords: Calcination, hydrothermal, magnesite, Padamarang.

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ABSTRAK Magnesit ($MgCO_3$) merupakan sumber utama untuk produksi magnesium dan senyawa-senyawanya. Di Indonesia, magnesit cukup jarang dan hanya dapat ditemukan dalam jumlah yang terbatas di Pulau Padamarang, Propinsi Sulawesi Tenggara. Oleh karena itu sifat magnesit dan derajat reaktivitas dari produk-produk magnesit penting untuk diketahui. Penelitian ini bertujuan untuk menganalisis karakteristik magnesit Padamarang dengan perlakuan kalsinasi dan hidrothermal. Proses dilakukan pada temperatur yang bervariasi dari 150-900°C selama 30 menit. Sifat kimia dan fisika dari magnesit dikarakterisasi dengan menggunakan *scanning electron microscopy* dengan *energy-dispersive X-ray spectroscopy* (SEM-EDX), *Fourier-transform infrared spectroscopy* (FTIR), dan *X-ray diffraction* (XRD). Gambar dari analisis SEM menunjukkan bahwa magnesit terbentuk dari lembaran-lembaran heksagonal yang tipis dan datar. Hasil analisis dengan FTIR dan XRD menunjukkan bahwa MgO terbentuk pada temperatur diatas 300°C, dimana sampel magnesit juga kehilangan massanya sekitar 50% pada suhu tersebut. Hal ini menunjukkan bahwa Magnesit Padamarang

terdekomposisi menjadi magnesium oksida dan karbon dioksida pada temperatur tinggi.

Kata Kunci: Kalsinasi, hidrotermal, magnesit, Padamarang.

INTRODUCTION

Magnesite refers to magnesium carbonate ($MgCO_3$, theoretically 47.8% MgO and 52.2% CO_2) (Deer et al., 1992). It is usually found as irregular veins as an alteration product of serpentine ultramafic rocks and other magnesium rich rock types and sometimes formed by replacement of dolomite and dolomitic limestone whereas calcium in the lattice of dolomite is replaced with magnesium. In this case the magnesite is said to be diagenetic (Mehmood et al., 2018; Indian Bureau of Mines, 2017; Joshi et al., 2009; Sharma and Joshi, 1997; https://www.sandatlas.org/magnesite/). Calcium and silica are, therefore, the most common impurities found in magnesite along with Fe_2O_3 and Al_2O_3 (Indian Bureau of Mines, 2017).

In addition there is a series of basic magnesium carbonates having the empirical formula $xMgCO_3.yMg(OH)_2.zH_2O$. These include hydromagnesite [$4MgCO_3.Mg(OH)_2.4H_2O$] and artinite [$MgCO_3. Mg(OH)_2.3H_2O$] (Shand, 2006).

There are two physical forms of magnesite: cryptocrystalline or amorphous magnesite and crystalline, macrocrystalline, or bone magnesite.

Deposits of massive cryptocrystalline magnesite occur in serpentized ultrabasic rock that has undergone a hydrothermal leaching of magnesium from the serpentine, $H_4Mg_3Si_2O_9$, in Eq (1). The hydrothermal solution contains dissolved carbon dioxide necessary for the dissolution process (Shand, 2006).

$$H_4Mg_3Si_2O_9 + 2H_2O + 3CO_2 \rightarrow 3MgCO_3 + 4H_2O + 2SiO_2 \dots\dots\dots\dots\dots\dots\dots\dots(1)$$

The magnesium carbonate is deposited in veins and the silica carried away in solution. Magnesite may also form through the serpentization of ultrabasic rock, under low-temperature and low-pressure conditions, which favor the exosolution of hydrothermal cryptocrystalline magnesite (Shand, 2006).

Equation (2) shows serpentization of olivine, $(Mg,Fe)_2SiO_4$, to form antigorite, $H_4(Mg, Fe)_2Si_2O_9$, and magnesite:

$$2(Mg,Fe)_2SiO_4 + 2H_2O + CO_2 \rightarrow H_4(Mg,Fe)_2Si_2O_9 + MgCO_3 \dots\dots\dots\dots\dots(2)$$
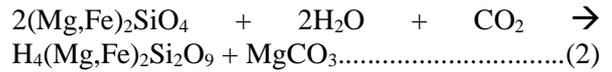
The magnesite occurs as massive bodies, lenticular (lens-shaped) masses, and veins of varying thickness (Shand, 2006).

The calcination of magnesium carbonate has not been as extensively studied as limestone (CaCO3). However, much of the theory of limestone
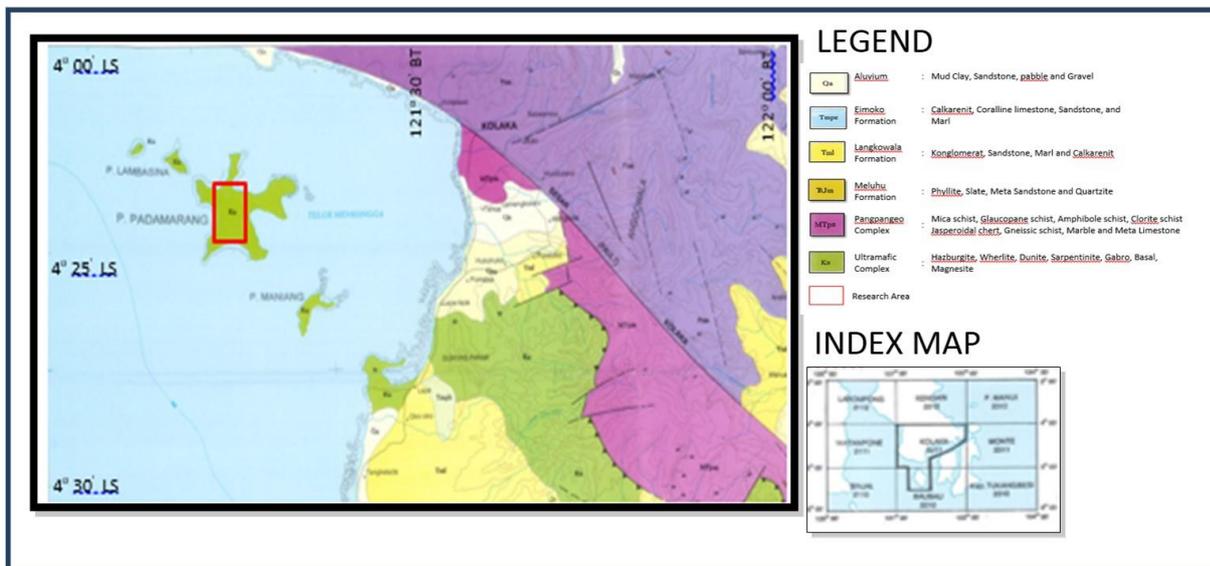
Figure 1. Location of magnesite in Padamarang Island, Southeast Sulawesi Provence. Map of geology Kolaka sheet (Simandjuntak et al., 1993).

calcination can be applied to magnesite. The essential reaction that occurs during heating is the loss of carbon dioxide from magnesite, with the corresponding formation of magnesium oxide, MgO.

$$MgCO_3 + heat \rightarrow MgO + CO_2\uparrow$$.........................(3)
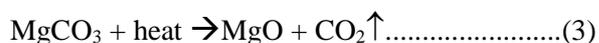
The decomposition of magnesite occurs between 402 and 750°C (Shand, 2006). The reaction proceeds rapidly above 550°C (Seeger, 2005). The differences are probably due to the different sources of magnesite with its impurity level, crystallographic structure, and microstructure that effect to its calcination properties (Shand, 2006).

Magnesite is a well-known raw material widely used for making magnesia refractories, which could be largely used in the steel industry, and was one of the original sources for magnesium oxide used in refractory products. Many countries produce natural magnesite. Although available production data varies considerably, global production of magnesite is probably 10 Mt to 12 Mt yearly. (https://www.resourcesandgeoscience. nsw.gov.au/__data/assets/pdf_file/0007/238156/ Magnesite.pdf).

Magnesite is quite rare in Indonesia and can be only found in limited amount in Padamarang Island, Southeast Sulawesi Provence (Suraji et al., 2015) (Figure 1). About 240,000 ton magnesite potency (with 40% MgO) has been surveyed (http://profilpnpmsultra.blogspot.com/p/provil-kab-kolaka.html) in Padamarang and other four different places. The properties of magnesite and the reactivity degree of the obtained product are of technological importance. Thus the characteristics of Padamarang magnesite need to be determined for future uses. This article describe the characteristics of Padamarang magnesite under calcination and hydrothermal treatment (the processes involves applying heat under presure to achive reaction in aqueous medium). Hydrothermal treatment has been attracting worldwide attention because of the fascinating characteristics of water as reaction medium at elevated temperatures and pressures (Savage, 1999). During the process, various reactions such as oxidation, hydrolysis, dehydration and thermal decomposition can be carried out energetically so that the reaction can be successfully used for decomposition of magnesite to CO_2 and other end products.

GEOLOGY

There are two different geology terranes based on the rocks formation, structure, and age of the Kolaka sheet. They are East Sulawesi geology terrane and *anjungan tukang besi buton* terrane. The characteristic of East Sulawesi geology terrane is combination between mafic, ultramafic (the oldest rock), and metamorfic rocks; meanwhile *anjungan tukang besi buton* terrane composed of continental sedimentary rock with pelagos sedimentary rock as cap rock.

Ultramafic rocks included inophiolite sequence, that consist of peridotite, serpentinit, wherlit, harzburgit, gabro, and basalt. Metamorphic rocks such as schist, malih sedimentary was found in Pongpangeo complex.

Research area was in Padamarang Island, Southeast Sulawesi Province. This area is on Kolaka sheet of geological map that included on Ultramafic Complex Formation (Ku) with Crateseous age (Simandjuntak et al.,1993). This formation consists of hazburgite, wherlite, dunite, sarpentinite, gabro, basalt, and magnesite (Figure 1).

Structure development in Kolaka sheet is separated from the evolution of the whole tectonic Sulawesi. Anggowala fault, as the main fault in Padamarang, is horizontal fault (dextral) with northwest − southeast direction. The type magnesite in research area are genetically affiliated with cryptocrystalline. They are commonly found in contact with or in close proximity to the peridotite ultramafic rocks. (Sasvári and Kondela, 2007; Gartzos, 2004). The ultramafic rocks release Mg, Ca, Fe and other metals via dissolution, leaching or other mineral-alteration reactions. The released Mg ions may react with water molecules to form brucite. Subsequently, Mg along with Ca and Fe can react with dissolved CO_2 to precipitate different carbonate minerals (Basir et al., 2009).

METHODS

Magnesite ore supplied from Padamarang, Southeast Sulawesi Provence. The crystal phase identification was obtained using X-ray diffraction (XRD, Multi Flex, Rigaku, Akishima, Japan) using Cu Kα radiation at 20 mA and 40 kV

and shown in Figure 5. In addition, morphology analysis was also conducted by using scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDX).

To evaluate the optical properties and microstructural characteristics of the magnesite, petrography analysis of magnesite ore thin section was conducted by using petrographic microscope. The results (such as color, shape, etc.) were compared with the data from literatures (Deer et al., 1992; Winchell, 1951). The results are shown in Figure 2.

For calcination and hydrothermal treatment, magnesite ore was ground and sieved to give -200 mesh size fraction. The calcination experiments

with 2 g of sample were carried out in the tube furnace at temperature range 150-900°C for 30 minutes, whereas hydrothermal treatments were carried out in an apparatus consisting of a steel pressure vessel (autoclave) at temperature range of 150-300°C (maximum temperature of autoclave is 400°C) for 30 minutes. The losses in weight during calcination and hydrothermal treatment are shown in Table 1. Solid resulted from the experiments were analyzed by Fourier-transform infrared spectroscopy (IRTracer-100 FTIR, Shimadzu, Tokyo, Japan [accumulation, 100 times; resolution, 4 cm-1]) and XRD. The data were compared with those for raw magnesite, as discussed below.
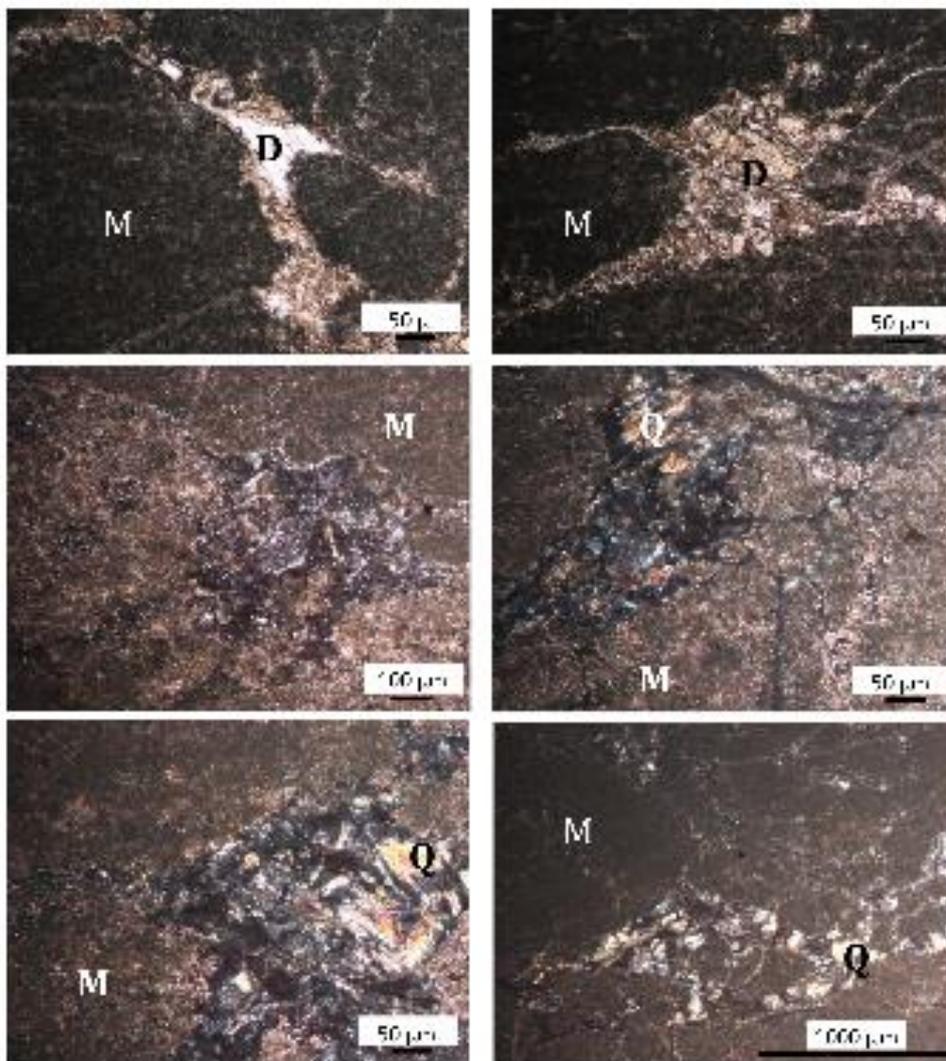
Figure 3. Photomicrography of Padamarang magnesite ore thin section. Magnesite (M) may occur by hydrothermal processes. The hydrothermal processes penetrate rock fracture resulting in quartz (Q) and dolomite vein (D).

Table 1. Weight losses of magnesite during calcination and hydrothermal treatment.

Temperature (°C)	Weight Loss (%)	
	Calcination	Hydrothermal
150	2.53	4.50
180	0.50	8.96
200	1.00	0.50
230	1.00	4.00
270	10.40	8.50
300	9.45	8.00
400	48.51	-
500	49.75	-
600	49.01	-
900	49.50	-
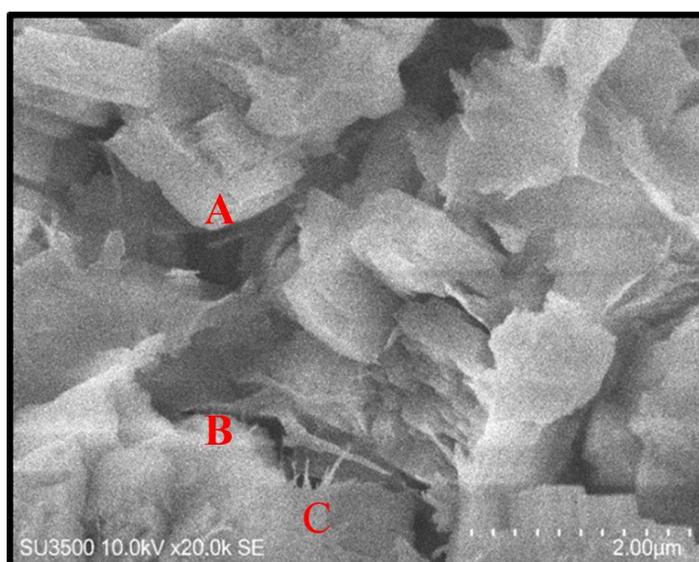
Figure 2. SEM image of Padamarang magnesite: (A) Magnesite morphology formed from thin and flat hexagon sheets. (B)Structure of magnesite consists of very fine hollow minerals. (C) Needle shaped morphology of magnesite.

RESULTS AND DISCUSSION

Morphology analysis

Scanning electron microscope analysis was carried out on magnesite sample. SEM image (Figure 3) indicates that magnesite was formed from thin and flat hexagon sheets indicating the structure of MgO. Besides that, needle shaped morphology indicating the structure of CaO was also found. In addition, the magnesite mineral consists of very fine hollow minerals that are clearly visible on the magnesite surface. From the EDX analysis, the elements of magnesite Padamarang contains of 30.69% Mg, 15.37% C, and 53.39% O.

Petrography analysis

Magnesite, usually white or yellowish with compact appearance, occurs in nature in three distinct textures as follow: 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% (Sadik et al., 2016).

Based on petrography analysis and comparison data from literatures, Padamarang magnesite sample may occur by hydrothermal processes.
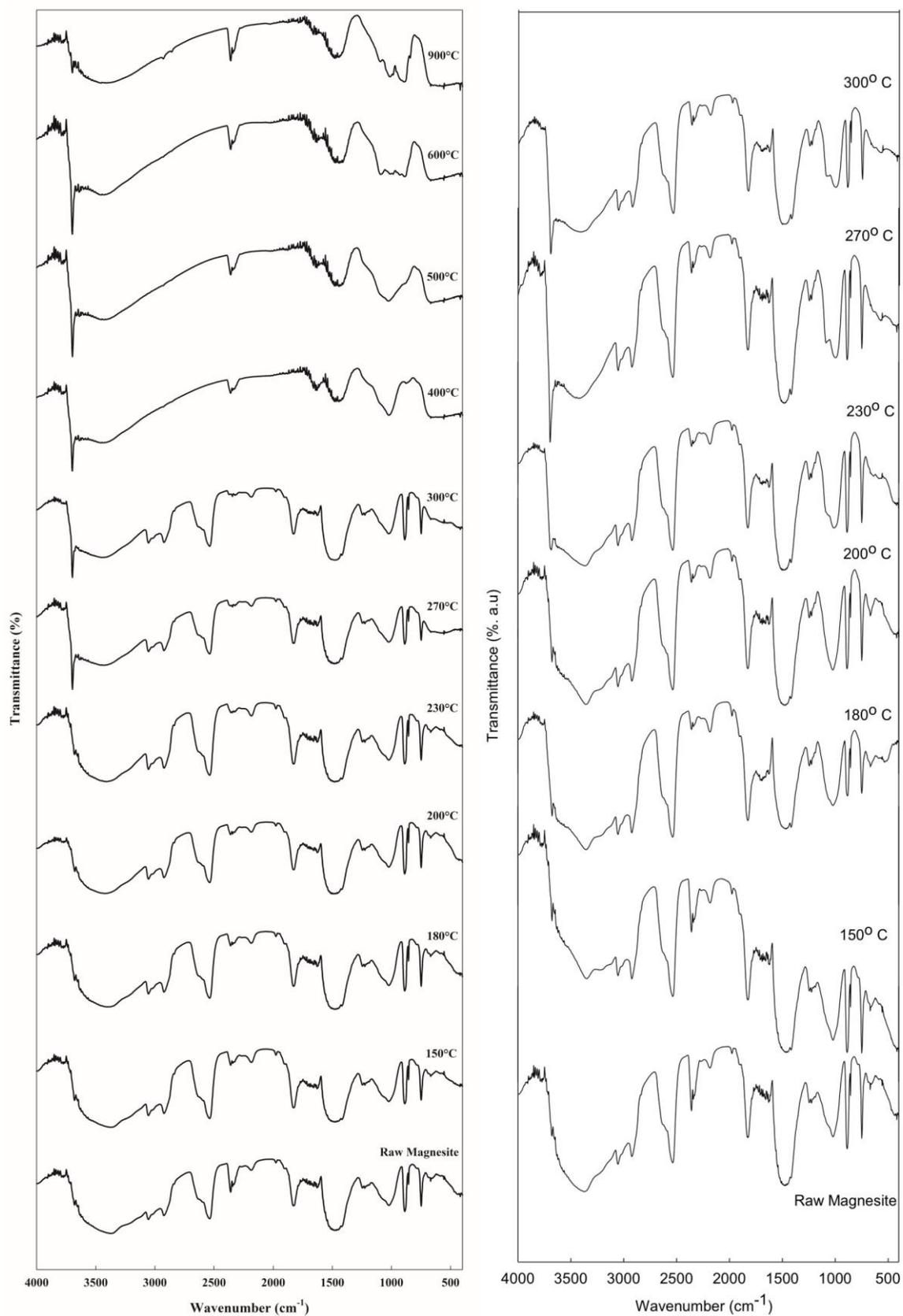
Figure 4. FTIR spectra of (a) calcined magnesite, (b) hydrothermal treated magnesite.
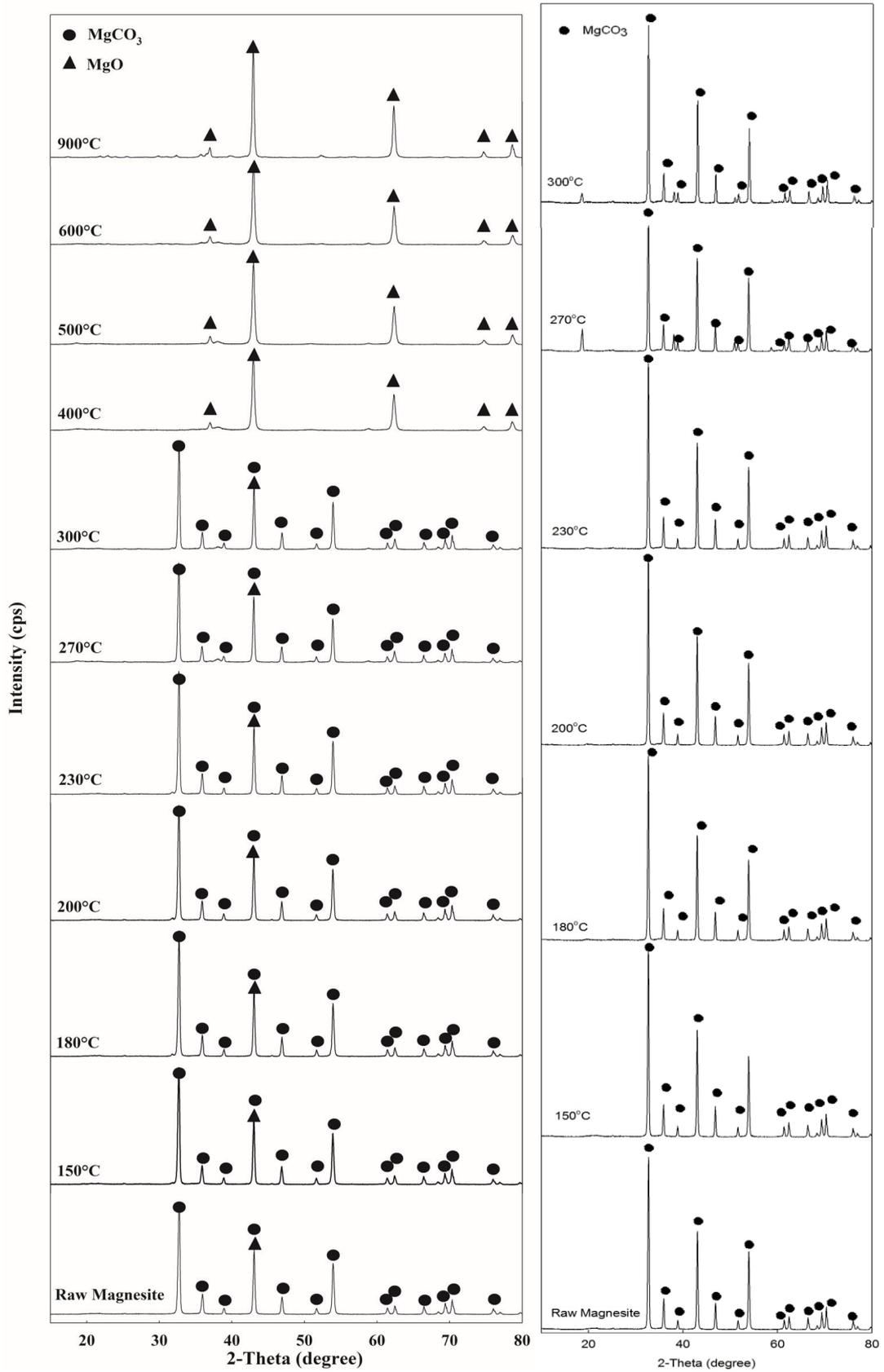
Figure 5. XRD pattern of (a) calcined magnesite, (b) hydrothermal treated magnesite.

Weight Loss

Calcination is thermal treatment of an ore to effect its decomposition and elimination of a volatile product, usually CO_2, water vapor, or other gases. As a result of calcination, carbonate ore is converted into its oxide. Calcination reactions usually take place at or above the thermal decomposition temperature or the transition temperature.

At high temperatures, $MgCO_3$ decomposes to magnesium oxide and carbon dioxide. This process is important in the production of magnesium oxide (Seeger et al., 2005) and it is called calcining (Eq. 3). However, calcination to the oxide is generally not considered complete below 900 °C due to interfering readsorption of liberated carbon dioxide.

As reported by Weast et al. (1978), the decomposition temperature of magnesite is at 350 °C. Table 1 shows the losses in weight during magnesite calcinations and hydrothermal treatments. It shows that above 300°C mass losses around 50% due to the decomposition of magnesite. These results are consistent with the explanation given above.

Although significant change in mass loss was not observed at the starting temperatures, both hydrothermal and calcination (150-300°C), significant changes occurred between 400 and 900°C. These were probably caused by the decomposition of magnesite into MgO and CO_2 as reported by Shand (2006) based on reaction in Eq. (3). Evaporated CO_2, water vapor or other gasses decreasing the final weight of sample.

Fourier Transform Infra Red (FTIR) spectroscopy analysis

The FTIR spectra of the magnesite calcined at 150-900°C for 30 minutes and hydrothermal treated at 150-300°C for 30 minutes are shown in Figures 4(a) and (b) respectively.

The FTIR spectra of calcined magnesite differ in the region between 2900-3700 cm^{-1}, the broad peaks assigned to stretching mode of –OH group (Ma et al., 2002) due to H_2O or OH vibration (White, 1971), that diminish with increasing calcination temperature. The CO_3^{2-} asymmetric stretching vibrations are observed as a strong band split in two at ~1420-1480 cm^{-1} (Sawada et al., 1978). This shows that the carbonate ion exist. The three absorption bands at ~800, 850 and 880 cm^{-1} are assigned to the CO_3^{2-} bending vibrations (Sawada et al., 1978 and Raade, 1970). It is expected that volatile product, CO_2, water vapor, or other gases would be removed from the crystal lattice during calcination. This was confirmed as calcination proceeded, the IR band assigned to – OH group and CO_3^{2-} became gradually obscure at above 300°C.

For hydrothermal treated magnesite, the changes were not significant among raw magnesite and treated magnesite due to the highest hydrothermal temperature of experiment was only 300°C. This is the highest temperature that can be reached by the autoclave in our laboratory to adapt its maximum temperature (400°C).

X-Ray Diffraction (XRD) analysis

Phase transformation of the magnesite calcined and hydrothermal treated for fixed duration at different temperatures were recorded by X-ray diffraction (XRD) in the 2θ range of 20°-80° and presented in Figures 5(a) and (b) respectively.

The characteristic peaks of $MgCO_3$ (JCPDS 08-0479) both of calcination and hydrothermal treated magnesite, observed at 2θ~32.50°, 35.70°, 39.00°, 43.30°, 47.20°, 51.80°, 54.00°, 61.40°, 62.50°, 66.50°, 69.80°, 70.80°, 77.10°.

However, most of the $MgCO_3$ peaks were disappeared above 300°C (on calcination treatment) and replaced by the appearance of MgO peaks that increase with increasing calcination temperature. The MgO peaks in observed at 2θ~37.1°, 43.1°, 62.4°, 74.7°, and 78.7° which are in good agreement with the standard JCPDS 78-0430 with 2θ~42.94°, 62.09°, and 78.44° (Bagheri Gh. and Kahaki, 2015). The most intense peak was observed at 2θ~43.1° and 62.4°, revealing the formation of well-crystallized MgO.

CONCLUSION

A combination of SEM-EDX, FTIR, and XRD was used to analyze the characteristics of Padamarang magnesite under calcination and hydrothermal treatment processes at various temperatures with range of 150-900°C for 30 minutes.The results of theoretical evaluation, microscopy, and spectroscopy analysis show that MgO formed at temperature above 300°C. The XRD patterns provided a clearer understanding of

MgO formation. Besides that, those results were also supported by significant change in mass loss occurred between 400 and 900°C that caused by evaporation of CO_2, water vapor or other gasses. All of the data led to the conclusion that Padamarang magnesite decomposes to magnesium oxide and carbon dioxide at temperature above 300-900°C.

ACKNOWLEDGMENTS

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