

Influence of crystallographic orientation on hydration of MgO single crystals

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Received 2 January 2009; received in revised form 13 January 2009; accepted 14 February 2009

Available online 11 March 2009

Abstract

This study has been performed in order to find out the influence of crystallographic orientation on hydration of MgO single crystal substrates with (1 0 0)-, (1 1 0)-, and (1 1 1)-orientations. The samples were left in a hydration chamber with an 88% relative humidity for 18 h at room temperature. The effect of humidity on the samples was examined by scanning probe microscope (SPM) and scanning electron microscope (SEM) which showed that the degree of hydration was noticeably influenced by the crystallographic orientation. It was found that the MgO with (1 1 1)-orientation has the highest tendency to hydrate than the other orientations. Second most affected sample was (1 1 0) crystal. Loss of MgO on the surface by hydration is most severe when the crystal is oriented in (1 1 1) plane with the maximum hydrate layer thickness of 174 nm after 18 h of exposure.

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Keywords: D. MgO; E. Refractories; Hydration behavior

1. Introduction

Basic refractories are widely used in steel and cement industries to contain slag or cement clinker melts at high temperatures [1,2]. They are composed mainly of MgO which is chemically compatible with the basic slag compositions that minimizes corrosion during service [3]. Microstructure of magnesia bricks consists of high melting magnesia crystallites surrounded by a bond phase like merwinite, monticellite, brownmillerite or dicalcium silicate [4–6]. Corrosive attack of the liquid slag or clinker to the brick is essentially resisted by the magnesia crystallites that have high melting temperatures (2850 °C). These magnesia crystallites are affected by moisture during storage of the bricks. Moisture in the air reacts with MgO to form brucite (Mg(OH)₂) [7]. Formation of brucite layer on periclase crystals means that the useful part of the refractory material is partially compromised and hence less magnesia is

present in the refractory to resist slag attack during service. Brucite layer formed on top of the refractory surface is weakly bonded and easily washed out by the liquid slag. Refractory specialists are concerned by the loss of valuable magnesia crystallites. When magnesia grains are observed under an optical microscope, scanning probe microscope (SPM) or scanning electron microscope (SEM), crystallites of periclase show varying degree of attack by the moisture depending on the crystallographic orientation of the crystallites. This is evident in most micrographs of industrial magnesia bricks stored for long times (Fig. 1a) or those exposed to high humidity (Fig. 1b). MgO single crystal substrates are also frequently used in epitaxial thin film growth [8,9]. Hence degradation of single crystal MgO by moisture related with storage conditions effects structural quality of thin films and devices made on MgO substrates for various microelectronic applications [10,11]. Delplancke-Ogletree et al. studied the effect of annealing and exposure time on brucite growth on (1 0 0) single crystals [12]. Lee et al. investigated the effects of moisture on single crystals of different orientations of MgO that are grown via thin film deposition [13]. But no study has yet been done on the degree of chemical attack of moisture on MgO bulk single crystals as function of crystallographic orientation. This study is

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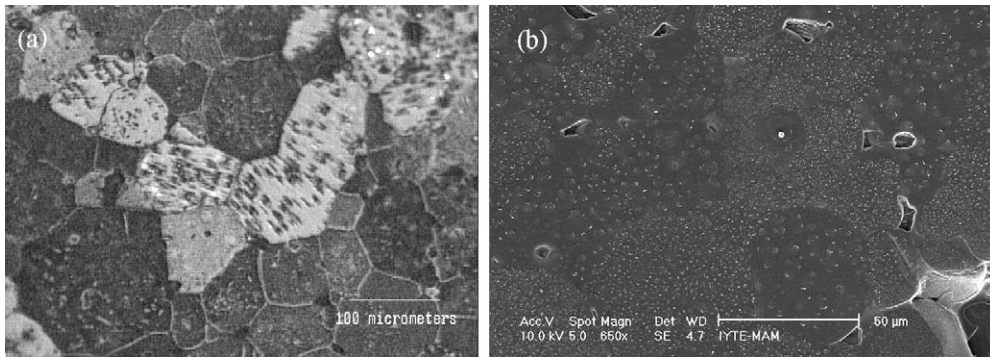


Fig. 1. Commercial magnesia refractory specimen: (a) optical microscope image in plane polarized light mode of polished surface, (b) SEM image of hydrated magnesia grains after exposure to 88% humidity for 18 h.

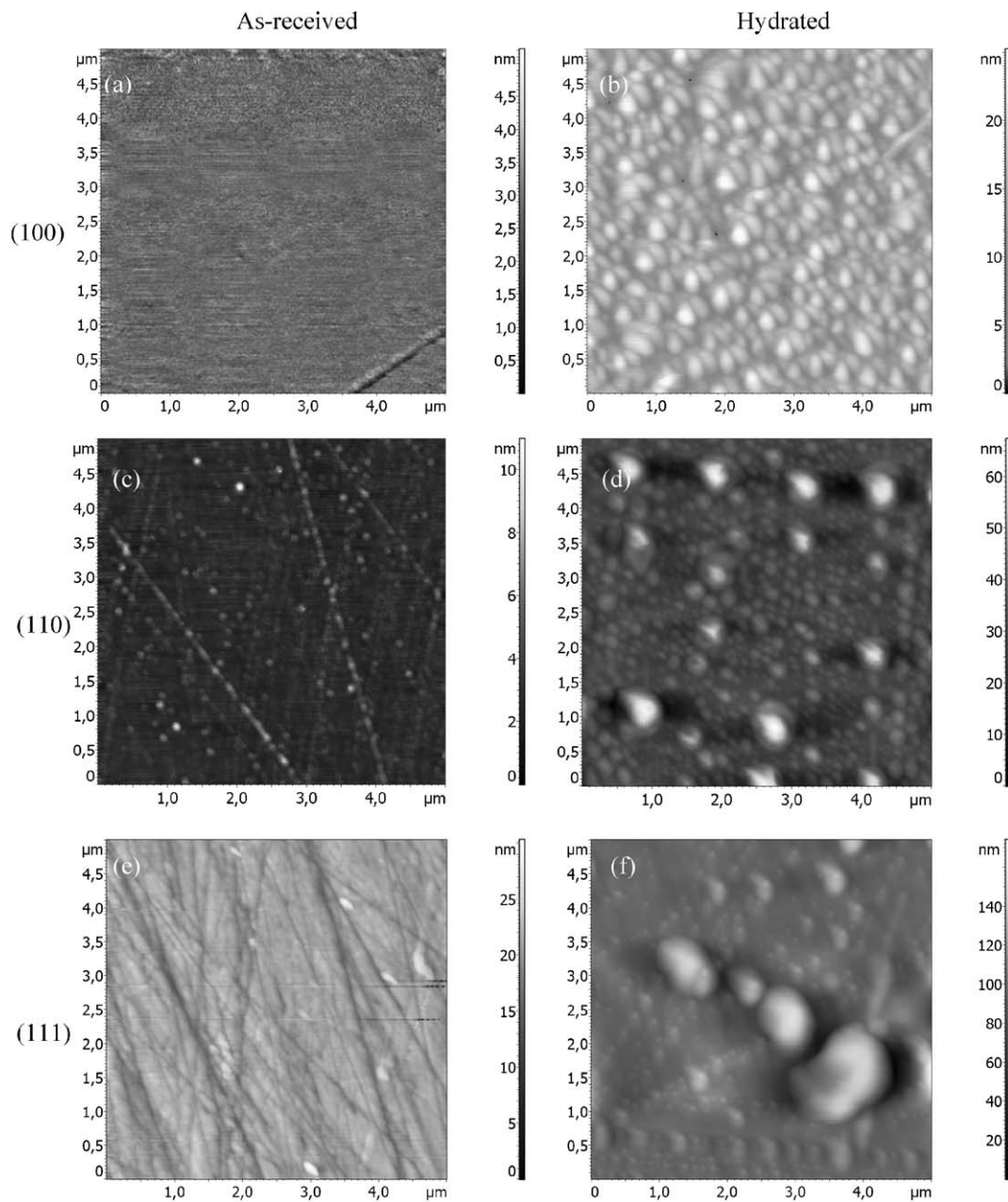


Fig. 2. 2D SPM images of MgO single crystals: (a) as-received (1 0 0), (b) hydrated (1 0 0); (c) as-received (1 1 0), (d) hydrated (1 1 0), (e) as-received (1 1 1), (f) hydrated (1 1 1).

performed in order to find out the influence of crystallographic orientation on hydration of MgO single crystal substrates.

2. Experimental

A commercial refractory brick was polished and observed in an optical microscope (Nikon L150). Three different (1 0 0)-, (1 1 0)-, and (1 1 1)-oriented and one-side polished MgO single crystals (Sigma–Aldrich) were used to investigate their hydration behaviors. First, the surface morphologies of commercially as-received MgO single crystals were examined by scanning probe microscopy (Solver Pro from NT-MDT, SPM) and scanning electron microscope (Philips XL-30SFEG, SEM). Then, polished surfaces of the samples were left in a hydration chamber with an 88% relative humidity for 18 h at room temperature. The effect of humidity on the samples was examined by SPM and SEM. The samples were scanned in SPM on a $5\ \mu\text{m} \times 5\ \mu\text{m}$ surface areas using semi-contact mode. The data of the AFM surface topography was analyzed using the Image Analysis 2.2.0 SPM software (NT-MDT). As-received and hydrated MgO single crystals were examined by X-ray diffraction (Panalytical X-Pert Pro, XRD). Also, grazing incidence (GIXRD) was performed using $\text{CuK}\alpha$ radiation at an angle of $\omega = 1^\circ$ to reveal the crystal structure of the hydrated MgO surfaces.

3. Results and discussion

Two different polycrystalline MgO brick specimens were used to investigate the effect of humidity. The first specimen was stored in a moist room for long periods of time while a second sample was polished and exposed to 88% humid air for 18 h in a chamber. Magnesia grains of the first specimen are shown in Fig. 1a in plane polarized mode which indicates different amount of moisture attack due to different crystallographic orientations of crystallites. Magnesia crystallites in the second specimen were also affected by humidity as shown in Fig. 1b.

Such differences in vulnerabilities to moisture by different grains prompted this study to understand which directions were more susceptible. Three MgO single crystals with (1 0 0)-, (1 1 0)-, and (1 1 1)-orientations and with the surface dimension of $10\ \text{mm} \times 10\ \text{mm} \times 0.5\ \text{mm}$ were subjected to a humid atmosphere to determine their hydration behavior and also the effect of the crystallographic orientation on hydration. Fig. 2 shows surface morphologies ($5\ \mu\text{m} \times 5\ \mu\text{m}$) of (1 0 0)-, (1 1 0)-, and (1 1 1)-oriented MgO surfaces, either as-received or hydrated.

The magnesia single crystals were tested in humid atmosphere inside a closed aluminum SPM hood. The MgO single crystal samples were clamped in the SPM sample holder, so that real time measurements could be made to check for the progress of Brucite formation. Fig. 3 shows how $\text{Mg}(\text{OH})_2$ grows on the oriented MgO crystal surface after 18 h. Polishing scratches were observed on the surfaces of as-received samples. After hydration, magnesium hydroxide formed both as clusters around the scratches and on flat areas. As shown in both Figs. 2

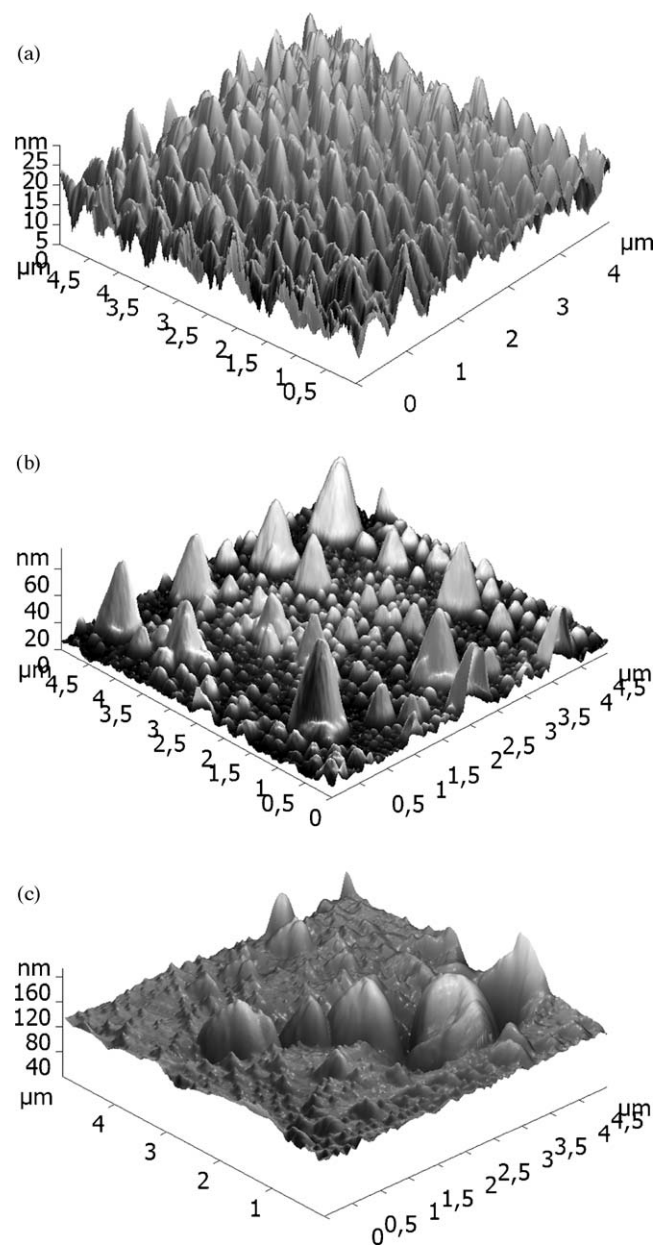


Fig. 3. 3D SPM images of hydrated MgO single crystal: (a) (1 0 0)-oriented, (b) (1 1 0)-oriented, (c) (1 1 1)-oriented.

and 3, the MgO crystals with (1 1 1)-orientation have larger brucite grains compared to (1 1 0) while smaller brucite grain features were observed on (1 0 0) surfaces. This implies that the MgO with (1 1 1)-orientation has the highest tendency to hydrate than the other orientations. As can be seen from hydrated (1 1 0)- and (1 1 1)-oriented samples, when the size of magnesium hydroxide clusters increased, their total number decrease. In the (1 1 1) sample a maximum hydrated layer thickness of 174 nm was achieved after 18 h of exposure to 88% humidity at room temperature. After a month of exposure to the same humid atmosphere a hydrated layer of roughly $7\ \mu\text{m}$ is expected to form on the surface. This is a significant amount of materials loss for refractories producers.

Fig. 4 shows SEM images of (1 0 0)-, (1 1 0)-, and (1 1 1)-oriented MgO surfaces, either as-received or hydrated.

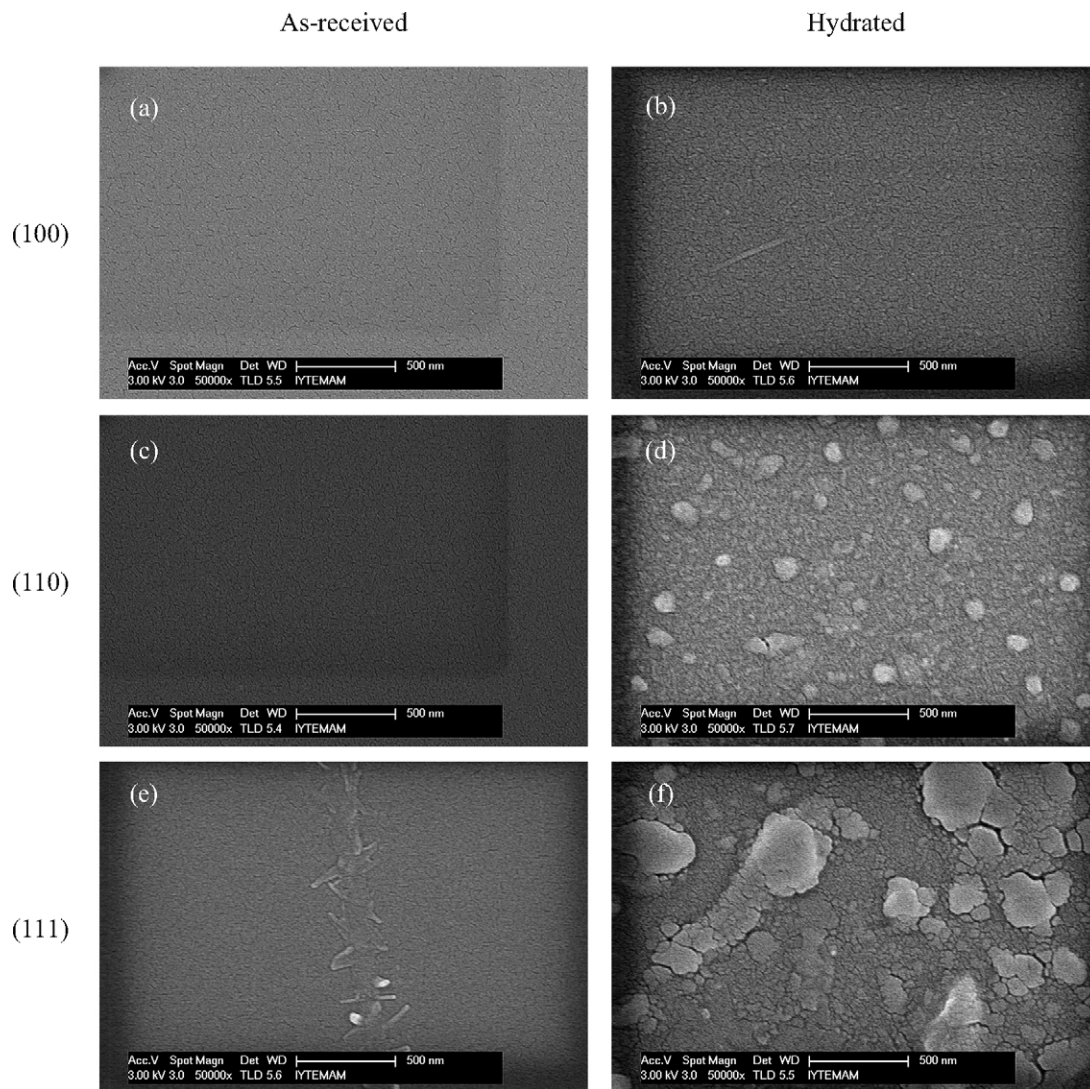


Fig. 4. SEM images of MgO single crystals: (a) as-received (1 0 0), (b) hydrated (1 0 0); (c) as-received (1 1 0), (d) hydrated (1 1 0), (e) as-received (1 1 1), (f) hydrated (1 1 1).

Polishing scratches on surfaces act like nucleating sites for hydrate formation. The (1 0 0)-oriented MgO surface showed a more stable attitude compared to other crystallographic orientations against air and humid effects. Magnesium hydroxide formed partially on (1 1 0) surface, whereas almost completely covered the (1 1 1)-oriented MgO surface. The hydrate formation occurred in the form of large clusters of roughly 400 nm in diameter in the (1 1 1) sample (Fig. 4f) and

smaller hydrates were observed in Fig. 4d and b for (1 1 0) and (1 0 0), respectively.

The SPM and SEM results showed that the crystallographic orientation has an important influence on hydration degree of the MgO. Refson et al. showed that water molecules physisorb readily on the perfect MgO (0 0 1) surface, while dissociative chemisorption of water is energetically favored at low-coordinated surface defect sites only [14]. Therefore, surface

Table 1
Surface roughness of MgO single crystals.

Orientation	As-received			Hydrated		
	(1 0 0)	(1 1 0)	(1 1 1)	(1 0 0)	(1 1 0)	(1 1 1)
Amount of sampling	65536	65536	65536	65536	65536	65536
Maximum height	5.2 nm	10.9 nm	30.2 nm	25.2 nm	67.2 nm	174.6 nm
Average (mean height)	2.8 nm	2.9 nm	20.6 nm	13.1 nm	26.9 nm	91.0 nm
Average roughness (R_a)	0.25 nm	0.48 nm	1.16 nm	2.95 nm	5.05 nm	10.28 nm
Root mean square (RMS) (R_q)	0.34 nm	0.70 nm	1.52 nm	3.69 nm	7.54 nm	16.23 nm

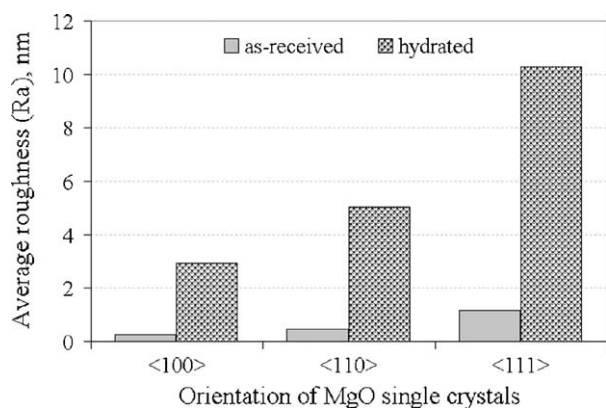


Fig. 5. Average roughness of single crystals.

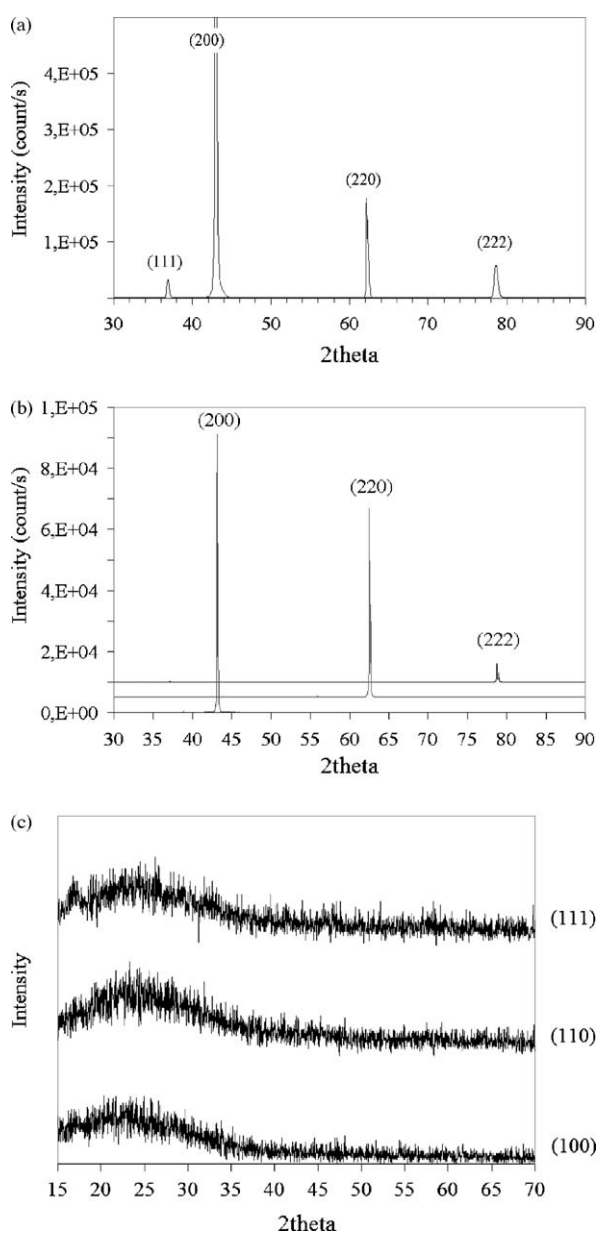


Fig. 6. XRD charts of MgO single crystals: (a) as-received, (b) hydrated, (c) grazing incidence measurement of the hydrated surface.

hydroxyl groups cause protrusions consisting of poorly ordered hydroxide. This is because the protonation of the MgO (1 1 1) creates a surface with the same structure as the Mg(OH)₂ (0 0 0 1) cleavage plane, and this may stabilize MgO (1 1 1) surface [14]. MgO has a higher tendency to hydrate when the atoms on the plane have a coordination number of 3 and a lower tendency to hydrate for a coordination number of 5 [13].

Surface roughness values of as-received and hydrated samples is given in Table 1. Average roughness value of hydrated (1 0 0) surface was about 3 nm, which was almost the same for similar times with that of Delplacke-Ogletree et al. [8]. As can be clearly seen from Fig. 5, average roughness values of (1 1 1) surface was higher than the others. Especially, (1 1 1)-MgO surface is more sensitive than the others to humid atmosphere. This could be attributed to the higher planar density in this particular orientation as the atoms on the surface of the MgO (1 1 1), (1 1 0) and (1 0 0) planes have a coordination number of 3, 4 and 5, respectively [13]. The magnesium oxide (1 1 1) plane will hydrate faster and (1 0 0) plane will hydrate slower.

Before and after exposure to humidity, surfaces of samples were characterized with 2θ - ω and grazing incidence X-ray diffraction (GIXRD) at low incidence angles of 1°. The purpose was to identify any brucite formation on the surface. The very thin layer of brucite, of course, could not be analyzed by powder XRD machine which operates at large incidence angles (e.g. 1–90° 2 θ). The incident X-ray beam in GIXRD will cover more distance in the surface layer at low incidence angles of 1°. As-received (1 0 0)- and (1 1 0)-samples had single peaks for (2 0 0) and (2 2 0) at 42.9° and 62.2°, respectively. But (1 1 1)-sample had two peaks for (1 1 1) at 36.9° and for (2 2 2) at 78.7° (Fig. 6a). No change was observed on the sample surfaces as a result of humidity exposure because whatever formed on the surface was not well crystallized (Fig. 6b). According to GIXRD results, the samples had one bump around 15–30° suggesting an amorphous structure after exposure to humidity (Fig. 6c).

In the literature it was found that MgO single crystals of (1 0 0) orientation is used for most electronic substrates. This orientation is least susceptible to moisture attack among other orientations [13,14].

4. Conclusions

It was found that crystallographic orientation of MgO single crystals affects the degree of hydration in moist atmosphere. (1 0 0)-oriented MgO surface is more stable as compared to other crystallographic orientations against air and humidity effects. (1 1 1)-MgO surface is worst affected from humid atmospheres. Hydrate of magnesium formation partly occurred at (1 1 0) surface, whereas almost completely observed on (1 1 1) surface. Degree of crystallinity of the hydrate layer on the surface was found to be little developed when GIXRD data was analyzed. SEM observations also confirmed the amorphous morphology of the surface layer. Polishing scratches on surfaces act like nucleating sites for hydrate formation. The differences in orientation of crystals can lead to different

hydration behavior of commercial MgO refractories during storage.

Acknowledgements

The authors would like to thank IYTE-MAM staff Mrs. Duygu Oguz Kilic for her helps in SEM analysis of the samples. Special thanks are due to Mr. Serdal Okur for GIXRD analysis.

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