

Examination on the mechanical performance of carbonate binders at micro level via combination of nano-indentation and backscattered electronic microscopy

Liwu Mo, College of Materials Science and Engineering/State Key Laboratory of Materials-Oriented Chemical Engineering, Nanjing Tech University, 30 South Puzhu Road, Nanjing, 211800, China. andymoliwu@njtech.edu.cn

Yuanyuan Hao, College of Materials Science and Engineering, Nanjing Tech University, 30 South Puzhu Road, Nanjing, 211800, China

Min Deng, College of Materials Science and Engineering, Nanjing Tech University, 30 South Puzhu Road, Nanjing, 211800, China

INTRODUCTION

Carbonate binders, which mainly consists of Ca- or Mg-bearing carbonates, attracted increasing attentions in recent years in the context of CO₂ emission cutting and development of alternative non-clinker cement. The carbonate binders are normally prepared via the accelerated carbonation of Ca and/or Mg rich raw materials, e.g. reactive MgO, steel slag, fly ash, etc. [1-3]. The mechanical performance improvement of the carbonated calcium or magnesium material is mainly attributed to the dense and interlocked network structures of the carbonate products. However, there is absence of study on understanding the relationship between the microstructure and macro performance of the carbonate binders.

Magnesium slag is a byproduct produced during the manufacture process of metal magnesium, which has high contents of CaO and MgO and thus might possess a high potential to be used as the raw material to prepare carbonate binder. In the present study, a carbonate binder was prepared via the CO₂ activation of magnesium slag pastes. The mechanical performance and microstructure of the carbonate binders were examined. To furthermore understand the performance development of the carbonate binder, the mechanical performance of carbonate binders at micro level via combination of nano-indentation and backscattered electronic microscopy. This study is believed to provide a new way for preparing novel alternative carbonate binders and also the way used for the examination on mechanical performance at micro-level worth sharing.

MATERIALS AND METHODS

Magnesium slag, a byproduct produced during the manufacture of metal magnesium, from Shanxi, China, was used in this study. The magnesium slag contains 53.86 wt. % CaO and 7.24 wt. % MgO. The magnesium slag mainly consists of calcium silicate

with various forms of beta-larnite, hatrurite, γ -dicalcium silicate, periclase, and a small amount of lime.

The magnesium slag powder was mixed in a paste mixer with water at a given water-to-slag ratio (W/S) at a low speed for 2 min and then at a high speed for another 2 min to obtain homogenous mixtures. Then the fresh mixtures were cast into molds to prepare cubic paste specimens with size of $20 \times 20 \times 20$ mm. After 2d of moist curing, the paste cubes were demoulded and cured under moist condition with a relative humidity of 98% for 3 more days. Then all the paste cubes were pre-dried under the condition with a temperature of 23 ± 2 °C and a relative humidity of 30~40% for 24 ± 2 h. One batch of the paste cubes were selected for performance examination before the CO₂ curing for reference. Another three batches of the paste cubes were then placed in the carbonation chamber. The chamber was vacuumed to remove air and then the CO₂ with a concentration of 99.9 wt. % was injected into the chamber. After being cured in the chamber for different curing ages, namely 1 d, 3 d and 14 d respectively, the magnesium slag pastes were used for relevant performance examination. For the test at each curing age, one batch of paste cubes were used.

The carbonated magnesium slag pastes were ground into fine powders with particle size smaller than 80 μ m, and then were examined with X-ray diffraction (XRD, SmartLab X-ray diffractometer, Rigaku Co. Japan) with Cu K α radiation ($\gamma = 1.5418$ Å) and a scanning 2θ range of 5°-80° to identify the mineral phases in the pastes. After 1 d, 3 d and 14 d of CO₂ curing, the compressive strengths of the magnesium slag pastes with various W/S ratios were test respectively. The pore structure of carbonated magnesium slag paste was examined via using Mercury Intrusion Porosimetry (MIP). Scanning Electronic Microscope (SEM) coupled with EDX spectroscopy was employed to investigate the morphology of the carbonated magnesium slag paste and the paste prior to CO₂ curing for comparison.

The paste was vacuum dried, epoxy impregnated, polished, and carbon coated. Then after, the polished sample was investigated by using SEM with a BSE mode. To examine the micro-mechanical property, the polished magnesium slag pastes were polished and investigated by using a NanoTest Advantage instrument (MicorMaterials, UK). For each test, a grid of 10×10 points, evenly spaced by 6 μ m, was performed on the polished sample. During the indentation, the load was linearly increased up to a maximum load of 5 mN in 10 s, kept constant for 10 s, and linearly decreased in 10s. BSE coupled with EDS was employed to investigate the same specimen tested by the grid indentation. After the nanoindentation test, the indentation zone was imaged with the BSE mode as well as the secondary electron mode to identify each indent. This facilitates to obtain the indentation modulus and hardness on each specific phase in the carbonated sample. Magnesium slag paste with a W/S ratio of 0.25 after 14 d of CO₂ curing was used for the nanoindentation test. For comparison, the nanoindentation was also conducted on the hydrated magnesium slag paste without CO₂ curing.

RESULTS

Figure 1 shows the XRD patterns of the magnesium slag pastes exposed to CO₂ curing for different ages. After CO₂ curing, regardless of exposure time and W/S ratios, obvious diffraction peaks of calcite and vaterite were observed, implying the calcite and vaterite were the main calcium carbonates formed in the magnesium slag pastes.

Figure 2 shows the compressive strengths of the magnesium slag pastes before and after CO₂ curing. After being subjected to CO₂ curing, the compressive strengths of the magnesium slag pastes are increased significantly.

Figure 3 shows the pore structures of magnesium slag pastes before and after CO₂ curing. In terms of the total pore volume, it is much smaller in the carbonated magnesium slag paste than that in the magnesium slag paste before carbonation. In addition with the increasing carbonation curing, the total pore volume is decreased.

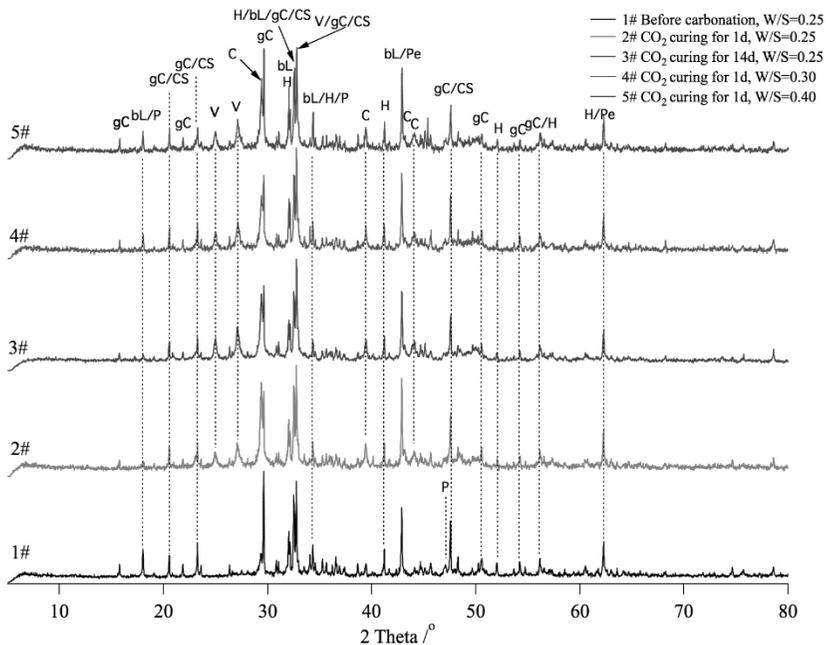


Figure 1: XRD patterns of the magnesium slag pastes before and after CO₂ curing (bL: β -larnite, C: calcite, CS: calcium silicate, gC: γ -dicalcium silicate, H: hatrurite, P: portlandite, Pe: periclase, V: vaterite)

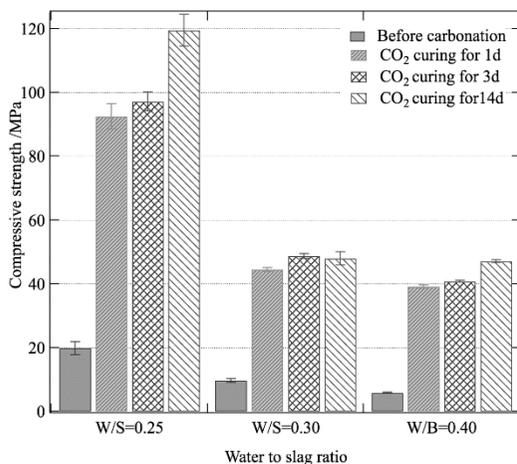


Figure 2: Compressive strengths of magnesium slag pastes before and after CO₂ curing

Figures 4 and 5 show the typical SEM morphology and BSE images of magnesium slag pastes before and after carbonation. Obviously before the CO₂ curing, the microstructure of the magnesium slag paste is very porous with abundant uncarbonated calcium silicate particles (Figures 4a and 5a). The microstructure of the carbonated magnesium slag paste is much denser than that of the paste before CO₂ curing as shown in Figures 4b and 5b.

Figure 6 shows the indentation grid and the maps of nanoindentation elastic modulus and hardness. A grid of 10×10 was drawn in the BSE image of sample and each crossing point of the dash lines represents one indentation (Figure 6a). The elastic modulus and hardness of each point are clearly illustrated via the combination of the grid and the maps. The average elastic modulus and hardness of the carbonate products substance are 50.5 ± 9.5 GPa and 2.2 ± 0.6 GPa respectively, while they are 85.9 ± 16.1 GPa and 4.0 ± 1.2 GPa for the uncarbonated calcium silicate particles. For the hydrated magnesium slag paste, the average elastic modulus and hardness of the hydration product substance excluding calcium silicate phases are 23.1 ± 3.8 GPa and 0.8 ± 0.2 GPa respectively (Figure 7), which are much lower than that of the calcium carbonate substance. In addition the modulus and hardness of the uncarbonated calcium silicate phase in the hydrated magnesium slag paste are 37.6 ± 10.4 GPa and 1.4 ± 0.6 GPa respectively, which are also lower than that of the uncarbonated calcium silicate phase embedded in the CO₂ activated magnesium slag paste.

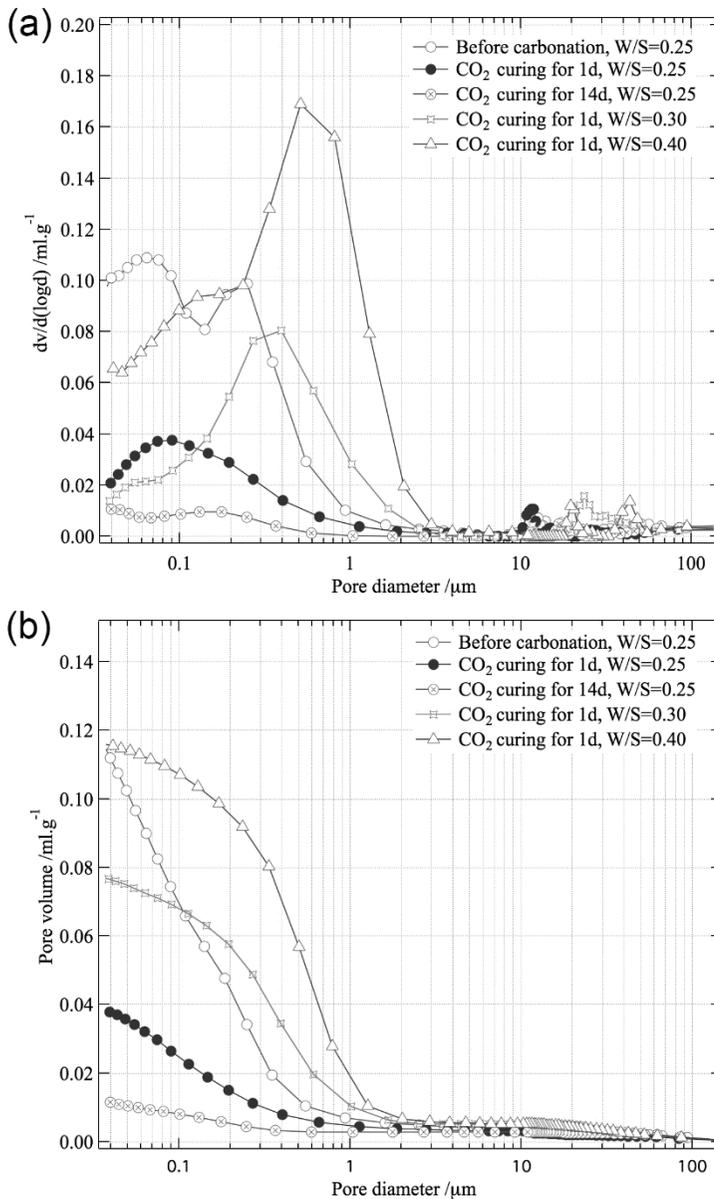


Figure 3: Pore structures of magnesium slag pastes before and after CO₂ curing. (a) pore size distribution and (b) cumulative pore volume.

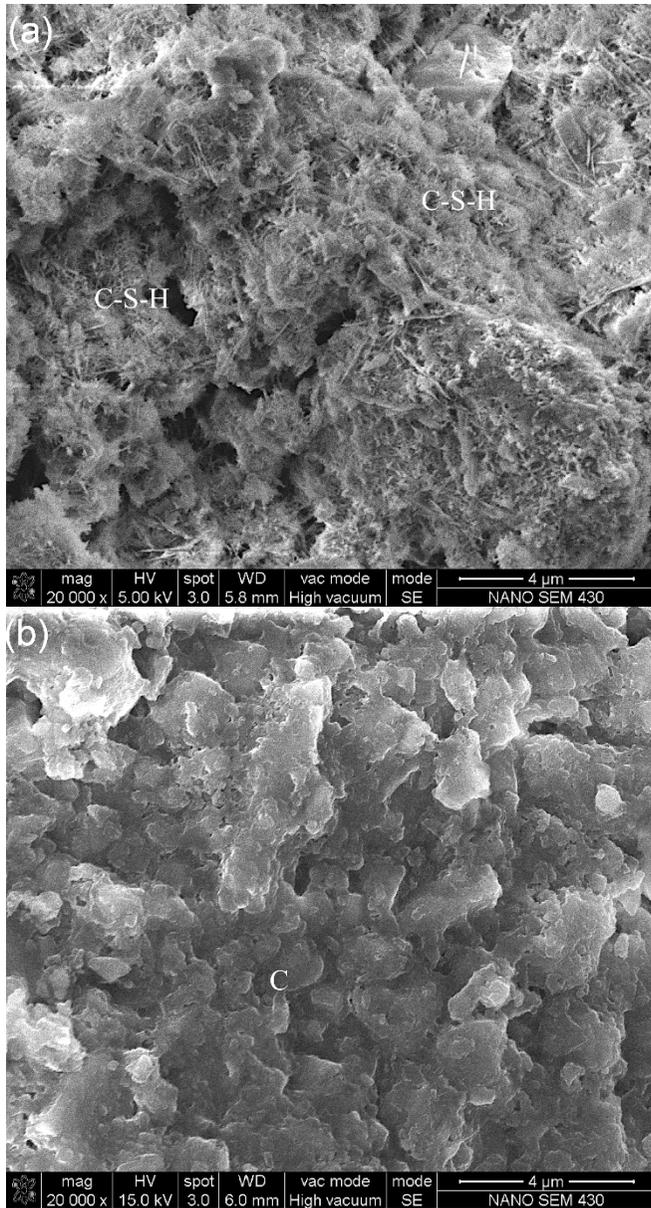


Figure 4: SEM morphology of the W/S magnesium slag pastes (a) before and (b) after 1 d CO₂ curing. C: calcium carbonate

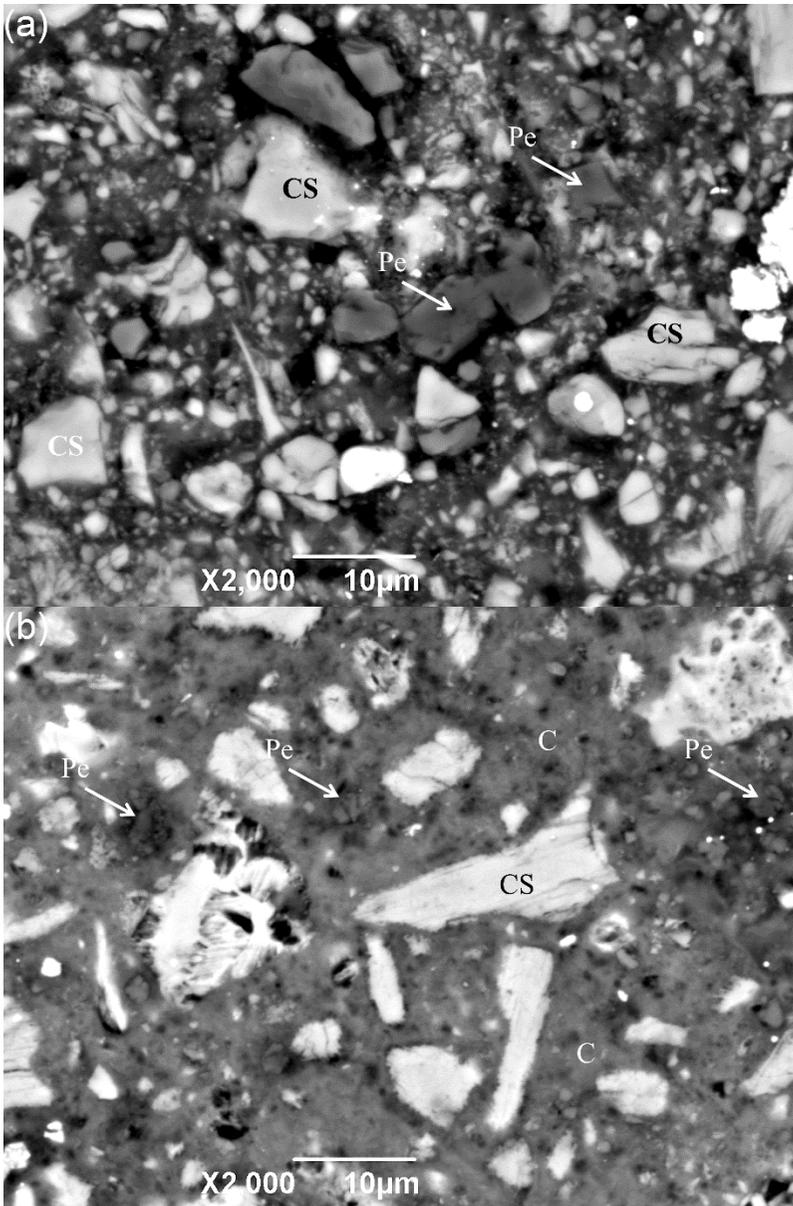


Figure 5: BSE image of the magnesium slag paste (a) before carbonation, and (b) after carbonation. C: calcium carbonate, CS: calcium silicate, Pe: periclase

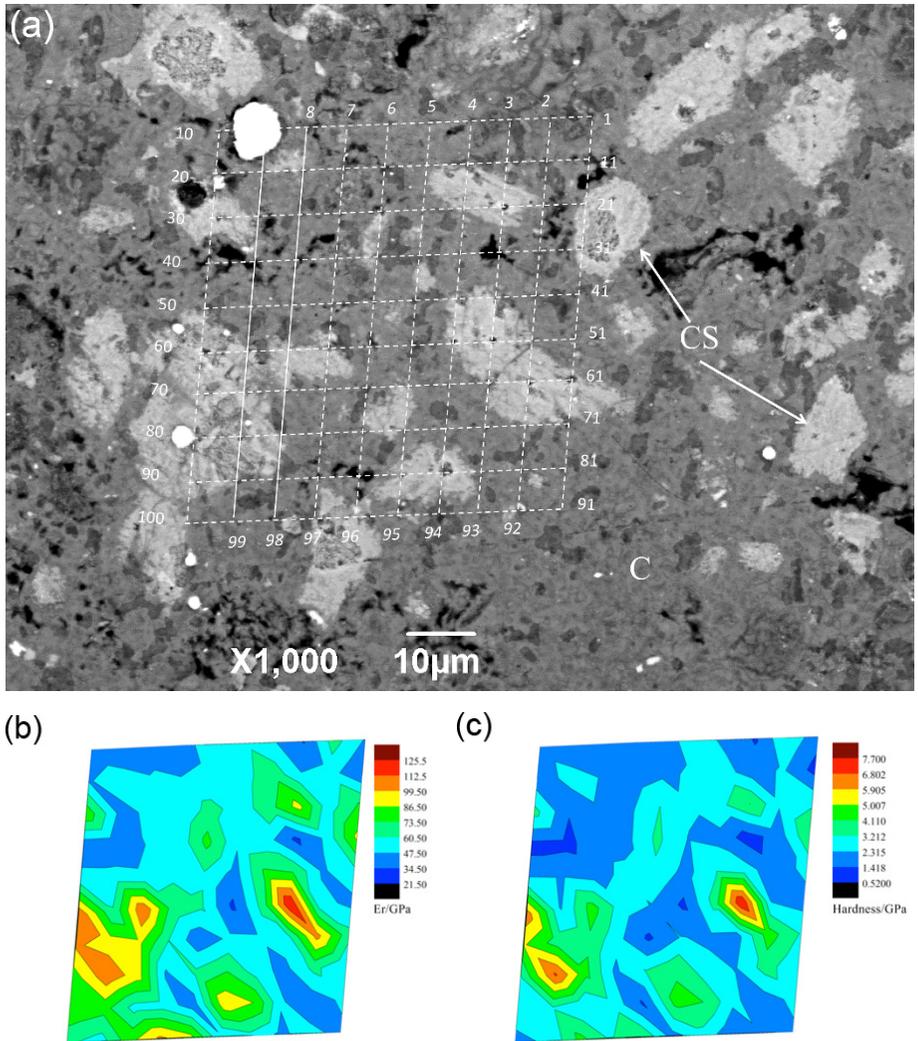


Figure 6: Nanoindentation of CO₂ activated magnesium slag paste. (a) indentation grid on the BSE image, (b) map of nanoindentation elastic modulus, and (c) map of nanoindentation hardness. C: calcium carbonate, CS: calcium silicate

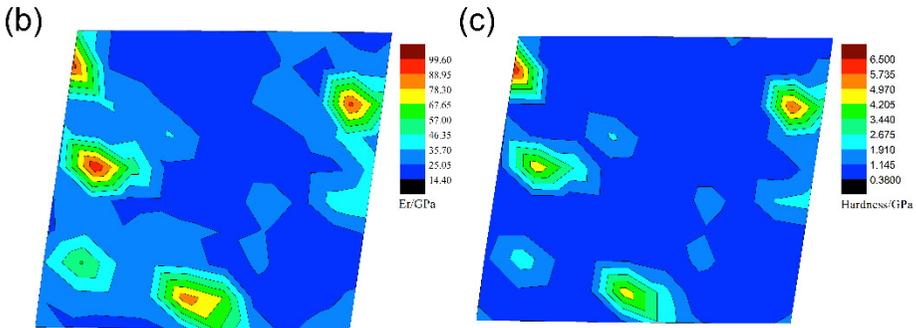
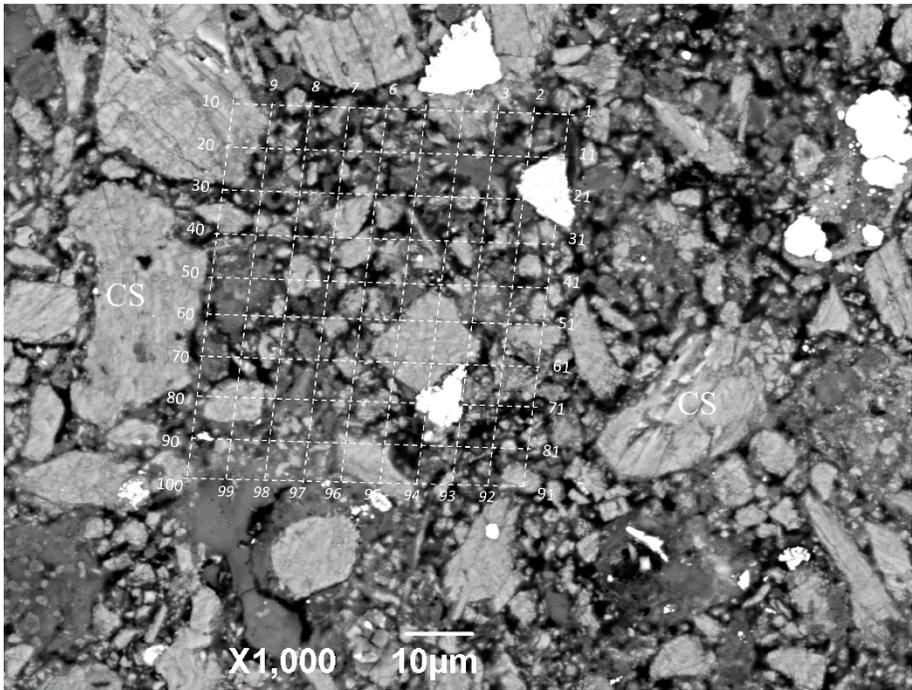


Figure 7: Nanoindentation on the hydrated magnesium slag paste. (a) indentation grid on the BSE image, (b) map of nanoindentation elastic modulus, and (c) map of nanoindentation hardness. CS: calcium silicate

CONCLUSION

Calcium carbonate binders with high and rapidly developed compressive strengths are prepared via carbonating the magnesium slag paste under CO₂ curing. The compressive strengths of the magnesium slag pastes after only 1 d of CO₂ curing are increased by up to 4.7 times in comparison to that of the pastes prior to CO₂ curing, and it reaches up to 119.5 MPa after 14 d of CO₂ curing. This is mainly attributed to the formation of calcium carbonates in terms of calcite and vaterite due to the carbonation of calcium silicates, which leads to an enhanced product matrix with dense microstructure in terms of reduced pore diameter and total porosity. The carbonate products matrix exhibits high nanoindentation elastic modulus and microhardness, being 50.5 ± 9.5 GPa and 2.2 ± 0.6 GPa respectively, which are much higher than 23.1 ± 3.8 GPa and 0.8 ± 0.2 GPa for the hydrated magnesium slag pastes. The reaction degree of periclase involved in carbonation is quite limited.

ACKNOWLEDGEMENTS

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