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Hydrothermally-grown Monetite ($CaHPO_4$) on Hydroxyapatite

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Abstract: Using sintered hydroxyapatite as substrate and reagent grade CaO, P_2O_5 and deionized water as raw materials for hydrothermal reaction, monetite ($CaHPO_4$) could be deposited on the surface of hydroxyapatite under an autogeneous pressure of 1.55–8.59 MPa at 200–300°C. The deposition rate of monetite increased with temperature and time of the reaction. Under 8.59 MPa at 300°C, small needle-like crystals of monetite were present after 8 h. After 72 h, the diameter and length of the needle-like crystals became larger and the clusters of crystals were more pronounced. After growing for 120 h at 300°C, the crystal morphology changed and the needle-like crystals coalesced into granular grains. © 1998 Elsevier Science Limited and Techna S.r.l. All rights reserved

1 INTRODUCTION

Much effort has been undertaken to develop and synthesize calcium phosphate ceramics because of the close chemical and crystallographical similarity of these materials to human bone. Thermal formation of hydroxyapatite powder (HAP) from $Ca_3(PO_4)_2$ and CaO in the presence of water vapour was studied by Monma and Kanazawa,[1] in which the conversion of $Ca_3(PO_4)_2$ to hydroxyapatite occurred within 50 min. at the firing temperature of 1300°C. Plasma spraying was employed commercially for coating hydroxyapatite on to total hip prostheses, and experimentally for coating amorphous calcium phosphate on to stainless steel by Liu *et al.*[2] By an alternative approach, Monma[3,4] studied an electrochemical method using an electrolyte of $Ca(H_2PO_4)_2{\cdot}H_2O$ solution to deposit brushite $(CaHPO_4){\cdot}2H_2O$, monetite ($CaHPO_4$) and apatite on to stainless steel substrates. Similarly, Ban and Maruno[5,6] produced calcium phosphate coatings by the electrochemical process, but the medium was a simulated body fluid. In this study, it was found that amorphous calcium phosphate coatings were obtained at temperatures of 5°C, 22°C and 37°C, but the coatings contained $Mg(OH)_2$, $CaCO_3$ and carbonate apatite of low crystallinity when processed at 52°C and 66°C. Kokubo and co-workers[7–11] have thoroughly studied the biomimetic processes. They immersed $CaO–SiO_2$ based glass, silica gel and titania in a simulated body fluid to induce apatite nucleation and growth on the substrates that contained polymer and alumina. Glass-reinforced hydroxyapatite composite was studied by Santos *et al.*;[12] the composite was immersed in a simulated physiological solution and bioactive apatite was produced after the Ca and Si ions leached out from the surface of the composite.

Under hydrothermal conditions, Hattori *et al.*[13–15] used $Ca_2P_2O_7$ and CaO as starting materials to prepare hydroxyapatite powders; after 3 h at 350°C and 30 MPa the synthesized powders were composed of aggregates of hydroxyapatite with diameters ranging from 1 to 2 μm. At 70 MPa and 398°C, transformation of $Ca_2P_2O_7$, CaO and H_2O into hydroxyapatite was quite rapid and almost complete within 1 h. When only $Ca_2P_2O_7$ and H_2O were used as raw materials at 80 MPa and 500°C, hydroxyapatite was detected after 96 h. The hydrothermal process enables formation of calcium phosphate more quickly than the electrochemical process or biomimetic methods which usually need several days/weeks to accomplish, yet the hydro-

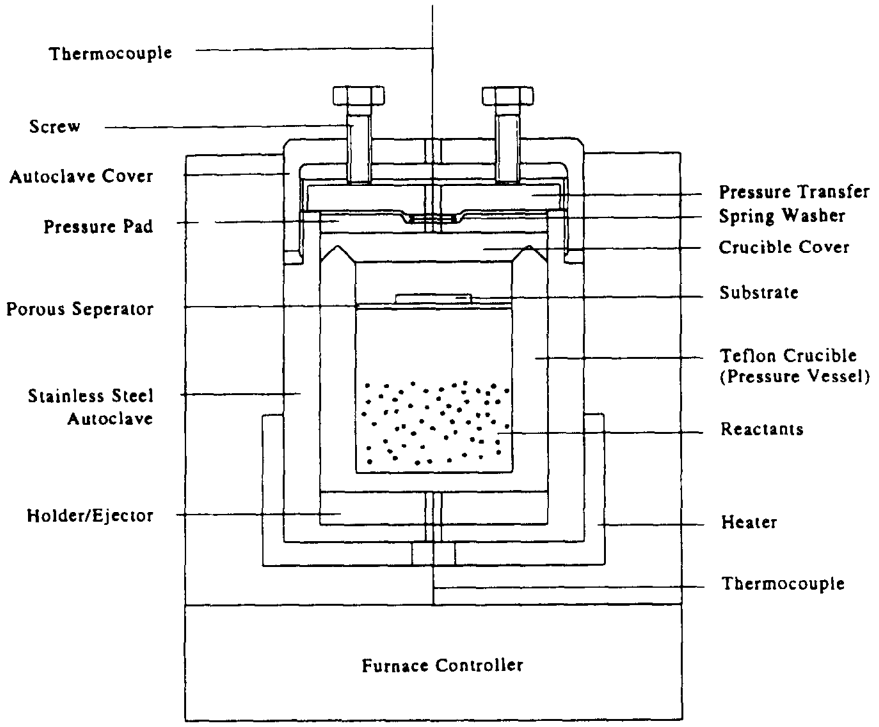

Fig. 1. Experimental setup for hydrothermal reaction.

thermal process needs higher temperature and pressure. The purpose of this study was to investigate and develop a hydrothermal process that would allow production of calcium phosphate coatings, instead of powders as in the previous work of Hattori *et al.*,[13,14,15] under a lower temperature and pressure.

2 EXPERIMENTAL PROCEDURE

Hydroxyapatite plates were used as substrate. To prepare the substrate, 0.4 g of reagent grade hydroxyapatite powders (Fluka Chemicals) were inserted into a 6 mm inner diameter die and then pressed uniaxially to 270 MPa. The compacts were then sintered at 1250°C for 1 h.

The raw materials for the hydrothermal reaction contained extra pure reagent CaO (Nippon Shiyaku Kogyo K. K.), pure reagent P_2O_5 (First Chemicals) and deionized water. Appropriate quantities of CaO (1.32 g) and P_2O_5 (1.00 g) powders were mixed in a mortar and inserted into a 12 ml cylindrical teflon crucible, into which was added 0.4 ml deionized water. The experimental setup is depicted in Fig. 1. This quantity of deionized water was enough for the vapour to be saturated at 300°C.[16] The cylindrical teflon crucible had a porous separator to divide the raw materials on the lower part of the autoclave from contacting the upper substrate directly for the purpose of preventing the hydroxyapatite plate from dissolving. Then, the crucible was sealed in a stainless steel autoclave and heated to 200–300°C. In the autoclave, only the lower half was heated and the upper part of the autoclave was subjected to natural cooling. A thermal gradient of $22 \pm 2°C$ for various experimental conditions was calculated between the raw material mix and the specimen by interpolation of temperature measurements on the top and bottom of the autoclave. The test conditions of temperature, pressure and time for hydrothermal synthesis of calcium phosphate coating on hydroxyapatite substrate are shown in Table 1.

After hydrothermal reaction the specimen was prepared to conduct the XRD measurement (Siemens D5000) with CuK_α radiation, FTIR (Fourier Transform Infrared) spectra measurement (JASCO 300E) and SEM morphology observation (ABT-55).

Table 1. Calcium phosphate coating synthesized from CaO, P_2O_5 and H_2O under various hydrothermal conditions of temperature, pressure and time

Test no.	Temperature (°C)	Pressure (MPa)	Time (h)
a	300	8.59	8
b	300	8.59	72
c	300	8.59	120
d	250	3.98	72
e	200	1.55	72

3 RESULTS AND DISCUSSION

In the crucible, a thermal gradient of about 22°C was maintained between the raw material mix and the specimen. By this arrangement, the convective vapour could transfer the CaO and P_2O_5 powders from the lower part of the autoclave to the upper substrate to deposit the calcium phosphate. The evidence of mass transfer is the reaction product coated on the specimen as shown below. The XRD patterns for products of the hydrothermal reactions under various conditions are shown in Fig. 2, in which monetite, portlandite ($Ca(OH)_2$), CaO and P_2O_5 can be indentified. All of the patterns are very similar and the results show that the monetite phase was easy to grow. However, a small quantity of residual CaO was found in all of the specimens, and small residual P_2O_5 was identified in specimens b, c and d. According to reference tables,[16] the autogeneous (self-generated) pressures of saturated water vapour at 200°C, 250°C and 300°C are 1.55 MPa, 3.98 MPa and 8.59 MPa, respectively. Under these conditions, single crystals of monetite ($CaHPO_4$) were easily grown.[17] In this experiment, the chemical compositions used in each batch fall in the hydroxyapatite + portlandite + liquid region of the $CaO–P_2O_5–H_2O$ system.[17] Yet, if the raw materials were not thoroughly reacted, the reaction products may fall in the monetite + liquid region. The composition of the product in this study indicated that powder reactants were not thoroughly reacted, with the consequent shift of the reaction to the higher $H_2O + P_2O_5$ region.

The results of FTIR patterns from the specimens are shown in Fig. 3. All of the patterns are very similar except for a small difference in specimen b, which had been additionally dried before FTIR measurement. The patterns were analysed as follows: The wavenumbers near 560 and 1060 cm^{-1} were identified as the PO_4^{3-} vibration. Near 880 cm^{-1} an absorption band of HPO_4^{2-} was found. The multiple vibrations of PO_4^{3-} and $CaO/Ca(OH)_2$ occurred near 1060, 1140 and 1440 cm^{-1}. A peak at 1650 cm^{-1} was associated with the H–O–H bending motion band, 2380 cm^{-1} was the P–H stretching vibration band, 2880 cm^{-1} was the O–H stretching vibration band of HPO_4^{2-}, and 3650 cm^{-1} was the O–H stretching vibration band of water and hydroxyl groups. The FTIR patterns confirmed that the main product of the hydrothermal reaction in this study was monetite.[6,18]

Figure 4 shows the micrographs of the specimens grown under 300°C and 8.59 MPa for various periods. The reaction product in Fig. 4(a) corresponded to 8 h of reaction, and the reaction products in Fig. 4(b) and (c) were formed after 72 and 120 h, respectively. After 8 h of reaction at 300°C and 8.59 MPa (Fig. 4(a)), needle-like monetite crystals were present; the length of the crystals was 1–2 μm and the diameter was sub-micron. In

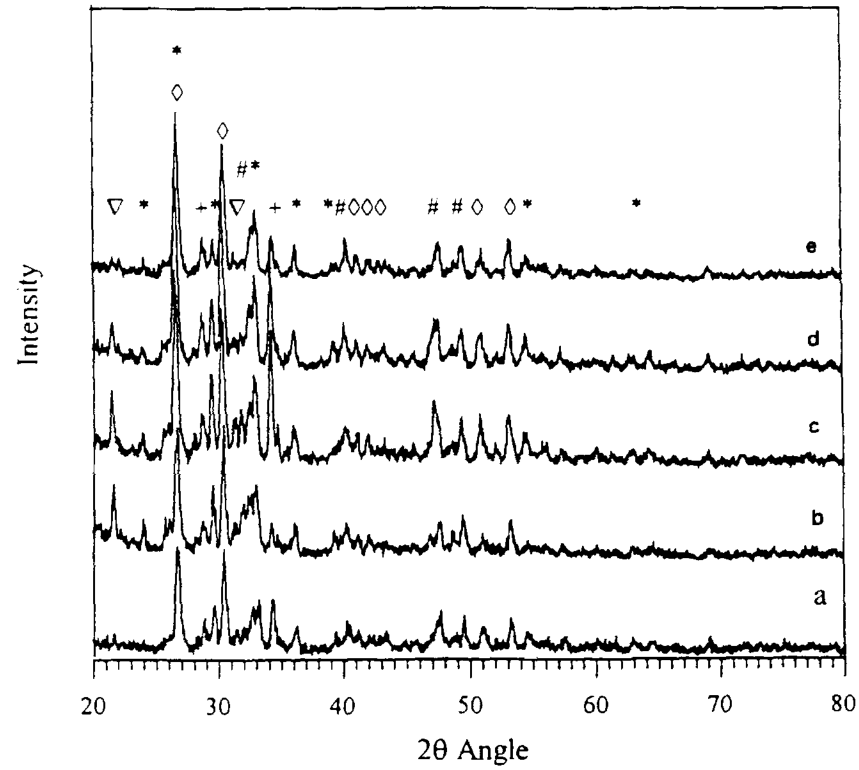

Fig. 2. The XRD patterns of the specimens grown at (a) 300°C and 8.59 MPa for 8 h, (b) 300°C and 8.59 MPa for 72 h, (c) 300°C and 8.59 MPa for 120 h, (d) 250°C and 3.98 MPa for 72 h, and (e) 200°C and 1.55 MPa for 72 h. ◇ $CaHPO_4$, # HA, P_2O_5, * CaO, + $Ca(OH)_2$.

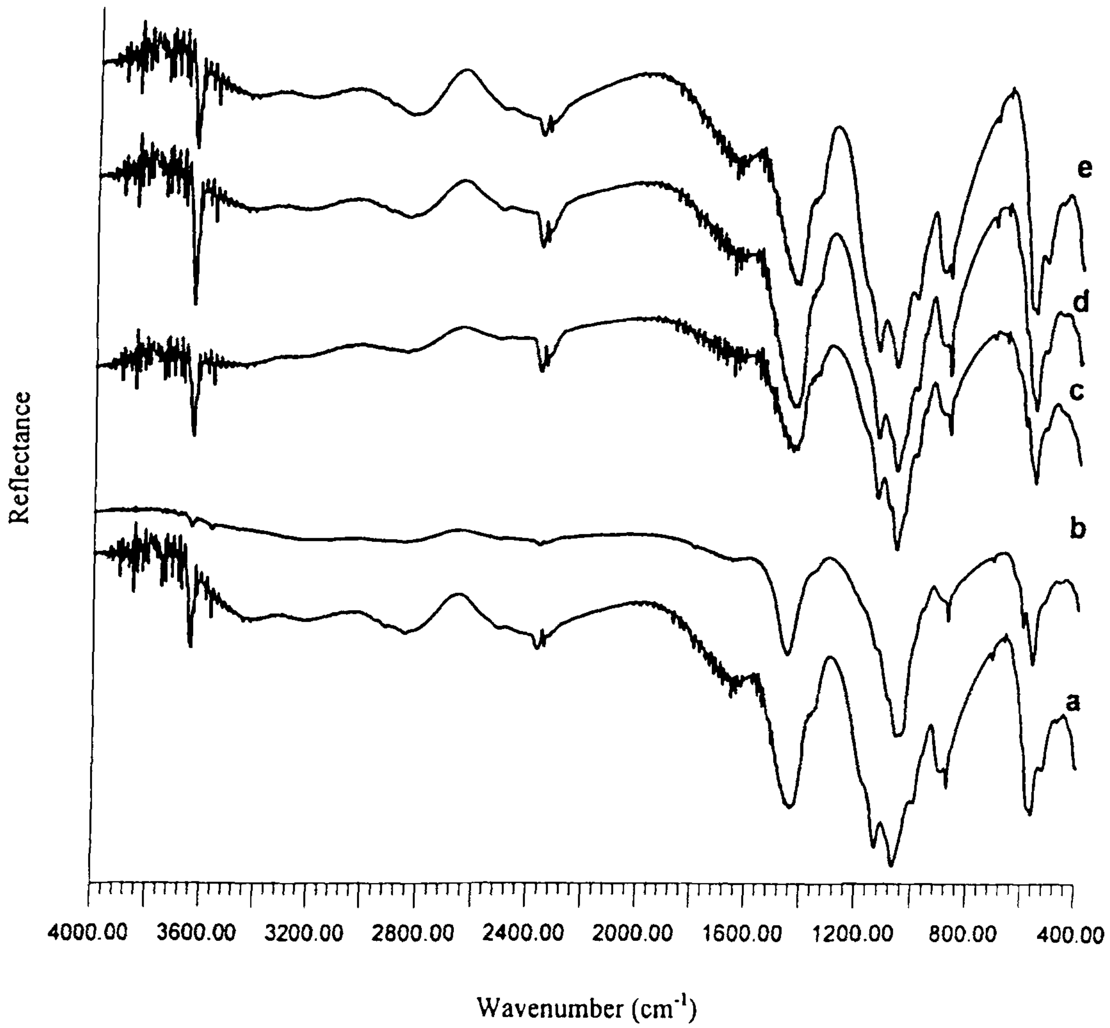

Fig. 3. The FTIR patterns of the specimens grown at (a) 300°C and 8.59 MPa for 8 h, (b) 300°C and 8.59 MPa for 72 h, (c) 300°C and 8.59 MPa for 120 h, (d) 250°C and 3.98 MPa for 72 h, and (e) 200°C and 1.55 MPa for 72 h.

the micrograph, some unreacted small particles can be observed. After 72 h of reaction (Fig. 4(b)), the length of the crystals was larger than 5 μm, their diameter was 1–2 μm, and the aspect ratio of these crystals was larger than 10. A few aggregates of granular crystals can be observed in this photograph, and the granular crystals were coalesced from the needle-like crystals. After 120 h of reaction (Fig. 4(c)), the needle-like crystals disappeared and all the crystals consisted of aggregates of granular grains with 2–3 μm in diameter. As shown in Fig. 4(c), a few small particles with diameters less than 0.5 μm existed on the substrate and they were considered to be unreacted powders.

Figure 5 compares the micrograph of the specimens after 72 h of reaction, in which the product shown in Fig. 5(a) was prepared at 200°C and 1.55 MPa, and the products shown in Fig. 5(b) and (c) were made under 250°C, 3.89 MPa, and 300°C, 8.59 MPa, respectively. In Fig. 5(a), the length of the cluster of crystals was 2–3 μm; at the bottom right of the picture, an abnormally grown petal crystal (indicated by an arrow on the micrograph) on the concave of the substrate can be detected, but the reason for its occurrence was not understood. In Fig. 5(b) and (c), the needle-like crystals were observed to exist preferentially in the concave cracks of the substrate, which confirmed that the crystals preferred to deposit on the defect sites. By comparing the crystals in all of the micrographs in this study, it may be concluded that under the same surface condition, the deposition or growth rate of the crystals increases with the temperature and time of the hydrothermal reaction.

4 CONCLUSION

Using $CaO–P_2O_5–H_2O$ as reagents for a hydrothermal reaction, monetite ($CaHPO_4$) crystals were grown easily on the hydroxyapatite substrates although the raw materials reacted incompletely. The crystal growth rate increased in proportion to the reaction temperature and time, and surface defects served as the preferred deposition sites. The morphologies of the grown monetite were needle-

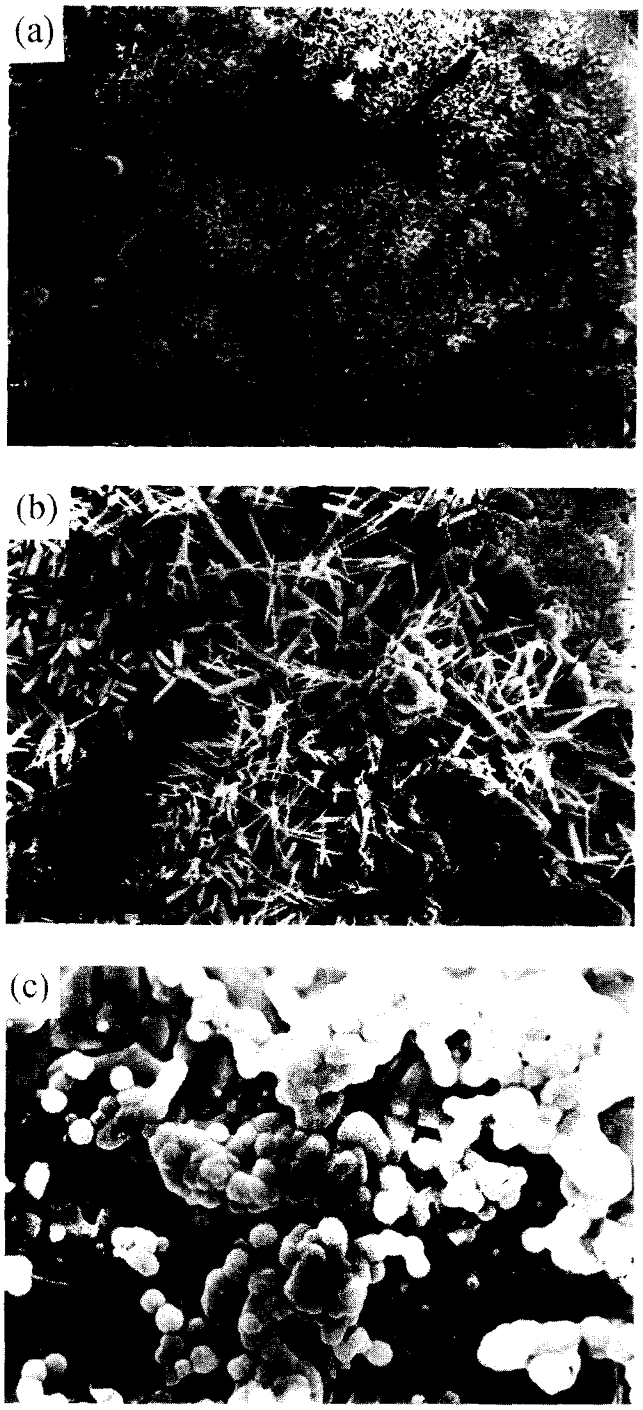

Fig. 4. The micrographs of specimens grown under the conditions of 300°C and 8.59 MPa for (a) 8 h, (b) 72 h, and (c) 120 h.

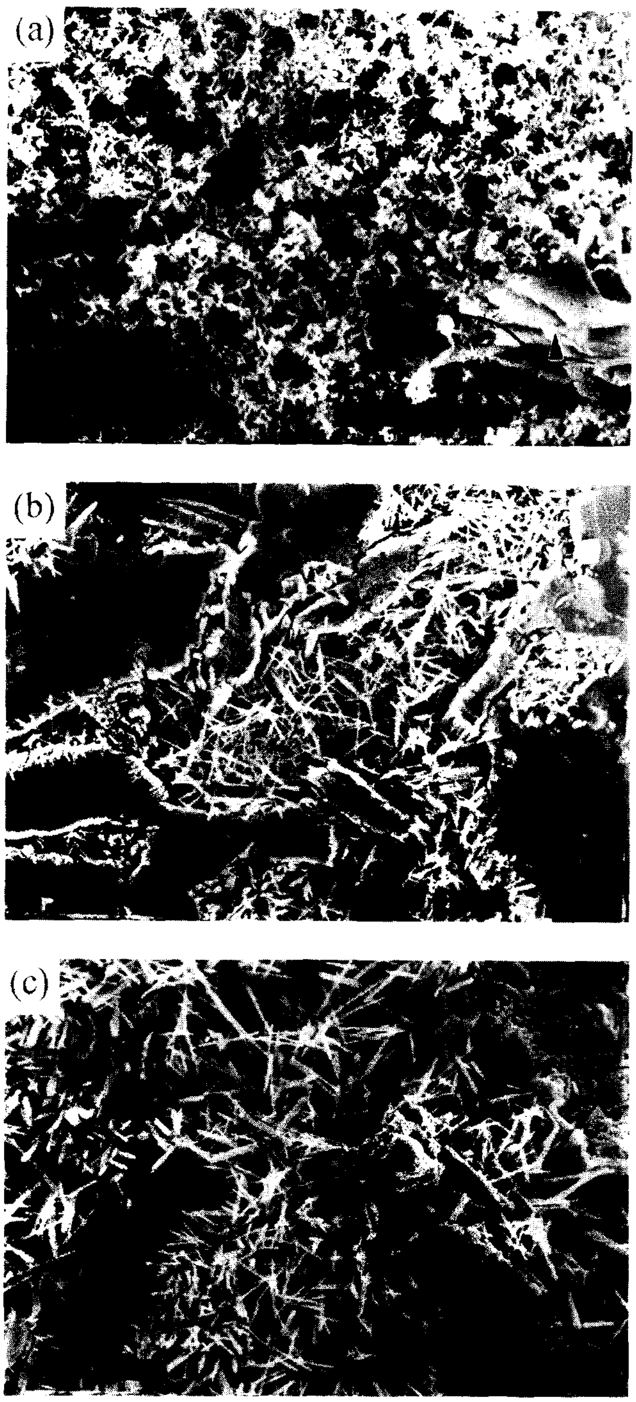

Fig. 5. The micrographs of specimens grown for 72 h under the conditions of (a) 200°C and 1.55 MPa, (b) 250°C and 3.98 MPa, and (c) 300°C and 8.59 MPa.

like or granular depending on the hydrothermal conditions.

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