Nanophase materials by a novel microwave-hydrothermal process*

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Abstract: While there are many techniques for the production of nanophase materials, we have been using a hydrothermal process because it is a low-temperature method that can lead to energy savings. A recent innovation is the introduction of microwaves in the hydrothermal system, and we named this process the microwave-hydrothermal (M-H) process. M-H synthesis is a novel processing technology for the production of a variety of nanophase ceramic oxide and metal powders under closed-system conditions. This closed-system technology not only prevents pollution at its source, but also saves energy and, thus, could substantially reduce the cost of producing nanophase powders of all kinds. With several examples, the value of this technique is reviewed here. The M-H technique leads to (a) rapid heating to temperature of treatment, which can save energy and time; (b) increased reaction kinetics by one to two orders of magnitude, which also saves time and energy; (c) formation of novel phases; and (d) selective crystallization.

INTRODUCTION

Microwave-enhanced chemistry is gaining wide acceptance in many types of reactions for different applications. The theory of microwave-assisted reactions or -enhanced chemistry has been thoroughly documented in several publications [1–4]. The extensive use of microwaves started with the invention of a device, magnetron to generate microwaves of a definite frequency around the time of World War II. Kitchen and commercial microwave ovens started to come on the market in the 1950s [2]. The application of microwaves for drying, sintering, dissolution, and other applications soon began [5–9]. The main feature of the microwave dielectric heating is that it utilizes the inherent properties of the liquids, solids, and their mixtures to convert microwave energy in situ into heat that promotes the reactions. As is well known, this is unlike the conventional heating where the solid or liquid is heated from outside the vessel through conduction. We have been very active in the use of microwaves for solid-state heating and sintering of materials starting about 1982 or so [5,10–11] and liquid-state heating to synthesize ceramic powders from the early 1990s [12–20]. Although hydrothermal (liquid-state) processing is a well-established technique for synthesis of many materials, the kinetics are slow owing to the low temperatures used, and for this reason, we started using microwave field to accelerate the kinetics of reaction. The combination of microwave field with the hydrothermal method was named the "microwave-hydrothermal" (M-H) process [12]. Similarly, the combination of microwave field with solvothermal and polyol processes can be termed "microwave-solvothermal" (M-S) and "microwave-polyol" (M-P) processes, respectively.

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EXPERIMENTAL

Initial M-H experiments were carried out in an MDS-2000 (CEM corporation) acid digestion system [12–19], which operated at 2.45 GHz frequency. This system was controlled by pressure and could operate at up to 200 psi. From the steam tables, one could calculate the temperature of pure water to be about 195 °C at 200 psi. The pressure in the vessels and the power (full power, 650 ± 50) were computer-controlled. The reactions were carried out at different pressures (and thus temperatures) and powers in double-walled digestion vessels with the appropriate solutions or suspensions loaded in the inner Teflon liner. Some of the variables used were: pressure, concentration of solutions, pH, and time. Subsequent experiments starting in 1998 were conducted using a MARS-5 apparatus, which was operated under controlled temperature or pressure conditions [20]. It also uses 2.45 GHz frequency, but has a maximum power of 1200 W. The power of this unit can also be controlled from 0 to 100 %. This system can be operated to a maximum pressure of 350 psi and 240 °C, and both parameters can be controlled by a computer. The temperature inside the vessels was measured by an optical probe using a phosphor as a sensor. M-H and M-P experiments were conducted using these two systems. For comparison with the microwave-assisted reactions, conventional-hydrothermal or polyol experiments were conducted using Parr vessels (Parr Instrument Co., Moline, Illinois).

RESULTS AND DISCUSSION

Thus far, we have investigated numerous unary, binary, and ternary oxide syntheses using the M-H process, which was shown to (a) lead to rapid heating to temperature of heat treatment, (b) increase the kinetics of reaction by one to two orders of magnitude, (c) lead to the formation of some novel phases, and (d) lead to selective crystallization of phases in the chemical system used. Results presented below give examples to show the above advantages of the M-H process over the C-H process.

Figure 1 compares the rates of heating with C-H and M-H methods. It is clear from the figure, that very rapid heating occurs with microwaves because of direct dielectric heating of the liquid, whereas indirect heating (i.e., conductive heating from outside to inside) leads to slower heating rate in the conventional heating. Depending upon the temperature and container conditions, about 60 to 100 min were needed to heat water up to 100–150 °C under C-H conditions, whereas it took only 1 to 3 min by using microwaves to attain the same temperatures. Thus, the heating rate is much higher with microwaves, and a rate of heating of about 1 °C/min can be achieved. This high rate of heating can lead to energy savings in the synthesis of nanophase materials.

Figure 2 shows the kinetics of reaction of conversion of gypsum to hydroxyapatite at various temperatures under M-H using the MARS-5 system and C-H conditions. The kinetics of the conversion of gypsum upon treatment with diammonium hydrogen phosphate to hydroxyapatite is much faster in the presence of microwaves at all the temperatures investigated. Figure 3 shows a dramatic enhancement of
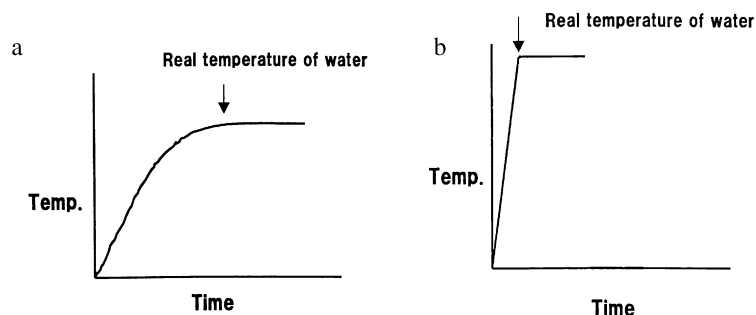

Fig. 1 Increase of temperature with time (a) conventional-hydrothermal and (b) microwave-hydrothermal.
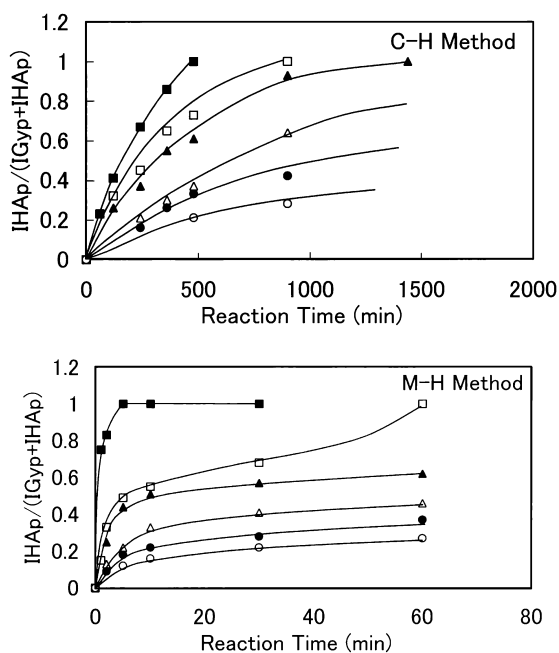
Fig. 2 Kinetics of reaction of conversion of gypsum to hydroxyapatite at various temperatures under M-H and C-H conditions. IHAp = intensity of hydroxyapatite peak, and IGyp = intensity of gypsum peak.
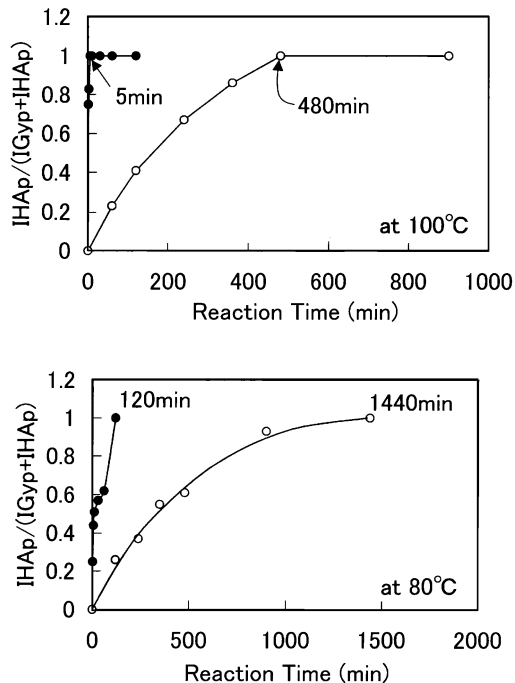
Fig. 3 Hydroxyapatite crystallization at 80 and 100 °C under M-H and C-H conditions. IHAp = intensity of hydroxyapatite peak and Igyp = intensity of gypsum peak.

hydroxyapatite crystallization at 80 and 100 °C under M-H conditions using MARS-5 system when compared to C-H conditions. This dramatic enhancement in crystallization kinetics may be attributed to the localized superheating of the solutions under M-H conditions [1], and, thus, there appears to be no specific "microwave effect" as has been postulated by others. Figure 4 shows the nanophase hydroxy-apatite obtained at 100 °C at two different durations. After 1 min of treatment at 100 °C, both lamellae and fibers were obtained (Fig. 4A). However, after 2 h of treatment at the same temperature, mostly nanofibers were produced (Fig. 4B) as a result of the transformation of lamellae to fibers.

Figure 5 shows the yield of hematite from 0.018 M $FeCl_3$ in the presence of 0.01 M HCl under both M-H and C-H conditions at 160 °C. These results again show that the crystallization of hematite was enhanced by an order of magnitude under microwave-assisted conditions. Figure 6 shows the nanophase hematite synthesized under M-H conditions at 120 °C/2 h using the MARS-5 system. Average particle size of hematite prepared by M-H and C-H methods from 0.018 M $FeCl_3$ in the presence of 0.01 M HCl is compared in Table 1. These results clearly show that microwave-assisted condi-
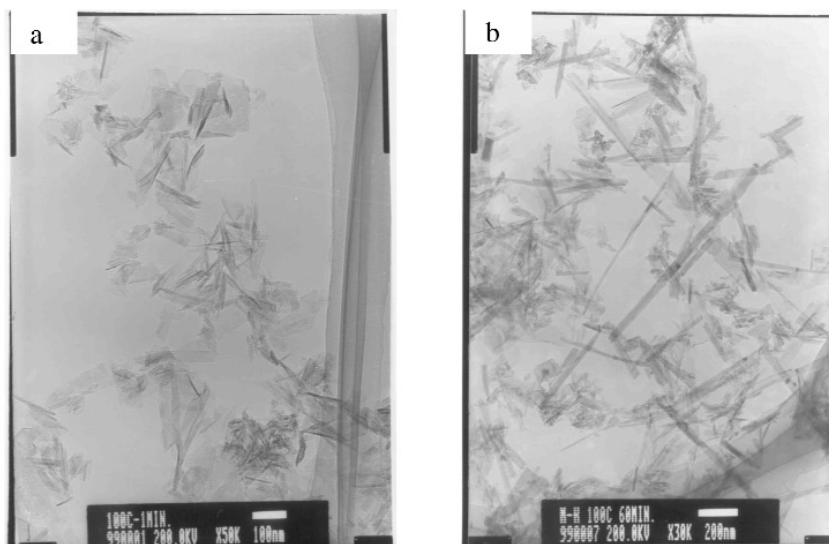

Fig. 4 Nanophase hydroxyapatite obtained at 100 °C at two different durations (a) after 1 min and (b) after 2 h.
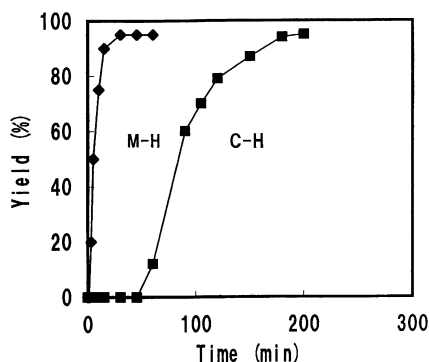

Fig. 5 Yield of hematite from 0.018 M $FeCl_3$ in the presence of 0.01 M HCl under both M-H and C-H conditions at 160 °C.
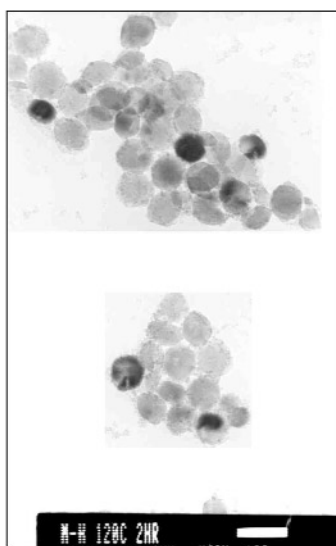
Fig. 6 Nanophase spherical hematite synthesized under M-H conditions at 120 °C in 2 h. Note the presence of 1–2-nm particles, which aggregated to form 60-nm spherical particles.

Table 1 Conventional and microwave hydrothermal synthesis of iron oxides.

Conditions		Average particle size (nm)		
Reactions	Temp (°C)	2 h	4 h	8 h
	100	β-FeOOH	β-FeOOH	β-FeOOH
C-H	120	β-FeOOH	95	105
	140	85	90	110
	100	31	45	52
M-H	120	49	56	58
	140	53	51	53
	160	66	65	62

tions led to somewhat smaller particles compared to the conventional method probably because of enhanced nucleation under the former method. Note the formation of metastable akagenite phase instead of hematite by the C-H method at certain temperatures and durations, while the M-H method led to only hematite under all the conditions reported.

The formation of three different novel phases has already been achieved under M-H conditions [12,14,21]. The reason why new phases were formed with the M-H method compared to the C-H conditions may be due to the rapid heating rate in the former. A new 0.98-nm aluminum hydroxide phase, a new 1.32-nm titanium phosphate phase, and a 1.5-nm Sn phosphate phase were synthesized under M-H conditions using an MDS-2000 system. Thus, either stable or metastable novel phases could be obtained using microwave-assisted reactions.

Elimination of metastable phases such as akagenite occurred during hematite crystallization using the M-H method (Table 1), apparently as a result of a very rapid heating rate. Crystallization of titania under M-H conditions led to rutile, the equilibrium phase, rather than anatase, while under C-H conditions anatase formed under similar conditions [12]. Rutile crystallized in the form of spheres, but the spheres are composed of nanophase rutile needles [22].
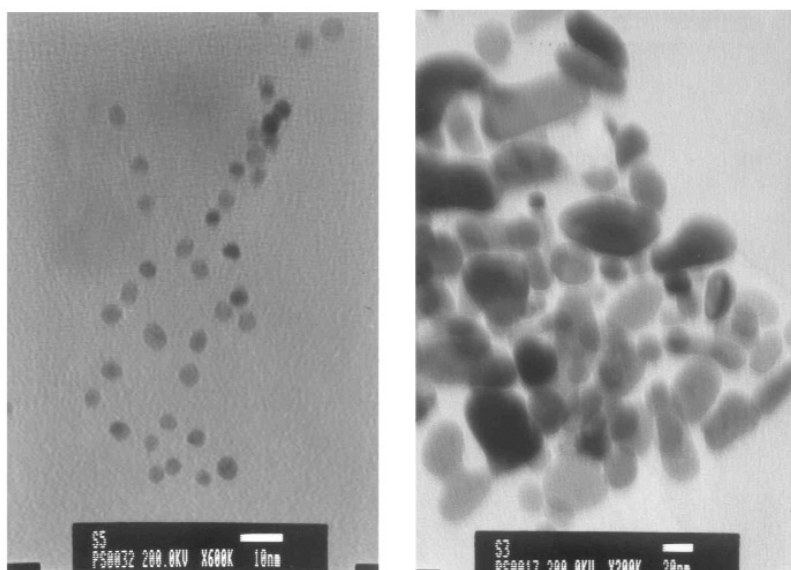
Fig. 7 Nanophase metal particles of Pt (a) and Au (b) synthesized in 15 min at 150 °C using the M-P process.

The M-P process was used to synthesize metals very rapidly [17,18] compared to the conventional polyol process [23–25]. Recently, we focused our attention in synthesizing nanophase metals by the M-P process. Figure 7 shows the nanophase metal particles of Pt and Au synthesized in 15 min at 200 °C and 150 °C, respectively, under M-P process conditions. These results show that nanophase metals can be synthesized very rapidly under microwave-assisted conditions compared to the conventional polyol process using reflux conditions [23–25].

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