MICROWAVE HEATING IN HIGH PRESSURE REACTION VESSELS

A. LARGETEAU[a,*], S. OREE[b], CL. MARZAT[b] and G. DEMAZEAU[a]

[a]*Interface Hautes Pressions;* [b]*Laboratoire Master, ENSCPB–Université Bordeaux 1, B.P. 108, Avenue Pey-Berland, 33402 Talence Cedex, France*

We report the use of microwave–hydrothermal processing to synthesize various ceramic powders. Microwave–hydrothermal processing is compared with conventional hydrothermal processing in the crystallisation of MoO_2. The presence of microwave field leads to accelerated kinetics of crystallization of the finely divided molybdenum dioxide particles. Existing microwave heated pressure vessels for chemical synthesis cannot be used above 250 MPa and 270°C because they contain parts made of polymeric materials. The objective of this work is to associate a microwave source to a high pressure vessel in a way such that it might be used to carry out reactions in acqueous media at pressures around 100 MPa and temperatures above the critical point of water.

Keywords: Solvothermal; Microwaves; Synthesis; Powders; Pressure vessel; Internal heating

INTRODUCTION

Solvothermal synthesis of fine powders of a vast range of inorganic compounds from aluminosilicates, phosphates, oxides, sulphides to nitrides and others have been successfully achieved in the past few years [1, 2]. The solvothermal technique is particularly attractive since it yields powders of high chemical purity having a small distribution of sizes. Such properties are highly desirable in important technological applications including magnetic recording, catalysis, pigment production and in the manufacture of ceramic precursors.

*Corresponding author. e-mail: Largeteau@icmcb.u-bordeaux.fr

Although microwave heating has been applied in a few hydrothermal reactions under mild conditions (less than 2 MPa and 200°C) [1, 3], most of them require temperatures and pressures comparable to the critical point of water (22.1 MPa, 374°C) or even higher [2]. Contrarily to external resistive heating, internal heating using microwaves acts directly on the reaction medium, avoiding inertia associated with heating the large mass of the pressure vessel. Reactions requiring rapid evolution of the temperature, otherwise difficult, can therefore be investigated in this manner.

The reaction vessel designs available for such treatments usually contain elements made of Teflon, which cannot be operated safely beyond 270°C [4]. In this work, we present a complete laboratory equipment for controlled heating of aqueous solutions to high temperatures and pressures (more than 400°C, 180 MPa) using microwaves at 2.45 GHz. Microwave power is transmitted inside the reaction vessel through two pressure resistant sapphire windows by means of high-power coaxial lines. This apparatus has been applied to produce finely divided molybdenum dioxide, MoO_2.

APPARATUS

The Pressure Vessel

A detailed view of the high pressure cell is shown in Figure 1. Its capacity is around 100 cm^3. The cylindrical pressure vessel, made in a special alloy, P.E.R. 5 from Aubert et Duval, has been designed for

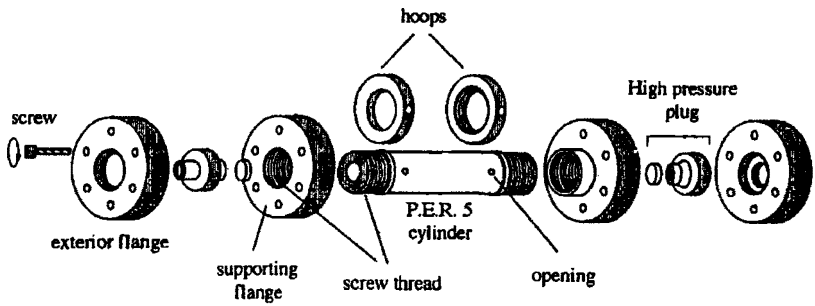


FIGURE 1 View of the parts of the disassembled high pressure cell. The hoops have been moved upwards for clarity in the drawing.

functioning up to 400 MPa pressure and 700°C. It has an internal diameter of 28.6 mm and an external diameter of 60 mm. At both ends of the cylinder, are found two high pressure plugs fitted with sapphire windows. A detailed view of the window mounting, similar in principle to that proposed by Poulter [5], is given in Figure 2. An important feature of the closure element is that the window rests on an optically flat ($\lambda/2$) metallic seat and that no sealing material is used. Moreover, the cap is only meant to hold the sapphire window in place without subjecting it to any pre-pressure.

Each high pressure plug is assembled to the ends of the pressure vessel by a cone closure mechanism as shown in Figure 3. Inlet and outlet holes enable the autoclave to be linked to a high pressure pump and the associated pressure control instrumentation. The entire device was tested up to 180 MPa at room temperature and remained leakproof in this range.

Microwave Coupling

In high pressure technology, it is highly recommended that the window aperture be minimised for safety reasons [5]. As a consequence, we have adopted a sapphire window having a diameter of 25.4 mm with

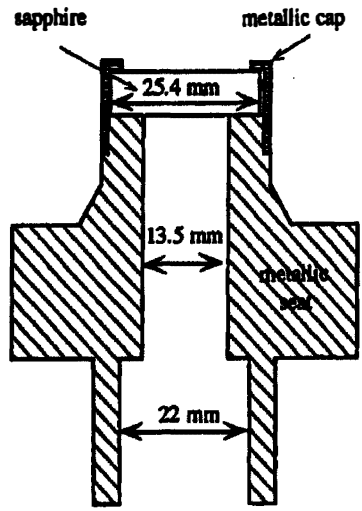


FIGURE 2 A two-dimensional view of the high pressure plug.

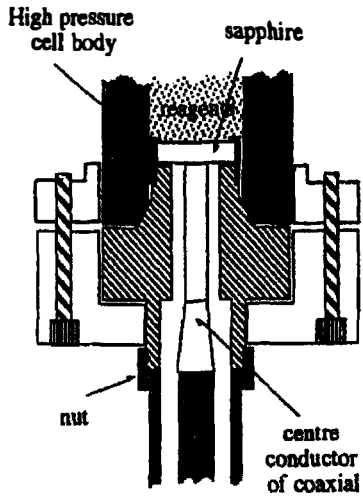


FIGURE 3 Coupling of microwaves in the pressure vessel through a coaxial line.

an unsupported diameter of 13.5 mm and a thickness of 6.35 mm. At such reduced dimensions and in order to avoid cut-off effects, excitation of the pressure vessel is conveniently done through a coaxial, the window having the same role as an iris. In addition to its exceptional mechanical resistance under compression, the use of sapphire for the windows is also justified because its high permittivity ($\varepsilon_r' = 9.41$ and $\tan\delta = 0.0001$) allows a significant reduction in window size.

Most high power generators at 2.45 GHz deliver microwave energy from a rectangular guide. We have therefore constructed a crossbar transition for converting the TE_{01} mode wave propagation of the rectangular guide into the TEM mode of a coaxial line. The end of the centre conductor of the coaxial is in close contact with the high pressure window (Fig. 3). In these conditions, TM_{01} mode is predominantly excited inside the autoclave. When water, ethanol or water–ethanol mixtures are present in the reaction vessel, the reflected power is less than 30%. This reflection can be further reduced to a few percent by using an impedance matching device.

The heating characteristics of water inside the vessel can be measured by a high pressure thermocouple placed in a region of the cavity where the electric field is low. Higher heating rates can be

obtained by insulating the inner walls of the vessel with a closely fitting borosilicate glass tube. For example, in the absence of insulation, water initially at room temperature attains a temperature of 65°C at the end of 5 minutes microwave heating at 450 W: when an insulating inner tube is used, a temperature of 160°C can be reached under equivalent conditions.

SOLVOTHERMAL SYNTHESIS

Molybdenum dioxide MoO_2 is a black compound conventionally prepared by the reduction of the trioxide or ignition of ammonium molybdate. However, the particle size of the powder obtained in this manner is not fine enough and varies greatly. Our objective is to explore the formation of finely divided MoO_2 by the microwave-solvothermal technique.

A few grammes of 99.8% pure ammonium molybdate crystals $(NH_4)_2MoO_4$ from Aldrich, in a small glass tube, was introduced in the reaction vessel containing a mixture of equal volumes of water and ethanol. The contents of the autoclave were then microwave-heated at 400 to 1200 W while the pressure was maintained between 40 and 50 MPa. When the temperature of the reaction medium reached 345°C after 28 minutes treatment, there was a rapid rise in temperature to around 410°C followed by a marked increase in reflected power which led to an equally rapid cooling to a stable temperature of 280°C. This phenomenon will be due to the decreases of microwave absorption of the reaction medium following the complete conversion of the soluble ammonium molybdate phase into an insoluble phase. The total treatment time did not exceed 35 minutes.

RESULTS

On cooling, the reaction vessel was disassembled and a black slurry was collected. After separation of the precipitate from the liquid phase and drying, a finely divided powder was obtained. X-ray diffraction confirmed that the powder was highly crystalline MoO_2. Figure 4 shows the X-ray diffraction pattern obtained.

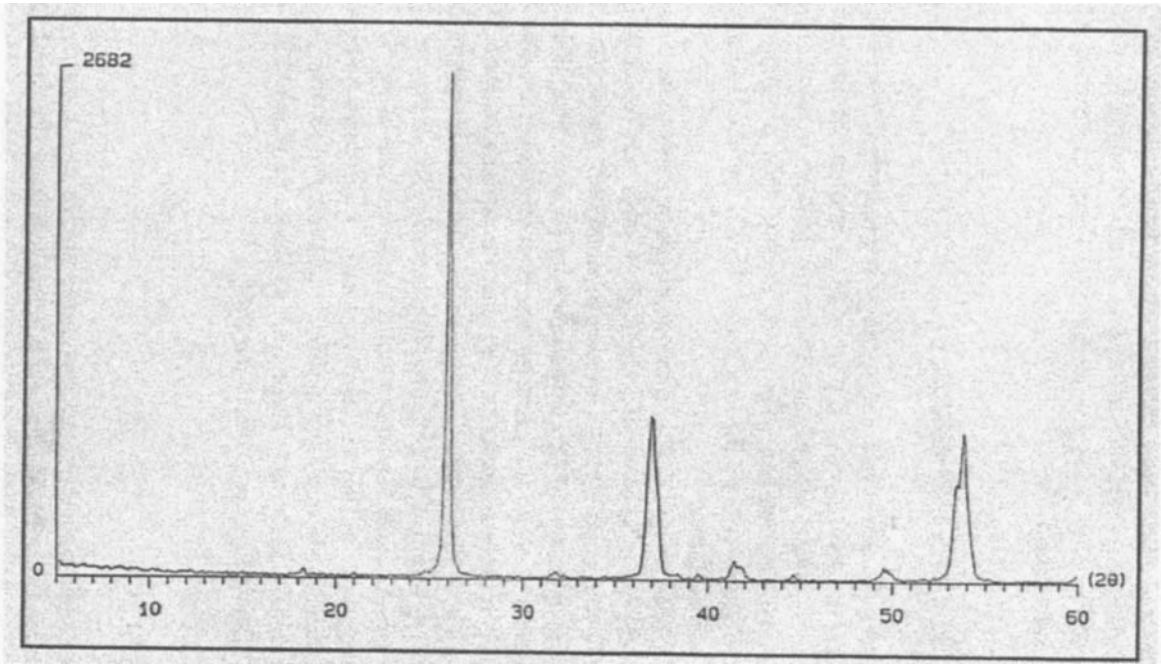


FIGURE 4 X-ray diffraction pattern of the MoO_2 powder obtained by the microwave–solvothermal method.

Scanning electron microscopy photographs reveal two types of particles present in the powder:

(i) monoclinic crystals of MoO_2 of size 1 to 4 μm representing less than 20% of the powder. It is through that formation of these particles occurs when the rate of temperature rise is slow (Fig. 5a);
(ii) small agglomerates of submicronic particles. These particles are supposed to nucleate when the rate of temperature rise is rapid (Fig. 5b).

In comparison, particles produced at 400°C and 44 MPa by the conventional hydrothermal method (Fig. 5d) are usually of spherical shape having a diameter of 1 to 2 microns.

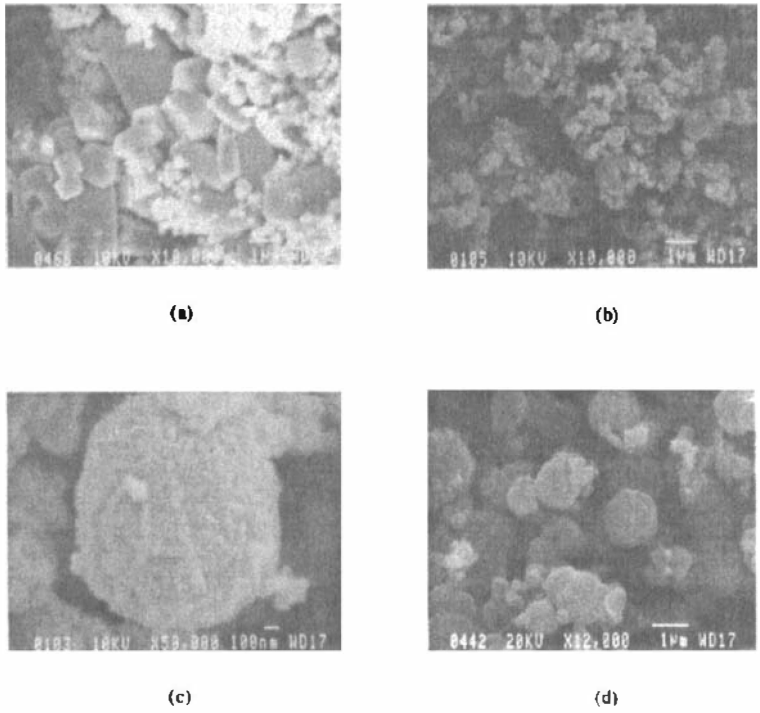


FIGURE 5 S.E.M. photographs of molybdenum dioxide particles: (a) faceted crystals, (b) agglomerated submicronic crystals produced by microwave–solvothermal synthesis at around 400°C and 40–50 MPa, (c) agglomerated crystals with a higher magnification, (d) crystals produced at 400°C and 44 MPa by conventional solvothermal synthesis.

CONCLUSION

The synthesis of a highly crystalline form of molybdenum dioxide using microwave heating has been demonstrated at about 400°C and 45 MPa. The powders produced have a different microstructure compared to the powders produced by conventional solvothermal synthesis. More experimentation is required to understand the role of the factors (temperature, reaction medium composition, time and pressure) governing the nucleation of the particles.

References

[1] Komarmeni, S., Li, Q. H. and Roy, R. (1996). Microwave hydrothermal processing of layered anion exchangers, *J. Mater. Res.*, **11**(8), 1866.

[2] Byrappa, K., *Handbook of crystal growth 2* (Elsevier Science B.V., Amsterdam, 1994), Chap. 9.

[3] Baghurst, D. R. and Mingos, D. M. P. (1992). A new reaction vessel for accelerated syntheses using microwave dielectric superheating effects, *J. Chem. Soc. Dalton Trans.*, p. 1151.

[4] Lautenschlager, W. (1995). Apparatus for performing chemical and physical pressure reactions, *U.S. patent No. 5 382 414.*

[5] Chervin, J. C., Syfosse, G. and Besson, J. M. (1994). Mechanical strength of sapphire windows under pressure, *Rev. Sci. Instrum.*, **65**(8), 2719.