Module 8_Unit-3_NSNT

Hydrothermal Synthesis

Hydrothermal processing has gained much interest for synthesizing advanced nanomaterials as well as composites exhibiting tailored properties. This technique has been used to produce nanostructured materials for a broad range of applications which include electronics and optoelectronic devices, catalysis, biomedicine, biophotonics, etc. The word ‘hydrothermal’ has its origin in geology and Sir Roderick Murchison, a British geologist, was the first to use it. He attributed the variations in earth’s crust and the subsequent forming rocks as well as minerals to hydrothermal action of water at very high temperatures and pressures. Incidentally, the largest naturally occurring single crystal (beryl crystal, more than 1kg), as well as the largest man-made single crystal (quartz crystal, of several kgs), both have originated via hydrothermal process [1-2].

Hydrothermal synthesis belongs to a group of syntheses techniques in which substances in high-temperature and high pressure aqueous solution are crystallized. This is also called as the “hydrothermal method” [1]. According to Byrappa [3], hydrothermal processing is “any heterogeneous chemical reaction in the presence of a solvent (aqueous or non-aqueous) above room temperature and at pressures > 1 atm in a closed system” [2]. Hydrothermal processing includes techniques such as hydrothermal synthesis, hydrothermal crystal growth, hydrothermal transformation, hydrothermal sintering, etc. Hydrothermal processing of nanomaterials yields highly pure, homogenous, symmetrical crystal structures having novel properties. It also allows greater size control, low temperature synthesis, more control over composition of the end product, dense compounds, and can be used to produce compounds in relatively short time durations.

Hydrothermal is a solution processing technique which involves processing of super heated aqueous solutions. The pressure-temperature plot of different synthesis procedures is shown in Figure 1 where, it is apparent that hydrothermal is an environmentally benign process.

![Figure 1 Pressure-temperature map of different synthesis approaches](image-url)
K.E. Schafhautl was the first to use hydrothermal method to grow micron sized quartz crystal in a pressure cooker containing as-precipitated silicic acid [4]. There have been reports of synthesizing artificial diamond by hydrothermal method.

Hydrothermal processing is an unconventional method to synthesize nanocrystalline inorganic materials. Direct precursor-product relation exists thereby allowing synthesis of roughly every material with no requirement of structure defining agents. It is well recognized that the majority of inorganic materials become soluble in water at high temperature and high pressure. Hydrothermal method is based on this premise wherein the materials are dissolved in water under high temperature and pressure conditions. These dissolved substances are then crystallized to obtain the desired end products. Being indicated in the name, water performs a crucial role in precursor material transformation process at elevated temperatures. According to the phase diagram of water, merely the branch between gaseous and liquid state warrants further considerations: less than 100 °C equilibrium vapour pressure of water (liquid state) is < 1 bar; and beyond the boiling point significant hydrothermal pressure range exists. Generally, two different operating modes can be identified.

Hydrothermal processing is usually performed in a steel pressure vessel also defined as autoclave wherein the processing conditions are controlled by adjusting the temperatures and/or pressures. The autoclave may or may not be coated with protective Teflon coatings. The processing is carried out in aqueous solution (Figure 2). Temperature is increased beyond boiling temperature of water, attaining the pressure of vapour saturation. Internal pressure depends largely on temperature and the quantity of solution put in the reaction chamber (autoclave). This procedure is extensively used for producing small particles in ceramics industry.

![Figure 2 Schematic of a hydrothermal experiment setup.](image)

**Principles and Operation**

Both chemical and physical parameters are varied steadily during processing such that there establishes direct relation between precursor-product. Nonetheless, this is a rather complex processing technique as a numerous interacting parameters (process variables) are present which can be controlled to give different results. The impact of these variables poses problems which are not yet satisfactorily resolved. Temperature controls the formation kinetics and thermodynamic stability of products. Pressure influences solubility, supersaturation range stipulating crystallization process and also the thermodynamic stability of the products (higher pressure $\rightarrow$ denser phases). To avoid the influence of the pressure generating temperature, external pressure mode is preferred since high pressure-low temperature processings are possible only through high pressure hydrothermal synthesis (HPHS) mode. Processing time too is an essential variable as formation of the kinetically stable phase is favored in short term whereas
thermodynamically stable phases are formed in long term processes under related temperature-pressure regions. This happens as a consequence of increased solubility and recrystallization of previously created phases. Nonetheless, some reaction related conditions like convection inside autoclave and aggregation of precursors can also affect the synthesis process.

**Instrumentation in Hydrothermal Approach**

Since hydrothermal processing frequently involves high temperatures and pressures, the reaction container must be able to sustain such conditions without undergoing any structural or compositional damage. Experimental facilities must be available for routine and reliable operation under extreme environments. Designing an ideal hydrothermal reaction container, often termed as ‘autoclave’, should consider the following:

- The vessel/container should not react with acid, base, or any other oxidizing agents.
- It must be easy to assemble and disassemble when required.
- Its dimensions must allow achievement of high temperatures.
- It must be leakage proof and should be able to sustain the highest possible temperature and pressure values likely to be encountered during its operating life.
- The material of the vessel as well as the vessel itself must be able to endure repeated elevated temperatures and pressures for long durations. Additionally, it should be stable and there should not be any requirement of any type of treatment or machining after each experiment.

In view of these requirements, the autoclaves are typically produced from high strength alloys and thick quartz cylinder. Thus, the most important parameters to be considered before selecting an autoclave include process temperatures and pressures along with the resistance to corrosion of autoclave material.

**Methods used in Hydrothermal Processing**

a. **Temperature-difference method:** The majority of hydrothermal syntheses and crystal growths use this technique. The temperature inside the crystal growth region is reduced to achieve supersaturation. The aqueous solution (containing the solute) is kept at the bottom section of the autoclave. The heating of autoclave results in the creation of two zones of different temperatures. The solute particles dissolve in the hotter zone. The convective movement of the solution transfers the saturated aqueous solution from the lower part towards the upper part of the autoclave. As the saturated solution ascends, a counterflow of cooler and denser solution present in the upper part occurs. This counterflow of solution results in the descend of cooler and denser solution towards the lower end of the autoclave. As the temperature is decreased, the solution in the upper part supersaturates resulting in the onset of crystallization.

b. **Temperature-reduction technique:** There is no temperature difference across the autoclave length. To achieve the supersaturation and thereafter, crystallization, the temperature of the solution present inside the autoclave is gradually reduced. However, the difficulties involved to control the growth process and introduce seed crystals are the major drawbacks of this technique due to which it is rarely employed.

c. **Metastable-phase technique:** Often the solubilities of the phase required to be grown and the precursor phase are not equal; and this inequality is exploited in this technique. The precursor is thermodynamically unstable under growth conditions. The metastable phase is more soluble than the stable phase. Therefore, the metastable phase begins to dissolve and the stable phase begins to
crystallize. Metastable-phase approach is generally used in combination with either the temperature difference or temperature reduction technique, as discussed above.

Hydrothermal processing of advanced materials

Hydrothermal method has been used for processing a wide variety of advanced materials. We will now discuss some of the most popular processing in the following sections:

a. **Metallic Nanoforms**: Recently, nanoparticles of many metals as well as metal alloys (e.g., Au, Pt, Ag, Co, Ni, Fe, FePt, etc.) have attracted huge interest owing to their size and morphology dependent novel properties. Most of these nanoparticles are formed in non-equilibrium conditions. Hydrothermal processing has been extensively applied to prepare these structures.

b. **Metal oxide Nanostructures**: Synthesizing metallic oxides via hydrothermal technique has gained much attention owing to its advantage in preparing highly monodispersed nanoparticles having carefully tailored size and shape. Such metal oxide nanostructures find practical applications in high-density data storage, bio-imaging, targeted drug delivery, photocatalytic, electronic and optical devices, etc. Recently, Adschiri [6-11] have elaborated the continuous fabrication of metal oxide nanoparticles by supercritical water based reaction medium. Metal oxide nanostructures are formed by contracting the metal nitrates with supercritical water in the flow system. Very tiny particles could be formed due to supercritical water assisted rapid dehydration of metal hydroxides prior to the growth. The reactions involved are called hydrolysis and dehydration, and can be written as:

\[
\text{M(NO}_3\text{)}_2 + \text{xH}_2\text{O} \rightarrow \text{M(OH)}_2 + \text{xHNO}_3 \\
\text{M(OH)}_x \rightarrow \text{MO}_{x/2} + (1/2) \text{xH}_2\text{O}
\]

Processing in supercritical water increases the dehydration rate while the particle is still small in size and the particle diffusion does not affect the reaction rate. Additionally, the critical region gas-like viscosity as well as the diffusivity of water results in very low mass transfer limit; leading to an overall large synthesis rate. Besides, the synthesis rate is also increased due to the high temperature. Metal oxides formed in this manner are: \(\alpha\)-Fe\(_2\)O\(_3\), Fe\(_3\)O\(_4\), ZrO\(_2\), NiO, Co\(_3\)O\(_4\), CeO\(_2\), etc.

c. **Metal Sulphides**: Sulphides of several di-, tri-, and penta-valent metals are an interesting group with numerous technological applications, and can be easily prepared via hydrothermal technique.

d. **Carbon Nanoforms**: The carbonaceous structures (such as graphite, diamond, amorphous and diamond like carbon, fullerenes, carbon nanotubes (CNTs), etc.) have been focus of colossal importance owing to exceptional size dependent properties. However, there are uncertainties regarding their phase stability, because some of these polymorphs do not appear in the pressure-temperature curve of carbon. Furthermore, all these structures exhibit rather contrasting properties. Several researchers have synthesized these compounds with varying successes and hydrothermal method has also gained much recognition.

Advantages
The hydrothermal processing proffers several merits over conventional and novel synthesis techniques. The cost of instrumentation, energy as well as precursors is far less in comparison to other advanced techniques. As discussed earlier, hydrothermal technique is environmentally benign. It gives good control over the particle shape and size.

Other advantage of using hydrothermal method than other techniques for crystal growth is that crystalline phases which are unstable at their melting points can also be grown with this technique. This technique can be used to grow the materials which have high vapor pressures at melting points. Moreover, hydrothermal processing can also be used for producing large and high purity crystals having well controlled compositions. The limitation of the method includes the inability to observe the crystal during its growth.

Hydrothermal synthesis is affected by the temperature and pressure below a critical point for the particular solvent. Some oxides are more soluble in the hydrothermal salt solutions in comparison to the pure water. These hydrothermal salts are termed as mineralizers. Furthermore, there exist solvothermal processing techniques which are analogous to the hydrothermal methods. The main difference between the hydrothermal and solvothermal processes is that the latter uses organic solvents and supercritical carbon dioxide [12].

Nanopowders can be synthesized by either:

a. directly hydrolyzing the precursors in the autoclave at elevated temperatures. In this case, an aqueous solution containing the precursor is placed inside the autoclave, or
b. room temperature hydrothermal processing of the reaction products. In second case the crystallization rate of amorphous phases rises abruptly under the hydrothermal processing conditions. In this case, the autoclave is loaded with a suspension of reaction products carried out at ambient.

In both cases, a temperature difference is not required to be maintained. Also, no specialized equipment is needed.

Substantial enhancements in hydrothermal processing facilitate in controlling the reactions by using external factors. For example, hydrothermal processing is being used in conjunction with microwave, ultrasonic, electrochemical and mechanochemical syntheses [12].

Zeolites (synthetic) are among the most frequently produced nanomaterials by using hydrothermal processings. Their growth strongly depends upon the presence of surface activation agents within the solution. These agents control the morphology of oxide products in hydrothermal solutions. The choice of synthesis conditions and type of surfactants can ensure the production of targeted porous nanomaterials with given pore size controlled in a fairly wide range of values [12].

References


Review Questions

1. When were hydrothermal vents discovered?
   a. 1900  
   b. 1977  
   c. 1990  
   d. million years ago

2. The water flowing out of hydrothermal vents is usually very cold, about 2 Celcius. (True/False)?

3. Animals living around the hydrothermal vents rely on sunlight for food (True/False)?

4. What kind of nanomaterials can be produced from hydrothermal synthesis?