

# Chapter 3: Experimental Materials and Methods

## 3.1 Materials Used

Borazane (H<sub>3</sub>BNH<sub>3</sub>), powder

Company: Aldrich

Purity: 90%

CAS Number: 13774-81-7

Molecular Weight: 30.87

Appearance: white powder, flakes or crystalline solid and/or chunks

Hazard: Heat may cause an explosion

Titanium (Ti), powder

Company: Strem

Particle size –325 mesh (44micron)

Purity: 98%

CAS Number: 7440-32-6

Molecular Weight: 47.87

Appearance: grey powder

Hazard: Spontaneously flammable in air.

Titanium(III) chloride ( $\text{TiCl}_3$ ), powder

Company: Aldrich

CAS Number: 7705-07-9

Molecular Weight: 154.23

Appearance: purple powder or crystalline powder

Hazards: Reacts violently with water. Spontaneously flammable in air.

Causes burns.

Magnesium Hydride ( $\text{MgH}_2$ ), powder

Company: Gold Schmidt AG

Molecular weight: 26.30

Particle size: 50 micrometer

Purity: 95%  $\text{MgH}_2$ , 5% Mg

Appearance: Light grey

### **3.2 Material Processing**

The only mechanical processing that is used is ball milling. Ball milling involves sealing ingredients in a hardened steel container along with a number of heavy metal balls, and then shaking or vibrating the container. The balls crash about, impacting each other, the container walls, and the materials inside. The random, chaotic motion of the heavy agitation creates tremendous numbers of collisions, imparting a great deal of energy and breaking existing bonds to allow for the formation of new bonds. When the container is opened, the ingredients have been transformed into an end product without the use of any additional chemicals.



**Figure 3.1** Spex-8000 ball mill Low-tech chemistry with a high payoff High-energy ball-milling, a relatively low-tech process in which metal balls are sealed in a vial with chemicals and shaken to produce new substances, may replace solvents in certain chemical reactions, offering at least a partial alternative to the use of toxic compounds such as benzene. [Environmental Health Perspectives, V. 111 (10) August 2003, pg. A534]

A Spex-8000 ball mill was used for high energy ball mill from Glen Crest Ltd. as shown in fig. 3.1. Before experiment, the ball milling vial and balls were cleaned with acetone than water. After that they were heated in oven for 1 hour at 150°C to get rid of moisture, and then were kept inside the glove box from Saffron Scientific Equipment (fig. 3.2). The Spex-8000 is fixed into the glove box, there is argon atmosphere inside the glove box, to protect the powder from oxidation during milling.

For the magnesium hydride ( $MgH_2$ ) milled for 20 hr Fritsch P5 planetary ball mill was used. This facility was used because we have the facility available, secondly we need quite a lot of powder for our test, which would be putting burden on the Spex. In Spex

we have to use it in 4hr duration, while in Frish P5 we can do ball milling at once or in duration of 10 hr.



Fig. 3.2 Glove box

### 3.3 Material Analysis

#### 3.3.1 TG/DSC

Thermogravimetry is one of the oldest thermal analytical procedures and has been used extensively in the study of polymeric systems. The technique involves monitoring the weight loss of the sample in a chosen atmosphere (usually nitrogen or air) as a function of temperature. The usefulness of TGA for analysing complex systems such as rubber vulcanisates was greatly enhanced by the introduction of the ability to record simultaneously the first derivative of the weight loss. This is sometimes referred to as derivative thermogravimetric analysis (DTA).

A mass spectrometer (MS) can be coupled to the TGA instrument for continuous, on-Line analysis and identification of the evolved gases during heating of the sample in

TGA. The gases are routed to the MS via a capillary, which can be heated up to 150 °C to keep the evolved gasses from condensing. The thermal analysis can be performed in a controlled atmosphere including oxygen, nitrogen or helium with adjustable flow rates.

Both diffraction scanning calorimetry (DSC) and thermogravimetry (TG) measurement were carried out using a setaram setsys 16/18 TG/DSC system (fig. 3.3) with a precision of 0.1 µg during heating under a controlled atmosphere (hydrogen, argon or vacuum). The apparatus was operated by using the software “setsoft” and can simultaneously collect the TG and DSC signals. The operation temperature range is from room temperature to 1600 °C. A small turbo pump was used in the system for high vacuum environment.

TG measures the instantaneous mass of specimen as the test proceeds, display mass loss in relation to temperature or time at an isothermal temperature. The aim of using TG in this project was to investigate the hydrogen desorption kinetics (hydrogen release versus time) and capacities of the material at different temperatures. DSC measurement plots the graph of the different rate of heating (in cal/sec) versus temperature. The area under the curve is directly proportional to the heat evolved or absorbed by the reacting sample, and the height of the curve is directly proportional to the rate of reaction. The DSC measurement in this study is to determine the starting deposition temperature and the temperature at which the highest reaction rate is obtained. The TG data collected simultaneously from the DSC measurement reflect the maximum hydrogen capacity in the material.



**Figure 3.3** Combined facility of TG/DSC/MS

In our experiment, 8-12 mg powder was used for both TG and DSC. The recommended amount of powder to be used is 25mg. We used less powder because after processing the powder get polymerised and expand in size and if we use more powder it expand and come out of the sample holder. One thing of interest that can be seen in detail is that our sample holder got damage and a hole was made on a platinum sample holder. The temperature used was 90°C and the melting point of platinum is 1768°C. After that, ceramic sample holder was used.

### **3.3.2 Mass spectrometry**

Mass Spectrometry is an analytical technique that is used to identify unknown compounds, quantify known materials and elucidate the structural and physical properties of ions. It is a technique associated with very high levels of specificity and

sensitivity. Analyses can often be accomplished with minute quantities - sometimes requiring less than picogram (10<sup>-12</sup> grams) amounts of material.

A mass spectrometer is an instrument that can separate charged atoms or molecules according to their mass-to-charge ratio. Relative molecular masses of organic compounds and biopolymers can be measured in this way and the instrument is capable of generating structural information. Mass spectrometry was performed on OmniStar mass spectrometer from the company Pfeiffer Vacuum. The unit monitors gas emissions continuously and can measure up to 64 different ones simultaneously in concentrations from 100% down to  $\leq 10$  ppm.



**Figure 3.4** OmniStar Mass spectrometer

### **3.3.3 X-ray Powder Diffraction (XRD)**

X-Ray Powder Diffraction is used for the identification of crystalline compounds by their diffraction patterns some specific uses, are listed below;

- Crystallographic structural analysis and unit-cell calculations for crystalline materials.
- Quantitative determination of amounts of different phases in multi-phase mixtures by peak-ratio calculations.

- Quantitative determination of phases by whole-pattern refinement.
- Determination of crystallite size from analysis of peak broadening.
- Determine of crystallite shape from study of peak symmetry.

There are four basic things in a diffraction pattern to notice

- 1) Peak Position: Tells you the phases present.
- 2) Peak width: tells you the crystallite size
- 3) Peaks height: tells you the amount of a phase
- 4) Background Hump: tells you the amorphous content.

The “angle” of the diffraction is related to the interplanar spacing,  $d$ , by the Bragg law, and the intensity of the diffraction maximum is related to the strength of those diffractions in the specimen. X-ray data are recorded in terms of  $2\theta$  (x-axis) vs. intensity (y-axis).

X-ray powder diffraction was performed on siemens D-5000 diffractometer, fig. 3.5. The source was Cu  $K_{\alpha}$  radiation from a conventional water-cooled x-ray tube, and the angle is  $2\theta$ . The software attached to the system is Diffracplus Basic 4.0, which allows rapid scan and longer data collection, and easy analyses of the data obtained. The powder samples were compressed in a plastic X-ray sample holder with a clean glass plate to make a flat sample. The samples are all powders. The slides are 0.1mm, 0.1mm and 0.06mm.



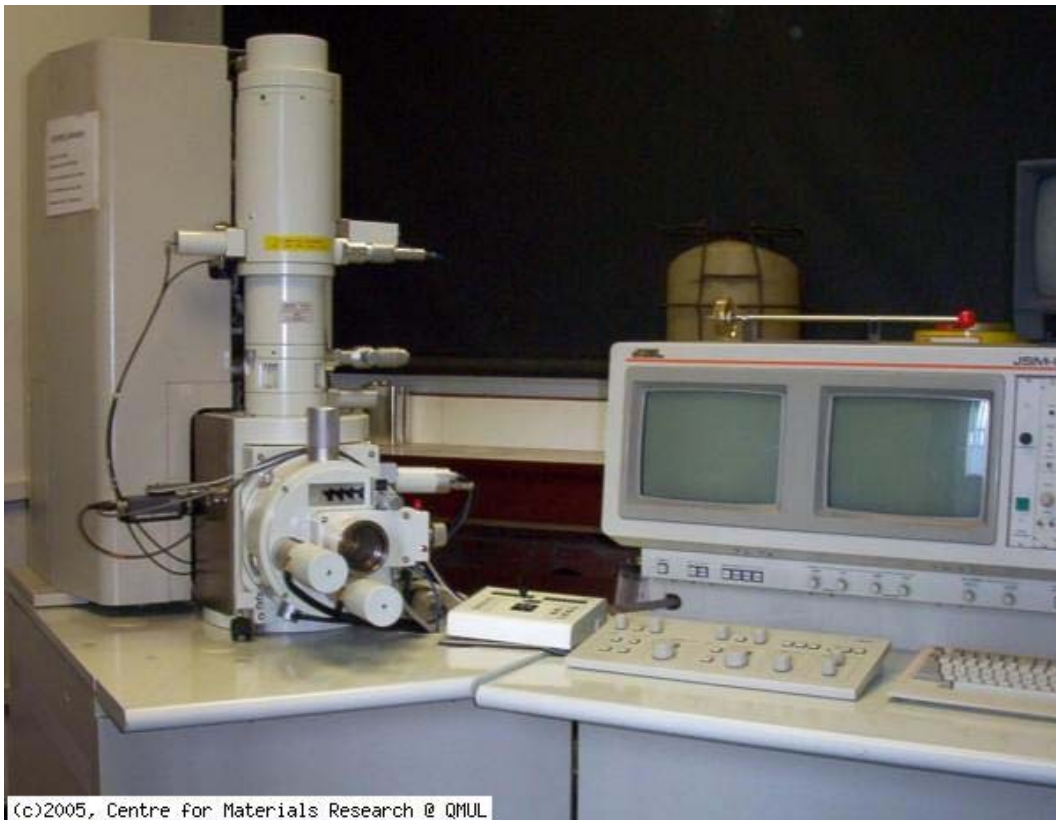


**Figure 3.5** Siemens D-5000 diffractometer

### 3.3.4 SEM

Scanning electron microscopy (SEM) was conducted using JEOL JSM 6300 field emission SEM (fig. 3.6), which consist of a cold cathode field emission gun and require a vacuum better than  $10^{-8}$  Torr. As we know that to have better SEM images the most important part is specimen preparation. The specimens were prepared by sprinkling powder on the sticky paper that is conductive as well and than placing that sticky paper on metal stubs. After that they were gold coated in gold coater. One thing of notice is that there is a little bit of blackish shade shown after the coating, which might be due to some moisture present in the specimen before coating. SEM was conducted to characterise the particle size, phase distribution and particle morphology.

The working parameters were normally that, the probe current was set on 6 or 7, voltage was 10 KV, and distance is 19mm. The magnification was x400, x4000, and x10000. Photograph of every sample was taken at x4000 so that is easy to benchmark and compare the pictures.



**Figure 3.6** Field Emission SEM