

CHAPTER 3

EXPERIMENTAL PROCEDURE

This chapter deals with the experimental procedure used to develop ABO_w based composites, conduct characterization of their microstructure, and investigate physical, mechanical, and tribological properties. As received commercial pure aluminium powder and aluminium (Al-319) alloy have been also cast and characterized for the same properties compared to developed aluminium-based composites.

3.1 Material selection for the synthesis of ABO_w as reinforcement

In the present study, commercial pure alumina powder and boric acid with a purity of 99% have been selected to synthesise reinforcement material using the hydrolysis route. Commercial alumina and boric acid were procured from CDH limited, Bangalore, India.

3.1.1 Synthesis of ABO_w as reinforcement

The particle size of alumina powder was reduced by using a high-energy planetary mill (Retsch PM 400) with yttrium stabilized zirconia ball at 300 rpm for 2 hours to obtain micro particles of size $<45 \mu\text{m}$. The zirconia ball to powder weight ratio in the milling process was 1:10. The hydrolyzation process was used to prepare a homogeneous mixture of alumina and boric acid (in atomic ratio 9/1) in distilled water at 80°C in a magnetic stirrer. The sol was dried at 110°C in the oven for 10 hours. The dry powder was calcined in a furnace at a $5^\circ\text{C}/\text{min}$ heating rate, in the temperature range $950\text{-}1400^\circ\text{C}$ followed by removal of residual B_2O_3 by soaking for 4 hours in the air atmosphere.

3.1.2 Sample preparation for various testing

After the sol was dried in an oven, the dried powder was selected for sample preparation. Green pellets were prepared in a hydraulic press by applying a uniaxial load of 300 MPa. Rectangular green samples of dimensions 50 mm ×10 mm ×10 mm were prepared [71]. The samples were fired in an electric furnace in a temperature range of 950-1400°C, at a heating rate of 5°C/min, followed by 4 hours soaking in air atmosphere for removal of residual B₂O₃, and the final samples were prepared. The process flow chart of synthesis of ABO_w is depicted in **Figure 3.1**.

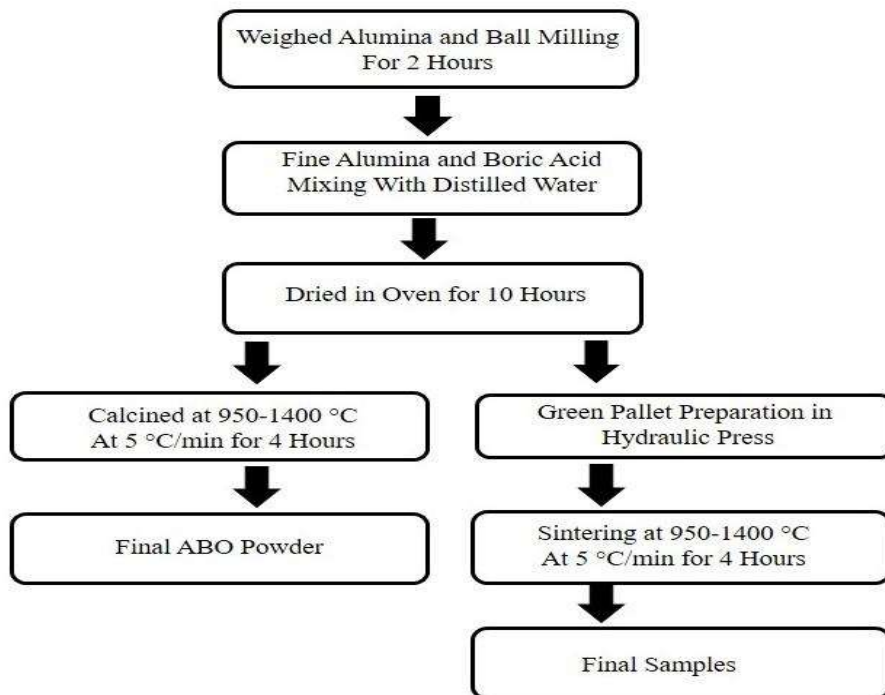


Figure 3.1: Process flow chart of development of ABO reinforcement

3.2 Material selection for coating of ABO powder

In the coating process of ABO powder, chromium nitrate, zinc nitrate, tetraethyl orthosilicate (TEOS), and tetra butyl titanate (TBT) having a purity of 99%, procured

from CDH Pvt Ltd, Bangalore, India has been selected and citric acid was selected for mixing. Coating of whiskers was done by hydrolysis process.

3.2.1 Coating of ABO powder

Starting material used for the coating was ABO_w (>10-20 μm) powder which was synthesized using the hydrolysis route. In this study, the mass ratio of all four oxides (1-4) to (ABO_w) powder selected was 1:10. The synthesis of coated alumina borate whiskers containing raw materials and their particle size is shown in **Table 3.1**.

Table 3.1: List of raw material

Sr. No.	Raw Material	Particle Size (μm)
1	Chromium Nitrate	80
2	Tetraethyl ortho-silicate (TEOS)	80
3	Zinc nitrate	80
4	Tetra butyl titanate (TBT)	80

For Cr₂O₃, SiO₂, ZnO, and TiO₂ coating, dissolution of each one of them were prepared using equal mole of chromium nitrate, tetraethyl orthosilicate (TEOS), zinc nitrate, tetra butyl titanate (TBT) respectively with citric acid, in distilled water in **Figure 3.2 (a)**. Subsequently, ABO_w powder was mixed with each sol and subjected to ultrasonic vibration to avoid powder agglomeration.



Figure 3.2: (a) Mixing (b) Oven (c) Furnace (d) Sonication (e) Heating (f) Coated ABO_w

Now, ABO_w powder-sol mixes were dried at 100°C for 10 h in **Figure 3.2 (b)** and calcined at 500°C in the air for 4 h in **Figure 3.2 (c)**. The calcined powder was further dispersed homogeneously in distilled water by ultrasonic vibration in **Figure 3.2 (d)**, and ultimately preforms were made in the hydraulic press. Finally, the preforms were calcined for 1 h at 1100°C **Figure 3.2 (e)** and each oxide coating was obtained on the surfaces of ABO_w powder **Figure 3.2 (f)**.

3.2.2 Sample preparation for various testing

Coated ABO powder selected for sample preparation of various tests. Green pellets of dimensions 50 mm x 10 mm x 8 mm were made in a hydraulic press for each preform applying a uniaxial load of 280 MPa. Different shapes of moulds are used for making various shapes for a) Rectangular sample (50 mm x 10 mm x 8 mm) for flexural strength at room temperature and high temperature, and compressive and density test, b) Square (25 mm x 25 mm) samples were made [72].

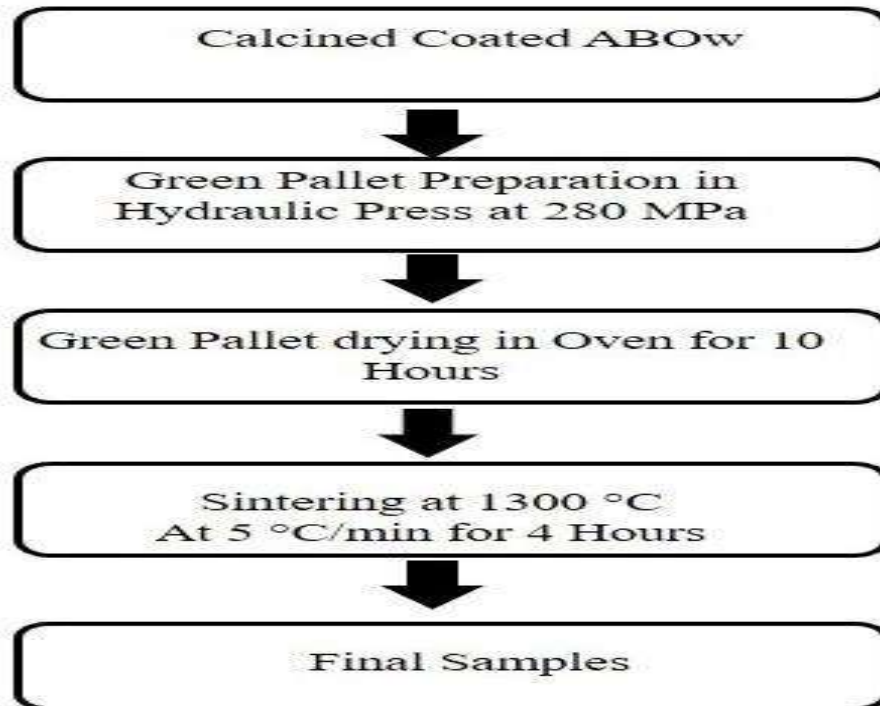


Figure 3.3: Process flow chart of development of oxides coated ABO_w powder

The green pellets were dried and pressure less sintered at a temperature of 1300°C for 4 h with a heating rate of 5°C/min in Okay (70 F6) electric furnace in the air atmosphere to remove residual B₂O₃. The process flow chart of the development of oxide-coated ABO_w powder is depicted in **Figure 3.3**.

3.3. Development of ABO_w reinforced in aluminium metal matrix composite by powder metallurgy process

3.3.1 Material selection and fabrication process for composite

Pure aluminium metal powder (purity of 99.5%) and particle size of 20–40 μm was used as a matrix and procured from Poly-chem Pvt Ltd, Bangalore, India. A simple method of semi-powder metallurgy was adopted for effective dispersion of the ABO_w whiskers in the matrix [72]. The constituent powders were mixed in non-reactive solvent

instead of ball milling. Al powder was vigorously mixed with ethanol with a magnetic stirrer for 40 min, and then ABO_w was added in varying contents of 5, 10, and 15 wt. % at 80°C in a vacuum and stirred for another 15 min. After hydrolysis, sol was dried in an oven at 110°C in a vacuum for 4 h, dried sol was then mixed with PVA (polyvinyl alcohol) solution, and at last, the pellet was pressed with the hydraulic press at 180 MPa.

3.3.2 Sample preparation for various testing

Rectangular specimens with the dimensions of 50 mm × 10 mm × 10 mm for flexural strength, cylindrical specimens with the dimensions of 30 mm (length) × 8 mm (diameter) for wear tests, and cylindrical specimens with the dimensions of 20 mm (length) × 15 mm (diameter) for compression tests were sintered in argon gas environment in a sintering furnace. The heating rate was 5°C/min to raise the temperature to 600°C and soaked for 2 h and subsequently cooled to room temperature.

3.4. Development of SiO_2 coated ABO_w reinforced in aluminium metal matrix composite by powder metallurgy process

3.4.1 Material selection and fabrication process for composite

For the development of coated ABO_w composites, the mass ratio of SiO_2 to ABO_w selected was 1:10 [73]. Fine SiO_2 (<40 μm; purity 99%) powder procured from CDH Pvt Ltd, New Delhi, was taken as a starting material to form a clear sol by mixing with distilled water for 20 min. SiO_2 and distilled water was taken in the ratio of 1.7. Aluminium powder (>45 μm; purity 99.5%; CAS: 1344- 28-1) was used as matrix material procured from Poly-chem Pvt Ltd, Bangalore, India. The aluminium metal powder was mixed with ethanol vigorously in a magnetic stirrer for 40 min [74], then SiO_2 coated ABO_w was added in various required percentages (5, 10, and 15 vol %) through a wet dispersion process and kept in an oven for 3 h. The dried mixture was

then cold-pressed isostatically through a die at 2 tons/cm² to get green compacts on a hydraulic press, which was degassed in an environment of elevated temperature.

3.4.2 Sample preparation for various testing

Rectangular pellets of dimension 50x10x10 mm³ were prepared for flexural strength measurement [75]. For diametral compressive strength and Young's modulus test, disc-shaped samples of 15 mm diameter and 5 mm thickness were prepared and fired in an argon gas environment in a sintering furnace at a heating rate of 5°C/min followed by heating at 600°C with 2 h soaking, and then cooled to room temperature. Internal bonding took place between the compact powder particles during the sintering process. Thus, solid-state bonding took place without melting of the pellets between the atoms, which may be referred to as solid-state sintering.

3.5 Development of SiO₂ coated ABO_w reinforced in aluminium (319) alloy composite synthesized by compo-casting

3.5.1 Material selection for the matrix of the composite

The pure commercial aluminium alloy (Al-319 ingots), also used as matrix material, was procured from the Khandelval aluminium work Pvt. Ltd., Mahmoorganj, Varanasi. The mg-turning fluxes (KCl and MgC₂.6H₂O) and degasser hexa-chloroethane (C₂Cl₆) were brought through the supplier R.K. scientific, Nadesar, Varanasi. The graphite rod for stirring purposes of 2.5 inch in diameter and 12.5-inch length was brought through Anil scientific PVT Limited, Varanasi.

3.5.2 Fabrication process of composites by compo-casting

Ingot pieces of Al-319 alloy were melted at 750 °C in a clay-graphite crucible in a resistance heating furnace and subsequently cooled to a semi-solid temperature of

610°C. Preheated ABO_w whiskers at 600°C were added through a coated injection tube with continuous stirring of the melt at 300 r/min for 30 min for better dispersions of whiskers. The synthesized composite slurry was bottom poured into a preheated permanent mould (280°C).

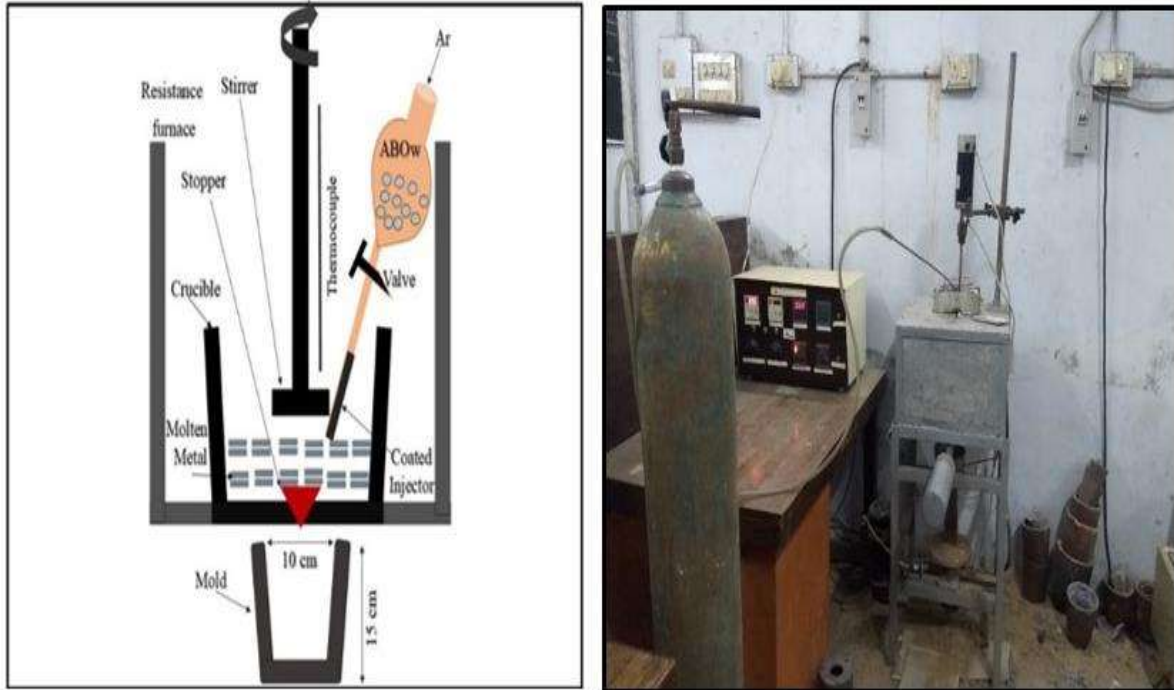


Figure 3.4: (a) Schematic of the experimental set-up used (b) pictorial view of compo-casting techniques

The schematic diagram is and pictorial view of the compo-casting technique shown in **Figure 3.4 (a& b)**. The chemical compositions of the matrix aluminium alloy (Al-319) and the composites were analyzed by an optical emission spectrometer (foundry master) and the same has been reported in **Table 3.2**.

Table 3.2 Compositional details of commercial aluminum (319) alloy

Elements	Si	Al	Fe	Cu	Mn	Mg
Wt%	5.71	90.00	0.628	3.21	0.421	0.028

3.6 Characterization

The following sub-section describes the techniques and procedures used to characterize the microstructural, physical (density/porosity), mechanical, and tribological behaviors of the reinforcement and aluminum matrix of the composites in the present investigation.

3.6.1 X-ray diffraction analysis of composites

X-ray diffraction investigation carried out the identification of phases present in both reinforcement and composites. It is a powerful non-destructive characterization tool for qualitative and quantitative phase analysis of crystalline materials. The technique is sensitive to crystal structure, and lattice spacing, various chemical phases, and compounds can be identified. Each phase or compound has a characteristic peak defined by positions (2θ) and intensities. X-ray diffraction (XRD) was performed by Rigaku desktop minflex II X-ray diffractometer (Tokyo, Japan) with a Ni-filtered Cu- $K\alpha$ radiation wavelength 1.541836\AA operated at 40KV/30mA with scanning speed of $3^\circ/\text{min}$ in the angle (2θ), the inter planner spacing, d , was evaluated using Bragg's law given by Eq.3.1, which is ultimately utilized for detection of different phases with the help of X-ray diffraction statistics details (JCPDS).

$$2d \sin\theta = n\lambda \quad (3.1)$$

Where, θ - Incident angle

λ -Wavelength of the X-ray

and an n -An integer representing the order of the diffraction [76].

3.6.2 Microstructural characterization of reinforcement and composites

For microstructural investigation, the specimen of base aluminium and composites were manually polished following the standard metallographic procedures as discussed below:

The surface of the metallic specimen was made plane through a specially designed motor-driven emery belt. The sharp edges of the specimen were then bevelled to avoid the tearing of the emery paper in the subsequent polishing. The specimens were then polished manually using the silicon carbide metallographic emery paper (400, 600, 800, 1200, and 1600 grit). During polishing on each emery paper, the grinding direction was changed at right angles from the previous grinding direction. The final polishing is carried out on a velvet cloth using Brasso and Kerosene oil on a polishing machine (Bainpol, Metco). After polishing, the specimen was etched using Keller's reagent for about 5-10 seconds, followed by washing and drying. Finally, dried samples were examined using an optical microscope (Dewinter Opticals Inc., New Delhi, India).

The microstructural study of the samples were performed by scanning electron microscopes (SEM), FEI, Quanta 200F, and high-resolution scanning microscope (HR-SEM) equipped with energy dispersive analysis of X-ray (EDAX) to explore the compositional analysis (Model no. Nova nano sem 450). HR-SEM helps better understand the coating of the ABO_w reinforcement and the bonding between the matrix and reinforcement phases at comparatively high resolution. The shape of the particles can also be observed through HR-SEM. These optical, SEM, HR-SEM microstructure, and EDAX spectrum are presented and discussed in Chapter 4, 5, 6, 7 and 8.

Transmission electron microscope (TEM) (Tecnai G²-20) operated at 200kV uses a particle beam of electrons to visualize specimens and generate a higher magnified

image than SEM and also shows the crystallographic structure and the composition of reinforcement and composites.

The behavior of worn surfaces under load conditions was examined by scanning/atomic probe microscope (SPM/APM) model no. NTEGRA Prima. For studying surfaces at the nanoscale level, an instrument scanning probe microscope (SPM) is used. It forms surface images by touching and scanning the sample surface with the help of a physical probe, thereby collecting the data in the form of a two-dimensional grid of data points displayed as a computer image.

3.7 Density measurement of reinforcement and composites

The experimental density of reinforcement samples and composites was evaluated using Archimedes' principle (ASTM C693) with the help of the calculated weight of samples in the air and water using an electronic balance having an accuracy of 0.001g. The bulk density is the mass per unit volume other than the pores. If all the pores in the body are removed, then the actual density of the material can be found. The experimental density of samples was evaluated. First, the dry weight of samples was measured (D). Then the samples were immersed using a thread into a boiling water bath for a period of up to 5 hours at 80°C. They are then removed from the bath, and tissue paper is used to remove the water on the surface only, and then soaked weight (S) was measured. Suspended weight (W) was determined by measuring the soaked samples suspended in the air. Then bulk density (BD) and apparent porosity (AP) of the reinforcement samples, base Al matrix, and composites were evaluated using the [77].

3.8 Thermal Analysis of the ceramic whiskers/reinforcement

3.8. Differential thermal analysis (DTA/DSC) and Thermo-gravimetric analysis (TGA)

It is a technique in which the difference in temperature between the sample and reference material is monitored against time or temperature. In contrast, the temperature of the sample, in a specified atmosphere is programmed. It is also called differential scanning calorimetry (DSC). The sample and the reference are placed symmetrically in the furnace model no. is DSC-60 Plus. The TGA model no. TGA-50 technique measures the mass of a sample as it is heated, cooled, or held at a constant temperature in a defined atmosphere. The properties and behavior that the TGA technique can measure include composition, purity, decomposition reactions, decomposition temperatures, and absorbed moisture content [78].

3.9 Hardness measurement of composites

The hardness of the base aluminium and the composites was measured using a Vickers hardness tester (Leco) with a load of 5 kg. The Vickers method is based on an optical measurement system. The micro hardness test procedure, ASTM E-384, specifies a range of light loads using a diamond indenter to make an indentation measured and converted to a hardness value. The micro-hardness methods are used to test metals, ceramics, and composites almost any type of material [79]. Since the test indentation is minimal in a Vickers test, it is helpful for a variety of applications: testing very thin materials like foils or measuring the surface of a part, small parts or small areas, measuring individual microstructures, or measuring the depth of case hardening by sectioning apart and making a series of indentations to describe a profile of the change

in hardness. Measurement of tensile strength/flexural strength/compressive strength of composites

3.10.1 Measurement of tensile strength of base alloy and composites

The uniaxial tension test provides an easy and efficient method to characterize the response of a material to loading .

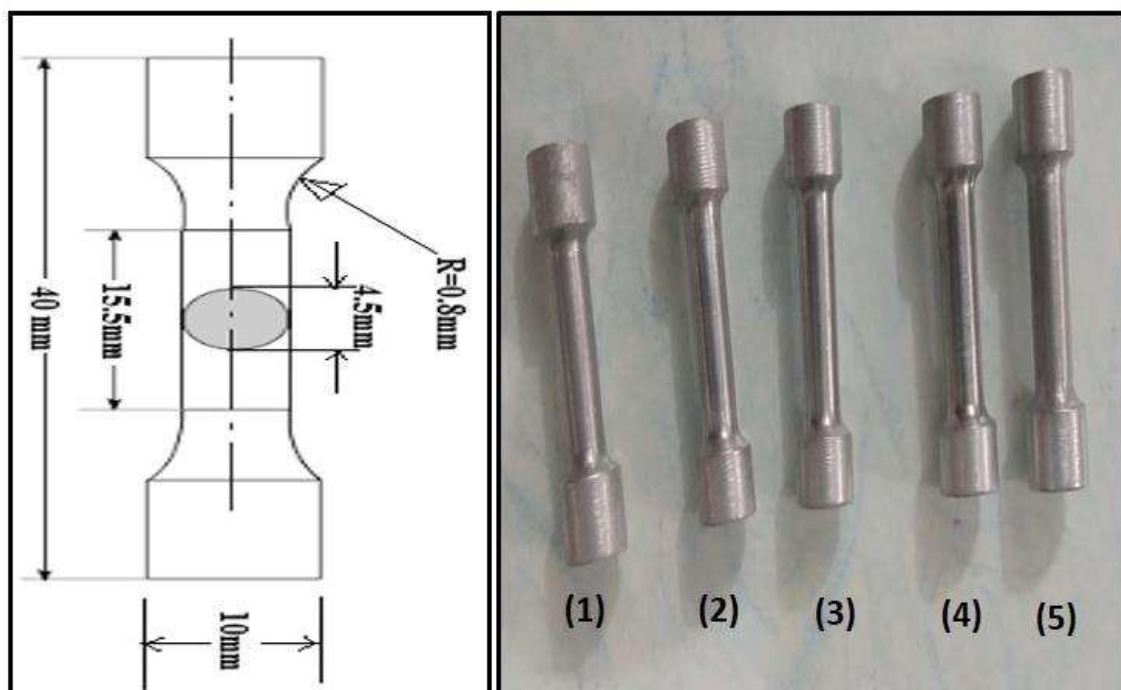


Figure 3.5: Schematic and pictorial measurement of a tensile test specimen

By subjecting a specimen to a controlled tensile movement along one axis, alter in dimensions and ensuing load can be recorded to evaluate a stress-strain, change in dimensions and elastic properties of materials can be evaluated from the profile [80]. The tensile test was executed on base aluminium alloy and composites ,and the ultimate tensile strength (UTS) was calculated. The uniaxial tensile test for base Al-319 alloy and composites was executed on the Instron tensile testing instrument having model no.5848 and crosshead speed of 0.15 mm/min. The test samples were developed as per

international standard ASTM E8; the schematic, pictorial and dimensional details of a tensile specimen is depicted in **Figure 3.5**. The uniaxial tensile test was executed on each material thrice for repeatability of the results and the average value of them was evaluated.

3.10.2 Measurement of flexural strength

The flexural strength at high temperature and the room temperature were measured. For high-temperature hot modulus of rupture (HMOR) measurements [81] were carried out by 3-point bending tests Nanotech (H7LKOUP) equipment with a crosshead speed of 0.10 mm/min at room temperature (27°C), 700°C, 800°C, 1000°C according to HMOR testing temperature (ASTM C583-8). The flexural strength represents the highest stress experienced within the material at its yield moment.

3.10.3 Measurement of compressive strength of base aluminium and composites

Compressive strength (CS) represents the ability of a product to resist failure under compressive load at room temperature **Figure 3.6 (a)**. A schematic diagram for measuring compressibility strength test specimen is shown in **Figure 3.6 (b)**. It has an indirect relevance to whiskers/composites performance and is used as one of the indicators of abrasion resistance. The higher the CS of material is, the greater should be the abrasion resistance. Base aluminium /aluminium alloy and composites with high CS are also expected to have higher resistance to load attack [82-83]. The compressive strength of P/M materials is measured using an extensometer clamped to the gauge length during the test. The stress at 0.1 % or 0.2 % permanent offset is usually reported. The determination of CS is also significant in the case of reinforcement samples where samples must be porous as well as strong.

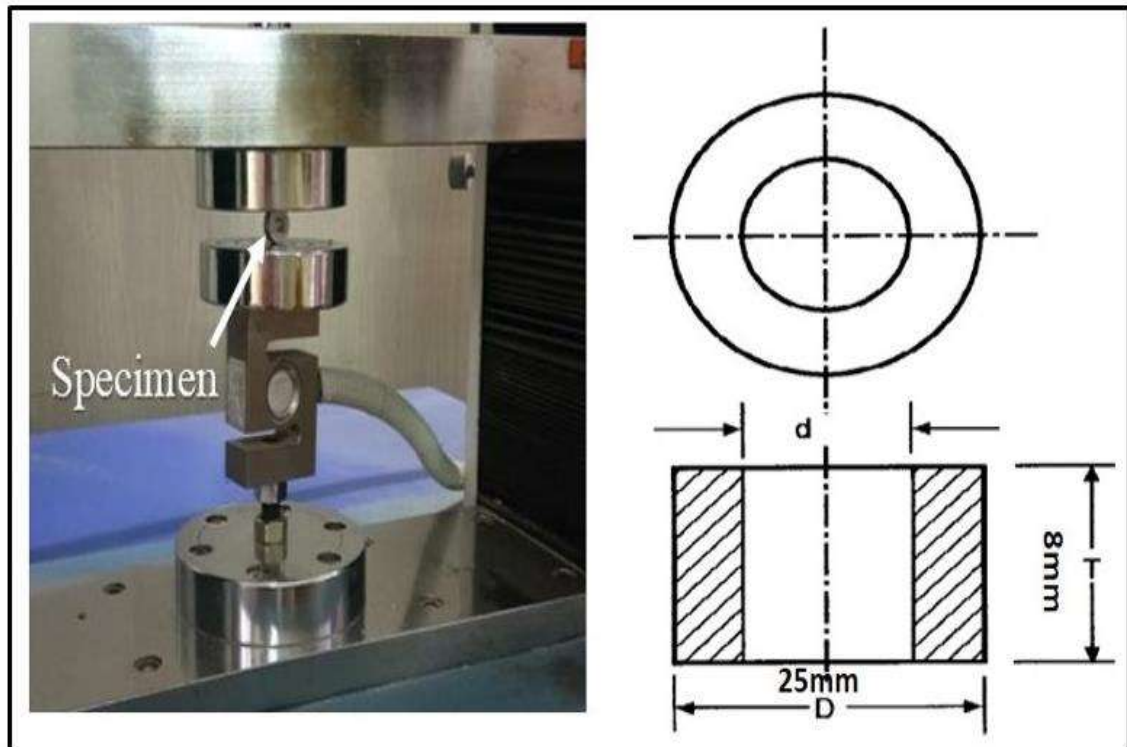


Figure 3.6: (a) DCS test set-up (b) schematic measurement of DCS test specimen

For the measurement of the CS, a steadily increasing compressive load is applied to the area (A) of the sample by a compressive force (F) until the sample fails.

3.10.4 Measurement of mechanical strength by non-destructive testing

Non-destructive test machine (Pundit Plus-215) was used for measuring the mechanical strength, e.g. Young's modulus. Longitudinal (V_L) and transverse (V_S) ultrasonic wave velocities of the test samples were measured.

The ultrasonic pulse-echo techniques were used to measure the velocity of a sound wave propagated in the polished samples. Adhesive materials like glycerin and burnt honey were used to bond between the sample and the transducer [84]. After that, Young's modulus (E) value of base alloy and composites was calculated using the following expression:

$$E = \frac{V_L^2 \rho (1 + \sigma)(1 - 2\sigma)}{(1 - \sigma)} \quad (3.2)$$

Where ρ is density and σ is the Poisson's ratio of the samples

3.11 Dry sliding friction and wear testing of materials

The base aluminium and developed aluminium alloy composites were dry sliding friction and wear tests were performed on the pin-on-disc machine (DUCOM, TL-20, Bangalore, India) as per the standard ASTM G99 in **Figure 3.7 (a)**. Friction and wear tests were performed using cylindrical specimens of 8 mm diameter and 30 mm length with flat surfaces in the contact region with round edges. The schematic diagram of the wear test specimen with dimensional details is depicted in **Figure 3.7 (b)**. The specimen was stationary against the rotating counter disc of 100 mm diameter EN-31 hardened steel with 60-62 HRC as provided in the pin-on-disc apparatus.

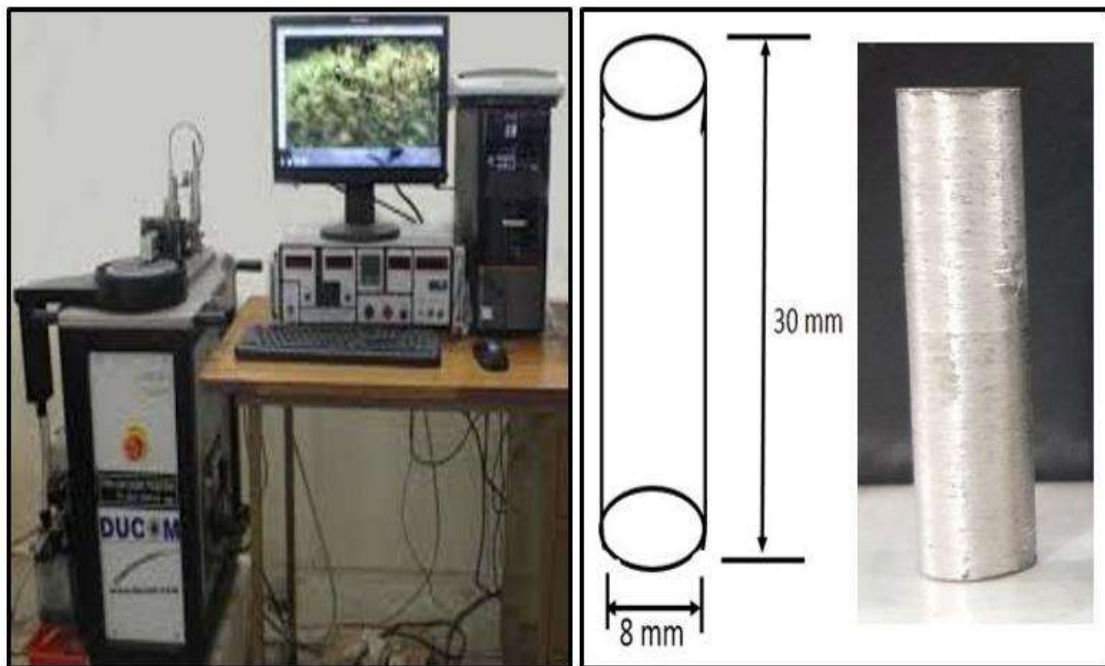


Figure 3.7: (a) Pin-on-disc type tribometer (b) schematic and diagram of the wear test specimen

The normal load was applied to the specimen through the lever ensuring continuous contact between the counter face and pin surface. The contacting surface of the specimen was polished with emery papers of 400, 600, 1200, 1600 grit size and cleaned with acetone earlier to conduct the wear and friction tests. The test was conducted under load and constant speed. Friction and wear tests were executed for a total time, and the loss of weight was calculated at the intervals of 10 min. To measure the weight loss, the specimen was uninvolved from the holder after 10 min of a run, allowed to down to room temperature, cleaned with brush smoothly to remove loose wear debris, weighed and fixed again in exactly in the same manner and position in the holder to avoid the disorientation of its sliding. An analytical balance having an accuracy of 1×10^{-7} Kg was used to weigh the specimen before and after the run. The result of weight loss was converted into volume loss utilising the density of the respective composite as measured by Archimedes' principle. The machine had a control panel showing the frictional force. The friction force was noted after every 60 sec and used to calculate the coefficient of friction dividing by the normal load [85].

