*CHAPTER-2*

# EXPERIMENTAL PROCEDURE

## 2.1 Introduction

This chapter provides the details of raw materials, procedure of synthesizing composites and details of different equipment used for the characterization of composite samples.

## 2.2 Raw Materials

AA5052 aluminium-magnesium alloy was acquired from Hindalco Industries, Renukoot, India and analysed for the constituents present as shown in Table 2.1.

**Table 2.1 -** Chemical composition of AA5052 alloy

| Element | Al | Mg | Si | Fe | Cu | Mn | Cr | Zn |
|---|---|---|---|---|---|---|---|---|
| Wt.% | 96.78 | 2.5 | 0.13 | 0.30 | 0.01 | 0.05 | 0.2 | 0.03 |

Two inorganic salts namely potassium hexa-fluoro-zirconate ($K_2ZrF_6$) with 97% purity and Potassium tetra-fluoro-borate ($KBF_4$) with 96% purity were obtained from Sigma Aldrich. These salts were used as flux to form the $ZrB_2$ reinforcement particles by *insitu* reaction of aluminium alloy and inorganic salts.

## 2.3 Synthesis of Composites

The amount of inorganic salts ($K_2ZrF_6$ and $KBF_4$) was calculated in the stoichiometric ratio and added in the mass ratio of 52:48 to prepare different compositions. These salts were dehydrated in an electric oven at 300°C for about 3 hours to remove the moisture present. Dehydrated salts were cooled, screened, mixed and wrapped into aluminium foils. AA5052 aluminium alloy was cut into small pieces and charged in required amount into a graphite crucible kept in a vertical muffle furnace. The furnace was equipped with bottom pouring arrangement and melting was done under controlled argon gas (99.99% purity) atmosphere. Reaction temperature and time are two important parameters which require optimization for preparation of the composites consisting only $ZrB_2$ particles. Several trial runs were conducted by varying the temperature and time to optimise the reaction temperature and time in which the *insitu* reaction completes. Once these parameters were optimised as 860ºC and 30 min, final castings were taken with these parameters to prepare composites with different compositions. Temperature of liquid melt was measured by K-type thermocouple. To prepare the composites with different vol. % (i.e. 0, 1.5, 3, 4.5, 6, 7.5, 9 and 10) of $ZrB_2$ particles, amount of salts was calculated (cf; Table 2.2) and added into the molten 0.5 Kg Al alloy at a temperature of 860°C [Kumar et al. 2015b; 2016a].

*Insitu* reaction took place at 860°C temperature and composite melt was maintained at this temperature for about 30 minutes to complete the reaction. During this period intermittent stirring was done by graphite stirrer to have uniform distribution of *insitu* formed $ZrB_2$ particles in the matrix. Before pouring, the melt was degassed and refined by hexa-chloro-ethane ($C_2Cl_6$) tablets, and the slag was removed. The melt was poured

into a preheated mild steel mould. The cast ingots were machined and cut to prepare the samples for different studies. The schematic diagram of experimental setup and flow chart for synthesizing the composites are shown in Figs. 2.1 and 2.2 respectively.

**Table 2.2 –** Amount of inorganic salts used to synthesize different composites

| S. No. | Material | $K_2ZrF_6$(× $10^{-3}$ Kg) | $KBF_4$ (× $10^{-3}$ Kg) |
|---|---|---|---|
| 1. | AA5052 - 0 vol. % $ZrB_2$ | 0 | 0 |
| 2. | AA5052 - 1.5 vol. % $ZrB_2$ | 43 | 38 |
| 3. | AA5052 – 3 vol. % $ZrB_2$ | 85 | 76 |
| 4. | AA5052 - 4.5 vol. % $ZrB_2$ | 128 | 114 |
| 5. | AA5052 – 6 vol. % $ZrB_2$ | 170 | 152 |
| 6. | AA5052 - 7.5 vol. % $ZrB_2$ | 215 | 190 |
| 7. | AA5052 – 9 vol. % $ZrB_2$ | 255 | 228 |
| 8. | AA5052 - 10 vol. % $ZrB_2$ | 284 | 253 |

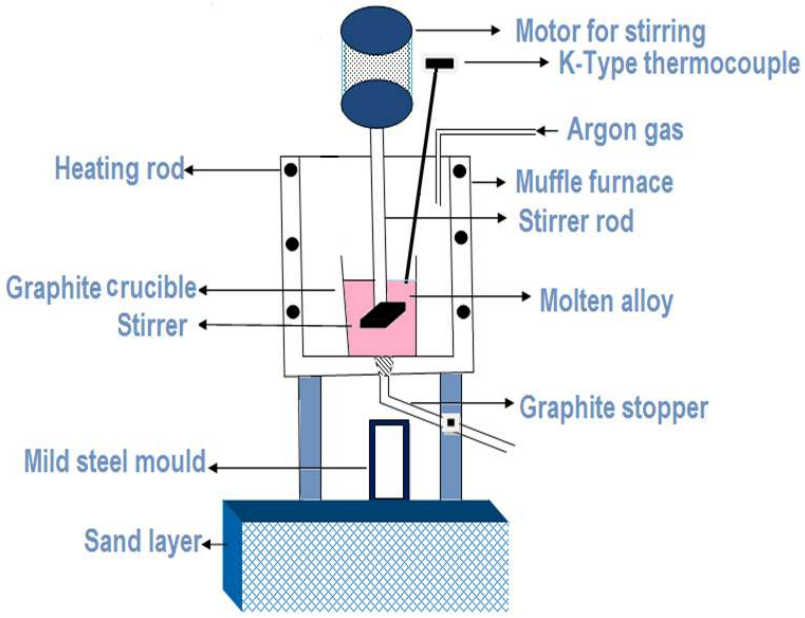



**Figure 2.1 -** Schematic diagram of experimental setup used for casting

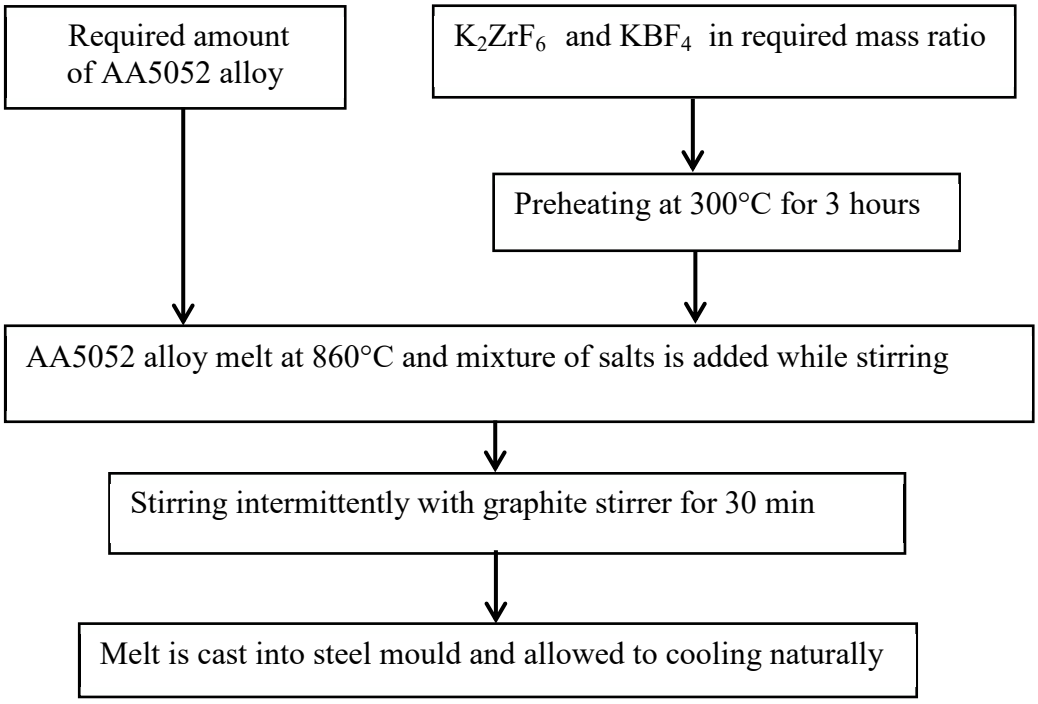



**Figure 2.2 -** Flow chart for synthesizing the composites

## 2.4 Characterization Using Different Techniques

### 2.4.1 Differential Thermal Analysis (DTA) Study

DTA (NETZSCH STA 449F3 STA449F3A-0843-M) study was conducted to find out the reaction temperature of *insitu* composites. The composite sample was heated at the rate of 10°C/min in the temperature range of 25-1100°C in an alumina crucible under nitrogen atmosphere. Figure 2.3 shows the DTA/TGA apparatus used for analysis.

**Figure 2.3 -** DTA/TGA apparatus for DTA analysis

### 2.4.2 X-Ray Diffraction (XRD) Study

Figure 2.4 shows the XRD (Rigaku Miniflex II X-ray diffractometer) machine used for identification of phases formed in the composites. $CuK_{\alpha}$ radiation of wavelength 1.541836 Å with Ni filter was used for analysis.


**Figure 2.4 -** XRD Machine

### 2.4.3 Extraction of $ZrB_2$ Particles

Actual amount of $ZrB_2$ particles in the composites was estimated by chemical extraction method. $ZrB_2$ particles were extracted from the composite by dissolving the known amount of composite sample in 10% HCl solution for several days. The solution was centrifuged at 15,000 rpm for 20 minutes and then supernatant liquid was filtered through Whatman ashless filter paper grade 42 to collect the $ZrB_2$ particles. Filtered residue of $ZrB_2$ particles was thoroughly washed, dried and weighed. The difference in weights of the extracted particles and composite sample was calculated to find the actual amount of $ZrB_2$ particles. Actual vol. % of $ZrB_2$ particles in the composites were found as given in Table 2.3.

**Table 2.3 -** Actual vol. % $ZrB_2$ in composites

| S. No. | Material | Theoretical vol. % $ZrB_2$ | Actual vol. % $ZrB_2$ |
|---|---|---|---|
| 1. | AA5052 - 0 vol. % $ZrB_2$ | 0 | 0 |
| 2. | AA5052 - 1.5 vol. % $ZrB_2$ | 1.5 | 1.23 |
| 3. | AA5052 – 3 vol. % $ZrB_2$ | 3.0 | 2.85 |
| 4. | AA5052 - 4.5 vol. % $ZrB_2$ | 4.5 | 4.20 |
| 5. | AA5052 – 6 vol. % $ZrB_2$ | 6.0 | 5.58 |
| 6. | AA5052 - 7.5 vol. % $ZrB_2$ | 7.5 | 6.95 |
| 7. | AA5052 – 9 vol. % $ZrB_2$ | 9.0 | 8.10 |
| 8. | AA5052 - 10 vol. % $ZrB_2$ | 10.0 | 8.55 |

### 2.4.4 Density and Porosity Measurement

The experimental density of base alloy and composites was determined by Archimedes principle which involved weighing the polished sample in air and in liquid of known

density. Application of the Archimedes principle leads to the following expression for the density measurement of composite ($\rho_c$ ) [Prasad et al., 2014],

$$\rho_c = \frac{m}{m-m_1}\rho_w \quad (2.1)$$

Where m is mass of the composite sample in air, $m_1$ is mass of same composite sample in distilled water and $\rho_w$ is the density of distilled water. The density of distilled water at 20°C is 998 Kg/$m^3$.

Porosity of composite is estimated by the following expression [Prasad et al., 2014],

$$\text{Porosity (\%)} = \frac{\rho_{th}-\rho_{exp}}{\rho_{th}} \text{ x } 100 \quad (2.2)$$

Where $\rho_{th}$ and $\rho_{exp}$ are the theoretical and experimental densities respectively. $\rho_{th}$ can be calculated from the rule of mixtures [Prasad et al., 2014],

$$\rho_{th} = \rho_m V_m + \rho_r V_r \quad (2.3)$$

Where $\rho_m$ is the density of matrix, $V_m$ is the volume fraction of matrix, $\rho_r$ is the density of reinforcement and $V_r$ is the volume fraction of reinforcement.

### 2.4.5 Optical Microscopy

Specimens were cut from the middle of all casting ingots and prepared for metallographic examination. Standard metallographic procedure was adopted in which specimens were mechanically ground and polished by using various grinding papers with grades ranging from 400 to 1200 and polished with 0.5 μm diamond paste using disc polishing machine. The polished specimens were etched with freshly prepared Keller's etchant containing 2.5 ml $HNO_3$, 1.5 ml HCl, 1 ml HF and 95 ml distilled

water. The microstructure was observed under Leitz Metallux-3 optical microscope as shown in Fig.2.5.

**Figure 2.5 -** Optical Microscope

### 2.4.6 Scanning Electron Microscopy (SEM)

SEM (FESEM Quanta 200FEG) and ZEISS (EVO18) (Fig. 2.6) were used for in depth analysis of distribution of *insitu* formed $ZrB_2$ particles. Morphology of the tensile fractured specimen and worn surface was also investigated under SEM.

### 2.4.7 Energy Dispersive Spectroscopy (EDS)

EDS (Model-51-ADD0048) has been used to analyse the worn surfaces and also to confirm formation of only $ZrB_2$ particles.

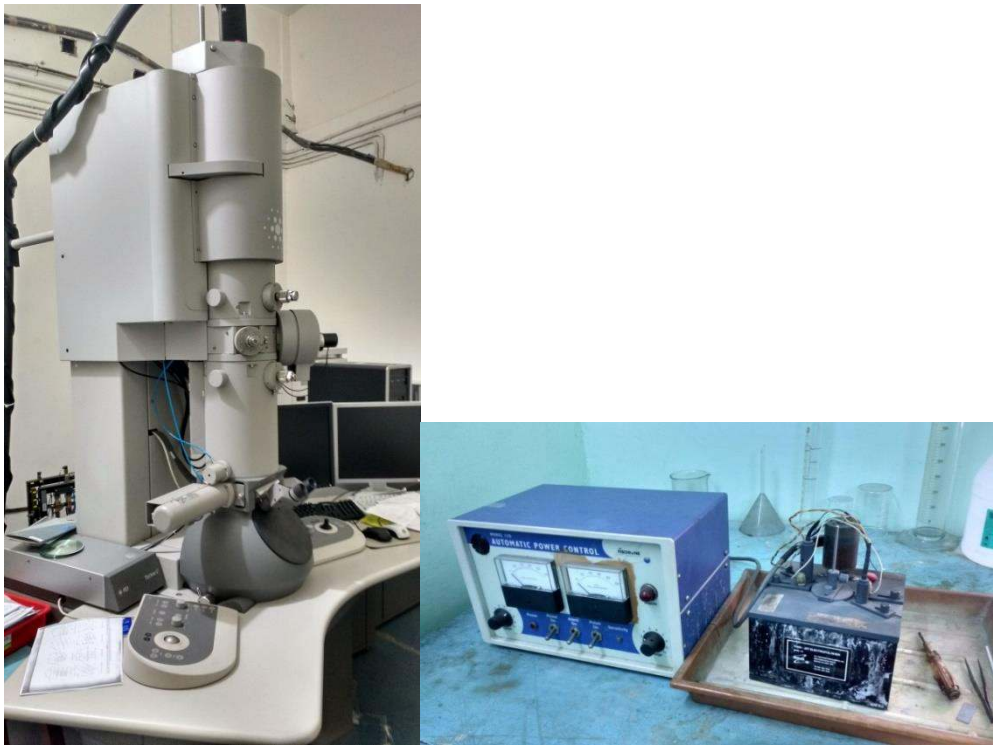

**Figure 2.6 -** Scanning Electron Microscope

### 2.4.8 Transmission Electron Microscopy (TEM)

TEM (TECNAI $G^2$ 20) shown in Fig. 2.7a was used to critically analyse the morphology, dislocations and interfacial characteristics. Thin slices of about 500 μm thickness were sectioned from composite sample using a thin diamond coated circular saw. The thickness of these slices was reduced to about 50 μm by emery paper. Discs of 3 mm diameter were punched from the thinned slice and TEM foils were prepared by electrolyte thinning in the electrolyte containing 90% ethanol and 10% perchloric acid cooled to - 35°C and 60 volts, using a twin jet polisher (FISHIONE, Model 110) as shown in Fig. 2.7b.

### 2.4.9 Hardness Testing

Hardness of the base alloy and composites was estimated by conducting Brinell hardness testing at 500 Kgf load for a dwell time of 30 seconds. Average of 5 readings of hardness values was taken. Brinell hardness tester used for the hardness measurement is shown in Fig. 2.8.




**(a)** **(b)**

**Figure 2.7 - a -** Transmission Electron Microscope and **b -** Twin jet polisher


**Figure 2.8 -** Brinell hardness tester

### 2.4.10 Tensile Testing at Ambient and High Temperature

Cylindrical tensile samples were prepared as per BS 12-1950 British Standards with a gauge diameter of 4.5 mm and gauge length of 15.4 mm [Kumar et al., 2014]. Tensile tests were carried out at ambient as well as high temperatures i.e. 50°, 100°, 150° and 200 ºC on computerised 100 KN screw-driven Instron$^{TM}$ Universal Testing Machine (model 4206) as shown in Fig. 2.9a, with a strain rate of 1.07 X $10^{-3}$ $s^{-1}$. Three specimens for each composition were tested and the average values are reported. Fig. 2.9b shows the geometry of tensile test specimen.

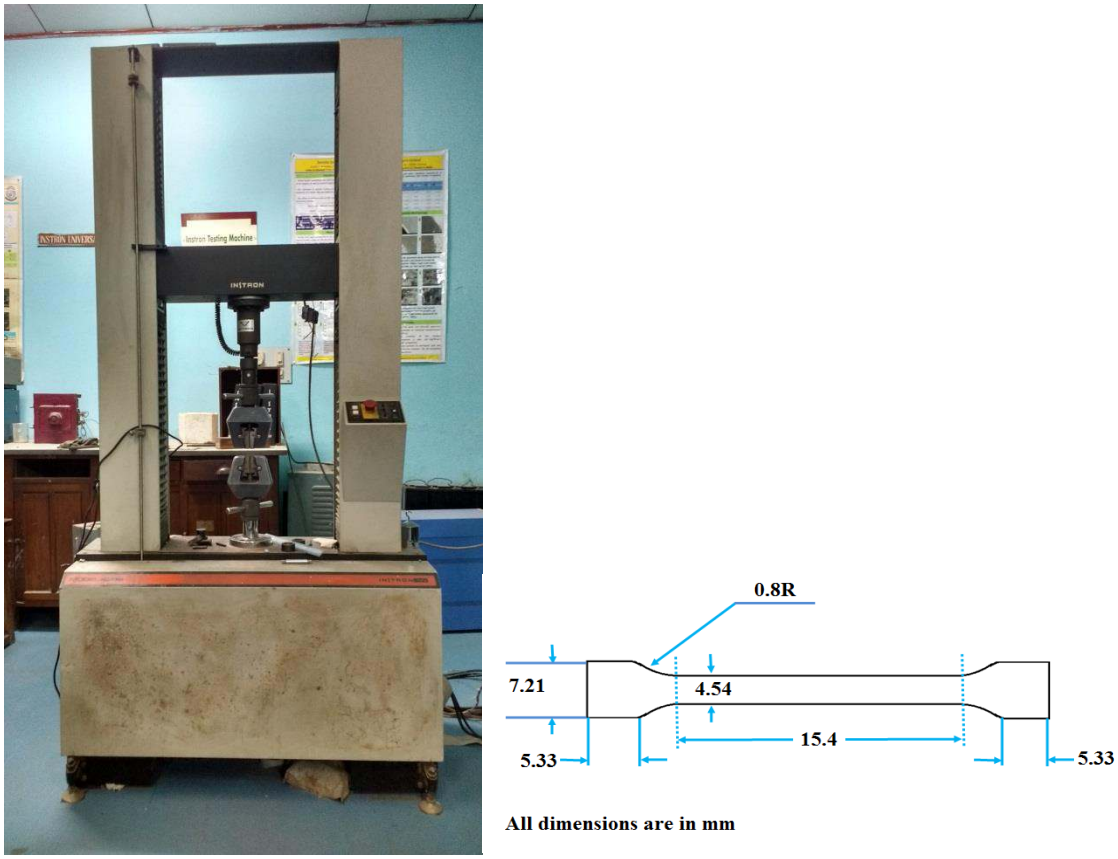



**Figure 2.9 - a -** Universal Testing Machine and **b** - Geometry of tensile test specimen

### 2.4.11 Ambient Temperature Tribology

Dry sliding wear and friction studies were carried out on Multifunctional Tribometer (Rtec-Instruments, USA) (Fig.2.10) at ambient temperature. Wear samples of composite and base alloy were prepared as per ASTM Standards [ASTM: G99-05, 2010] in the form of cylindrical pin having dimensions 30 mm height and 8 mm diameter. The wear samples were tested against a rotating hardened steel disc grade EN31 having diameter 50 mm, thickness 6 mm and hardness 62 HRC. Schematic diagram of pin-on-disc apparatus is shown in Fig. 2.11


**Figure 2.10 -** Multifunctional Tribometer

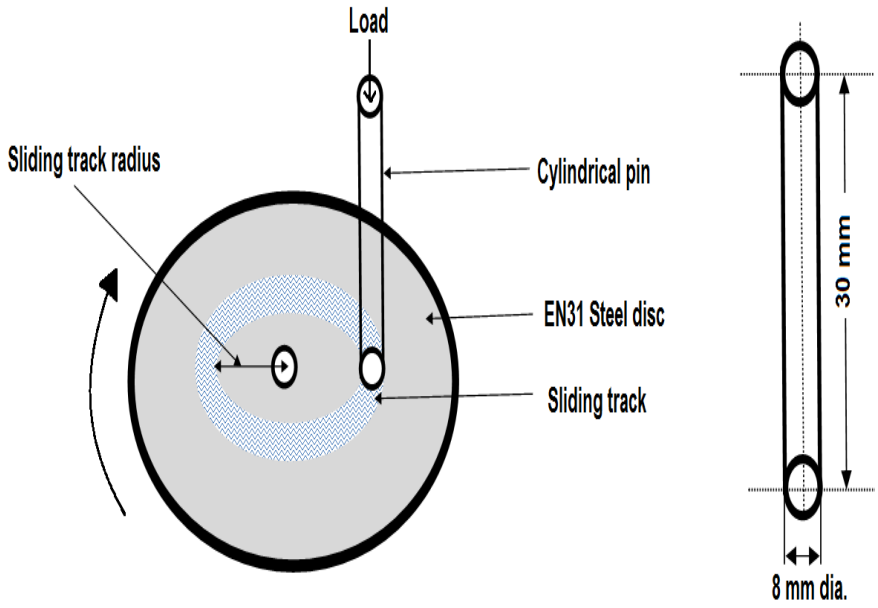



**Figure 2.11 -** Schematic diagram for pin-on-disc apparatus

Wear tests were carried out at four loads i.e. 10, 20, 30 and 40 N and four sliding velocities i.e. 0.5, 1.0, 1.5 and 2.0 m/s for a fixed sliding distance of about 3 Kilometres. All tests were conducted at ambient temperature under dry sliding conditions. After each test the pin sample was ultrasonically cleaned with acetone and weight loss was measured with a digital balance with least count of 0.1 mg. Wear rate was calculated from the weight loss measurements. Coefficient of friction was monitored continuously during the test and average value is reported. Worn surfaces of alloy and composite samples were analysed under SEM and Profilometer (Fig. 2.12) attached to the Multifunctional Tribometer.

### 2.4.12 High Temperature Tribology

High temperature dry sliding wear and friction tests were carried out on Multifunctional Tribometer at four temperatures i.e. 50°, 100°, 150° and 200°C. Cylindrical pin samples

(12 mm Ø 9 mm) were tested against hardened steel disc of grade EN 31 under normal loads 10, 20, 30 and 40 N at constant sliding velocity of 0.5 m/s and sliding distance of 1000 m. Figure 2.13 shows the various accessories used during wear testing at high temperature.

**Figure 2.12 -** Profilometer attached to Multifunctional Tribometer

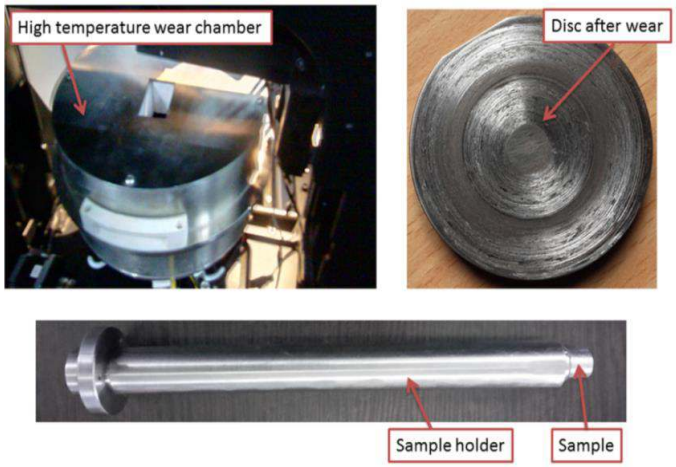



**Figure 2.13 -** High temperature chamber, disc and sample holder