CHAPTER 2

EXPERIMENTAL DETAILS

2.1 INTRODUCTION

This chapter provides details of fabrication of ZA alloy & ZA/ZrB_2 composites and different techniques used for their characterization.

2.2 MATERIALS

Raw materials required for fabricating ZA/ZrB_2composite were commercially pure Zn (99.20% pure), commercially pure Al (99.20% pure) and inorganic salts potassium tetra-fluro- borate (KBF_4) and potassium-hexa-fluro-zirconate (K_2ZrF_6). These were procured from Someshwar Metal Pvt. Ltd Nasik Maharashtra, Hindalco Industries Limited, Renukoot Uttar Pradesh and Sigma Aldrich Chemicals Private Limited, Bangalore Karnataka, India respectively. Table 2.1 shows the composition of ZA alloy used for fabrication of ZA/ZrB_2 composites.

Table 2.1 Composition of ZA alloy

Elements	Al	Mn	Cu	Si	Zn
Weight %	26.70	0.05	0.05	0.25	Balance

2.3 CASTING PROCEDURE

Small pieces of aluminum were charged into the graphite crucible placed in microprocessor PID controlled vertical muffle furnace at 850 °C (Fig. 2.1(a)). Once aluminum was in molten condition, inorganic salts wrapped in aluminum foil (commercially pure) were also charged. The amount of salts for different compositions is given in Table

2.2. These salts were pre-heated in an electric oven at 150 °C for 5 hour to remove the moisture content (Fig. 2.1(b)). The stoichiometry of the salts was maintained. Intermittent mechanical stirring was employed during *insitu* reaction using graphite stirrer for 30 min, which was the tentative time of completion of reaction. Then the required amount of cleaned small pieces of Zn were also charged, which were also preheated at 100°C for 1 hour in order to avoid any moisture present and allowed to melt. Intermittent stirring was continued at 300 rpm for homogenization of molten melt. Hexa-chloro-ethane (C_2Cl_6) was used for degassing of molten metal before pouring. Finally melt was poured into a preheated (at 300 °C for 3 hour) copper mold of 45 mm diameter (Fig. 2.1(c)). The as cast sample is shown in Fig. 2.1 (d). Five compositions were prepared with 0, 3, 4.5, 6 and 9 vol.% of ZrB_2. Test samples of required shape and size were cut from ingots as per requirements of various tests such as optical microscopy, XRD characterization, Hardness, Tensile and compressive strength etc. Likely reactions are given in following equations [Vineet et al. 2019]:-

$$3K_2ZrF_6 + 13Al \rightarrow 3Al_3Zr + 4AlF_3 + 6KF \quad (2.1)$$

$$2KBF_4 + 3Al \rightarrow AlB_2 + 2AlF_3 + 2KF \quad (2.2)$$

$$Al_3Zr + AlB_2 \rightarrow ZrB_2 + 4Al \quad (2.3)$$

Table 2.2 Amount of Inorganic salts required for 0.6 kg ZA alloy

Composites	**K_2ZrF_6 (g)**	**KBF_4 (g)**
ZA/0 Vol.% ZrB_2	0	0
ZA/3 Vol.% ZrB_2	56	50
ZA/4.5 Vol.% ZrB_2	84	75
ZA/6 Vol.% ZrB_2	112	100
ZA/9 Vol.% ZrB_2	168	150

Fig. 2.1 (a) Stir-casting set up (b) Electric oven (c) Copper mould (d) As cast sample

2.4 X-RAY DIFFRACTOMETER FOR PHASE ANALYSIS

Rigaku MiniFlex 600, X- ray Diffractometer using Cu-Kα radiation (wavelength 1.5 $A^{0)}$ has been employed to carry out phase analysis of the as cast *insitu* reinforced composite having different Vol.% of ZrB_2. To validate the presence of *insitu* formed particles, "d" spacing's were compared with the standard JCPDS files. The presence of these particles in the composites was further confirmed by the XRD analysis of extracted particles. The particles were extracted from the composite dissolving in 30% HNO_3, which took 10-12 days. The matrix of ZA was dissolved in 30% HNO_3. The solution was filtered by ash less filter paper. Later the extracted particles were heated in electric oven at 150°C for 5 hours to eliminate the moisture content.

2.5 COMPOSITIONAL ANALYSIS

Optical emission spectroscopy (OES) (Foundry master with frequency 100-400 Hz and voltage 300- 500 V) was carried out to determine the actual composition of alloy.

Polished samples cleaned with acetone were used to eliminate the problem of electric spark during testing. The test was done at three different regions and average was taken to calculate the final wt.% of the constituents.

2.6 DENSITY AND POROSITY

The experimental density was calculated using Archimedes principle. The required size and shape of as-cast samples were cut from both the end and from middle section of ingot. The equation is given below [Prasad et al., 2014]-

$$\rho = \frac{W_a}{W_a - W_w} \tag{2.4}$$

where,

$\rho -$ Density in g/cc,

$W_a -$ Weight in air in g

$W_w -$ Weight in water in g

The Rule of Mixture was employed to calculate the theoretical density of alloy and composite. The equation is given below [Varin, 2002] –

$$\rho_c = \rho_p VF_p + \rho_a VF_a \tag{2.5}$$

where, ρ_c, ρ_p *and* ρ_a denote density of composite, particle reinforced, and alloy respectively, and VF_p and VF_a are volume fraction of particle reinforcement and alloy phase respectively.

where, density is in g/cm^3 and weight of samples in air and water is in g.

The porosity was evaluated with the help of theoretical and experimental densities for all composite samples as given below [Prasad et al., 2014] –

$$\%\, porosity = \frac{\rho th - \rho e}{\rho th} \times 100 \quad (2.6)$$

where, ρ_{th}-theoretical density, ρ_{ex}-experimental density

2.7 MICROSTRUCTURAL CHARACTERIZATION

2.7.1 Optical Microscope (OM)

The Leitz Metallux-3 optical microscope was used to study the morphology of Zn-rich grain in composites with different vol.% of reinforcement particles. For microstructural analysis, Optical Microscopy (OM) has been performed. To carry out the sample preparation, a series of emery papers starting with 400 grit size to 2500 grit size were used followed by cloth polishin using Brasso paste (mixture of powdered abrasive with kerosene oil) of 2–4 micron. 10 ml of HNO_3 with 100 ml of distilled water have been used as etchant. ASTM E112 standard has been taken for the analysis of average grain size of composites and was calculated using optical micrograph using line intercept method [ASTM Standard E112, 1996]. Then the samples of all compositions were studied under optical microscope.

2.7.2 Scanning Electron Microscope (SEM)

Scanning Electron Microscope (SEM analysis was done using NOVA Nano SEM (Nova Nano SEM 450) attached with EDS. Particle size distribution of composites was calculated from the SEM image.

2.8 MECHANICAL PROPERTIES

2.8.1 Hardness Test

To analyze the effect of vol.% of ZrB_2 particles on hardness, macro hardness tests were carried out using Vicker hardness tester (Model number LM 248B AT). The samples

were prepared and tested according to ASTM standard E384. To verify the repeatability of data, 3 samples from different section and 8 tests per sample were done and average of all the data was calculated to determine hardness value of alloy and composites.

2.8.2 Tensile and Compressive Test

Tensile and compressive tests were performed at ambient temperature with strain rate of 0.01 s^{-1} using 100 KN screw-driven Instron™ Universal Testing Machine (UTM). For tensile testing ASTM E8 standard were used with specimens' size of 15.5 mm gauge length and 4.5 mm dia. While for compressive strength measurement ASTM E9 standard with specimen size of 15 mm length and 12 mm of diameter were used. The plots between engineering stress and engineering strain were used to determine the value of ultimate tensile strength (UTS), yield strength (YS) and percentage elongation. Average of four tests were conducted for UTS, YS and % elongation. The fractured surfaces were studied using NOVA EVO 18 SEM.

2.9 TRIBOLOGICAL PROPERTIES

2.9.1 Wear and Friction

Tribological properties of alloy and composites were analysed in dry and lubricating sliding conditions at ambient temperature. To carry out the tribology test pin on disc (PoD) tribometer setup from was used (Ducom TR-20 M26) ASTM G99-17 standard was used to perform tribology test at ambient temperature, and specimen was taken from midsection of as-cast sample. A cylindrical sample was prepared using a lathe machine with dimension of 30 mm length and 6 mm diameter. EN31 steel was employed as counter disc with 60 HRC. Samples were polished using number of emery paper followed by cloth polishing. The

average surface roughness value of polished samples was 150 ± 10 nm. To analyse the behaviour of alloy and composites in lubricating condition SAE 20W40 Motor oil was used. To assess the load-bearing capacity of the sample accurately, the emery paper of grit size 2000 was initially arranged on disc sample, and at lower load and velocity, the flattening of pin sample was carried out. The counter disc and pin sample were carefully cleaned using acetone before and after conducting the test. The weight of the pin sample was measured using a METTLER TOLEDO weighing machine with the least count of 0.1 mg. Tribology tests were performed at applied loads (10 N-50 N) and sliding distance (1000 m to 5000 m) at a constant sliding velocity of 2.5 m/sec and a lubricant flow rate of 5 ml/min. Weight loss was taken manually by measuring the weight before and after the test, and coefficient of friction was taken using data acquisition software attached to tribometer setup. The tribological data are represented in the terms of wear volume, wear coefficient and coefficient of friction. Each test was conducted three times to check the repeatability of obtained results. The wear volume is defined as the volume loss of material per unit density, while coefficient of friction is defined as the frictional force divided by normal force.

Volume loss has been defined by following equation according to ASTM standard [ASTM standards G99, 2010]:

$$volume\ loss = \frac{mass\ loss}{density} \times 1000 \qquad (2.7)$$

where, volume loss is in mm^3, mass loss is in gram, and density is in g/cm^3.

The wear coefficient is a better parameter to elaborate wear characteristics of material which is determined by the following equation [Banerjee et al., 2020]:

$$Wear\ coefficient\ (K) = \frac{\Delta W * H}{\rho * L * S} \qquad (2.8)$$

where, ΔW-weight loss, H-hardness (HV), ρ-density, L-applied load and S-sliding distance

The coefficient of friction was calculated with the help of recorded frictional force data during experiment.

2.9.2 Surface Topography

In order to understand the wear mechanism, worn surface texture studies were carried out using FESEM (Nova Nano SEM 450) attached with EDS. Atomic force microscopy (AFM) using INTEGRA Prima microscopy and SJ210 Surface Roughness Tester Mitutoyo were used to investigate the surface morphology and average surface roughness value (R_a in μm) of alloy and composites respectively. Further, the wear depth was also calculated for in-depth analysis of worn surfaces according to the following equation [Banerjee et al., 2020].

$$Wear\ depth = \frac{K*L*S}{A*H} \tag{2.9}$$

where, K-wear coefficient, H-hardness (HV), L-applied load, S-sliding distance, and A-cross sectional area of pin sample.

The wear debris was also analyzed by energy-dispersive X-ray spectrometer (EDS) to confirm the presence of elements under different operating conditions [Gautam et al., 2016, 2016a].

Table 2.3 presents the nomenclature of alloy and composites, while Table 2.4 presents the process parameters used to fabricate the alloy and composites. Table 2.5 presents the properties of synthetic motor oil used for lubrication.

Table 2.3 Nomenclature of ZA alloy and composites [Vineet et al., 20222]

Sr. No.	Composition	Nomenclature
1	Zn-27wt.% Al/0 vol.% ZrB_2	C0.0
2	Zn-27wt.% Al/3 vol.% ZrB_2	C3.0
3	Zn-27wt.% Al/4.5 vol.% ZrB_2	C4.5
4	Zn-27wt.% Al/6 vol.% ZrB_2	C6.0
5	Zn-27wt.% Al/9 vol.% ZrB_2	C9.0

Table 2.4 Parameters kept constant during fabrication [Vineet et al., 2022]

Sr. No.	Parameters	Value
1	Furnace temperature	840 ^{0}C
2	Pre heating temperature and time for inorganic salts	150 ^{0}C for 4 hours
3	Stirring time and speed	40 minutes at 300 rpm
4	Pre heating temperature and time for Zn	100 ^{0}C for 2 hours
5	Mold material	Copper
6	Mold dimension	220 × 40 × 40 mm
7	Pre heating temperature and time for mold	300 ^{0}C for 2 hours

Table 2.5 Properties of SAE20W40 motor oil [Wani et al., 2016]

Parameters	Kinematic viscosity at 40^{0}C, in mm^2/s	Dynamic viscosity at -10 °C, in mPas	Density in kg/m^3	Flash point, in °C	Pour point in °C	Viscosity Index
Values	116	2800	879	236	-30	135

2.10 STATISTICAL MODELLING USING RSM AND ANN

In the present study, the Response surface methodology (RSM) has been used to optimize the tribological parameters and Artificial neural network (ANN) is used to further validate the efficacy of the statistical model.

To analyze tribological behaviour the ANOVA analysis was conducted using RSM by Design-Expert 13 (DOE) software which suggested use of quadratic model. DOE is a productive technique that can be utilized in different experimental conditions. Response surface methodology (RSM) is an assembly of statistical and mathematical method that is used for modelling, investigation, and optimization, where the output is affected by many variables [Montgomery, 2001]. RSM reduces number of experiments and economically viable and powerful technique of optimization. Linear or square polynomial functions is mostly used in RSM in order to explain and investigate experimental conditions, second-order models are mostly employed in RSM owing to its flexibility and offer a good approximation to the true response surface [Palanivel, 2013].

In present study, a three-factor, three-coded level (low: -1, centered: 0, and high: +1) central composite design (CCD) based RSM was utilized to verify the optimal parameters for wear for alloy and composites. Load (A), sliding speed (B) and varying ZrB_2 vol.% were taken as independent factors, with wear as response variable. The whole process gives the influence of individual and combined parameters on wear (response variable), an analysis of mathematical models for the process optimization, and a check on the adequacy of the model. The depiction of lower and higher levels of independent factors is given in Table 2.6 by considering the optimized parameter value which is in between input variables (Load: 10–50 N; sliding distance: 1000- 5000 m and ZrB_2 content: 0-9 vol.%) based on the experimental optimization. Alpha is the distance of each axial point (a point lies on any of the axes of a co-ordinate system) from the centre in a central composite design. An alpha value less than one (<1) keeps the axial points inside of cube; a value equal to one (=1) keeps them on the faces of the cube, and

a value greater than one (>1) keeps them exterior to cube. In present study, alpha is taken as 1 and the axial points lie on the faces of the cube and due to this minus alpha and plus alpha values are also equal to the lowerand higher values of the variables as given in Table 2.6.

Table 2.6 RSM parameters for alloy and composites

Name of the factors	**Units**	**Low (-1)**	**High (+1)**	**-alpha**	**+alpha**
Load	N	10	50	10	50
Sliding speed	M	1000	5000	1000	5000
ZrB_2 Content	vol.%	0	9	0	9

ANN is stimulated from function of human brain and embody of extremely interlinked processing elements in family and termed as neurons. Interconnected neurons in specific pattern are termed as ‘‘architecture’. Execution of the neural network hinges on many invisible layers and some neurons in invisible layers, which is called as network structure [Rajasekaran et al., 2003]. Figure 2.2 presents schematic of the ANN structure used in this experimental study. Three input variables (applied load, vol.% of ZrB_2, and sliding distance) and one output (wear or COF) is taken for ANN network.

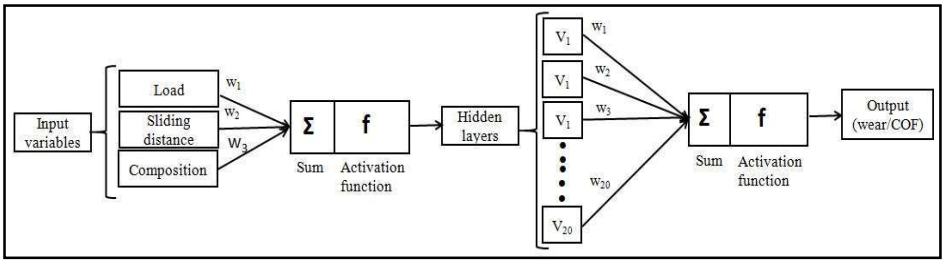

Fig. 2.2 ANN structure