DEVELOPMENT OF ZA/ZrB_2 INSITU COMPOSITE FOR TRIBOLOGICAL APPLICATIONS

Thesis submitted in partial fulfilment for the

Award of Degree

Doctor of Philosophy

By

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I would like to dedicate this Thesis

To my

Beloved Parents

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1. Abbreviation

Zn	Zinc
Al	Aluminium
Cu	Copper
Fe	Iron
C	Carbon
Zr	Zirconium
B	Boron
K	Potassium
F	Fluoride
Si	Silicon
Mn	Manganese
Mg	Magnesium
O	Oxygen
N	Nitrogen
Sn	Tin
Pb	Lead
Ni	Nickel
Gr	Graphite
Cr	Chromium
Ti	Titanium
W	Tungsten
N	Newton
µm	Micron
m	meter
cm	Centimetre
mm	millimetre
gm	gram
θ	Theta
α	Aluminium phase

β	Zinc phase
ε	metastable phase
η	Supersaturated phase
ρ	Density
Vol.%	Volume percentage
Wt. %	Weight percentage
MPa	Mega Pascal
HV	Vickers's Hardness
^{0}C	Degree centigrade
Sec	Second

2. Acronyms

ZA	Zinc- Aluminium
MMCs	Metal matrix composites
PMCs	Polymer matrix composites
CMCs	Ceramic matrix composites
ASTM	American Iron and Steel Institute
VHN	Vickers's hardness number
SAE	Society of Automotive Engineers
C0.0	Zn- 27 wt. % Al
C3.0	Zn- 27 wt. % Al/ 3 Vol.% ZrB_2
C4.5	Zn- 27 wt. % Al/ 4.5 Vol.% ZrB_2
C6.0	Zn- 27 wt. % Al/ 6 Vol.% ZrB_2
C9.0	Zn- 27 wt. % Al/ 9 Vol.% ZrB_2
RSM	Response Surface Methodology
CCD	Centre Composite Rotatable Design
DOE	Design of Expert
ANN	Artificial Neural Network
UTS	Ultimate tensile strength
YS	Yield Strength
SEM	Scanning Electron Microscopy
OM	Optical microstructure

EDS	Energy Dispersive X-ray Spectroscopy
XRD	X-ray Diffraction
TEM	Transmission Electron Microscopy
AFM	Atomic force microscopy

PREFACE

Tribology extends a wide range of answers to meet sustainability through improvement in working life and reducing frictional losses. From a Socio-ecological point of view, wear preservation can aid to increase the utility value with the same resource-consuming. Researchers have suggested reduction in CO_2 emission by improving tribological performance either through improving surface topography or by introducing microcavities in lubrication conditions, which increases mechanical parts' load-bearing capacity. Tribology has a wide range of applications such as in automobiles, marine, medical technology, etc. The automobile sector has the biggest potential for energy saving by applying advanced technology. Bronze-based alloys are extensively used for tribological applications, especially in automobile and machinery parts such as bearings, bushings, etc. However, owing to their high fabrications temperatures which requires lot of energy and low strength-to-weight ratio motivated researchers to look into alternative suitable materials.

Zn-Al based alloy are found to be suitable material for tribological applications due to its excellent castability, high strength-to-weight ratio, high wear resistance, and low fabrication cost. They are widely used as frame housing, gear housing, Zinc roofing, toothed wheel, plain bearing, gears, structural rods, etc. However, to widen and commercialize the applications of Zn-Al based alloys, further improvements in mechanical and tribological properties are required. This created an interest for suitable reinforcement. ZrB_2 reinforcement shows excellent interfacial bonding with Zn based alloy which results in an improvement in strength.

Zn-Al based composites can be fabricated either by *exsitu* technique, while adding particulates directly to matrix or by *insitu* process, where particulates are generated within the matrix. However, *insitu* processes are preferred over *exsitu* due to finer & homogenous particle distribution, clean interfaces, and more thermodynamically equilibrium phases with matrix. Liquid metallurgy route is one of the potential *insitu* methods for commercial production of composites due to its simplicity, low cost, and near net-shape forming capabilities. Present work has been divided into 8 chapters:-

Chapter 1: This chapter presents an introduction and literature review. It describes different types of composites, metal matrix composites (MMCs), advantages of MMCs, applications, and fabrication techniques with different matrices and reinforcements. It also embodies different types of wear and friction and their mechanisms. Developing materials for automobile applications that can exhibit high strength-to-weight ratio and good wear resistance requires a proper choice of the matrix, reinforcement material, and also suitable fabrication method.

Therefore, in the present study, Zn-Al alloy has been chosen as matrix phase and ZrB_2 as reinforcement phase as it is ultra-high temperature ceramic exhibiting high hardness (36 GPa), high melting point (3246°C), superior high-temperature strength, high thermal and electrical conductivities. ZrB_2 could be a good candidate for reinforcement to improve the mechanical and tribological properties of Zn-Al alloy. The stir casting technique is one of the promising *insitu* techniques that has been chosen for the fabrication of composites.

The objective of the present study is to develop the Zn-Al/ ZrB_2 composites to provide superior tribological properties than few of existing materials to extend life and efficiency of certain parts.

Chapter 2: This chapter deals with a brief introduction of equipment used for the characterization of the composites. Composites have been prepared using stir casting route.

The formation of second-phase particles in the composites was identified using a Rigaku Miniflex X-ray Diffractometer using Cu-Kα radiation (λ = 1.5405 Å). Actual volume of formation of particles was also confirmed by the chemical extraction method using 15% HCl solution. Chemical compositions were evaluated by the optical emission spectrometer. The morphology of the grains was examined under Leitz Metallux-3 optical microscope (OM). The distribution of particles and their morphology were observed under FESEM Quanta 200FEG scanning-electron microscope (SEM), and ZEISS (Model-EVO 18) SEM. The theoretical density was calculated by the rule of mixture, the experimental density of the composites was evaluated using the Archimedes principle and porosity was calculated with the help of theoretical and experimental density.

The tensile and compressive tests were conducted at room temperature at a strain rate of 1.05×10^{-3} s^{-1} using a 100 KN screw-driven Instron™ Universal Testing Machine (Model 4206). Hardness was evaluated by LM 248AT Vicker hardness tester at 30N load with 30s dwell time. Friction and wear properties were evaluated on a pin-on-disc configuration of a multi-function tribometer in dry and lubricating sliding conditions at room temperature at constant velocity (2.5 m/s) with varying sliding distance (1000 m – 5000 m) and applied loads (10 N- 50 N). Samples after tests were observed by SEM/ EDS, AFM, and surface profilometer to understand the operative wear mechanism under different conditions.

Chapter 3: It deals with the fabrication of composites with varying vol.% of ZrB_2 particles in the Zn-Al alloy, identification of different phases formed by XRD, compositional analysis by optical emission spectrometer, and effect of vol.% of ZrB_2 particles on the mechanical and tribological properties. Morphology studies show grain refinement of the Zn-rich phase on the incorporation of ZrB_2 particles. SEM analysis reveals uniform particle distribution with hexagonal morphology of particles. Mechanical test results indicate improvement in strength parameters such as ultimate tensile strength (UTS), yield strength (YS), and compressive strength with an increase in the vol.% of ZrB_2 particles. A comparative study with already existing materials reveals that present materials exhibit high strength-to-weight ratio and has potential for tribological applications.

Chapter 4: It deals with the tribological behavior of alloy and composites in dry sliding conditions. Cumulative volume loss and coefficient of friction (COF) increase with an increase in sliding distance and applied load. Decrease in wear while an increase in COF was observed with increasing ZrB_2 content and at 9 vol.% of ZrB_2 composites shows the least wear. The worn surface study was carried out by SEM attached with EDS, AFM, and Surface profilometer. At a lower sliding distance and applied load, mild/oxidative mode of wear while at higher load and sliding distance, severe/oxidative-metallic modes of wear were observed. AFM analysis and surface profilometer study exhibit smoother topography with low average surface roughness with increasing the ZrB_2 content. These results are in agreement with wear and friction data. The obtained properties reveal that the present material can be used for low wear and high friction applications such as disc and brake etc.

Chapter 5: Last chapter showed that this composite could be an alternative to brake material. However, to see its behavior with lubricants to explore its possibility in other application study with lubrication was also conducted. SAE20W40 motor oil was used as a lubricant with a flow rate of 5 cm^3/hr. Tribological behavior is investigated under varying sliding distance, applied load, and varying volume % of ZrB_2 at constant velocity. Worn surfaces have been investigated using SEM with an EDS surface profilometer and AFM. Observed results are investigated with the support of morphology, hardness, and texture studies. In lubricating conditions very less wear was observed at lower load and sliding distance while at higher loads and sliding distance mild wear is observed for composites while for alloy relatively more wear. However, it was interesting to note that in the presence of lubricant, the COF values also decreased even with an increase in ZrB_2 content. It could be due to the presence of microcavities, which act as pockets for lubricant retention and the material system behaves as self-lubricating material and making them a suitable material for bearing applications. AFM and surface profilometer study reveals smooth topography minimum average surface values even at higher load and sliding distance (50 N and 5000 m) and least COF at 9 vol.% of ZrB_2 which indicates less wear loss of material and less frictional losses thus an overall reduction in materials footprint and energy losses.

Chapter 6: This chapter deals with the comparative study of tribological properties in dry and sliding conditions. Comparison has been done by comparing their wear and COF behavior along with wear mechanism in both dry and lubricating sliding conditions using. It was found that with the addition of lubrication volume loss decreases drastically even at higher loads and sliding distances which offers even wider scope of applications of the present materials. Observation also reveals that in presence of lubrication the severity of damage is very less, with less wear depth and low average surface roughness.

Chapter 7: This chapter is categorized into two sections. The first section deals with statistical modelling of tribological parameters in dry sliding conditions while the second section deals with statistical modelling of tribological parameters in lubricating sliding conditions. Response surface methodology (RSM) using Design expert 13 (DOE) was used to optimize the response parameter (wear and COF) also the Artificial neural network (ANN) was used to further verify the results. Based on RSM, CCD was generated, and based on the best-fitted curve quadratic model was suggested for both wear and COF with R^2 value very close to 1 and a p-value less than 0.05 signifying the efficacy of the model. Predicted and experimental values found to be very close, which confirms that this model can be used for prediction of properties to minimize unnecessary experimentation. ANN results also show high accuracy to predict and optimize the tribological parameters with R^2 value close to 1 for both training and test and an error value below 5% for all the predicted and experimented data suggesting the accuracy of the model. Further, the optimum tribological parameters were obtained using both models. Master regression was developed to predict or optimize tribological parameters at any given set of input parameters. Also, the 2D and 3D plot for both RSM and ANN are given to see the wear and COF behavior with varying input variables and the results are in agreement with experimental results. The correlation matrix was generated and composition was found to be the most contributing factor.

Chapter 8: It summarizes the main conclusions on the morphology, mechanical, and tribological properties of Zn- Al/ ZrB_2 composites as discussed in different chapters of the thesis. In addition, wear properties in terms of specific wear rates and COF have been compared with earlier work, and the scope of the present work has also been presented.