PREFACE

During the last few decades, Metal Matrix Nanocomposites have attained an important position in the industries as they are being used successfully in a wide range of applications due to improvement in the structural, mechanical and electrochemical properties. Metal Matrix Nanocomposites (MMNCs) basically consist of ductile metallic matrix with the dispersion of hard ceramic reinforcements it. MMNCs have several advantages over other general wrought materials such as a higher specific strength, higher specific modulus, lower coefficient of thermal expansion, higher wear resistance and better properties at elevated temperatures. Lot of investigations have been carried out using aluminium, magnesium and copper as the matrix, however, no systematic attempt has been made to study the iron based nanocomposites. Therefore, in order to investigate iron based composites and to explore its scientific importance, the present thesis is divided into following ten chapters:

Chapter 1 Metal Matrix Composites (MMC) – *An Overview*: Composite materials are engineered or naturally occurring materials made from two or more constituent materials with significantly different physical or chemical properties which remain separate and distinct at the macroscopic or microscopic scale within the finished structure. General applications of composite materials are in automobile, aerospace and aeronautical industries. Present chapter also gives an overview on various types of composite materials such as Metal Matrix Composite (MMC), Polymer Matrix Composite (PMC) and Ceramic Matrix Composite (CMC) Materials, various techniques for processing MMC products and their wide engineering applications. This chapter also discusses powder metallurgy processing route which is an attractive process to synthesize MMCs. It helps in manufacturing products with homogeneity and high dimensional accuracy and avoids large number of operations, high scrap losses and high energy consumption.

Chapter 2 Literature Review: Metal Matrix Composites (MMCs) have high modulus, fracture and compressive strength. They also show improved thermal, wear and corrosion resistance. The characteristics of powder metallurgy processed metal matrix composites are greatly influenced by: (i) Percentage of the reinforcement (ii) Phase and microstructure which depend on the processing parameters and heat treatment schedule (iii) Bonding between the dispersoids and the matrix.

The present chapter briefly reports available literature about the investigations on metal matrix composites (MMCs) describing (i) Processing of composites by stir casting and powder metallurgy, (ii) aluminium, copper, magnesium and iron based metal matrix composite systems, their structural, mechanical and electrochemical behavior and effect of processing parameters on their properties.

Chapter 3 Aims and Objectives of Present Investigations: The aims and objectives of the present investigations are focused on the preparation and characterization of Fe-Al_2O_3, CoO and CeO_2 doped Fe-Al_2O_3 and Fe-Al_2O_3-ZrO_2 hybrid metal matrix nanocomposite specimens. On the basis of the results of the initial work a detailed work plan was prepared to explore the optimum composition and processing parameters for development of Fe-Al_2O_3 Metal Matrix Nanocomposites with good mechanical, erosive and corrosive properties. The characteristics of materials also depend on doping, them with suitable dopants and additives as secondary phases. Therefore, in order to investigate the effect of doping we have selected one transition metal oxide CoO and one rare earth oxide CeO_2 to selected compositions of Fe-Al_2O_3 nanocomposites. These compositions were processed with optimum sintering schedule to study the effect of doping on mechanical and electrochemical behavior. Similarly, to investigate the effect of addition of secondary ceramic reinforcement, we investigated Fe-Al_2O_3-ZrO_2 hybrid metal matrix nanocomposite to study the effect of composition and processing parameter on structural and mechanical behavior. Synthesized specimens were characterized for phase, microstructure, energy dispersive spectroscopy, density, hardness, wear, deformation and corrosion respectively.

Chapter 4 Synthesis and Characterization Methods: This chapter describes (i) synthesis of composite specimens by powder metallurgy route with sintering in the temperature range 900-1100°C in inert argon atmosphere, (ii) XRD, SEM, EDAX methods for structural characterizations, (iii) density, hardness, wear, deformation methods for mechanical characterizations and (iv) Tafel polarization for electrochemical (corrosion) studies.

Chapter 5 Sintering and Hardness Behavior of Fe-Al_2O_3 Metal Matrix Nanocomposites: The present chapter focuses on the structural and mechanical behavior of Fe-Al_2O_3 metal matrix nanocomposites. The specimens were synthesized by varying the percentage of Al_2O_3 followed by sintering in the temperature range of 900 - 1100°C for 1-3 hour respectively. XRD results revealed the formation of iron aluminate phase whose quantity increased with the increase in the percentage of alumina. SEM results show dense phase structure with the presence of nano size dispersion of iron aluminate phase. Amount of iron aluminate phase formation also depends upon the sintering temperature and time respectively. Nano size particles were found to be highest in the 20% Al_2O_3 reinforced specimens. Density of the specimens increased with an increase in the sintering temperature and time respectively. It was also found that density value depends on the iron aluminate phase formation. The hardness of the formed specimens was also found to be dependent on the density as well as on the iron aluminate phase formation.

Chapter 6 Wear and Deformation Characteristics of Fe-Al_2O_3 Metal Matrix Nanocomposites: The present chapter describes wear characterization of Fe-Al_2O_3 metal matrix nanocomposites. Dry sliding wear test was carried out on the specimens at a load of 0.5, 1.0 and 2.0 kg respectively. Scanning electron micrographs of the worn out specimens were also taken. The wear rate values and the worn micrographs helped the researcher to get the deeper understanding of the subject. It was found that the wear behavior of the specimens depends on the iron aluminate phase formation. For 5% of Al_2O_3 addition, the adhesive wear was more prominent at lower load whereas abrasive wear was more prominent at higher load. For the 10% of Al_2O_3 reinforcement, the removal of the material is due to fragmentation of asperities and removal of material is also due to cutting and flowing actions of penetrated hard asperities into the softer surface. It can also be seen from table 6.1 that the wear rate of 5% Al_2O_3 reinforced iron matrix composites showed low values of wear rate at 0.5 kg load whereas the wear rate values were high at higher loads i.e. at 1.0 and 2.0 kg in comparison to 10% Al_2O_3 reinforced iron matrix nanocomposites. Thus, it can be concluded that the wear rate values reduced significantly on increasing the amount of Al_2O_3 reinforcement.

In the last part of the present chapter test specimens having different height to diameter (h/d) ratios have been synthesized by compacting and sintering at 1100°C for 1 h and deformed at room temperatures under different interfacial friction conditions. The deformation patterns of different specimens were studied and it is found that the dry specimens show more bulging than the lubricated ones. The test specimen show more surface movement on top surface than the bottom surface in all the deforming conditions. SEM images of $h/d<1$ showed the crushing action between the grains, $h/d=1$ shows the grain growth formation in the form of nano flakes and nano rods whereas the $h/d>1$ images shows the sliding action between the grain boundary and grains respectively. Apart from this the present chapter also focuses on the verification of the experimental deformed density with the theoretical deformed density.

Chapter 7 Studies on Structural and Mechanical Characterization of CoO and CeO_2 Doped Fe-Al_2O_3 Metal Matrix Nanocomposites: The present chapter discussed the effect of CoO and CeO_2 doping on Fe-Al_2O_3 metal matrix nanocomposites synthesized via powder metallurgy technique. In the current chapter it is observed that how small amount of doping can change the structural and mechanical behavior of the formed nanocomposites. It has been observed that on increasing the cobalt oxide percentage from 0.5 to 1.0%, there was a significant reduction in the iron aluminate ($FeAl_2O_4$) phase formation. However, the density and hardness values were found to improve. Microscopic images showed the nano size particles of Fe and Al_2O_3 separately. It was found in the present case that CoO particles bonds in between the particles of Fe and Al_2O_3 thereby reducing the reactive sintering rates. In the similar manner on increasing the cerium oxide (CeO_2) percentage from 0.5 to 1.0% in the nanocomposite specimen there was a formation of iron aluminate ($FeAl_2O_4$) phase along with the presence of separate cerium oxide phase. The hardness values were found to increase with an increase in the percentage of cerium oxide. Values of wear rate were found to decrease with the increase in the percentage of cerium oxide. It can be concluded that various structural and mechanical properties were found to improve by doping CoO and CeO_2 in Fe-Al_2O_3 metal matrix nanocomposites.

Chapter 8 Studies on Structural and Mechanical Characterization of Fe-Al_2O_3-ZrO_2 Hybrid Metal Matrix Nanocomposites: In Fe-Al_2O_3-ZrO_2 hybrid metal matrix nanocomposites the consolidation and phase formation mechanism depends upon the sintering temperature and time respectively. At lower sintering temperature i.e. 900°C and sintering time of 1, 2 and 3h the reaction rate between the various particles is less due to which the amount of iron aluminate ($FeAl_2O_4$) and iron zirconium oxide (Zr_6Fe_3O) phase formation is reduced. Due to the lower temperature and time of sintering, the specimen shows low values of density and hardness. However, on increasing the sintering temperature to 1000 and 1100°C for all time of sintering shows more amount of iron aluminate and iron zirconate phases respectively. At higher temperature and time of sintering the bonding between iron aluminate and iron zirconium oxide particles with the iron particles is improved. Due to the higher bonding strength the structural and mechanical properties is improved. Density and hardness values are found to increase with an increase in the sintering temperature and time respectively. Hardness value of Fe-Al_2O_3, Fe-ZrO_2 metal matrix nanocomposites was found to be in the range of 40-45 HRH and 40-52 HRH whereas the hardness value of CoO doped Fe-Al_2O_3 nanocomposites were found to be in the range of 38-43 HRH. Hardness values [55-60 HRH] of the hybrid metal matrix nanocomposites were found to be better in comparison to the Fe-Al_2O_3, Fe-ZrO_2 and CoO doped Fe-Al_2O_3 metal matrix nanocomposites. Wear rate of the Fe-Al_2O_3 and CoO doped Fe-Al_2O_3 metal matrix nanocomposites was found to be high. Wear of the hybrid nanocomposite specimens was also found to be less in comparison to Fe-Al_2O_3 and CoO doped Fe-Al_2O_3 metal matrix nanocomposites.

Chapter 9 Corrosion Behavior of Fe-Al_2O_3 Metal Matrix Nanocomposites: The present chapter describes the corrosion behavior of 5 - 10% Al_2O_3 reinforced, CoO doped Fe-Al_2O_3 and CeO_2 doped Fe-Al_2O_3 metal matrix nanocomposites. XRD and SEM of the corroded specimen were also recorded in order to study the effect of HCl on the respective phase as well as on the morphology of the specimen. Following are the important findings of the present chapter:

1) During corrosion in Fe-Al_2O_3 metal matrix nanocomposite system carried out in freely aerated 1N HCl solution leads to the formation of aluminium chlorate ($AlCl_3O_{12}$) phase. Aluminium chlorate phase forms a film on the surface of the specimen due to the chemical reaction of alumina with hydrochloric acid. Formation of aluminium chlorate film is in nano size.

2) CoO doped Fe-Al_2O_3 metal matrix nanocomposite system showed the formation of nano size film of $AlCl_3O_{12}$ and $CoCl_2$ due to the chemical reaction between hydrochloric acid and alumina alumina and cobalt oxide respectively. Finer nano size particles of aluminium chlorate are found after the corrosion. Specimen 10AFe1.0Co1100(1) and Pure Fe+0.5% CoO showed the highest corrosion protection.

3) CeO_2 doped Fe-Al_2O_3 metal matrix nanocomposite system showed the formation of nano amorphous layer on the specimen surface. 10AFe0.5Ce1100(1) sample showed the highest corrosion protection.

Chapter 10 Conclusions and Scope for Future Research Work: The present thesis reports the successful synthesis of Fe-Al_2O_3 (5-30 wt%) metal matrix nanocomposites synthesized via powder metallurgy technique. Specimens were synthesized by compacting and sintering in argon atmosphere in the temperature interval of 900 - 1100°C for 1 – 3 hours respectively. Fe-(5/10%) Al_2O_3 metal matrix nanocomposite specimens shows the presence of iron aluminate phase. Iron aluminate phase formation depends upon the sintering temperature and time respectively. High amount of iron aluminate as is present in (20/30%) Al_2O_3 reduces the bonding strength between the particles and thus increases the brittleness. 5% and 10% of Al_2O_3 reinforced metal matrix nanocomposite show better hardness, wear, deformation and corrosion characteristics respectively. In the next stage of the investigation successful synthesis of CoO and CeO_2 doped Fe-(10%) Al_2O_3 nanocomposites were carried out by sintering at 1100°C for 1 h. It was found that the doping of cobalt oxide reduced the iron aluminate phase formation however cerium oxide doping enhanced the iron aluminate phase formation. Properties of both CoO and CeO_2 doped specimens were found to improve. Corrosion behavior of CoO doped specimen was found to be best among all the specimens. Corrosion resistance improved on increasing the percentage of cobalt oxide doping. However, 0.5% CeO_2 doped specimen showed the best corrosion characteristics. The last investigation focused on the successful synthesis of Fe-Al_2O_3-ZrO_2 hybrid metal matrix nanocomposites synthesized via powder metallurgy technique. The specimens were compacted and sintered in the temperature range of 900-1100°C for 1-3 hour respectively. Specimens showed improved mechanical properties. Iron aluminate and iron zirconium oxide phases were formed due to the reactive sintering between the iron – alumina and iron –

zirconia particles respectively. Hardness values were found to be high in comparison to Fe-Al_2O_3 metal matrix nanocomposites. Wear rate of the specimens were found to be reduced in comparison to the synthesized Fe-Al_2O_3 metal matrix nanocomposites. It is expected that the outcome of the present investigation will be helpful in designing and developing metal matrix nanocomposites for heavy duty applications.

On the basis of above investigations there is an ample amount of scope for further research work for the development of iron based metal matrix nanocomposites.

- Synthesis of few more specimens can be done using different dopants such as titanium di-oxide etc.
- Wear behavior of the same specimens can be carried out by varying the sliding velocity and keeping the sliding time and load as a constant factor.