PREFACE

The surge for the design and development for new and advanced materials have always been enticing to the materials engineering & science community. The intermetallics and metal matrix composites (MMCs) are receiving increasing attention among the advanced materials due to their high strength, stiffness and high-temperature properties. The intermetallic compounds have emerged as technologically important materials widely used for high-temperature applications. The discovery of aperiodic intermetallics i.e., quasicrystals in 1984 by Dan Shechtman has been a path-breaking development, which has redefined the conventional concept of crystallography. The inherent room temperature brittleness and reduced dislocation activity of periodic and aperiodic intermetallics have resulted in its low fracture toughness. This low values of fracture toughness often restrict its large scale structural applications. Similarly, in the year 2004, yet another paradigm shift in the materials development strategy has given birth to the concept of high-entropy alloys (HEAs) having five or more than five alloying elements in equiatomic, near equiatomic or non-equiatomic ratio. These HEAs was first reported by Brian Cantor and J W Yeh independently and despite having five or more elements in equiatomic proportions mostly resulted in disordered solid solution. On the other hand, the aluminium matrix composites (AMCs) falling under the class of MMCs have received much attention due to their high strength to weight ratio. Designing and finding suitable reinforcement for these AMCs has always been challenging as well as awarding. For developing high strength AMCs, Al-based metal matrices have been reinforced with quasicrystals and HEAs.

The processing of these advanced materials is equally necessary for developing materials for engineering applications. The nanostructured alloys and AMCs have better properties compared to their conventional counterpart. The nanostructuring of the aperiodic intermetallics (i.e. quasicrystals) and AMCs improves its strength and toughness. These nanostructures alloys and AMCs can be synthesized by solid-state techniques, i.e. mechanical milling. Non-equilibrium processing routes can synthesize the nanostructured alloys and AMCs for tailoring their physical and mechanical properties. The consolidation of these nanostructured alloys and AMCs are challenging and can be accomplished through various non-equilibrium consolidation techniques like spark plasma sintering (SPS), vacuum hot-pressing (VHP), and hot isostatic pressing (HIP).

The present work deals with the synthesis and processing of the nanocomposites of Al-Cu-Fe quasicrystalline matrix reinforced with Sn particles and AA 6082 Al matrix reinforced with Al-Cu-Fe icosahedral quasicrystal (IQC) and non-equiatomic AlSiCrMnFeNiCu HEA. The study aims at understanding the structural transformation, thermal stability and microstructural features of these nanocomposite powders. Attempts were made to consolidate these nanocomposite powders through SPS, hot-pressing (HP) and pressure-less sintering. The structure, microstructure and mechanical properties of these bulk composites were studied in detail.

The thesis is divided into six chapters. **Chapter-1** presents the introduction and current understanding of the theme of the work based on the reviewed literature available. This chapter briefly describes the timeline for design and development of the new materials, i.e. quasicrystals, high-entropy alloy and high strength Al matrix composites. The crystallography, properties and applications of quasicrystals was described along with present shortcomings for its application as a structural material. The section on the AMCs briefly discusses the AMCs reinforced with various unconventional reinforcement such as quasicrystals and HEAs. This chapter also concerns the different material processing methodology being used in the present work. The objectives of the present study are listed at the end of this chapter.

Chapter-2 describes the details of the materials and experimental procedure used for the present work. This chapter mentions the equipment and protocol required for materials processing and its characterization. Vacuum induction melting was used for preparing as-cast quasicrystalline and non-equiatomic high-entropy alloy (HEA) and was further crushed into a particle size of $\leq 100\ \mu m$. Mechanical milling (MM) was used for synthesis nanocomposite powders of quasicrystalline and Al matrix composite through high energy planetary ball milling. The structural and microstructural features of these nanocomposites were studied through X-ray diffraction (XRD) and transmission electron microscopy (TEM), and scanning electron microscopy (SEM) equipped with energy dispersive spectroscopy. The thermal stability of these nanocomposite powders was established through differential scanning calorimetry (DSC). The heating events in the DSC thermogram were co-related with the phases evolved by ex-situ XRD of annealed composite powder or by in-situ XRD. The hardness and indentation behaviour of these nanocomposite powders studied through microindentation and nanoindentation techniques. Further, these nanocomposite powders were consolidated through SPS, HP and pressure-less sintering for fabricating bulk composite. The phase analysis and microstructure of bulk composites were studied through XRD and TEM, and optical microscopy (OM) and SEM, respectively. The mechanical properties of these bulk composites were investigated through microhardness and compressive testing.

Chapter-3 presents the investigation on the mechanically driven structural transformation in Sn reinforced Al-Cu-Fe quasicrystalline (IQC) matrix nanocomposite (NC). The sequence of structural transformation, phase composition, thermal stability and hardness of mechanically milled IQC-Sn NC powder were studied. The XRD result suggests the formation of nanostructured composites. The IQC phase co-existed with $Al_{13}Fe_4$ (a=1.549 nm, b=0.808 nm, c=1.248 nm, α=β=90˚, γ=107.720˚; mC102; C2/m) and B2-type Al (Cu, Fe) (a=0.29 nm; cP2; $Pm\bar{3}m$) phase, in IQC-Sn NC powder subjected to MM for 40 h. The double diffraction was observed due to the layering of nanocrystalline B2 and IQC phase in the NC powder. The inner concentric and outer ring corresponds to the B2-type and (422222) reflection of the IQC phase, respectively. The phases formed during MM transforms to stable IQC phase along with crystalline phases during subsequent annealing treatment as confirmed by XRD and nano-beam diffraction (NBD). The structural transformations occurring during MM have a remarkable effect on indentation hardness, which is in the range of ~ 4 to 7 GPa. This nanocomposite powder was consolidated by SPS, HP, and pressure-less sintering. The phase evolved in SPSed IQC-Sn composite was also found to be dependent on the volume fraction of Sn reinforcement in the IQC matrix. The bulk composite prepared by SPS has shown significant enhancement in the compressive yield strength ~75% for IQC-20Sn. The fracture toughness of the IQC-10Sn HPed composite was found to increase by ~22%. The increase in the compressive yield strength and fracture toughness of these bulk composite was attributed to the inhibition of cracks by soft Sn particles homogeneously dispersed in the IQC matrix by milling and sintering.

Chapter-4 deals with studying the effect of Al-Cu-Fe IQC reinforcement on the structure, morphology and phase composition of AA 6082 Al matrix nanocomposites processed through mechanical milling and SPS. The characterization of these milled and SPSed AMCs was done through XRD, TEM, and SEM. The MM induces microstructural refinement of the matrix, and the extent of improvement was dependent on the volume fraction of the IQC. However, the partial structural transformation of IQC phase to $Al_{13}Fe_4$

crystalline phase (a=1.549 nm, b=0.808 nm, c=1.248 nm, α=β=90˚, γ=107.720˚; mC102; C2/m) was only evident for AMCs reinforced with 40 vol% of IQC. The presence of (311111) diffraction peak of the IQC phase in AMCs confirms the existence of face-centred IQC phase even after 50 h of MM. The Al-IQC was consolidated at 300 °C (573 K) with a pressure of 500 MPa, and another set of the sample was consolidated at 450 °C (723 K) and 550 °C (823 K) with a pressure of 50 MPa. It was observed that on increasing the reinforcement in AMCs, the relative density of the composite increases and reaches a maximum value of 99.5% for Al-40IQC. The compressive yield strength and ultimate strength of these AMCs is ~519 MPa and 639 MPa respectively. However, the Al-30IQC SPSed at 300 °C (573 K) with a pressure of 500 MPa for 30 min has resulted in a significant rise in the compressive yield strength ~900 MPa. The enhancement in the mechanical properties may be attributed to strong interfacial bonding of the Al matrix and IQC reinforcement due to interfacial reactions.

Chapter-5 concerns with investigating the effect of non-equiatomic AlSiCrMnFeNiCu high-entropy alloy (HEA) reinforced Al-based metal matrix composite. These HEA used as reinforcement was prepared by vacuum induction melting followed by 30 min milling for its fragmentation. The HEA was reinforced into the AA 6082 Al matrix by MM followed by pressure-less sintering. The structure, microstructure and morphology, compositional analysis, and thermal stability of these HEA and Al-HEA nanocomposite powders were ascertained using XRD and TEM, SEM-EDS, and DSC respectively. The HEA used as reinforcement was found to have a two-phase microstructure with a major phase corresponding to the B2-type and a minor phase of Cr_5Si_3. The MM imparts significant refinement of the Al matrix, and a nanostructured grain of ~10-12 nm was observed for Al-30HEA nanocomposite powder. For AMCs with a higher fraction of reinforcement, the HEA was found to be well embedded in the 6082 Al matrix and has an excellent interfacial bonding. The Al-30HEA nanocomposite powder was found to be thermally stable up to 650 °C (923 K). This was confirmed by correlating the DSC thermogram with the in-situ XRD investigations. It provided a basis for the consolidation of Al-HEA composite at high temperature through pressure-less sintering. The pressure-less sintering of Al-30HEA has led to the formation of a thin ~500 nm transitional layer at the interface of 6082 Al matrix and HEA reinforcement. The microhardness of Al-HEA composite was found to be encouraging, and a maximum microhardness of ~1.72 GPa was observed for Al-30HEA composite. This high value of microhardness was attributed due to the formation of the transitional layer and indirect strengthening of Al-HEA composite.

Chapter-6 presents a summary of the work indicating major findings and observation arising out from the present work along with the suggestions for future work.

Reference section provides the list of relevant references (~400) cited in Chapter 1-6 of the thesis.