Abstract

Mechanical Alloying (MA) is a versatile technique, for developing a wide variety of conventional as well as novel materials, with unique microstructures having unusual properties. Mechanical Alloying involves milling of powders in a desired weight ratio in an ambient or inert atmosphere, during which, repeated welding, fracturing and rewelding of powder results in a homogeneous mixing of powders with fine structures. Apart from its ability to synthesise conventional alloy systems, Mechanical Alloying can also be used to produce alloys of immiscible systems, intermetallics, nanocrystalline phases, ceramics and composites. In addition, MA has been used directly in the synthesis of metals from compounds such as oxides by milling in a reducing atmosphere.

Alloys of the immiscible Copper-Iron system have potential applications in automotive, electrical and electronic industries. The main difficulty in the processing of copper-iron alloys is the immiscibility of the elements in each other. Therefore these alloys have to be processed by nonequilibrium techniques. Several techniques such as vapour deposition; ion mixing and Mechanical Alloying (MA) have been used to prepare copper -iron alloys. Among the various techniques, Mechanical Alloying is a very versatile technique for synthesising equilibrium phases, metastable phases such as quasicrystalline and nanocrystalline phases, composites and the like. Mechanical Alloying of several metallic and non -metallic systems has been done. Mechanical Alloying is being used commercially for manufacturing several commercially important alloys and composites. In this work, Mechanical Alloying has been chosen for preparing copper - iron alloys because of its commercial application potential.

Chapter 1

Chapter 1 gives an introduction to Mechanical Alloying, its advantages over conventional and other new material processing techniques such as Rapid Solidification Processing (RSP) .The processing capabilities of MA are also explained.

Chapter 2

A detailed literature review on the formation of several metastable phases by MA and in particular on studies on MA in Cu-Fe system have been presented in chapter 2. Mechanical Alloying of Cu-Fe system has been investigated by several workers, covering

the entire range of compositions from copper rich end to the iron rich end of the phase diagram. Various aspects of MA of copper - iron system such as formation of solid solutions, formation of metastable supersaturated nanocrystalline phases, crystal structure and compositions of the metastable phases have been investigated using X-ray diffraction, optical microscopy Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Differential Scanning Calorimetry (DSC) and Energy Disperse Xray Analysis (EDAX). Also the thermal stability of the alloys formed on MA during annealing have been investigated. Magnetic property studies using Mossbauer spectroscopy, Extended X-ray Absorption Fine Spectroscopy (EXAFS), as well as measurement of Giant Magento Resistance (GMR) have also been done. XRD investigations have confirmed the formation of solid solutions having a FCC structure (when the copper content exceeds 70 at %), and a BCC structure for Copper less than 30 at %, or a mixture of both FCC and BCC phases (Copper 30 to 70 at %). Grain sizes calculated from XRD patterns have shown the formation of nanocrystalline grains. Optical microscopy and Scanning Electron Microscopy (SEM) studies have confirmed the particle deformation and fracture resulting in finer particle sizes as milling progressed. Transmission Electron Microscopy (TEM) studies has shown the evidence for the formation of a lamellar structure typical of Mechanical Alloying. TEM studies on thermally annealed samples have shown evidence for a reverse martensitic type of transformation during annealing. Magnetic measurements using Mossbauer Spectroscopy have shown evidence for the formation of solid solutions during MA, confirming the XRD results. Extended Fine Absorption Spectroscopy (EXAFS) investigations to study the near neighbour environment in the milled powders have confirmed the alloying of copper and iron powders. Giant Magneto Resistance (GMR) studies on MA Cu- Fe samples have shown a sharp increase in the magnetic resistance of the alloyed samples which decreased on subsequent annealing.

Quasicrystalline phases have been observed in Copper -iron alloys prepared by ion mixing and solid state inters diffusion (SSI). Though extensive work on MA of Copper- Iron system has been done, the formation of quasicrystalline phases have not been reported. The present work has been taken up to investigate the possibility of solid state crystalline lattice instability, inducing formation of Quasicrystalline or amorphous phases, by continued milling under favourable milling conditions. Interest was particularly focussed on understanding the role of defect generation rate-millingmilling intensity), types of defects and their mobility (milling temperature) under the chosen milling conditions in governing the formation of metastable phases on MA. The objective of the present work was also to study the effect of the nanocrystalline state formed on MA on the phase stability of a wide range of systems including Cu-Fe with a positive enthalpy of mixing and to compare with systems showing a negative heat of mixing like Cu-Ti, Cu-Al etc. The thermal stability of the phases synthesised by MA was also of interest, considering the varying tendencies for alloying in these two classes of systems.

Chapter 3

The scope of the present investigations is presented in Chapter 3. These include investigation of the influence of defect density on the formation of equilibrium phases, formation of metastable phases on MA, factors influencing the formation of such metastable phases as well as thermal stability of the phases formed on MA.

Chapter 4

Chapter 4 discusses in detail the various experimental procedures adopted in the study. In the present work MA of 65 Copper - 35 iron powders were carried out using both a vibratory ball mill and an attritor mill. Milling was carried out for varying time durations including 2 to 100 hours for ball milling and 15 min to 10h in the case of attritor.

The milled powders were subjected to investigation by particle size analyser, optical microscopy, Scanning Electron Microscopy (SEM), x-ray Diffraction and Transmission Electron Microscopy (TEM) to study the:

i) Evolution of microstructure during milling (particles shape and size change)

ii) Formation of metastable phases

iii) Thermal stability of metastable phases formed

iv) Detailed microstructural characterisation of the phases formed

v) hot forging of MA powders and evaluation of properties.

In the present investigation , Mechanical Alloying of the immiscible copper-iron system (positive heat of mixing) was taken up as the main work. As copper -iron system has a positive heat of mixing, it was considered appropriate to compare the Mechanical Alloying of copper -iron with few other alloy systems having a negative heat of mixing. So MA of copper-titanium and copper-aluminium systems (exhibiting negative heat of mixing) were also studied for comparison . The process of alloying in these systems, formation of metastable phases such as amorphous phases and intermetallics, (if any), during milling was examined, as well as their stability on thermal annealing. In the case of Copper-Titanium system, powders of Copper and Titanium (in the ratio 75:25) were milled for varying times from 10 to 100 hours. Similarly in the case of Copper-Aluminium, powders of Cu and Al (20:80) were alloyed for times varying from 10 to 200 hours. The MA powders were hot forged at 873 K and evaluated for hardness and oxidation resistance.

Chapter 5

In the case of copper-titanium as well as copper-aluminium systems, in spite of their high negative heat of mixing, no evidences of formation of intermetallic phases could be found. The high density of defects induced on MA, and the sensitive dependence of the thermodynamic stability of intermetallic phases on defect content can restrict their formation and lead to formation of metastable supersaturated NC phases, which can accommodate higher fraction of defects. Formation of intermetallic phases were observed on post annealing of MA powders. Annihilation of defects on annealing trigger the formation of the thermodynamically stable intermetallic phases leading to the decomposition of the metastable supersaturated NC alloys. Oxidation resistance of hot forged Al-Cu compacts was found to be superior compared to that of hot forged Cu-Ti powders.

Mechanically Alloyed copper-iron powders were characterised for their size by ultrasonic particle analyser. Microstructures were characterised by optical, XRD, SEM and TEM. The average particle size of the powders were found to decrease continuously with milling time. Optical Microscopy and SEM studies of both ball milled and attritor milled copper - 35 wt% iron powders showed a marked change in the particle size and shape. X-ray diffraction revealed the formation of supersaturated NC solid solution during the early stages of MA, (including 15 mins to 1 h) in attritor mill and (1 h to 10 h) in a ball mill. TEM investigations of annealed attritor powders have also confirmed the formation nanocrystalline phases, showing the typical spotty ring diffraction pattern characteristic of nanocrystalline materials. The positive heat of mixing precludes the formation of compound phases on milling. NC State as an important microstructural criterion to accommodate the excessive plastic energy has been explained. The higher diffusivities and higher solubilities in NC phases aid the formation of these NC supersaturated solid solutions. The mechanism of NC state formation via increase in dislocation density, reconfiguration into energy efficient configurations including cell formation, and finally their transformation into NC high angle grain boundaries, have been illustrated by TEM investigations.

The formation of supersaturated NC phases during the early stages of alloying Copper - 35-wt % iron powder were discussed earlier. Since the formation of compounds in this system is impossibility from thermodynamic considerations, the effect of continued milling on the stability of these phases was of interest. XRD studies of ball milled and attritor-milled powders have revealed the formation of quasicrystalline phases in all the compositions in copper iron system. XRD studies of both ball milled and attritor milled copper – 35 wt% iron, revealed peaks corresponding to new phases apart from elemental copper and iron peaks. The new phases in the ball-milled samples were indexed using the Bancell indexing scheme, to quasicrystalline phases. In the case of attritor samples also, XRD patterns showed new peaks corresponding to QC phases after just 1h of milling (compared to ball milled powders, where QC phases were observed only after 20 h). However the material constants of the QC phases are process dependent and are slightly different for the ball milled powders in comparison to the attrited powders. Thermal stability studies were performed on both ball milled and attritor milled samples, to investigate the stability of the metastable phases formed on alloying. It was found that in ball milled and attritor milled samples, the metastable phases showed a strong tendency to decompose into Nanocrystalline (NC) pure copper and pure iron. The grain sizes calculated using Scherrer's formula from XRD results showed the formation nanocrystalline pure copper and iron on thermal annealing even at temperatures as low as 323 K.

TEM studies on Copper - 35 wt% iron powder samples, Mechanically Alloyed using attritor, have provided important information regarding the Mechanical Alloying process. Detailed TEM characterisation of TEM have shown (i) flattening of particles during deformation (ii) alloy formation during milling (iii) evidence for formation of quasicrystals (iv) nucleation and growth of new structures resembling fractals (v) formation of nanocrystalline phases.

From the XRD and TEM investigations it is obvious that the milling results in the formation of nanocrystalline phases prior to destabilisation of crystalline phases and subsequent formation of quasicrystalline phases. The role of disclination defects in aiding the transformation of NC state in to QC state on MA, and vice versa on thermal annealing have been described in more detail in the thesis.

Hot forged Cu-Fe powders resulted in a NC composite showing high hardness compared to elemental iron and copper. The oxidation resistance was also found to be superior.

Chapter 6

The major conclusions of this work are summarised in this chapter. They include:

(i) MA of Copper -25 wt % Titanium and Cu – 80% Al powders confirmed the formation of only supersaturated NC solid solutions. The formation of intermetallic phases was observed only after post annealing. The oxidation resistance of hot forged Al-Cu powders showed superior oxidation resistance.

(ii) Mechanical Alloying of elemental copper and 35-wt% iron powder results in transformation of crystalline to quasicrystalline phases via a metastable supersaturated NC Solid Solution State.

(iii) The composition of QC phases formed as well their material constants are found to be process dependent.

(iv) Thermal annealing resulted in decomposition of quasicrystalline phases into elemental copper and iron phases.

(v) Nanocrystalline state plays an important role in destabilising crystalline matrix by two main mechanisms, namely: (a) chemical free energy driving force and (b) mechanical instability. Nanocrystalline State is an important microstructural criterion in solid state reactions inducing continuous transformation from crystalline to quasicrystalline phases and vice-versa.

(vi) Hot forging of Cu-Fe powders results in a NC composite.

(vii) Oxidation resistance of hot forged Cu-Ti and Cu-Fe was found to be superior.