CHAPTER 1

INTRODUCTION

1.1 Background

Copper alloys are one of the major groups of commercial alloys. These alloys are widely used in many engineering applications such as bearings, bushings, ship propellers, heat exchanger condenser tubes and valve bodies because of their excellent thermal and electrical conductivity, good corrosion and wear resistance, good mechanical properties and fatigue strength and good anti-seizure characteristics. These traditional alloys are strengthened by the following methods: (i) grain boundary strengthening (ii) strain hardening (iii) solid solution strengthening (iv) dual phase strengthening (v) precipitation hardening and (vi) order hardening. Recently, researchers have adopted three new methods in-order to further improve the properties of copper alloys: (i) alloy addition, (ii) dispersion hardening, (iii) surface modification, (iv) spinodal hardening. In case (i), alloying elements like Ni, Cr and Ti are added to the traditional copper alloys. In case (ii) ceramic particulates TiC, B₄C, SiC, WC and Al₂O₃ are added to the bulk of the copper alloys so as to form a metal matrix composite. In case (iii) the wear and corrosion properties of the surface are modified using surface modification processes. In case (iv) by adding Ni to traditional Cu-Sn bronze alloy that becomes hardenable by a process known as spinodal hardening.

1.2 Traditional hardening methods

1.2.1 Grain boundary strengthening

It is a strengthening mechanism where, the grain boundary acts as a barrier to the motion of dislocation. The mechanical property of a poly-crystalline metal is influenced by the grain size. Grain boundaries arise since the grains have different crystallographic orientations. The slip motion tends to take place while undergoing deformation. The discontinuity of slip planes from one grain to another and due to the different orientation of grains the dislocation changes its direction of motion are the two reasons for the grain boundaries to act as an impediment to the dislocation motion. In order to deform a material plastically, the stress required to move a dislocation from a single grain to another mainly depends upon the grain size. The average grain size decreases with the average number of dislocation per grain. The lower dislocation...
pressure at the grain boundaries is resulted due to the lower number of dislocation per grain which makes the dislocation hard to move into the adjacent grains. This is called as Hall-Petch equation and it is explained as follows \( \sigma_y = \sigma_0 + kd^{-1/2} \) where, \( \sigma_y \) is the yield stress for a poly-crystalline material, \( \sigma_0 \) is the certain shear stress required to ensure gliding dislocation in a mono-crystal, \( d \) is the average grain size and \( k \) is the Hall-Petch parameter.

1.2.2 Strain Hardening

Strain hardening is the phenomenon where the ductile metals become hard and strong when they are plastically deformed. Strain hardening can also be referred as work hardening. During strain hardening, usually the strength, hardness and elastic modulus of the copper and its alloys are enhanced by forging, rolling and drawing operation. Hardness and elastic modulus are increased, but the ductility of the metals gets decreased. Annealing is the process that is carried out to remove the effect of cold work. Strain hardening is carried out on the materials that does not respond to heat treatment.

1.2.3 Solid Solution Strengthening

The common strengthening mechanism is solid solution strengthening of copper. Alloying elements such as aluminium, nickel, tin, beryllium, silicon and zinc etc. are added to the molten copper to completely dissolve them and to form a homogeneous microstructure (a single phase) upon solidification a stress field is created around the solute atoms that is present in the substitutional sites interact with the stress fields of moving dislocation which increases the stress required for plastic deformation. Traditional bronze and brass are the major alloys of this category which are not heat treatable.

1.2.4 Dual Phase Hardening

The strengthening mechanism where the second phase forms an impediment for the dislocation motion is called dual phase hardening. Aluminium is the major alloying element added to bronze to get aluminium bronze alloy in contrast to standard bronze (Cu-Sn) and brass (Cu-Zn). The composition of aluminium in aluminium bronze that is used for industrial application vary from 5wt-% to 11wt-% aluminium. Nickel, manganese, silicon and iron are the other common alloying elements sometimes added to aluminium bronze. When aluminium is added above 10wt-% formation of another phase is observed. The second phase that is formed also contributes to the strengthening of the alloy.
1.2.5 Precipitation Hardening

The precipitation hardening involves two steps: (i) solutionising / quenching (ii) aging. In the first step the alloying element is brought into solution by heating the specimen above the solvus temperature for a specified period of time. By quenching the specimen the alloying elements are released in the matrix to become a super saturated solid solution. When the specimen is heated below its solvus temperature a process referred as aging for a period of time the intermediate phases formed initially and upon further aging the equilibrium phase precipitate form the solid solutions. The strain field around the intermediate phase is usually high and the strain field impedes the motion of dislocation thus, increasing e and strength of the alloys. This type of strengthening mechanism is seen in Cu-Be alloys. There are many distinct advantage for precipitation hardening. By varying the temperature and time, the following properties like ductility, hardness, impact resistance, and strength can be obtained.

An outstanding combination of properties such as tensile strength, yield strength, wear resistance and corrosion resistance are possessed by Cu-Be alloys. These alloys can be cast or hot worked. Even though these alloys exhibit excellent mechanical and wear properties the cost and health hazardous for these alloys are very high.

1.3 New approach of hardening

1.3.1 Dispersion Hardening

Due to the effects of recrystallization, particle coarsening and dissolution, conventional strengthening mechanisms like precipitation hardening and cold working are inefficient at high temperature. Copper base alloys are found good choice of application in hydrogen or oxygen environment with high thermal conductivity and high elevated temperature strength. Another important advantage of copper alloys is its low elastic modulus, which minimizes thermal stress in actively cooled structure. Further, copper offers good formability, good machinability. Copper has an excellent resistance to neutron displacement damage for fusion applications. However, a considerable amount of improvement is required in the strength of copper in order to meet the design experiments for high temperature applications. An enormous amount of research work have emphasized on particle and fibre strengthening of copper composites with up to 40 vol% of reinforcing phase. In the recent literature dispersion hardening is called as metal matrix composites. Copper based composites are suitable for the engineering
applications due to their excellent thermos-physical properties and mechanical properties compared to the base copper alloys. In order to enhance the properties of copper base alloys, reinforcing particles like SiC is commonly added to form copper based metal matrix composites.

Further, the metal matrix composites reinforced with ceramic particles possess superior combination of properties such as specific strength, high elastic modulus and desirable coefficient of thermal expansion, high wear resistance and temperature resistance. Metal matrix composites are now widely used for automobile, structural and aerospace industry, sporting goods and general engineering industries. Copper matrix composites can be used as wear resistance and heat resistance material. The metal matrix composites also finds applications in brush and torch nozzle materials and electrical sliding contacts such as those in homo-polar machines and railway overhead current collector system where high thermal and electrical conductivity and excellent wear resistance properties are required. Dispersion particles such as carbides, oxides and borides which are thermally stable at high temperature and insoluble in the copper matrix are being considerable used as the reinforcement particle.

1.3.2 Surface Modification

Surface modification process is an emerging method alternative to the other traditional coating process in order to improve the tribological and corrosion properties of ferrous and non-ferrous alloys. Surface modification can be defined as the process in which the surface gets modified by bringing out changes in the properties different from those found originally on the surface of the material. The main application of the surface modification process is to form hard and fine structure on the surface of the material which improves the properties of the material. Surface modification process can be classified into two methods, (i) surface refining process (ii) surface alloying process. In the surface refining process the surface of the material is melted by using a heat source to form a molten pool. The heat source is moved along the material so that a solidified layer forms on the surface of the material upon solidification. A fine grain structure is obtained upon solidification in surface refining process due to rapid cooling of the material. Due to fine grain structure the modified layer shows improved properties. A superior wear resistance can be achieved by using this process.

The second method is surface alloying process. This method is similar to the surface refining process. The major difference is that in this process the alloying element/ ceramic particles are added to the modified layer. In the surface modification process, surface properties
are commonly improved by the method called hard-facing. For the improvement of hardness and wear resistance without significant decrease in toughness and ductility of the substrate, welding is a process which is used to deposit an alloy homogeneously on to the surface of a soft material. For the protection against wear, a huge variety of hard-facing alloys are available.

In recent years spray atomisation or spray forming and deposition are considered to be the emerging science and technology in the field of materials development and production. The spray forming technology is considered as an advanced processing that has advantage similar to rapid solidification and semi-solid processing. By using this technology new materials can be developed and microstructure and properties of the commercial materials can be improved. An example for new developed spray formed material is Cu-15Ni-8Sn alloy where the Ni and Sn are sprayed over the substrate of Cu. Due to its high strength, high conductivity and good corrosion resistance, Cu-15Ni-8Sn spray formed alloy may be suited for engineering applications in electronic equipment, electrical switch gear, contacts, springs and connectors replacing Cu-Be alloys.

1.3.3 Spinodal Hardening

The spinodal decomposition theory was introduced by Cahn-Hilliard. Several authors have discussed about spinodal decomposition in detail. The principle concept of this theory is explained below

A miscibility gap is shown in the temperature-composition diagram where a pair of partially miscible solids, i.e. solid that do not mix in all proportions in all temperatures. Figure 1.1 (Favas et al. 2008) depicts a phase diagram with two frames.
Figure 1.1: Phase diagram with a miscibility gap (Favvas et al. 2008)
The upper frame considered to be the diagram of free energy and lower frame is the miscibility gap. Line (1) is considered as the phase boundary. Above the line (1) the solids are stable and the system is said to be stable (region-s). Below the line (1) is the meta-stable region (m). Within the region (from point a to b) the system is said to be stable (where, $\Delta G = \text{Free energy of mixing}; X_B = \text{concentration of element B}$) Line (2) is considered to be the spinodal line. Below line (2) the system is said to be unstable (region –u) (where, $\partial^2 \Delta G / X_B^2 < 0$). The unstable will decompose into solute rich and solute lean region within the spinodal region (u). This process is termed as spinodal decomposition. Figure 1.2 shows the spinodal structure which causes the hardening of the alloys. The spinodal decomposition depends upon the temperature ($T_c$). For example above $T_c$ (Figure 1.1) the spinodal reaction will not takes place.

![Modulated spinodal microstructure](Zhao and Notis (1998))

**1.4 Nucleation versus Spinodal**

Nucleation or growth and spinodal decomposition occurs within a meta-stable supersaturated solid solution. The nucleus form and grows subsequently in the case of nucleation and growth as shown in Figure 1.3 (a)
The nucleation and growth take place by the diffusion of solute atoms from the matrix towards the nucleus and this phenomenon is termed as down-hill diffusion. The new phase that is formed by this process may exhibit different structure from the parent matrix. A sharp interface also exists between the parent matrix and precipitate. Figure shows the graph of nucleation and growth. Process. Normally an incubation period is observed in this process.

During spinodal hardening, a small fluctuation is observed in the solute concentration and the fluctuation enlarges gradually as shown in Figure 1.3 (b). An absence of new phase is observed but there exists a composition gradient depicting solute-lean and solute-rich regions with an absence of sharp boundary between these two. This process is accomplished by the diffusion of solute atom from one region to another as shown in Figure 1.3 (b). This phenomenon is termed as up-hill diffusion. A same crystal structure is observed for the solute lean and solute rich region. An absence of incubation period is observed in this process.
1.5 Spinodal bronze

The spinodal bronze (Cu-Ni-Sn) alloy constitute the addition of Ni from 4 to 15 wt-% and Sn from 4 to 12 wt-% to Cu matrix. A modulated structure is observed in the Cu-Ni-Sn bronze alloys during heat treatment process. The modulated structure creates a strain field that impedes the dislocation motion thus enhancing the mechanical properties of the Cu-Ni-Sn alloys comparable to those of Cu-Be alloys. The Cu-Be alloys are found to be very expensive and hazardous to the environment. The increase in mechanical properties is attributed to a) Condition of the alloy (wrought or cast) b) composition of the alloy c) aging temperature d) aging time e) amount of cold work prior to aging. The Cu-Ni-Sn spinodal bronze may be used as an anti-wear and friction reducing material to make bearings of high performance for roller-cone cock bit, submarines and war ships for defence purpose.

1.6 Scope of present study

Previous studies on spinodal bronze reported in the literature were conducted to determine the hardness and the yield strength (YS) of a few alloy compositions mostly in wrought condition (cold worked) of the Cu-Sn-Ni bronze alloys. Limited studies were carried out to determine the mechanical properties and the wear rate with respect to investment and sand casting processes. However, the optimum aging temperature and time with respect to the alloy composition (Ni and Sn content) were not determined in these studies. Further, most of the studies have not determined the ultimate tensile strength (UTS), YS and elongation with respect to the alloy composition (Ni and Sn content).

If the Cu-Sn-Ni spinodal alloys are expected to be used in bearings, bushings, propellers and wear plates in order to improve the performance in service, a separate set of data base for various properties with respect to the specific manufacturing process such as forming and casting (sand, gravity die and investment casting) are required. Therefore, the present study is carried out to determine a) the optimum aging temperature and aging time, b) the mechanical properties such as hardness, UTS, YS and elongation and c) the wear rate and the coefficient of friction with respect to the gravity die casting (metal mould process). It is to be noted that the gravity die casting is a very important manufacturing process. Further, these properties were also investigated by varying the Ni content (3, 5, 9, 11 and 14 wt-%) and the Sn content (4, 6, 8, 10 and 12 wt-%). The significance of the present work is that the property values thus obtained in this investigation will become the basic data required in the design of various
components such as bearings, bushings used in automobile, industrial, aircrafts and marine applications.

1.7 Objectives

The objectives of this research work are as follows:

1. To make various compositions of spinodal bronze alloys (Cu-Sn-Ni) using gravity die casting process or permanent mould casting (metal mould casting) and to evaluate various properties.

2. To determine the optimum aging temperature and time for each alloy.

3. To measure the hardness of the age-hardened spinodal alloys.

4. To determine the UTS, YS and elongation of these alloys.

5. To determine wear rate and coefficient of friction of these alloys.

6. To investigate the effect of Ni content on the aging temperatures and aging time.

7. To investigate the effect of Ni contents on the microstructure, hardness, wear properties and mechanical properties (UTS, YS and elongation).

8. To investigate the effect of Sn content on the aging temperatures and aging time.

9. To investigate the effect of Sn content on the microstructure, hardness, wear properties and mechanical properties.

10. To compare the effect of Ni and Sn content on the properties.
1.8 Organization of the thesis

Chapter 1 introduces the various traditional method of strengthening the copper alloys. The new approach of strengthening by spinodal decomposition is also discussed. The objectives of this research work are highlighted.

Chapter 2 presents a detailed literature review of the work carried out on Cu-Ni-Sn wrought spinodal alloys system by various authors in relation to origin of the alloys, manufacturing process, need, spinodal decomposition, hardness, YS, wear properties and summary of the previous investigation.

Chapter 3 describes the experimental procedures such as die making, casting method, heat treatment technique, experimental set up and various mechanical and tribological test methods.

Chapter 4 presents the results and discussion of the effect of Ni content on optimum aging temperature, aging time, microstructure and hardness of spinodal alloys cast in metal mould (gravity die casting) while Sn content is kept constant.

Chapter 5 presents the results and discussion of the effect of Ni content on wear and mechanical properties of Cu-Ni-Sn spinodal alloys cast in metal mould.

Chapter 6 presents the results along with a discussion of the effect of Sn content on optimum aging temperature, aging time, microstructure and hardness of spinodal alloys cast in metal mould (gravity die casting) while Ni content is kept constant.

Chapter 7 presents the results and discussion of the effect of Sn content on wear and mechanical properties of Cu-Ni-Sn spinodal alloys cast in metal mould.

Chapter 8 gives the overall findings and summary of the results with conclusion followed by suggestion for future work that may be attempted.

1.9 Conclusions

This chapter introduces the various traditional strengthening methods and the new approach of strengthening. In the new approach of strengthening, the spinodal hardening of Cu-Ni-Sn spinodal alloys were explained in detail. Apart from the above discussions, the present study, objectives and organization of the thesis were highlighted.