**Chapter 1 - Introduction** 

# **1. Introduction**

# **1.1 Background**

In the electronic packaging industries soldering materials are essential in joining various microelectronic networks (Abtew and Selvaduray, 2000). Solders assure the reliability of joints and protect the microelectronic packaging devices. They provide electrical, thermal and mechanical continuity among various interconnections in an electronic device (Abtew and Selvaduray, 2000; Suganuma, 2004). Lead containing solders are in use for years resulting in an extensive database for the reliability of these materials (Tu and Zeng, 2001). The service performance of all the electronic appliances depends on high strength and durable soldering materials.

### **1.2 Environment concerns**

Through history it is already known that in the electronic packaging devices, the most common solder is Sn-Pb. However, with rise of electronic market, there is a hot issue over the toxicity of Pb among the electronic manufacturers. In the last few decades, the effect of lead contamination on human health has received significant attention. Leaching of this toxic lead from electronic wastes results in contamination of the human food chain and causes serious health hazards. The toxic fumes on burning these wastes can cause lung cancer and affect the nervous system, reproductive systems, kidney and cardiovascular organs over prolonged exposure and may eventually lead to death (Puttlitz and Stalter, 2004). Every year, lead is accumulated in our landfills through our used and waste domestic appliances. If one such unit contains 10 g lead, it can be shown that total lead accumulated per year becomes about 200 ton, which is definitely a huge amount. As a consequence, several European Union countries have passed legislations that impose elimination of lead from electronic solders (Suganuma, 2004; Puttlitz and Stalter, 2004). In view of these serious environmental health problems and legislations, the scientific community across the world have started to ban the use of Pb in their electronic assemblies. These activities have fuelled an extensive research in the electronic

manufacturers to find promising lead free solders all over the world. Besides the environmental issue, use of lead in electronic devices also poses a radioactive threat over prolonged use. These radioactive Pb generates  $\alpha$ -particles during its decay causing failure of memory chips. This is often called soft errors in electronic memory devices (Heijmen, 2002; Seifert *et al.*, 2001; Tu *et al.*, 2003). Therefore, not only strict control but almost a complete removal of Pb in high capacity memory goods is necessary.

#### **1.3 Current Scenario**

There is tremendous research going on to search for a better lead free solder alloy but still none has replaced completely the traditional Sn-Pb solder in terms of performance, ease of manufacture, cost, availability, wetting characteristics, mechanical strength, and intermetallic compound formation (Coombs, 2001; Subramanian, 2007).

In the present state the advanced solders that have been developed so far are mostly Sn rich alloys containing Cu, Ag, Zn, Bi, Sb, Ni etc. (Guo, 2006; Alam *et al.*, 2009; Lai and Duh, 2003; El-Daly and Hammad, 2010; Miao and Duh, 2001; Nogita and Nishimura, 2008; Lin and Shih, 2008). Among all the binary eutectic Pb-free alloys, SnAg, SnZn and SnCu are considered to be the potential candidates to replace Sn-Pb. As for ternary alloys, those in the SnAgCu system is considered promising due to its lower melting temperature and superior mechanical properties compared to the binary compositions (Wu *et al.*, 2004). However, there are some issues of reliability problems over long term use such as formation of large and brittle intermetallics of Ag<sub>3</sub>Sn and Cu<sub>6</sub>Sn<sub>5</sub> in ternary alloys which may have negative effect on mechanical properties (Suganuma, 2001).

Though these lead free Sn rich alloys are perfect replacement for lead based solders, their mechanical properties make their durability less than satisfactory. Moreover, these Sn rich alloys are prone to whisker growth with ageing causing short circuiting in electronic devices and ultimate failure. The driving force for Sn whisker formation is believed to be the internal stresses caused by the volume expansion due to the formation of intermetallic compounds like Cu<sub>6</sub>Sn<sub>5</sub>, Cu<sub>3</sub>Sn etc with time (Suganuma, 2004).

# Chapter 1

To meet the requirement, lead free solder alloys must be developed that are not only having superior strength but also have a minimum tendency of whisker growth. Recently, research activities are aimed at the development of solder alloys reinforced with nanoceramic particles in order to achieve the desired properties. Such reinforced solder alloys are known as nano-composite solders. Composite solders are more reliable because the reinforcing particles can suppress grain-boundary sliding, refine the intermetallic compound (IMC), suppress grain growth, and redistribute the stress uniformly (Shen and Chan, 2009; Guo 2006). This new modern approach to develop these solders would provide higher strength and reliability of solder joints. Researchers have been working on their development in order to achieve a better combined properties (Shen and Chan, 2009; Jin and McCormack, 1994).

Various synthesis routes like metal casting route, powder metallurgy, mechanical alloying, physical vapour deposition, sol-gel, plasma sprayed deposition, chemical reduction method, electrodeposition etc. have been used to produce solder materials (Miller, *et al.*, 1994; Alam *et al.*, 2009; Lai and Duh, 2003;; Aggarwal *et al.*, 2007; Conway *et al.*, 2002; Hsiao and Duh, 2005; Hsiung *et al.*, 2007; Ruythooren *et al.*, 2000). Among all these routes, electrodeposition is the most versatile method for producing these solders in coating form, bulk form and as composites (Bicelli et. al., 2008; Hovestad and Janssen, 1995).

Most of the solder matrix composites are reinforced with ceramic particles like  $Al_2O_3$ ,  $ZrO_2$ , SiC, TiO\_2, Cu<sub>2</sub>O, SnO<sub>2</sub> etc. (Zhong and Gupta, 2008; Shen *et al.*, 2006; Liu *et al.*, 2008; Tsao and Chang, 2010; Sivasubhramaniyam *et al.*, 2008; Babaghorbani *et al.*, 2009a; Abtew and Selvaduray, 2000; Shen and Chan, 2009). However, there is a limited research on co-electrodeposited solders. Some studies on Sn based nanocomposite solders are already reported for the Sn-CNT and SnBi-SiC systems (Choi *et al.*, 2008; Shin *et al.*, 2009). It can be found in the literature that CeO<sub>2</sub> has been rarely used for reinforcing the solder matrix by electrodeposition process inspite of its attractive properties. It possess high strength, high wear and corrosion resistance and highly inert

towards acids and bases. Ceria based ceramics are in demand because of their higher ionic conductivity than zirconia for the same solute concentration (Aruna *et al.*, 2006). Ceria base catalysts are in use in gas sensors, electrodes in SOFC, high temperature coating for oxidation prevention (Zhitomirsky and Petric, 2001). Well dispersed nanosized ceramic particles in a metal matrix can significantly improve the mechanical strength, and wear and corrosion resistance of the matrix without sacrificing significantly the electrical and thermal properties [Mangam, (2010, 2011)]. Therefore, it opens up potential applications of the Sn based nanocomposite solder materials in microdevices.

### **1.4 Objectives**

The specific objectives of the present investigation are

- To synthesize pure Sn coatings by pulse electrodeposition technique from different aqueous solutions.
- To study the effect of the pulse electrodeposition parameters (e.g., current density, additive concentration, duty cycle, frequency, pH, temperature, and stirring rate) on the morphology of pure Sn coatings.
- To synthesise the nanocrystalline CeO<sub>2</sub> by high energy ball milling method.
- To synthesize the Sn/CeO<sub>2</sub> and near eutectic Sn-Ag/CeO<sub>2</sub> composite films with varying amount of CeO<sub>2</sub> and their subsequent microstructural characterization.
- To evaluate the microhardness, density, porosity, melting behavior, wear and friction characteristics, corrosion behavior, electrical resistivity, and residual stress of the developed composites.

# **1.5 Contributions**

(1) An optimized set of parameters have been developed to obtain desired morphology and grain size distribution of the coatings. The optimized parameters for pulse electrodeposition of tin from sulfate bath are current density =  $0.2 \text{ A/cm}^2$ , amount of additive (Triton X-100) = 0.2 g/L, duty cycle = 10%, frequency = 100 Hz, pH = 1, bath temperature =  $28 \text{ }^{\circ}\text{C}$ , and stirring rate = 300 rpm.

(2) It has been shown that the  $Sn/CeO_2$  and  $Sn-Ag/CeO_2$  nanocomposites can be synthesized using pulse co-electrodeposition method and an incorporation of  $CeO_2$  in the Sn/(Sn-Ag) matrix leads to a significant increase in microhardness, wear and corrosion resistance and minimises the chances for whisker growth.

(3) This study proposes the incorporation of an optimum amount of ceria in the Sn basedceria nanocomposites for the enhancement of various properties and thus improved coating life.

## 1.6 Research Plan and thesis outline

The whole thesis is devided into 5 chapters.

Chapter 1 gives a brief introduction about the background and the current scenario of the soldering materials.

Chapter 2 gives a detailed literature survey of the existing solders, next generation solders and the composite approach of soldering.

Chapter 3 gives the information about the materials synthesised, methodology used for the synthesis of monolithic and composite solders and their characterization, and property evaluation.

Chapter 4 presents and discusses the obtained results from the investigated experiments. Chapter 5 summarises the findings and suggests future directions for the next generation

research based on this work.

Chapter 2 – Literature Review

# **2.1 Introduction**

Lead-bearing or lead containing solders are in use for a relatively long time; however, the increased health concerns over the use of lead combined with strict legislations have enforced the fabrication of lead free solders. In the following sections, a brief literature review on microelectronic packaging, levels of packaging, the various types of solders (conventional and lead free) in electronic packaging devices, metallurgical overview of Sn, lead free Sn based solders and their development, various synthesis routes of solder fabrication, pulse electrodeposition of Sn and Sn alloys, nanocomposite solders produced by pulse co-electrodeposition and various properties relevant to soldering applications have been presented.

#### 2.2 Microelectronic packaging

Prior to the discussion of various soldering materials, a brief survey of micro electronic packaging technology is required. Electronic devices such as computers, cellular phones, and portable laptops and ipads have become thinner and lighter whereas their multitasking capability has become more demanding. Historically, the various wires are used to interconnect the different components into an electric board/cable. With time, printed circuit boards (PCB) or printed wire boards (PWB) are developed in 1950s which is a great revolution in electronics world. Further in 1947, the invention of transistors and Integrated Circuits (ICs), analog to digital electronics changed the life style of the common man. This technology of interconnecting various IC's and other electronic components such as transistors, capacitors and resistors to form a circuit over a PCB to form an electronic device is known as electronic packaging (Tummala, 2000; Alam, 2004). Some examples of microelectronic packaging are shown in Fig. 2.1.



Fig. 2.1: Examples of Microelectronic Packaging (Tummala, 2000)

The electronic packages serve four functions: providing electrical connection and distribution of the signals to and from the ICs; dissipation of the heat and stress generated between ICs and the PCB during service; maintaining mechanical support and environmental isolation to the components and interconnections (Datta *et al.*, 2005). There are various types of miniaturized packaging devices like Ball Grid Array (BGA), Wafer Level Packaging (WLP), Chip Scale packaging (CLP) and Flip Chip Packaging (FCP) where usage of soldering materials also increases accordingly.

## 2.2.1 Packaging materials and electrochemical technology

In general, packaging materials includes papers, polymer, ceramic, metals or a combination of these. However, the materials used in electronic packaging includes interconnections, printed circuit boards, electrical contacts, encapsulations, solders, brazes, heat sinks, passive and active components (i.e., resistors, capacitors, inductors, transistors, diodes etc). These IC chips are attached to the base substrate where the interconnections are drawn. The electronic components are soldered on the PCBs. The PCB is attached to the heat sink and the whole assembly can be further placed in the metallic thermally conducting housing (Chung, 1995). In order to integrate these high performance components, the electrochemical processing technologies are expected to make a significant impact on microelectronic packaging. Electrochemical processing entered the electronics industry in the 1940s to fabricate PCBs by chemical etching of patterned copper laminates. The first commercial application of electroless plated copper

# Chapter 2

is reported in the 1950s with the development of plating solutions for Plated Through Hole (PTH) technology (Datta *et al.*, 2005).

# 2.2.2 Classification of packaging devices

There are different levels of integration in these packages used in electronic devices. Level 1 packaging involves joining of ICs (chip level) to a substrate, Level 2 packaging involves joining of Level 1 packages to PCB, and Level 3 interconnections include cable connector assemblies used to transmit signals between PCBs and the mother board (Tummala, 2000; Datta *et al.*, 2005; Puttlitz and Stalter, 2004) as illustrated in Fig. 2.2.



Fig. 2.2: Schematic Representation of Microelectronic Packaging Levels in a Personal Computer (Tummala, 2000).

The number of levels may vary depending on the scale of integration and packaging needs. High performance servers may contain several numbers of levels whereas the consumer electronic goods contain one or two packaging levels. In this thesis, only Level 1 and Level 2 interconnections are of interest.

# Chapter 2

# 2.2.2.1 Chip level packaging - Level 1

Level 1 packaging is described as the interconnections between chips and substrate. In general there are of two types of IC packages in this level: Through Hole Packages (THT) and Surface Mount Packages (*SMP*). The packages having pins that can be inserted in PCB through holes are called THT and if the packages have no pins but are mounted on surface of PCB are called *SMP*. The advantage of THT is high packaging density since both sides of the PCB can be utilised (Tummala, 2000). THT provides strong mechanical bonds when compared to *SMP* techniques, however, the extra drilling makes this packaging expensive. They also limit the available routing area for signal traces on multilayer boards. The connections are made through wire bonding, tape automated bonding and flip chip packaging, ball grid arrays (Gilleo, 2002).

In FCP and BGA, solder balls or bumps are used in place of wires. An array of solder balls is deposited on wetting/solderable layer on the IC chip and a matching footprint of solderable layers is deposited on the substrate. The IC die is then flipped over to join to the substrate. Most solder balls used in flip-chip packaging are made from Pb-rich, Pb-Sn alloys such as Pb-3Sn and Pb-5Sn. They are typically deposited by evaporation or electrodeposition on the IC bond pads. On the chip side, normally three different layers, (1) an adhesion layer, such as Cu, Al or Ti/Cr, (2) a diffusion barrier layer, such as Ni, and (3) a wetting/solderable layer, such as Au or Cu are deposited on the IC bond pads (Al or Cu) to improve wetting and joining to the pads. These seed layers are also referred to as the under bump metallization (UBM). The intermetallic compound forms due to the dissolution of the UBM wetting layer (Cu) into the molten solder during the reflow (Tummala, 2000; Chung, 1995; Puttlitz and Stalter, 2004; Islam, 2006; Gilleo, 2002). Figure 2.3 illustrates the difference between SMT and THT.



Fig. 2.3: Schematic Illustration of Level 2 Interconnection Technologies (a) SMT, (b) THT (Lee, 2002) and (c) Schematic Diagram of Flip Chip Package (Ho *et al.*, 2007).

# 2.2.2.2 Board level packaging - Level 2

Level 2 packaging comprise of the solder joints that join Level 1 packages to PCB, which provide both mechanical support and electric path for the devices. Commonly used PCB in electronic devices is made from epoxy resin composites reinforced with glass fibres (Harper, 2004). PTH and SMT are the two most popular Level 2 packaging styles. The technique for making interconnections usually includes wave soldering. In this technique, component leads are placed through holes on the PCB, and the board is then moved over a stationary solder wave. The solder is drawn upwards and forms a bond between the IC package leads and the PCB pads. It is a low cost and simple technology. For both the wave soldering and the SMT, those leads are typically made from Cu or Fe-Ni alloy with a Cu or Ni solderable finish and an electroplated Sn or Pb-Sn protective layer. Leadless chip devices use a thick Ag film as a conducting medium covered by a Ni or Cu solderable coating and then an electroplated Pb-Sn protective finish. Ball grid arrays are one type of surface mount technology, with solder balls covering one side of the package and Cu pads deposited on the PCB. Once the device package is placed on the PCB, the assembly is heated either in a reflow oven or by an infrared heater to melt the solder balls which hold the package in alignment with the PCB. In both Level 1 and Level 2 packaging devices, it is observed that the most common materials that come across a solder joint are Cu|solder|Cu, Cu|solder|Ni, and Ni|solder|Ni.

### 2.3 Soldering science and technology in microelectronics

Soldering science and technology has become indispensable for the interconnection and packaging of electronic devices and circuits. During packaging, a solder is the main component for the interconnection from IC, chips, and other electronic components to board. Also, it acts as a surface finish on the PCB on which the components are to be soldered (Shangguan, 2005).

#### 2.3.1 Solder

The term "solder " refer to a group of metals or alloys with low melting point that joins two other similar or dissimilar metals together. The temperature at which joining operation takes place is normally below 400 °C. The commonly used elements in solder materials include Sn, Pb, Cu, Ni, Ag, Au, In, Bi, Sb and Cd (Gilleo, 2002; Puttlitz and Stalter, 2004). The use of solders dates back to about 4000 BC and served as an important factor through the Bronze and Iron Ages up to the current so-called "Silicon Age." Around 350 BC, the Greeks used solder as a sealant for bronze-based water pumps and air pumps with Sn–Pb alloys, and the Romans used Sn-Pb solders extensively in the construction of aqueducts (Puttlitz and Stalter, 2004) and to close the seams of lead water pipes. Early in the 20<sup>th</sup> century, soldering was introduced for connecting copper wires. More recently, the solder joints took on the dual function of serving both a mechanical and electrical connection, challenging the strength, creep, and fatigue resistance of Sn-Pb solders (Gibson *et al.*, 1997). In electronics packaging industries till now, soldering materials continues to be the predominant means to attach devices to printed circuit boards or microelectronic chip carrier packages.

# 2.3.1.1 Conventional solders

Conventional Sn-Pb solder includes the eutectic composition 63Sn-37Pb and near eutectic composition 60Sn-40Pb solders. These are the largest group of alloys utilized in electronics products used extensively for PCB assemblies. Solders used in the Level 2 interconnections are limited to eutectic and near eutectic compositions having a relatively

low melting point that is most suitable to a PCB. The melting point or range of these alloys is sufficiently low to maintain the integrity of both components and PCBs. The higher melting point compositions like 95Pb-5Sn or 90Pb-10Sn are used in flip-chip technology to join the IC dies to a ceramic substrate (Level 1 packaging) before attaching it to the PCB (Level 2 packaging) (Puttlitz and Stalter, 2004).

Lead bearing solders are in use till date due to its indispensable properties. Firstly, it is very cheap, available in abundance and provides good physical and chemical bonding to the substrate without interfering with the substrate. Secondly, Pb reduces the surface tension of pure tin, which is 550 mN/m at 232°C, and the lower surface tension of 63Sn-37Pb solder (470 mN/m at 280°C) facilitates wetting (Vianco, 1993) The presence of Pb also helps to prevent the white tin ( $\beta$ -Sn) to gray tin ( $\alpha$ -Sn) allotropic phase transformation from occurring in high-Sn solders upon cooling below 13°C (Plumbridge, 2007). This makes it a prime choice for soldering.

#### 2.3.1.2 Replacement of Pb

There are many technology based problems for reasons for elimination of Sn-Pb solders. First, it has been already proved in the past that many lead-free candidate solders exhibit significantly better strength and fatigue life properties. Secondly, Pb and Pb compounds have been cited by the Environmental Protection Agency (EPA) as one of the top 17 chemicals posing the greatest threat to human life and the environment. Prolonged exposure to lead causes nervous and reproductive system disorders, delays in neurological and physical development, cognitive and behavioral changes, reduced production of haemoglobin resulting in anaemia and hypertension which are some of the adverse effects of lead on humans (Abtew and Selvaduray, 2000). Recent studies have found that a Pb level even well below the established official threshold could be hazardous to a child's neurological and physical development. When the level of lead in the blood exceeds 50 mg/dL of blood, lead poisoning is considered to have occurred (Avram et al., 2005). Figure 2.4 depicts the lead pollution as a result of electronic waste accumulating in landfills every year.



Fig. 2.4: Lead Pollution and its Effect on Human Beings (Islam, 2006).

In view of these reasons of Pb from electronics is necessary in electronics packaging (Puttiltz and Stalter, 2004; Abtew and Selvaduray, 2000).

# 2.3.1.3 The lead free definition and regulations

Legislations to restrict the use of Pb are first implemented in the USA in 1991 with the Lead Exposure Reduction Act of 1991 and the Lead Exposure Act of 1992, which bans Pb in some applications and limits Pb content in others to less than 0.1% (Gilleo, 2002). In the United States, the National Electronics Manufacturing Initiative (NEMI) program was developed to research on lead free alternatives. In Japan, this movement is connected to the Lead-Free Soldering Research Council (1994 to 2000) within the Japan Institute of Electronic Packaging. Japan Electronics and Information Technology Industries Association (JEITA) have set guidelines for lead-free products, published in 1999. These companies aimed to use leadfree solders in mass-produced consumer products and to implement lead-free soldering technologies in their products by 2003 (Suganuma, 2004). In Europe the EU directives (WEEE) and (RoHS) had issued a ban on the use of lead on consumer goods (Puttiltz and Gaylon, 2007; Pecht *et al.*, 2004).

### 2.4 Metallurgical overview of Sn

Pure Sn has two allotropes white tin ( $\beta$ -Sn, metallic) and gray tin ( $\alpha$ -Sn, semiconductor). The most common form in real life is white tin which transforms to gray tin at temperatures below 13°C (Plumbridge, 2007). The β-Sn possesses body centred tetragonal crystal structure with lattice parameters a = b = 0.5820 nm and c = 0.3175 nm (Wang et al., 2011). This c/a ratio of 0.546 gives rise to highly anisotropic behaviour in Sn. The mechanical properties are very poor, the hardness being 11 Hv and tensile strength 44 MPa (Alam et al., 2009). This is largely due to its lower melting point relative to common engineering metals like Al, Cu and steel. Chemically, pure Sn is a relatively inert metal which does not react with air, water, nitrogen, hydrogen or weak electrolytes and Sn-rich alloys display largely similar traits. Pure tin tends to form intermetallic compounds rather than solid solutions, although it has a smaller solubility of univalent metals such as Cu, Ag and Au (Snugovsky et al., 2004; Moon et al., 2000). Neighbouring elements to Sn in the periodic table such as In, Sb and Bi do however have appreciable solid solubility and form eutectic mixtures with, it (Harrison et al., 2001). All these elements have been experimented with, along with others, in the quest to replace Pb in solders and the alloys which have been suggested and studied in the literature are discussed below.

# 2.4.1 Lead free Sn alloys

A relatively large number of Pb-free solder alloys have thus far been proposed, Sn being the primary or major constituent. The two other elements that are major constituents are In and Bi. Other alloying elements are Zn, Ag, Sb, Cu, and Mg and in one case a minor amount of Pb (Abtew and Selvaduray, 2000).

#### 2.4.2 Requirements for lead free solder alloys

Lead-free soldering is now taking the position of the conventional leaded solders. The most popular Pb free alloy system candidates are listed in a thorough review paper by

Abtew and Selvaduray (2000). The most important characteristics that must be considered in selecting suitable lead-free solder candidates are listed in Table 2.1.

Table: 2.1: Criteria and Desired Attributes for Lead Free Solders (Puttlitz and Stalter, 2004)

- Not toxic
- Available in sufficient quantities to meet current and future requirements
- Exhibit sufficient electrical and thermal conductivity
- Possess adequate mechanical properties: strength, toughness, fatigue and creep resistance
- Compatible with typical terminal metallizations (e.g., Cu, Ni, Ag, Au, Sn, etc.
- Affordable (i.e., economically viable)
- Have acceptable melt and process temperatures
- Not too different from eutectic Sn-Pb
- Avoid deleterious temperature effects on cards, boards and components
- Low dressing characteristics

### 2.4.3 Solder reactions

From previous sections it can be inferred that most Pb-free solders developed till date are Sn-rich solders and Sn being the major component. For level 2 interconnections, the common base materials for the PCB surface finishes Cu is the most important and common substrate. Ni, Ni-P, Co and Ag are also used as an underlying metallization in PCBs (He *et al.*, 2004; Chen MN *et al.*, 2008; Kumar *et al.*, 2006; Magagnin *et al.*, 2005; Horvath *et al.*, 2011). Ni has been used as a diffusion barrier layer between Cu and Sn to prevent excessive formation of IMCs, since the reaction rate of Ni with liquid Sn is typically slower than that of Cu and the growth rate of IMCs is slower in the solder/Ni system than in the solder/Cu system (Chen MN et *al.*, 2008). In case of conventional Sn-Pb solder there is no intermetallic formation with the base metal (Puttlitz and Stalter,

2004). Pb does not react with Cu to form intermetallic compounds. But while adopting lead free solders, it is therefore essential to be familiar with the solder reaction to the base metals. Solder reaction is the wetting of a solder material on the substrate surface (Cu). In molten state a tiny droplet solder touches a large Cu surface, it spreads and forms a hemisphere on the substrate. The wetting reaction forms Cu-Sn intermetallic compounds at the interface between the molten solder and Cu, and the interface achieves metallic bonding after cooling, hence two pieces of Cu can be joined by the solder in a solder joint. The solubility of the substrate metal into the molten solder will thus accelerate IMC formation (Laurila *et al.*, 2005; Tu and Zeng, 2001)

# 2.4.4 Intermetallic compounds and whisker growth

Due to the Pb-free solder implementation, pure Sn and Sn-Cu, Sn-Ag are commonly used to replace eutectic Sn-Pb as the surface finish on the lead-frames and metal terminations of passive devices. However, in Sn rich lead free finish, Sn whiskers have been found to form, which poses a serious threat for the reliability of passive devices. The Sn whisker formation was first reported in 1946 (Brusse *et al.*, 2002). It is generally accepted that the driving forces of Sn whiskers mainly attribute to the internal stresses, the dissolution of the metal under-layer, and the interfacial compound formation. Based on these three main root-causes of Sn whiskers formation; (1) choosing optimal thickness of the finish layer, (2) alloying with other metal elements, and (3) adding a reaction barrier layer beneath the finish layer (Gaylon, 2003).

2.4.5 Reactions to copper substrates

The phase diagram for the Sn-Cu system (Baker, 1992) is shown in Fig 2.5. There are two intermetallic compounds of Cu and Sn below 300 °C; they are Cu<sub>6</sub>Sn<sub>5</sub> and Cu<sub>3</sub>Sn. The Cu<sub>6</sub>Sn<sub>5</sub> forms at room temperature while Cu<sub>3</sub>Sn forms after annealing at elevated temperatures (Tu, 1996; Takenaka *et al.*, 2005). They form during the wetting reaction as well as the solid state reactions between Sn and Cu according to the binary phase diagram of Cu-Sn. Some IMCs, such as AuSn<sub>4</sub> for Sn/Au couples, Cu<sub>6</sub>Sn<sub>5</sub> for Sn/Cu couples, and



Ni<sub>3</sub>Sn<sub>4</sub> for Sn/Ni couples even form at room temperature (Nakahara *et al.*, 1981; Simic and Marinkovic, 1980; Tang *et al.*, 2010; Marinkovic and Simic, 1982).

Fig. 2.5: Binary Phase Diagram of Sn-Cu (Baker, 1992)

The dissolution rate of Cu is different in different molten solders due to the IMC morphologies and the solubility of the substrate in molten solders. Yeh *et al.* (2006) investigated the dissolution behavior of a Cu substrate in molten Sn for Sn based solders, and found out that the dissolution rate followed the order of Sn > Sn-3.0Ag-0.5Cu > Sn-58Bi > Sn-9Zn. Similar results were obtained by Yen *et al.* (2008) with the Cu dissolution rate in the molten solders decreasing in the order of Sn, Sn-3.5Ag, Sn-4.0Ag-0.5Cu, Sn-37Pb, and Sn-8.6Zn at temperatures between 300 °C and 400 °C. Under suitable conditions, the IMCs in the interior of the solder act as a strengthening phase. For the IMCs at the solder/substrate interface, their presence usually reduces the interfacial energy between the liquid solder and the substrate and improves the wettability of liquid solder (Abtew and Selvaduray, 2000). Wetting on the substrate followed by the formation of a thin layer of IMCs is necessary to make permanent solder bonds. However, solder joint failure may occur if the IMCs layer becomes too thick. Cracks are often initiated around the interfacial area under stressful conditions when excessive IMCs

develop along the solder/substrate interface and impair the solderability (Laurila *et al.*, 2005).

#### 2.5 Synthesis routes and technologies for solder fabrication

There are many synthesis routes for the fabrication of solders varying from solid state mechanical alloying, powder metallurgy, sol gel, melting and casting route, chemical routes, or gaseous phase sputtering or evaporation methods, electrodeposition method etc. (Liangfeng *et al.*, 2009; Hong *et al.*, 2010; Aggarwal *et al.*, 2007; Hao *et al.*, 2007; Hsiao and Duh, 2005; Conway *et al.*, 2002; Hsiung *et al.*, 2007; Ruythooren *et al.*, 2000). Among all these methods we will discus techniques related to thin film pulse electrodeposition of solders. The other methods are not discussed here because they are out of the scope of this thesis.

# 2.5.1 Electrodeposition

Both evaporation and sputter deposition techniques require high vacuum and/or high temperature processing which increases operation cost and cause interdiffusion problems. Compared to these fabrication processes, electrodeposition is an economically viable process. It can be used to plate either a single layer or multilayer deposits, with easy and precise control of the thickness and composition of each layer. Electrodeposition can be performed on substrates with varying sizes and complex shapes and the deposit can be very thin or very thick (Paunovic and Schlesinger, 2006). There are, however, safety and environmental concerns related with chemical treatment and safe disposal of wastes. Numerous metals and metal alloys have been successfully electrodeposited from aqueous solutions. The most useful electrodeposited metals include Sn, Cr, Cu, Ni, Ag, Au, Zn, and alloys such as Cr-Ni, Fe-Co and various Sn alloys.

# 2.5.2 General aspect of electrodeposition

In electrodeposition, metal ions present in a solution, the electrolyte, are reduced at the surface of an electrode to form a metal layer, as shown in Fig. 2.6.



Fig. 2.6: A Schematic for Electrodeposition Process

This process essentially consists of : (1) an anode (the positive electrode), (2) a cathode (the item to be electroplated, which is the negative electrode), (3) the electrolyte acts as a transport medium for the tin ions to be deposited at the cathode as a coating on the item to be electroplated, (4) an electric current or voltage source for controlling the deposition, (5) various peripherals for contacting the electrodes, stirring and heating the solution etc.

The electrochemical deposition of a metal onto a conductive substrate involves passage of electricity through the conductive solution to provide sufficient energy to cause an otherwise non-spontaneous oxidation-reduction reaction to occur. Metal ions in solution receive these electrons and become neutral metal atoms which then leave the solution and deposit as metal onto the cathode. The relationship between the weight of material deposited and the various plating parameters can be stated by the Faradays laws (Brown, 2004).

$$\frac{Thickness}{time} = \frac{J(ECE)(CCE)}{density} \qquad \dots (2.1)$$

... (2.3)

Where, thickness of the deposit is in mg, time in seconds, J = current density, ECE = electrochemical equivalent, CCE = current efficiency (ratio of actual/theoretical weight deposited), density of deposit is in g/cm<sup>3</sup>.

# 2.5.3 Cathodic and anodic reactions

Electrochemical deposition of metals and alloys involves the reduction of metal ions from aqueous, organic, and fused-salt electrolytes. In this thesis, electrodeposition from aqueous solution is being considered. The reduction of metal ions  $M^{n+}$  in aqueous solution is represented by (Bard and Faulkner, 2001):

$$M^{n+} + ne^- \rightarrow M$$
 ... (2.2)

Reaction (2.2) is often accompanied by hydrogen evolution. In acid solutions, we have

$$2H^+ + 2e^- \rightarrow H_2$$

In neutral and basic solutions, hydrogen evolution follows the equation:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad \dots (2.4)$$

At the anode, the anodic reactions are as follows. In an acidic solution, we have

$$2H_2O \rightarrow O_2 + 4H_1 + 4e^-$$
 ... (2.5)

In an alkaline solution, the anode reaction is:

$$4OH^{-} \rightarrow O_2 + 2H_2O + 4e^{-}$$
 ... (2.6)

For a soluble anode, oxidation reactions, which will dissolve the anode into solution,

$$M \to M^{n^+} + ne^- \qquad \dots (2.7)$$

The equilibrium electrode potential between a metal and a solution of its ions is given by the Nernst Equation:

$$E_{M/M^{n+}} = E^{o} + \frac{RT}{nF} \ln C_{M^{n+}}, \qquad \dots (2.8)$$

where  $E^{o}$  is the standard electrode potential, R is the gas constant, F is the Faradaic constant, and  $C_{M^{n+}}$  is the metal ion concentration. It can be noticed that the value of  $E_{M/M^{n+}}$  depends on the concentration of metal ions to be plated, addition of additives, current density etc.

# 2.5.4 Electrode interactions

Various electrodeposition models have been proposed to explain the interaction mechanism when metal deposition takes place in aqueous solutions. The important models for a single solution bath are (1) Helmholtz double-layer model, (2) Gouy–Chapman model, and (3) Stern model. There are some more advanced models, such as for a combination of electrolytes Grahame proposed triple layer model, which is successfully developed to explain the interface phenomena between metal and solution. A comparison of theoretical and experimental data shows that this model represents an improvement of the others (Paunovic and Schlesinger, 2006).

### 2.5.5 Polarization and overpotential

When an electrode is made a part of an electrochemical cell through which current is flowing, its potential will differ from the equilibrium potential. If the equilibrium potential of the electrode (potential in the absence of external current) is E and the potential of the same electrode as a result of external current flowing is E(I), the difference between these two potentials,

$$\eta = \mathcal{E}(\mathcal{I}) - \mathcal{E} \qquad \dots (2.9)$$

is called overpotential. In terms of current and the voltage it is expressed as given by Tafel equation (2.10),

 $\eta = a + b \log I$ 

... (2.10)

where *a* and *b* are constants.

The overpotential  $\eta$  is required to overcome hindrance of the overall electrode reaction, which is usually composed of a sequence of partial reactions, charge transfer, diffusion, chemical reaction, and crystallization (Bard and Faulkner, 2001; Paunovic and Schlesinger, 2006). The overpotential is generally used as a measure of the extent of polarization. Polarization demonstrates departure of the electrode potential from the equilibrium value upon passage of a Faradaic current. Depending upon the nature and sites of the inhibition factors, there may be different kinds of overpotentials, such as charge transfer overpotential or activation overpotential which is caused by inhibition of the charge transfer taking place across the close proximity of solution/cathode interface. The mass-transfer overpotential (also called concentration overpotential) is caused by inhibition of the transfer processes of the potential-determining ions or complexes towards cathode. These are processes by which atoms are either incorporated into or removed from the crystal lattice. Hindrance of these processes results in crystallization overpotential.

Thus, four different kinds of overpotential are distinguished and the total overpotential  $\eta$  can be considered to be composed of four components: where  $\eta_{ct}$ ,  $\eta_d$ ,  $\eta_r$ , and  $\eta_c$  are, as defined above, charge-transfer, diffusion, reaction, and crystallization overpotentials, respectively. The electrode reaction can then be represented by a resistance,  $R_E$ , composed of a series of resistances (or more precisely, impedance) which represent the different steps:  $R_{mt}$ ,  $R_{ct}$ , and  $R_{ixn}$ . A fast reaction step is characterized by a small resistance, while a slow reaction step is represented by a high resistance (Fig. 2.7).



Fig. 2.7: Processes in an Electrode Reaction Represented as Resistances and Overpotentials (Bard and Faulkner, 2001)

# Chapter 2

# 2.5.6 Pulse current electrodeposition

In olden times, direct current (DC) electrodeposition there is only one parameter, namely current density that is variable. In modern times, pulsed current (PC) plating where the potential or current density alternates rapidly between two different values is used (Chandrasekar and Pushpavanam, 2008). This is accomplished with a series of pulses of equal amplitude, duration, and polarity, separated by a period of zero current as shown in Fig. 2.8. Each pulse consists of an on-time ( $T_{on}$ ) during which potential and current is applied, and an off-time ( $T_{off}$ ), during which open circuit potential and zero current is applied.  $J_a$  is the average current density and  $J_p$  is the peak current density.



Fig. 2.8: Typical Direct Current and Pulsed Current Waveform

The duty cycle is given by the equation below:

Duty Cycle (%) = 
$$\frac{T_{on}}{T_{on} + T_{off}}$$
 ... (2.11)

The average current density is defined as:

$$J_a = (J_p) \times \text{Duty cycle}$$
 ... (2.12)

The average current density in PC plating is similar to the current density used in DC plating. For a given average current density, a number of combinations of different peak

current densities and on-off times are available. This gives PC plating two important features. Firstly, a very high instantaneous current density, one to two orders in magnitude greater than the steady-state limiting current density as reported, can be used without depleting the metal ions at the electrode surface. This favors the initiation of the nucleation process and greatly increases the number of grains per unit area, resulting in a finer grained deposit with better properties than conventional DC plating. Secondly, during the off-time period, adsorption and desorption, as well as recrystallization of the deposit occurs, which can control the microstructure of the deposits (Paunovic and Schlesinger, 2006; Djokic, 2010).

### 2.5.7 Electrolyte conductivity

The conductivity of an electrolyte depends on the degree of dissociation, the mobility of individual ions, temperature (and thus viscosity) and the electrolyte composition. In aqueous solution, the ionic conduction depends on the degree of dissociation of dissolved species in the solution. In order to increase the conductivity of electrolyte, certain salts and acids or alkali are added, known as supporting electrolytes. For acid electrolytes chlorides and acids are useful, for neutral electrolytes chlorides and for alkaline electrolytes sodium hydroxide or cyanides are useful. Some values of specific conductivities of selected electrolytes versus their concentration are plotted in Fig. 2.9.



Fig. 2.9: Conductivity of Various Electrolytes as a Function of Their Concentration (Kanani, 2004).

A marked decrease in conductivity at higher concentration is due to the greater coulombic forces acting between the ever closer ions in solution. This leads to loose association of opposite charged ions which are effectively neutral and thus no longer contribute to overall conductivity (Kanani, 2004).

# 2.6 Electrodeposition of Sn and Sn alloys

Sn can be electrodeposited from both acidic and alkaline aqueous solutions (Tan, 1993). In acidic baths, Sn usually exists as  $Sn^{2+}$  ions, while in alkaline baths;  $Sn^{4+}$  is the more stable species. The various Sn plating baths available in literature are as follows.

# 2.6.1 Electrodeposition of Sn

#### 2.6.1.1 Sodium stannate baths

The alkaline stannate electrolytes usually contain sodium or potassium stannate and the corresponding alkali metal hydroxide. These electrolytes are environment friendly, as

they are non-corrosive in nature and do not require other organic additives. The alkaline tin baths have a very high throwing power and can be operated over a wide current density range. The tin coatings electroplated from alkaline electrolytes possess improved solderability, since they do not require any organic additive agents. This leads to a great improvement in wettability. One major disadvantage of alkaline plating baths is that highly alkaline baths may dissolve the photoresist used to define areas on semiconductor wafers. Alkaline plating baths also usually require higher plating temperatures (60-70 °C) as compared to acidic ones (Schlesinger and Paunovic, 2010).

#### 2.6.1.2 Stannous sulfate baths

Sulfate baths are primarily used for bright acid Sn plating. Organic agents are necessary if bright and dense films are to be obtained. Electroplating of tin from acidic stannous (divalent Sn) solutions consumes less electricity than alkali stannate solutions (tetravalent Sn) (Schlesinger and Paunovic, 2010). The major drawback of this system is Sn oxidation. At high current density, soluble Sn anodes are passivated due to the formation of SnO<sub>2</sub>. Irregular, dendritic, needle-like electrodeposits of tin are in general obtained from acidic electrolytes without organic additives. To improve the surface finish, morphology and adhesion during acidic tin plating, various organic chemicals as additives have been investigated in the past. From literature we found that sulfate baths have been used widely to plate pure Sn and various Sn alloys in electronics industries (Lowenheim, 1974; Rehim *et al.*, 1996; Tzeng *et al.*, 1996; Nakamura *et al.*, 1994; Fukuda *et al.*, 2003; Medvedev and Makrushin, 2001)

### 2.6.1.3 Stannous chloride baths

For tin electroplating sulfate baths use a number of additives to produce a homogeneous deposit. However, inspite of these advantages, the use of additives is undesirable from health concerns. Moreover, adverse effect on plating efficiency and working environment has been observed. In case of alkaline baths, same is true as it requires heating the solution that causes bubble formation. Also tin is tetravent in alkaline baths causing more

power. In view of these disadvantages, recently, He *et al.* (2008) developed a bath containing citric acid or its salt and an ammonium salt.

#### 2.6.1.4 Methanesulfonic acid baths

The problem of oxidation of  $\text{Sn}^{2+}$  to  $\text{Sn}^{4+}$  can be minimized by using a reducing acid Methanesulfonic acid (MSA) bath as compared to sulfate bath. MSA is much less corrosive to electronic materials than sulfuric acid. It forms a clear solution, have high dissolving power and less sensitive to Sn oxidation at higher current densities (Gillman *et al.*, 2001). Different combinations of methanesulfonate baths have been developed to electrodeposit both pure Sn and various Sn alloys by adding different additives (Martyak and Seefeldt, 2004; Low and Walsh, 2008).

# 2.6.1.5 Pyrophosphate baths

There are a number of pyrophosphate baths available in the literature. These types of baths containing  $P_2O_2^{2^2}$  is considered as one of the most stable systems and is widely used for Sn plating (Kim *et al.*, 2010; Vaid and Char, 1957). However, its use is limited in literature due to one disadvantage that it requires more control and maintenance than the other plating baths. The operational temperature should not exceed 43-60 °C, because the pyrophosphate complex hydrolyzes to orthophosphate at temperatures higher than 60 °C, which degrades the solution (Harper, 2004).

# 2.6.2 Electrodeposition of Sn alloys

Electrocrystallization of alloys is more difficult to study than pure metals, due to the codeposition of at least two metals, and formation of the various possible crystallographic structures according to the phase diagram (Winand, 1994). According to the electrochemical series of metals, we know that the reduction potential of two elements would be different. For a solution containing two or more different metal ions, at low overpotential, the metal with the most noble reduction potential will deposit at a faster rate. If the electrode potential difference is far apart then metal alloy electrodeposition

may be impossible. The difference can be eliminated in view of the Nernst equation by modifying the activity values and feasibility of the codeposition can thus be determined (Paunovic and Schlesinger, 2006; Kanani, 2004). This can be achieved by inducing a considerable change in ionic concentrations via complex ion using certain complexing agents. In the past thiourea has been utilised as a complexing agent for the electrodeposition of Sn-Ag and Sn-Ag-Cu alloys (Ozga, 2006; Fukuda *et al.*, 2002). The formation of complexes by bonding the metal ions with complexing agents will decrease the concentration of the free metal ions in solution significantly and modify the reduction potential of the metal ions. As overpotential increases, the overall reaction will shift from charge transfer control to the mixed control and then to mass-transfer control. At higher overpotentials, where the electrodeposition reaction is under mass-transfer control, the relative deposition rates of two or more metals will depend on their concentrations and the diffusion coefficients of the metal ions (Kanani, 2004).

The reduction potential can also be brought closer by changing the concentration of metal ion(s). The Nernst equation (2.8) as shown in section 2.5.3, shows that the concentration term is a logarithmic function of the reduction potential and for far difference in standard potential values, it gives negligible change. Therefore, simple adjustments of metal concentrations may not give the desired deposit composition. For individual metals, the chemistry between metal ions and different complexing agents is fairly well known. When many ions are present in the solution, it is difficult to determine a suitable complexing agent and this requires extensive study. The basic mechanism of Sn and Sn alloy deposition both remains the same as Sn deposition discussed in previous section.

# 2.7 Electrodeposition process parameters

The electrodeposition method is dependent on several processing parameters involved in the electrodeposition process. Therefore to obtain desired properties it is essential to optimise the operating parameters. The effect of these parameters on tin electrodeposition is discussed in the following sections.

# 2.7.1 Current density

The current density is the primary controlling parameter in pulse electrodeposition. The average current density  $J_{a}$  is given by peak current density  $J_p$  x Duty Cycle. This enables us to achieve a very high current density in pulse electrolysis without depleting the metal ions at the electrode surface (Ibl, 1980). A high overpotential associated with higher pulse current density raises the nucleation rate resulting in fine grained deposit and thus improved properties can be obtained (Djokic, 2010). The critical radius of the electrodeposited nucleus for stable growth is inversely proportional to the cathodic overpotential and the nucleation rate also increases with the cathodic overpotential. Thus, the higher the cathodic overpotential, the finer is the grain size of the electrodeposits. A higher current density also leads to the development of dendritic morphology of the deposits (Watanabe, 2004). The change in alloy morphology have been noted by several researchers with increases current densities. For the case of Sn-Ag alloy pulse electro deposition, Kim *et al.* (2004) noticed that the content of silver, whose deposition potential is higher than that of tin, dropped with increasing current density.

# 2.7.2 pH

Effect of pH in tin plating has not been discussed in detail in the literature. The majority of the tin plating baths available in literature are acidic in nature. As a general statement the rate of deposition increases with pH (Durney, 1984). Bath pH not only affects the deposition rate but modifies the crystal orientation. Some people have noted a pH induced texture in Sn grains from acidic electrolyte (Teshigawara *et al.*, 2001). Ebrahimi *et al.* (1999) investigated the effect of pH on nickel deposits. He found that the pH values of 4.5, 4.7 and 5.0 resulted in grain size of 79, 45 and 56 nm, respectively. The increasing pH value from 2.8 to 5.1 enhanced the nucleation rate of nickel crystals, which corresponded to decreasing grain size from 343 to 35 nm. For copper electrodeposition, Natter and Hempelmann (1996) reported the smallest copper grain size of 8 nm at pH 1.5 - 2.0 and a continuous increase of the grain size up to 100 nm at pH 11.5.

# 2.7.3 Temperature

The majority of acid type formulations operate at a room temperature while alkaline tin baths are needed to be heated at higher optimum temperatures. As the temperature increases the rate of deposition also increases (Natter and Hempelmann, 1996). The velocity (diffusion and migration) of the metal ions and inhibitor molecules are functions of the temperature. The viscosity of the electrolyte decreases at high temperature, therefore, the diffusion rate and the velocity of copper ions and inhibitor molecules are increased. Sahaym et al. (2010) studied the effect of bath temperature in Sn electrodeposits and found the pyramid type morphology at elevated temperatures. They varied the bath temperature from 35 °C to 85 °C and explained that the higher the temperature of the plating solution (substrate), the slower would be the cooling rate of these adatoms. This means that at higher temperatures they can diffuse longer distances on the substrate surface. Therefore with an increase in the plating temperature, the grain size increases and the film surface becomes increasingly smooth. Increasing the plating temperature to 85 °C resulted in the formation of large faceted grains. These features increased in size with increasing temperature as the base film became increasingly smooth. The plating temperature also affected the morphology of the whiskers that formed upon aging at room temperature (Sahaym et al., 2010).

## 2.7.4 Additives

Although literature review about composite films and nanocrystalline films contains information about additives, additives for conventional metal deposition are still important as those additives would provide another aspect of information about deposition mechanism and novel additives. Popular organic additives that have been used in electrodeposition are gelatine, thiourea, EDTA (Ethylenediaminetetracetic acid), citric acid, benzotriazole (BTA), and inorganic additives such as chloride are covered in this review. Nakamura *et al.* (1994) used various organic additives such as benzalacetone (BA) and N, N-bis (tetraoxyethylene) octadecylamine. They found that on increasing the concentration of BA the smaller grains are obtained and roughness increases, further

when both are used with a high concentration of BA fine grained deposits are obtained due to a synergistic action of these adsorbed species. Tzeng et al. (1996) studied the behavior of aliphatic and aromatic aldehyde groups in tin electrodeposition. They found that as compared to formaldehayde and propionoaldehyde, benzaldehyde is hydrophobic in nature showing more overpotential and thus acts as best grain refiner. Surface active agents like Triton X-100, aromatic carbonyl compounds, and amine-aldehyde reaction products, methane sulphonic acid and its derivatives, etc. (Medvedev and Makrushin, 2001; Nakamura et al., 1994; Martyak and Seefeldt, 2004; Low and Walsh, 2008; Lee et al., 2004; Aragon et al., 1992) are used in plating solutions. Excess organic additives, higher current density and high metal ion concentration in the plating solution may have a bearing on solderability. Because tin readily forms an oxide, aging will also play a role in the success and failure of the deposit in presence of organic brighteners (Lal and Moyer 2005). Fine grained and smooth deposits were obtained from acid stannous sulphate solutions containing some aromatic ketones (Nakamura et al., 1994). It was found that these organic compounds were adsorbed on the cathode surface and enhanced the overpotential. In the acidic solutions, many other chemicals, such as polyoxyethylene laurylether, triethanolamine, sorbitol, sodium gluconate, 1, 4- hydroxybenzene, Trion X-100 or polypropylene glycol, may be added as complexing agents. The additives are necessary to improve solution stability and deposit morphology. However, an excess amount of additives would make the coating less solderable (Lal and Moyer 2005).

For alkaline stannate baths additives, usually few reports are available in literature. They usually do not require any additives since deposition occurs at a very negative potential and hydrogen evolution runs parallel with tin deposition acts as a leveller. However, the disadvantage is the diffusion of hydrogen inside the tin deposits (Broggi *et al.*, 2006). In literature effect of additives have not been discussed in detail for chlorides electrolytes. Sekar *et al.* (2010) investigated the effect of additives in detail on pulse elctrodeposition of tin containing Gelatin,  $\beta$ -naphthol, polyethylene glycol, peptone and histidine as additives. They observed a grain refinement brought about by additives but a marked decrease in current efficiency and found that the bath containing peptone has the lowest

crystallite size with better corrosion properties. The choice of the additive(s) is often dependent upon the nature of the metal being electrodeposited and the pH and temperature of the electrolyte. For example, organic additives used in semi-bright or bright nickel are not amenable in acid zinc solutions. Additives used in acid tin plating are different than those used in alkaline tin solution yet the tin coating may have similar morphologies and deposit properties from both solutions. In MSA acid baths, glycol type additives, PEG, PPG and Phenolphthalein have been tried in literature (Martyak, Seefeldt, 2004). Glycol-type additives are effective in minimizing hydrogen gas evolution at low overpotentials and refine the grain structure across a wide current density range. These additives are active in the presence of Phenolphthalein. Low and Walsh (2008) used the perfluorinated surfactant in MSA bath and observed that the adsorption of the surfactant hindered the hydrogen evolution and reduced the peak and limiting current densities. There is a little information on pyrophosphate baths in literature. Pyrophosphate baths include mostly glycol additives used in SnAg type solder bumps. These baths require more control of the electrodeposition parameters. Normally chelating agents and organic additives such as triethanolamine, sodium gluconate, 1, 4hydroxybenzene, Triton X-100 have been added in pyrophosphate baths (Neveu et al., 2006; Vaid and Char, 1957; Teshigawara et al., 2001; Correia et al., 2007).

# 2.7.5 Duty cycle and frequency

The deposition rate in the pulse technique is governed by the pulse current density and other parameters such as 'on' time  $(T_{on})$  and 'off'  $(T_{off})$  time. The pulse length  $T_{on}$  and  $T_{off}$  time has significant effect on grain size. An increase in pulse current density at constant length  $T_{on}$  and constant average current density with an increase in  $T_{off}$  time cause an increase in grain-size, because grain growth takes place during the  $T_{off}$  time. But an increase in pulsed current density at constant pulse charge and at constant  $T_{off}$  implies a decrease in grain-size. Therefore, a short  $T_{on}$  prevents grain growth and increases the nucleation rate (Chandrasekar and Pushpavanam, 2008).

The frequency of the pulse is the reciprocal of the total pulse duration consisting of  $T_{on}$  and  $T_{off}$ . The pulse length  $T_{on}$  and  $T_{off}$  time had significant effect on grain size. Thus, at lower pulse frequencies the pulse duration is higher. This means that more time is available for the charging and discharging of the double layer during  $T_{on}$  and  $T_{off}$ , respectively. At higher pulse frequencies the double layer does not have sufficient time to fully charge during  $T_{on}$  and to discharge during  $T_{off}$  time. Thus, lower frequencies cause bigger grains while higher frequencies results in a grain refinement of the electrodeposits (Shanthi *et al.*, 2008).

### 2.7.6 Effect of agitation

Agitation in the plating solution can be produced either by agitating the electrolyte or by moving the cathode (Tan, 1993). Agitation has very little effect on deposit composition at low agitation rates; however at high agitation rates the tin content in deposit decreases with increasing agitation rate. Furthermore, agitation increases the deposit roughness of the surface, although not markedly. Agitation has the beneficial effect of increasing the plating rate and permits the use of higher current densities by lowering of polarization (Paunovic and Schlesinger, 2006). Wen and Szpunar (2005) studied the nucleation and growth of tin and pointed out that agitation should not exceed beyond a certain limit where turbulent flow occurs that cause the difficulty of tin ions supply to the cathode even at high current densities. Thus the cathode coverage is poor and the deposition rate decreases.

# 2.8 Pulse co-electrodeposition

Pulse co-electrodeposition was initially developed to improve the surface properties of metals like wear and friction resistance, micro-hardness, corrosion resistance, by incorporating fine particles ( $<30 \mu m$ ) into the electrodeposited film (Hovestad and

Janessen, 1995). Recently, more attention has been placed on the incorporation of nanoparticles, 100 nm or less in size, to obtain much improved properties.

The properties of the composite deposits are largely influenced by the amount of particles incorporated into the metallic matrix. Numerous process parameters have been found to affect the particle incorporation in composite deposits directly or indirectly. The plating parameters include: (1) Particle properties, such as particle materials, particle size, and particle shape; (2) Suspension properties, such as pH, constituents, additives, aging; (3) Deposition variables, such as particle concentration in suspension, current density, agitation, and temperature (Hovestad and Janessen, 1995). Combined with the variety of metals, which can be electrodeposited, electrochemical composite deposition enables the production of a wide range of composite materials. Compared to the plain metal coatings the composite coatings have improved physical and (electro) chemical properties (Kedward *et al.*, 1974; Stankovic and Gojo; 1996).

# 2.8.1 Composite co-electroplating of solders

The different nanocomposite solders produced in literature are shown in Table 2.2. The composite approach has been developed mainly to improve the strength and reliability of solder joints. Nanosized reinforcement particles in conventional solder matrices due to their effectiveness in improving the creep resistance by being distributed at the grain boundaries to limit grain boundary sliding (Liu *et al.*, 2004; Choi *et al.*, 2001).
Matrix & Reinforcement	Processing Methods	Properties Enhanced	Applications	Reference
Sn-37Pb/Cu and TiO <sub>2</sub> nanoparticles	Conventional blending and mixing	Higher mechanical strength	Soldering in common devices	Lin <i>et al.</i> , 2003
Sn-0.7Cu/Si <sub>3</sub> N <sub>4</sub> nanoparticles	Powder Metallurgy	Wettability, IMC growth is prevented	Wettability, IMC Lead free M growth is prevented	
Sn-3.5Ag/Cu <sub>6</sub> Sn <sub>5</sub> , Ni <sub>3</sub> Sn <sub>4</sub> , FeSn <sub>2</sub> nanoparticles	In situ methods	Creep Lead free		Choi <i>et al.</i> , 2001
Sn-3.5 Ag/ SnO <sub>2</sub>	Powder Metallurgy	Hardness and Tensile Strength	Sensors, Solder Joints	Babaghorbani et al., 2009a
Sn-3.8Ag- 0.7Cu/SiC	Mechanical Mixing	Microhardness	Lead free	Liu <i>et al.</i> , 2008
Sn-3.5Ag-0.7Cu/ MWCNT	Powder Metallurgy	Higher strength	Lead free	Nai <i>et al.</i> , 2006a
Sn-MWCNT	Electrodeposition	Shear energy	Lead free Flip Chip Technology	Choi <i>et al.</i> , 2008
Sn-Ag-Cu/ TiO <sub>2</sub>	Melting and Casting	Increased Microhardness	Solder Joints (cellular phones,)	Tsao and Chang, 2010
Sn-0.7Cu/ Al <sub>2</sub> O <sub>3</sub>	Powder Metallurgy	Stiffnes, Hardness, Strength	Solders	Zhong and Gupta, 2008
Sn-Bi/ Yttria	Powder Metallurgy	Shear strength and wetting properties	Solders	Liu <i>et al</i> , 2010
Sn-Bi/SiC	Electro Deposition	Increased shear strength	Solder bumps	Shin <i>et al.</i> , 2009
Sn-Ag-Cu/ TiB <sub>2</sub>	Powder Metallurgy	Tensile Strength	Solders	Wei <i>et al.</i> , 2005
Sn-Cu/Cu nanoparticles	Powder Metallurgy	Higher strength	Solder joints, wire interconnects.	Alam <i>et al.</i> , 2009
Sn-3.5Ag/ZrO <sub>2</sub>	Casting	Higher strength	Solders	Shen <i>et al.</i> , 2006

Table 2.2: Reinforcement of Nanoparticles into Sn Deposits by Various Routes

# 2.8.2 $CeO_2$ as a reinforcement

After doing a thorough literature survey on the co-electrodeposited nanocomposites we find that co-electrodeposition technique is not new but it has been rarely used for

reinforcing any solder matrix. Earlier routes like, powder metallurgy, ball milling and conventional casting has been utilised tremendously. In literature, powder metallurgy route has been oftenly used to fabricate the lead-free solders reinforced with Cu nanoparticles, SiC, ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, SnO<sub>2</sub>, Y<sub>2</sub>O<sub>3</sub>, TiB<sub>2</sub>, CNT, Rare earth, (Alam et al., 2009; Wang et al., 2009; Shen et al., 2006; Fouzder et al., 2010; Zhong and Gupta, 2008; Babaghorbani et al., 2009a; Liu X et al., 2010; [Nai et al., (2006a; 2006b)]; Chen et al., 2003). However, in the development of nanocomposite an optimum fraction of the reinforcement phase must be added, otherwise it will deteriorate the solderability. Recently, Choi et al. (2008) synthesized Sn reinforced with carbon nanotubes using pulse co-electrodeposition technique, but there is limiting research on the synthesis of lead free solders by an electrodeposition process. It is noticed that ceria nanoparticles CeO<sub>2</sub> has rarely been used for reinforcing a solder materials inspite of being considered an excellent candidate for a reinforcement material of a nanocomposite solder. CeO<sub>2</sub> possess not only superior mechanical properties, but also excellent electrical and thermal characteristics. The main advantages of ceria are (a) higher electronic conductivity in solution as compared to its other counterparts like zirconia. (b) better corrosion resistance (c) resistance to oxidation and corrosion (Aruna et al., 2006). In this thesis an effort has been made to overcome the strength related concerns by incorporating the reinforcement nanoparticles within the solder matrix using co-electrodeposition process.

# 2.9 The co-electrodeposition mechanisms

Codeposition mechanisms for the dispersion of inert particles into metallic coatings have been developed initially for investigations of micron sized particles. The co-deposition mechanism proposed by first model given by Guglielmi (1972) has been adopted by various authors. In general this model is based on two consecutive adsorption processes. This model enables a quantitative treatment of the influence of particle concentration and current density on the incorporation rate of particles into a metal deposit but excludes hydrodynamic effects and particle characteristics. During the first step, an initial loose physical adsorption of the particles arriving at the electrode surface takes place. The loosely adsorbed particles are most likely still coated by a thin layer of adsorbed ions and solvent molecules which substantially screens the particle-electrode interactions. In the second step which is thought to be field-assisted and electrochemical in nature, the particles become strongly adsorbed onto the electrode due to the applied electrical field, as shown in Fig. 2.10 (a).



Fig. 2.10: (a) Codeposition Mechanism into a Metal Deposit and (b) The Five Stages in the Codeposition of a Particle (Guglielmi, 1972; Celis, 1987).

Finally, the strongly adsorbed particles are incorporated in the growing metal matrix. This model has been applied successfully to several systems, however some important process parameters such as, hydrodynamics, particle type, size and size distribution, pH and composition of the electrolyte are not taken into account.

Another model was presented by Celis *et al.* (1987) who attempted to predict the amount of particle codeposition for a given particle-metal combination by analyzing the particle transfer from the bulk electrolyte to the electrode surface. They proposed a five-step

process for the codeposition of particles with metals, which is schematically depicted in Fig. 2.10 (b).

The proposed mechanism of electrolytic codeposition of inert particles with metals is based on two fundamental postulates: (1) An adsorbed layer of ionic species is created around the inert particles when the particles are added to the plating solution or during the pretreatment of these particles in ionic solutions. (2) The reduction of some of these adsorbed ionic species is required for the incorporation of particles in the metallic matrix. The Celis model describes that the inert particle has to proceed through five stages on its way from the bulk of the solution to the site of incorporation at the active cathode surface as follows: (1) Adsorption of ionic species upon the particle surface, (2) Movement of the particle by forced convection towards the hydrodynamic boundary layer at the cathode, (3) Diffusion of the particle through the diffusion double layer, (4) Adsorption of the particle, still with its adsorbed ionic cloud, at the cathode surface, (5) Reduction of some adsorbed ionic species by which the particle becomes irreversibly incorporated in the metal matrix. Later on several models have been proposed for non-Brownian motion of particles given by Fransaer et al. (1992) and Veerecken et al. (2000) studied kinetics and settling time of nanoparticles, which is beyond the scope of this thesis and is not discussed. The models proposed so far are still unable to predict the process conditions necessary to achieve a given film composition for a given system without an initial set of experiments to find the empirical fitting parameters used in the model.

# 2.10 Key properties in the development of nano-composite solders

The original driving force for the preparation of nano-composite solders was to improve the mechanical, thermal, and corrosion resistance of the solder alloys to utilize them in high temperature, harsh service conditions. The properties that are improved compared to the conventional Pb-Sn solder are summarized as follows:

# 2.10.1 Density

For portable electronic goods density of the device is of primary concern. Several researchers have noticed an appreciable reduction in the density of the nanocomposite solders developed. Zhong and Gupta (2008) reported that the incorporation of nano  $Al_2O_3$  particulates in the Sn matrix aids in the reduction of density, while Babaghorbani *et al.* (2009a) found that in Sn-3.5Ag/SnO<sub>2</sub> solder the density is very close to the matrix because of the similar density values of the both phases.

#### 2.10.2 Electrical conductivity

For the fine pitch electronic devices, the electrical conductivity is the most important factor. The electrical resistivity of a nano-composite solder is affected by a combination of the following factors such as the reinforcement fraction, type, shape and size, presence of porosity and the matrix (Chang SY *et al.*, 2003; Weber *et al.*, 2003). Nai *et al.* (2008) reported that the addition of the CNT in the solder matrix does not degrade the resistivity of the matrix. They believed this could be attributed to the low volume fraction of porosity found in the composite solders and the small amount of reinforcement additions. While, Babaghorbani *et al.* (2009b) investigated the effect of micron sized and nanosized ceramic reinforcements, Cu, Y<sub>2</sub>O<sub>3</sub>, TiB<sub>2</sub> and SnO<sub>2</sub>, and ZrO<sub>2</sub>+8 mol% Y<sub>2</sub>O<sub>3</sub> inside the resistivity of the solder matrix adversely, while there is no significant change in resistivity when reinforcements are nanosized.

# 2.10.3 Melting point

Research reports on the melting behavior of solders are ambiguous. Often a decrease in the melting point of the composite solders is observed with increasing amount of ceramic nano reinforcements. Liu *et al.* (2008) studied the melting behavior of Sn-Ag-Cu alloy reinforced with nano-SiC. They argued that the reduction in melting point of the solder

alloys is possibly ascribable to an increase in the surface instability rendered by the addition of SiC nanoparticles with a higher surface free energy. Also, the size effect of the SiC nanoparticles can significantly alter the grain boundary/interfacial characteristics of the solders to induce this change in physical properties. Kumar *et al.* (2008) have also noticed a slight decrease in the melting point while reinforcing CNT in the solder matrix, while Nai *et al.* (2006c) observed no significant change in the melting behavior. Later on Shen *et al.* (2006) investigated the melting behavior of Sn-3.5Ag-ZrO<sub>2</sub>. They noticed no difference in melting point but solidification time increased. They argued that the ZrO<sub>2</sub> nano-particles acted as nucleation centres to promote the nucleation of solid in the molten alloy.

#### 2.10.4 Wettability/solderability

During soldering, in order to form a proper metallurgical bond between two materials, wetting must take place. In literature it is reported that the nanoparticles improve the solder wettability. It has been found that too much incorporation of the ceramic nanoparticles may also degrade the solderability because of an increase of the viscosity of the solder (Nai *et al.*, 2006b)

#### 2.10.5 Microhardness

The nano-composite solders developed have better microhardness as required for the electronics packaging industry. The addition of ceramic nanoparticles (Shen *et al.*, 2006; Liu *et al.*, 2008; Tsao and Chang, 2010; Zhong and Gupta, 2008) significantly enhanced the hardness, tensile strength and creep resistance of nano-composite solders. Moreover the additions of nanoparticles refine the grains of the matrix as well as are adsorbed on the intermetallics to refine them.

# 2.10.6 Wear and friction behavior

Tin-plated contacts have gained acceptance in many consumer applications such as separable connectors, press fit interconnectors, where wear resistance is of prime concern. Since mechanical and electrical properties and their changes caused by the sliding stress are critical to limits of application of contact finishes, frictional and wear behavior is important to study through the systematic wear tests and microscopic wear analyses (Baumann et al., 1983). Based on the performance and cost criteria, tin plating is considered as the best candidate in lead-free applications and has been recommended as the finish of choice for connectors. However, the susceptibility of tin-plated contacts for fretting corrosion is considered to be a major limitation for its use in automobile connectors (Wu and Pecht, 2002; Sankara Narayanan et al., 2007). Pure tin based interconnectors are sensitive to wear because they are relatively soft. In literature two types of wear we come across in relation to tin based solders, fretting and sliding wear. However, research on sliding wear has rarely been reported (Nagakawa and Matsukawa, 2002). Hammam et al. (1999) studied friction, wear, and electric properties of different tin coating prepared by different techniques (hot dipping, electroplating, and reflow), and reported that property differences among the techniques correlate to the thickness of the tin layer and the intermetallic compound. There is a limited research on sliding behavior of tin based solders. The ball on disk geometry has been successfully applied for fretting tests in literature (Hammam, 2006). Recently, Jun et al. (2009) reported that the wear and friction improves on adding the carbon fiber fraction in tin bronze matrix.

## 2.10.7 Electrochemical Corrosion

When the corrosion is present in the solder joints, it may change the microstructure of corroded regions and decreases the mechanical properties of solder joints by providing a crack initialization. In case of marine applications, chlorides from sea spray can react with the solder alloys and form soluble tin corroded products, which may damage solder joints and cause malfunction of electronic devices. Also, residual salt deposits combined

with humidity can promote the accelerated deterioration of solders. Solder joints in heat transfer systems can be susceptible to corrosion due to direct contact with heat transfer fluids (Song at al., 2006). Failure may occur as leaking through corroded solder joints. The mechanisms can be general corrosion, localized corrosion (e.g., pitting, crevice), and/or galvanic corrosion of dissimilar metals (e.g., solder and substrate). Improper soldering (e.g., flux remains and gaps between soldered parts) can also affect the corrosion process. Thus, understanding of corrosion of solder in heat transfer fluids is needed for the design and materials selection of heat transfer systems. However, they are susceptible to corrosion should they have long-time contact with corrosive vehicles such as salt or acid matter combined with moisture. Very little information is available on the corrosion resistance of solder alloys (Rosalbino et al., 2009; Mohanty and Lin, 2007). For the corrosion researches on Pb-free solders, It has been reported that the presence of Bi in Sn–Bi solders slightly increased the preferential dissolution of Sn in H<sub>2</sub>SO<sub>4</sub> solution and dramatically accelerated the dissolution in HNO<sub>3</sub> solution, compared with that of pure tin (Wu et al., 2006; Mohanty and Lin, 2007). There have been very few papers on the corrosion behavior of lead free composite solders. However, presently very little is known about the metallurgy and corrosion aspects of lead free solder systems. Recently, it has been found that lead free solders exhibit better corrosion resistance as compared to Sn-Pb solders due to their lower passivation current density, lower corrosion current density after the breakdown of passivation film and a more stable passivation film on the surface (Li et al., 2008).

# 2.10.8 Residual stress measurement

The growth of the intermetallic compound formation (IMC) has been investigated a lot in the past. These IMC produce compressive stresses (a drive for whisker growth in Sn coating) due to their volume expansion in the coating. Both reactive metal nanoparticles and inert nanoparticles are found to suppress the growth of IMCs particles in solder matrices, and are also effective in the redistribution of the stresses present in the material. The refinement of the IMCs can be explained on the basis of the surface adsorption theory (Shen *et al.*, 2006). Compared with the IMC particles, the size of nano-particles is very small. So, they are regarded as effective surface active agents, which are adsorbed on the surface of the IMC particles and suppress their excessive growth (Shen *et al.*, 2006; Amagai, 2008).

Chapter 3 – Experimental Procedure

This chapter provides the details about the various experimental steps involved in the synthesis of pure Sn coatings from various baths, monolithic Sn-Ag films as well as  $Sn/CeO_2$  and  $Sn-Ag/CeO_2$  nanocomposite solder films by pulse electrodeposition technique, different techniques employed for the microstructural characterization of monolithic and composite samples, and evaluation of different properties. The flowchart (Fig: 3.1) shows various experimental steps involved in this work.

# **3.1 Materials and Methods**

The materials (chemicals) for bath preparation used in this study are of electrolytic grade. The various steps involved in the pulse electrodeposition are as follows:

#### 3.1.1 Plating bath preparation

The electrolyte solution is prepared using deionised distilled water. Different types of aqueous plating baths (Bath 1, Bath 2, Bath 3, Bath 4 and Bath 5) are utilized for pure tin deposition. The plating bath chemicals used are of the highest purity (99.8%, Merck India) and are dissolved in 500 mL of distilled water contained in a borosilicate glass beaker (Tarsons Products Pvt Ltd, India) of 1 L volume. The solution is stirred mechanically with magnetic stirrer for about 1 hour for homogenization and kept overnight. The pH of the bath solution is also adjusted with the addition of 10 % dilute sulphuric acid and ammonia solution whenever required. The electrolytic solution pH and conductivity measurements are done by using Sartorius Professional meter PP-50. The compositions of the aqueous electrolytic baths are given in Table 3.1.

For composite preparation, the 20 h ball milled  $CeO_2$  powder (Loba Chemie, 99.9%) of different concentration (0, 1, 2, 5, 10, 15, 20, 25, 30 g/L) is added in the bath. Two types of baths are prepared for Sn/CeO<sub>2</sub> and Sn-Ag/CeO<sub>2</sub> composites and designated as Bath A and Bath B, respectively. The resultant solution is subjected to the ultrasonication (Sartorius, Labsonic M) for 6 h in order to achieve uniform dispersion of CeO<sub>2</sub> nanoparticles in the electrolyte. The plating bath is also stirred by a magnetic stirrer

(Tarson Spinot) during co-electroplating at 300 rpm. The bath compositions for composite samples are shown in Table 3.2.



Fig: 3.1: Flowchart Showing Various Experimental Steps Involved in this Work

Bath 1	Na <sub>2</sub> SnO <sub>3</sub> .2H <sub>2</sub> O	NaOH (15g/L)		
	(90 g/L)			
Bath 2	SnSO <sub>4</sub> (30 g/L)	H <sub>2</sub> SO <sub>4</sub> (200 g/L)	Triton X-100	
			(0.1 g/L)	
Bath 3	$SnCl_2$ (50 g/L)	C <sub>6</sub> H <sub>17</sub> N <sub>3</sub> O <sub>7</sub> (100 g/L)		
Bath 4	(CH <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub> Sn (30	CH <sub>4</sub> SO <sub>3</sub> (130 g/L)	PEG (2.5 g/L)	Hydroquinone
	g/L)			(1 g/L)
Bath 5	SnCl <sub>2</sub> (30 g/L)	K <sub>4</sub> P <sub>2</sub> O <sub>7</sub> (100 g/L)		

|--|

Table 3.2: Bath Compositions for Sn/CeO<sub>2</sub> and Sn-Ag/CeO<sub>2</sub> Composites

Bath A	concentration	Bath B	concentration
SnCl <sub>2</sub>	50 g/ L	SnCl <sub>2</sub>	50 g/ L
$C_{6}H_{17}N_{3}O_{7}$	100 g/L	$C_{6}H_{17}N_{3}O_{7}$	100 g/L
CeO <sub>2</sub>	(0-30 g/L)	AgNO <sub>3</sub>	0.24 g/L
		Thiourea	0.1 g/L
		CeO <sub>2</sub>	(0-30 g/L)

# 3.1.2 Substrate preparation

A copper plate (Loba chemie, 99.8%) of dimension 50 mm x 30 mm with a thickness of 0.1 mm is used as a cathode substrate. The cathode substrate is metallographically polished and thoroughly cleaned with soap, water, and acetone. It is then rinsed with a 10% sulfuric acid solution for 2-3 minutes, followed by a final rinse in deionized water and dried in alcohol. The anode used is electrolytic grade pure tin (99.8% purity, Merck Pvt. Ltd.) of dimension 10.0 cm x 2.5 cm x 0.5 cm. Prior to pulse electrodeposition experiment, the copper cathode is mounted on a rectangular pyrex glass slab. The desired

area (6 cm<sup>2</sup>) on cathode is exposed by masking it with a good quality cellophane tape. For composite preparation, the cathode used is the polished steel plate which is masked using a cold setting polymer to expose the required surface area ( $\sim$ 6 cm<sup>2</sup>) for the cathodic deposition. The substrates are ultrasonically cleaned to remove contaminants. All these preliminary treatments like polishing, ultrasonic cleaning have been done in order to eliminate the surface irregularities.

#### 3.1.3 Synthesis of reinforcement

As received  $CeO_2$  powder (Loba Chemie, 99.9%) is subjected to high energy ball milling in a vario-planetary milling machine (Fritsch Pulverisette-4, Germany), Fig. 3.2, which consists of WC twin vials rotating simultaneously on a revolving main disk.



Fig. 3.2: P4 Vario Planetary High Energy Ball Milling Setup

It provides an extra parameter namely, the transmission ratio  $(r_c)$  which is defined as the ratio between vial rotational speed and main disk revolution speed. The mill is operated at a main disc speed ( $\Omega$ ) of 300 rpm and planet speed ( $\omega$ ) of 540 rpm with a transmission ration of - 1.8, and the ball to powder ratio (BPR) is 10:1. After each hour of milling, the mill is allowed to cool for 45 to 60 minutes. Toluene is used as a process control agent (PCA) which prevents excessive cold welding of the powders and their oxidation. The powders are milled for 20 h and samples are collected regularly during milling to observe

the progress of the size reduction. After drying, the  $CeO_2$  powder is washed in alcohol followed by distilled water. The powder is characterised using XRD. Once it is confirmed that the powder is suitable for deposition, the electrodeposition is carried out. The various important parameters for the ball milling operation are listed below in Table 3.3.

Parameters	Value		
Apparatus	Fritsch Pulverisette - 4 Planetary Ball		
	Mill with Tungsten carbide balls and		
	vials		
Raw Material	Ceria (CeO <sub>2</sub> ), 99.5%		
d <sub>v</sub> (diameter of vial)	75 mm		
d <sub>b</sub> (diameter of ball)	10 mm		
R (revolution radius)	125 mm		
$l_{\rm c}$ (distance from rotating shaft to the centroid	32.5 mm		
of the ball that contacts with the mill)			
r <sub>c</sub> (critical speed ratio)	2		
$\Omega$ (rotational speed of main disk)	300 rpm		
$\omega$ (rotational speed of vial)	540 rpm		
Milling time	20 hours		
BPR	10:1		
PCA	Toluene		
Milling atmosphere	Ambient		

Table 3.3: Important Parameters for the Ball Milling Operation

# 3.1.4 Pulse electrodeposition

This is the most important step as far as the total work is concerned. The pure tin coatings are synthesised by pulse electrodeposition technique. The experimental setup for pulse electrodeposition is shown in Fig. 3.3. The cathodic pulse electrodeposition is carried out in galvanostatic mode using Potentiostat galvanostat (Autolab PGSTAT 30) with a 10 A

# Chapter 3

current booster. The Autolab is interfaced with a personal computer which controls the pulse waveforms with GPES software supplied by the Ecochemie, Netherlands. Auto lab PGSTAT 30 is also employed for polarization measurements wherever required. For these measurements, three electrode cell configuration is used. The copper is used as a working electrode. The saturated Ag/AgCl in 3 M KCl solution and platinum rod are used as reference and counter electrodes, respectively. The experiment is performed at a scan rate of 1 mV/s.



Fig. 3.3: Pulse Electrodeposition Experimental Setup

The composites are synthesised by pulse co-electrodeposition method with an addition of ball milled nanosized  $CeO_2$  powders in the electrolyte. One of the most important aspects of the co-electrodeposition process is to have the uniform dispersion of  $CeO_2$  powders in the solution. A magnetic stirrer is used to stir the solution bath having  $CeO_2$  nanoparticles to get a uniform colloidal suspension. Ultrasonication of the electrolyte is carried out for 6 hours to achieve better dispersion of ceria in the electrolyte. The as deposited coatings

are cleaned ultrasonically and finally washed with alcohol before the characterization. The various parameters used for the pulse-co-electrodeposition are given in Table 3.4.

Table 3.4: Operating Conditions and Electrical Parameters for Pulse Co-Electrodeposition

Bath A, Bath B	Sn/CeO <sub>2</sub> , Sn-Ag/CeO <sub>2</sub>	
Nanosized ceria particles	0, 1, 2, 5, 10, 15, 20, 25 and 30 g/L	
Current density	$0.2 \text{ A/cm}^2$	
Temperature	~28°C	
Agitation	Magnetic stirrer at 300 rpm	
рН	~4.3	
Pulse mode	DC square wave	
Pulse on, off time	0.001, 0.01s	
Pulse frequency	90 Hz	
Duty cycle	9%	

# **3.2 Characterisation Details**

#### 3.2.1 X-ray diffraction (XRD)

The XRD experiments are carried out in an X-ray diffractometer (Bruker's D8 Advance) with Co or Cu-target operating at 40 kV and 30 mA current. The phases formed are identified by comparison of the recorded diffraction peaks with the International Center for Diffraction Data (ICDD) database using Philips X'Pert HighScore software. Profile fitting is carried out using X'Pert HighScore which uses the Pseudo-Voigt profile function.

Structural broadening for the calculation of crystallite size is obtained using

$$\beta^2 = \beta^2_{observed} - \beta^2_{standard} \qquad \dots (3.1)$$

Where,  $\beta_{standard}$  and  $\beta_{observed}$  are full width at half maximum of any particular reflection from the standard silicon disc and the powder, respectively and  $\beta$  is the full width at half maximum of the particular reflection peak. The crystallite size analysis has been done by Williamson-Hall method. This method assumes that both size and strain broadening of profiles follow Lorentzian distribution (Williamson and Hall, 1953). According to this assumption, the mathematical relation involving the integral breadth ( $\beta$ ), volume weighted average crystallite size (D<sub>v</sub>) and the lattice strain ( $\varepsilon$ ) can be given as,

$$\frac{\beta\cos\theta}{\lambda} = \frac{1}{D_{\nu}} + 2\varepsilon \left(\frac{2\sin\theta}{\lambda}\right) \qquad \dots (3.2)$$

The plot of  $\left(\frac{\beta \cos \theta}{\lambda}\right)$  versus  $\left(\frac{2\sin \theta}{\lambda}\right)$  gives the value of the lattice strains from the slope and crystallite size from the ordinate intercepts.

# 3.2.2 Scanning electron microscopy (SEM)

The morphology and grain size of the matrix, and distribution of nano  $CeO_2$  particles in the electrodeposited coatings are analysed using scanning electron microscope (SEM) (Carl Zeiss Supra EVO 60) coupled with energy dispersive X-ray spectrometer (EDS), which detects the energy of the chacteristic X-rays. This is used to detect the elemental distribution present in the sample. The high resolution field emission microscope (FESEM, Zeiss Supra 40) is also utilised for visualization of CeO<sub>2</sub> nanoparticles.

#### 3.2.3 Transmission electron microscopy (TEM)

The transmission electron microscopes (JEOL JEM 2100 and Philips Technai 2 Twin G220S) operating at 200 kV are used to characterize the  $CeO_2$  powders and bulk composite samples. The powder samples for TEM analysis are prepared by simply ultrasonicating the dispersed powder in acetone for 2 hours. A drop of homogenized solution is taken and dropped on to a carbon coated copper grid followed by drying at room temperature. For composite sample preparation both twin jet electro polishing

(Fishione Model 120) and ion milling (Gatan PIPS) are employed. The twin jet polishing is carried out in an electrolyte containing 75% ethanol and 25% (by volume) phosphoric acid at -12  $^{\circ}$ C and 5 V. The ion milling is carried out after dimpling (Gatan) to a thickness of 20  $\mu$ m using argon as the ionizing gas at 5 keV with the double beam modulation technique.

#### **3.3 Property Evaluation**

#### 3.3.1 Microhardness

Microhardness of electrodeposited monolithic Sn, Sn-Ag as well as Sn/CeO<sub>2</sub> and Sn-Ag/CeO<sub>2</sub> nanocomposite coatings has been determined by Leica Vickers micro hardness tester (UHL VMHT). The indentation is imaged on a computer screen which is software controlled. The applied load is 25 gf for a dwell time of 20 seconds. The Vickers hardness tester uses a square based diamond pyramid as the indenter. The included angle between opposite faces of the pyramid is 136 °C. The Vickers microhardness number is given as the load divided by surface area of the indentation:

Vickers microhardness, (Hv) (kgf/mm) = 
$$1.854 \text{ F/d}^2$$
 ... (3.3)

Where, F is the indenter load in kg and d is the diagonal length of the impression in mm. For microhardness measurement, a representative sample is cut from the deposit. To average out any variations, samples are collected from different parts of the deposits. Multiple observations, about 10 measurements, are recorded for a single sample and the average hardness values are determined.

# 3.3.2 Surface profilometry

The surface profilometer (Veeco Dektak 150) is used to measure the surface roughness of the pure tin coatings as well as composite sample, 2D and 3D surface profile, penetration depth and width of the wear tracks. This technique utilizes a diamond stylus that is moved vertically in contact with a sample and then moved laterally across the sample for

# Chapter 3

a scan length of 2000  $\mu$ m and specified contact force. It measures small surface variations in vertical stylus displacement as a function of position. The height position of the diamond stylus generates an analog signal which is converted into a digital signal and is stored, analyzed and finally displayed on a computer screen.

3.3.3 Ball on disc wear and friction monitor

The friction and wear tests are performed using a ball-on disc friction and wear monitor (TR 208 M1) supplied by Ducom, India. The schematic diagram is shown in Fig 3.4.



Fig. 3.4: Ball-on-disc Wear and Friction Monitor Set up.

It mainly consists of hardened steel ball of 2 mm diameter loaded against a horizontal rotating disc of 25 mm in diameter and 0.5 mm in thickness. The samples are prepared as square shaped (of 2.5 x 2.5 cm dimensions) which are mounted on the horizontal disc. Normal load, rotational speed, and wear track diameter can be varied to suit the test conditions. The experimental data like wear and friction are recorded and displayed graphically using a microcomputer via an analogue to digital converter. Friction testing conditions employed in this study are listed in Table 3.5.

Parameters	<b>Experimental Conditions</b>
Load	4 to 10 N
Sliding distance	9 m
Temperature	Room Temperature
Ball and size	Hardened steel and 2 mm
Counter material	Sn, Sn/CeO <sub>2</sub> , Sn-Ag/CeO <sub>2</sub> composites
Ball hardness	1710 VHN

Table 3.5: Ball on disc Wear Test conditions and Parameters

The friction and wear of the samples are recorded for a total time of 1800 seconds. The coefficient of friction ( $\mu$ ) is calculated by using the frictional force data and is given by

$$\mu = \frac{F}{N}, \qquad \dots (3.4)$$

where F and N are the frictional force and normal force in Newton, respectively. Sliding speed S (m/s) is given by,

$$S = \frac{\pi D N}{60,000} \qquad ... (3.5)$$

The sliding distance L (m) is given by,

$$L = S \times T$$
 ... (3.6)

Where,  $\pi = 3.142$ , D = Diameter of wear track in mm, N = Disc speed in rpm and T = Test duration in s.

The wear rate of the worn out samples is given by

$$W = \frac{V}{NL}, \qquad \dots (3.7)$$

Where V is the worn out volume as calculated from the track profile geometry, L is the sliding distance, and N is the normal load applied (Jun, 2009). The volume loss governing the track geometry can be calculated using the following equation given by the ASTM standard G99 (Shafiei and Alpas, 2008):

$$V = 2\pi r \left( R^2 \sin^{-1} \left( \frac{H}{2R} \right) - \frac{H}{4} \left( 4R^2 - H^2 \right)^{1/2} \right) \qquad \dots (3.8)$$

Where R and r are the radius of the mate steel ball, and the round sliding track, respectively. Width of the wear track, H is measured from the surface profile of wear track after wear experiment.

#### 3.3.4 Electrochemical corrosion behavior

Autolab PGSTAT 302 N which can generate DC current waveforms pulses upto 10 A is used for the electrochemical corrosion studies. Experiments are conducted using the standard three electrode cell configuration with a platinum rod as a counter electrode, Ag/AgCl (1M KCl) electrode as a reference electrode, and the sample as a working electrode. A schematic diagram for the experimental set up is shown in Fig. 3.5. The surface of the examined specimens exposed to corrosive medium is about 1 cm<sup>2</sup>. The corrosive medium is chosen as 3.5 % NaCl aqueous solution with a pH of ~6.4. The sample is immersed in corrosive medium for 30 min to attain steady state potential or open circuit potential (OCP). After attaining a stable OCP, the measurements are carried out by potentiodynamic polarization measurements polarizing the specimen from -1000 mV to + 1000 mV with respect to  $E_{corr}$ , at a scan rate and 1 mV/s and step potential of 0.45 mV.



Fig. 3.5: Schematic Diagram Showing the Corrosion Investigation Setup

After the Potentiodynamic polarization test the samples are cleaned with alcohol, dried in air and then surface morphology of the corroded samples is examined using SEM. The corrosion rate is calculated by the Stern Geary relation which is embedded in the software program, the GPES (General Purpose Electrochemical System, Ecochemie module, version 4.9).

# 3.3.5 Electrical resistivity measurements

The electrical resistivities ( $\rho$ ) of Sn and Sn-3.5Ag solder materials and their composites are measured using a four-point probe set up. Probe spacing (*s*) of 1.5 cm is used. Typical size of the samples used in this measurement is 6 cm x 1 cm x 25 cm. The block diagram is shown in Fig. 3.6



Fig. 3.6: Schematic Diagram Showing the Four-Point Probe Configuration used for the Electrical Resistivity Measurements

A constant current from Keithley voltage/current source is passed through the sample across outer leads and the corresponding voltage is measured across the inner leads using a Keithley Digital Multi-Meter (DMM). Current is set at 1 A in this study, as tests conducted using lower range of applied current result in large variations in voltage value. The current used here is within the range of values (10 mA to 50 A) used by other investigators for four point probe testing. In this study, the following equation is used to calculate the sample's electrical resistivity value:

$$\rho = 2\pi s \left(\frac{V}{I}\right) \qquad \dots (3.9)$$

Where, V is the voltage between the inner probes, I is the current passing through the outer probes and s is the probe spacing.

Thus,

$$V = IR \qquad \dots (3.10)$$

and,

$$\rho = 2\pi s \times R \qquad \qquad \dots (3.11)$$

There are two cases, 1) the sample is infinitely thick (i.e., h>>s), and 2) the sample is infinitely thin (i.e., h<<s). For these two cases the resisitivity values can be given by the following equations

$$p = \frac{\pi}{\ln 2} \times h \times \left(\frac{V}{I}\right); \text{ for h} << s \qquad \dots (3.12)$$

and,

$$\rho = 2\pi \times s \times \left(\frac{V}{I}\right); \text{ for } h >> s \qquad \dots (3.13)$$

For the two-dimensional case, the quantity  $\rho/h$  (which has units of Ohms) is called the two dimensional resistivity, sheet resistance, or resistance-per-square. It is used in many thin film applications, where one does not know the film thickness or resistivity, only the sheet resistance.

## 3.3.6 Differential scanning calorimetry

A Pyris Diamond DSC (Perkin Elmer) is used to measure the melting point of the developed composites. The calorimetric investigation is carried out using alumina  $(Al_2O_3)$  pans in which 5 to 10 mg of the material is kept during testing. The samples are heated from 50 to 250 °C at a rate of 10 °C min<sup>-1</sup>, under a N<sub>2</sub> atmosphere with a flow rate of 50 ml min<sup>-1</sup>.

# 3.3.7 Density

The density of samples is determined using Archimedes principle. The composites are weighed separately in air and distilled water by high precision electronic balance (Sartorius CPA 225D) and the density is calculated based on the following equation:

$$\rho_{sample} = \left(\frac{W_{air}}{W_{air} - W_{water}}\right) \times \rho_{water}$$
(3.12)

Where  $W_{air}$  = Weight of the sample in air, and  $W_{water}$  = Weight of the sample in water

# 3.3.8 Residual stress measurement

The residual film stresses of the selected compositions on copper substrate are measured by  $\sin^2 \psi$  method of X-ray diffraction analysis using Philips Panalytical X'Pert Pro (PW 3040/60, Netherland) with a stress Goniometer attached to it. This method is performed by measuring the diffraction angle 20 in the  $\psi$  tilt axis ( $\psi$ = 0, 45° and 90°) against the direction of stress measurement and generating  $\sin^2 \psi$  diagrams (Cullity, 1978). All stress measurements are done along the same in-plane direction in the specimen frame of reference and thus only one component,  $\sigma \parallel$  (stress parallel to the surface), of the stress tensor will be reported. The  $\sin^2 \psi$  method is suitable for isotropic materials but when applied to anisotropic materials, a reflection peak that exists at a higher diffraction angle is selected for residual stress measurement (Satoa, 2003). The peak intensity corresponding to the (312) plane of the Sn structure is measured. This has been selected previously in the literature by a number of researchers (Sobiech *et al.*, 2011; Buchovecky *et al.*, 2009). The final residual stress is calculated using X'pert Stress Software.

# 3.3.9 Sample designations

Table 3.6: The Sample Codes used for the  $\mbox{Sn/CeO}_2$  and  $\mbox{Sn-Ag/CeO}_2$  and  $\mbox{Nanocomposites}$ 

Concentration of Caria $(g/I)$	Material code		
concentration of certa (g/L)	Sn/CeO <sub>2</sub>	Sn-Ag/CeO <sub>2</sub>	
0	CO	D0	
1	C1	D1	
2	C2	D2	
5	C5	D5	
10	C10	D10	
15	C15	D15	
20	C20	D20	
25	C25	D25	
30	C30	D30	
		<b></b>	

# 3.3.10 Plating baths designations

Table 3.7: The Plating Bath Codes used for the Pure Sn and Different Composites

Plating Baths	Systems
Bath 1	Alkaline Stannate Bath
Bath 2	Acidic Sulfate Bath
Bath 3	Stannous Chloride-Citrate bath
Bath 4	Methyl Sulfonic Acid (MSA) Bath
Bath 5	Pyrophosphate Bath
Bath A	Composite Bath For Sn/CeO <sub>2</sub> films
Bath B	Composite Bath for Sn-Ag/CeO <sub>2</sub> films

# Chapter 4 – Results and Discussion

4.1 A study on pulse electrodeposition of pure tin from aqueous plating baths

This chapter presents the detailed results and discussion about the investigated experiments, i.e., synthesis and characterisation of pulse electrodeposited pure tin from different aqueous solution baths, synthesis of CeO<sub>2</sub> reinforcement, development of the Sn/CeO<sub>2</sub> and Sn-Ag/CeO<sub>2</sub> nanocomposite solders, evaluation of various properties such as microhardness, density, melting point, resistivity, wear and friction, electrochemical corrosion, and residual stress measurement. This whole chapter is divided into the following sections:

In section 4.1, a detailed description about the experiments on pulse elctrodeposition such as common tin plating baths employed, their chemical compositions, rationale behind their selection and their characterization by bath conductivity and cathodic current efficiency, microstructural characterization of as deposited and aged tin coatings, and whisker growth morphology are provided and the results obtained are summarized.

In section 4.2, the effect of pulse electrodeposition parameters such as current density, additive concentration, pH, duty cycle, frequency, temperature, and stirring speed on microstructural characteristics of the coating obtained from sulfate bath and their effect on grain size distribution have been presented.

In section 4.3 microstructural characterization of the ball milled  $CeO_2$  and different composites has been presented. The evaluation of the various properties of the developed composites has been reported in section 4.4.

# 4.1.1 Plating baths

The Sn plating baths that have been used to study the morphology of the tin plated films are Alkaline sodium stannate bath (Bath 1), Acidic stannous sulfate bath (Bath 2), Triammonium citrate bath (Bath 3), Methyl sulfonic acid bath (Bath 4), and Potassium pyrophosphate bath (Bath 5). The bath properties, i.e., solution conductivity, pH, current efficiency as well as the roughness of the deposited films for each bath are also reported in this section. Table 4.1 shows the composition, conductivity, pH and CCE of all the baths.

Plating	Composition	Conductivity	pН	CCE (%)
bath		(mS/ cm)		
Bath 1	Na <sub>2</sub> SnO <sub>3</sub> .3H <sub>2</sub> O (90 g/L)	10.9	13.04	70-80
	NaOH (15 g/L)			
Bath 2	SnSO <sub>4</sub> (30 g/L)	46.2	1.0	85-90
	H <sub>2</sub> SO <sub>4</sub> (200 g/L)			
Bath 3	SnCl <sub>2</sub> (50 g/L)	13.8	4.3	90-96
	C <sub>6</sub> H <sub>17</sub> N <sub>3</sub> O <sub>7</sub> (100 g/L)			
Bath 4	(CH <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub> Sn (30 g/L)	58.1	0.24	65-75
	CH <sub>4</sub> SO <sub>3</sub> (130 g/L)			
	Hydroquinone (1 g/L)			
	PEG (2.5 g/L)			
Bath 5	SnCl <sub>2</sub> (30 g/L)	11.6	5.88	50-60
	K <sub>4</sub> P <sub>2</sub> O <sub>7</sub> (100 g/L)			

Table 4.1:	Different	Plating	Bath	Compos	sitions	and	Prop	perties
		<u> </u>						

Bath 1: Alkaline sodium stannate bath

This type of bath generally comprises of sodium stannate and sodium hydroxide, and there is no organic additive added to this type of bath. Usually the alkaline bath contains 90-110 g/L of sodium stannate (Durney, 1984; Schlesinger and Paunovic, 2010; Stoychev *et al.*, 1984). Based on the previous studies the selected composition in the present investigation consists of 90 g/L sodium stannate and 15 g/L sodium hydroxide (Table 4.1) NaOH acts as a stabilizing agent and improves the bath stability (Sharma *et al.*, 2012).

Bath 2: Acidic stannous sulfate bath

The sulfate bath usually contains 20-100 g/L of  $SnSO_4$  and the sulfuric acid is added upto maximum of 200 g/L (Ilgar, 1998; Medvedev and Makrushin, 2001; Rosenberg, 1976). It is observed in the present investigation that a higher amount of sulfuric acid above 200 g/L increases the conductivity from 46.2 to 67.3 mS/cm, but deteriorates the ionic mobility. Thus, the upper limit of sulfuric acid concentration is selected to be 200 g/L in the present investigation. There is one more point to note that in case of acidic baths the addition of organic additives is required to obtain uniform and smooth cathode coverage, and to prevent or inhibit dendritic powdery growth and promote nucleation (Vittal *et al.*, 2006). In the present investigation a nonionic surfactant (Triton X-100) is used as an additive.

#### Bath 3: Citrate bath

The triammonium citrate bath which is weakly acidic is used recently by He *et al.* (2008) for pure tin electrodeposition. The triammonium citrate ( $C_6H_{17}N_3O_7$ ) acts as an additive. The composition of the citrate bath used for tin electrodeposition in the present investigation is given in Table 4.1.

# Bath 4: Methyl sulphonic acid (MSA) bath

MSA is a reducing acid and thus has been developed by previous researchers to minimize the propensity for stannous oxidation,  $\operatorname{Sn}^{2+} \to \operatorname{Sn}^{4+}$ , as compared to sulfate baths. MSA is highly conductive (Table 4.1). It is completely soluble in tin salts and forms a clear solution unlike sulfate baths. However, this bath is more expensive as compared to sulfate and citrate baths. In this bath, Poly ethylene glycol (PEG) is used as an additive and hydroquinone as an antioxidant (Martyak and Seefeldt, 2004). Bath 5: Pyrophosphate bath

The pyrophosphate bath is also used in this study which also has a higher pH compared to the citrate bath. This type of bath has been also used for Sn plating in literature (Watanabe, 2004).

# 4.1.2 Cathodic Current Efficiency

The cathode current efficiency (CCE) of a bath is an important parameter to decide the final microstructural properties in a deposit. The CCE during plating from these baths are shown in Table 4.1.

The cathode current efficiency CCE is calculated by the equation:

CCE (%) = 100 x 
$$\frac{M_a}{M_c}$$
 ... (4.1)

where CCE is the ratio between actual amount of metal deposited,  $M_a$  to that calculated theoretically from Faraday's laws,  $M_i$ . CCE in plating, in general, depends on a number of key parameters of the electrolyte, such as chemical component concentrations, pH, additive, agitation, current density, temperature, rotation etc (Paunovic and Schlesinger, 2006). It is found that the CCE of sulfate bath (Bath 2) and citrate bath (Bath 3) is high while others have lesser current efficiency. It is well known that the hydrogen evolution occurs in all the plating baths, indicating that a lower CCE means a higher hydrogen production in the bath. This hydrogen diffuses in to the deposits and impairs the microstructural properties. Therefore, a reasonably higher CCE is required in order to obtain the desired properties and improved coating life (Jiang and Xian, 2008).

### 4.1.3 Microstructural characterization of the as deposited tin coatings

#### 4.1.3.1 SEM

Figure 4.1 shows the surface morphology of Sn coatings electrodeposited from different baths at various current densities (0.1 to 0.5 A/cm<sup>2</sup>). It is observed that the Sn coatings have different grain sizes when electroplated from different baths. The surface of the coatings plated from Bath 1 and 2 is uniform. It is noticed that the morphology of the grains plated from Bath 1 and 2 is polygonal while the coating plated from Bath 3 exhibits pyramidal shaped structure (since current efficiency is higher in this case, as noted from Table 4.1). In case of Bath 4 and 5, the grains are spherical/nodular or faceted with unsatisfactory cathode coverage.



Fig. 4.1: SEM Micrographs Showing the Surface Morphology of the Tin Coatings Deposited from Different Baths at Different Current Densities

Bath 1, 2 and 3 give more regular smooth surface which is also quite dense and no tendency to dendritic growth is observed below  $0.5 \text{ A/cm}^2$ . The electrodeposited Sn coatings obtained from Bath 3 have large grain size indicating a very high deposition rate of this bath (Table 4.1). The deposits obtained from Bath 4 and 5 represent a different type of morphology characterised by lumps of non-uniform and irregular shaped nodules. A general trend is noticed for each bath within the investigated current density range  $(0.1-0.5 \text{ A/cm}^2)$ . At lower current densities, the electrodeposited coatings with uniform grains are formed but the regular grain structure is deviated after a particular current density is reached which is different for different baths.

It can be concluded from the above discussion that a satisfactory cathode coverage with well developed grains may be obtained from each baths if the current density is kept around 0.2 A/cm<sup>2</sup>. A very high current density (i.e., 0.5 A/cm<sup>2</sup> for Bath 1, 2 and 3, 0.4 A/cm<sup>2</sup> for Bath 4 and 0.3 A/cm<sup>2</sup> for Bath 5) will in the lowering of the current efficiency and thus porous, nodular and non uniform deposits are obtained (Kim *et al.*, 2010). The porosity comes mainly from the hydrogen adsorption in the coatings while the nodular and dendritic morphology occurs due to the faster deposition rates at higher overpotentials caused by the concentration polarization effects occurring at the solution/cathode interface (Paunovic and Schlesinger, 2006). The nodular features observed in the microstructures plated from Bath 4 and 5 increase in number with current density upto 0.5 A/cm<sup>2</sup> due to poor cathode coverage. These nodules are reported to be detrimental to the tin deposits as whiskers may nucleate at these nodules in due course of time (Jiang and Xian, 2008).

# 4.1.3.2 X-ray diffraction

X-ray diffraction (XRD) patterns of electrodeposited Sn coatings from each bath plated at a current density of 0.2 A/cm<sup>2</sup> (where the cathode coverage is sufficient for characterization) are shown in Figure 4.2. All the diffraction patterns show that the electroplated tin film has the tetragonal ( $\beta$ -Sn) crystal structure. X-ray patterns of the coatings obtained from Baths 4 and 5 show peaks of Cu substrate and  $\beta$ -Sn, and a small peak of  $\eta$ -Cu<sub>6</sub>Sn<sub>5</sub> is also observed. The peaks of  $\eta$ -Cu<sub>6</sub>Sn<sub>5</sub> are not observed in the XRD patterns of the coatings obtained from Bath 1, 2 and 3. XRD patterns also reveal that each coating is having a specific set of preferred orientations.

The preferred orientation of the  $\beta$ -Sn films has been evaluated by Harris texture coefficient (Kaur *et al.*, 2007), given by the following equation (4.2):

$$T_{c} = \left(\frac{I_{hkl}}{I_{hkl}^{std}}\right) / \frac{1}{n} \sum_{hkl} \left(\frac{I_{hkl}}{I_{hkl}^{std}}\right) \dots (4.2)$$

Where  $I_{hkl}$  is the measured intensity of reflection hkl and  $I_{hkl}^{std}$  is the hkl reflection intensity of the standard sample, and n is the number of reflections. If the texture coefficient (T<sub>c</sub>) is greater than 1.0, it indicates the existence of a preferred orientation.


Fig. 4.2: XRD Patterns of Sn Coatings on Copper Substrate (a) Bath 1, (b) Bath 2, (c) Bath 3, (d) Bath 4 and (e) Bath 5

The preferred orientations of the deposits are shown in Table 4.2. It is observed that the (220) plane orientation is one of the preferred orientation for deposits from Baths 1, 2, 3 and 5. The other coexisting dominant planes are (321) for Bath 3, 4 and 5, (420) for Bath 2 and 3, (211) for Bath 4 and 5. Madra *et al.* (2003) have performed a detailed tensor analysis and reported that (110), (210), (220), (320) and (420) grain orientation do not favour whisker growth, while (211) and (321) are highly favourable for whisker growth (Gaylon, 2003; Lal and Moyer, 2005). These whisker resistant orientations are believed to restrain the whisker growth in tin coatings by minimizing the compressive stress. It can be inferred from the above discussion that among all the baths, Bath 2 and 3 possess desired whisker resisting orientations, i.e., (220) and (420).

Table 4.2: Texture Index of Different Planes in Sn Coatings Plated from Various Baths

Planes	200	101	220	211	301	321	420
Bath 1	1.4	0.7	1.7	0.9	0.4	0.7	1.0
Bath 2	0.2	0.02	3.6	0.1	0.2	0.6	2.2
Bath 3	0.03	0.01	2.9	0.2	0.07	0.7	3.1
Bath 4	0.1	0.6	0.7	1.8	0.4	2.5	1.0
Bath 5	0.8	0.34	1.5	1.9	0.3	1.6	0.6

These results are consistent with the reports that non-MSA (Bath 1, 2, 3 and 5) bath usually possess (220), while MSA bath (Bath 4) possess (211) texture (Gaylon, 2003). The type of texture in the coating will thus determine the whisker propensity of the coating.

### 4.1.4 Microstructure of the aged coatings

The microstructure of all the Sn coatings has been investigated after ageing at room temperature (~ 26 °C) for a period of 1 year. Figure 4.3 shows the microstructures of all the deposits after ageing. As shown in Fig. 4.3, different types of whiskers grow in each coating. The whisker nucleated in the coating plated from Bath 1 is nodular, along with a few short length whiskers with a diameter of about 1-2 µm. The whiskers that are generated in the coating plated from Bath 2 are also bright and short with a diameter of 2-4 µm but exist in branch like ribbon shape with a few nodules. This type of whisker growth is observed in the past by Jiang and Xian (2006) for sulfate baths. While the coating plated from Bath 3 shows rod shaped flute type whiskers which are of much less diameter, around 0.2-0.3 µm and have shorter length as compared to others. The coating plated from Bath 4 shows very thick whiskers, about 10 µm and a huge dendritic growth is also observed on the surface, which may have formed in the as deposited condition. There are some striation marks also observed on the whisker surface. These types of marks are supposedly form during ageing in order to relax the compressive stresses developed in the coating [Jiang and Xian, (2006, 2008)]. The coating plated from Bath 5 also shows a very thick, about 15-20 µm and non uniform long whisker.



Fig. 4.3: SEM Micrograph Showing the Surface Morphology of the Tin Coatings Plated From Different Baths after Ageing

It is likely that a nodule is a natural location for whisker nucleation. A thicker and longer whisker growth in Bath 4 and Bath 5 may be related to the whisker prone grain orientations, i.e., (211) and (321), as seen in Table 4.2, which help in formation of intermetallics and thus compressive stresses are developed in the coating. These

compressive stresses result in the increase in whisker growth (Lal and Moyer, 2005; Whitlaw *et al.*, 2004). This is also confirmed by the XRD patterns which show the presence of the few peaks of  $\eta$ -Cu<sub>6</sub>Sn<sub>5</sub> in the coating plated from Bath 4 and 5.

### 4.1.5 Summary

The current efficiency of Bath 3 is found to be the highest followed by Bath 2. The surface morphology of the coatings obtained from Bath 1 is uniform with equiaxed grains but at a very high current density  $(0.5 \text{ A/cm}^2)$  porous deposits are obtained. The deposits obtained from Bath 2 also show uniform surface morphology and dendritic growth occurs at 0.5 A/cm<sup>2</sup>. The deposits obtained from Bath 3 show very big sized grains due to its highest deposition rate among all the baths. Whereas, the deposits obtained from bath 4 and 5 possess non uniform and nodular surface morphology.

The microstructures of the coatings that are deposited from Bath 1, 2 and 3 show short length whiskers after ageing due to the presence of orientations like (220) and (420) while the coatings plated from Bath 4 and 5 exhibit thick and long whiskers after ageing due to the presence of whisker favourable orientations such as (211) and (321). Therefore, selection of plating bath is very important while studying tin deposits and to obtain the desired properties. In view of the above observations, Bath 2 and 3 which are acidic in nature have been selected for the study of morphology evolution of pure tin coatings and the synthesis of monolithic and composite solder coatings, respectively.

4.2 Effect of pulse electrodeposition parameters on the surface morphology of tin coatings plated from sulfate baths

In this section the effect of various electrodeposition parameters on the surface morphology of the electrodeposits plated from sulfate electrolyte (Bath 2) has been investigated. The various electrodeposition parameters studied are current density, pH, additive, duty cycle, frequency, temperature, and stirring speed.

### 4.2.1 Effect of current density on Sn electrodeposition

## 4.2.1.1 XRD

Figure 4.4 shows the XRD pattern of Sn coatings plated at current densities of 0.083, 0.1, 0.2, 0.3 and 0.5 A/cm<sup>2</sup>. It is observed that the deposits consist of tetragonal structure ( $\beta$ -Sn). It is also observed that the deposits have a preferred orientation which changes with a change in the current density. At lower current density  $(0.083-0.2 \text{ A/cm}^2)$  the intensity of the (220) plane is quite high, which indicates a (110) preferred orientation. This (110) type of texture is useful in preventing the whisker growth in electrodeposited coatings as it is believed to impart minimum compressive stress in tin coatings (Whitlaw et al., 2004; Lal and Moyer, 2005). The intensity of the (220) peak disappears as the current density increases to 0.3 and 0.5 A/cm<sup>2</sup> and at the same time, the intensity of other peaks, i.e., (211) and (321) increase. The most intense peak at 0.3 A/cm<sup>2</sup> is (200) and at 0.5 A/cm<sup>2</sup> is (101). This may be due to the fact that at higher current densities, inherent hydrogen gas evolution occurs at a higher rate causing build up of internal stresses in the deposits. The surface energy anisotropy is thus modified and consequently a change in texture occurs (Li and Szpunar, 1997; Reddy and Rajagopalan, 1963). These results on texture evolution with current density are consistent with previous reports; however, the results may vary from one type of bath to the other type (Moon et al., 2010; Sarobol et al., 2010).



Fig. 4.4: XRD Patterns of Tin Electrodeposited at Various Current Densities a) 0.083, (b) 0.1, (c) 0.2, (d) 0.3 and (e) 0.5 A/cm<sup>2</sup>.

## 4.2.1.2 SEM

Current density (J) is one of the most important parameters in electrodeposition. It controls the nucleation and deposition rate. When the current density is varied, a marked

# Chapter 4

change in the morphology of the deposit is observed. Figure 4.5 shows the morphology of the electrodeposited Sn coatings in response to the different applied current densities.



Fig. 4.5: SEM Micrographs Showing the Morphology of the Deposits Plated with Different Current Densities (a) 0.083, (b) 0.1, (c) 0.2, (d) 0.3 and (e)  $0.5 \text{ A/cm}^2$ 

Figure 4.5 (a-d) shows the morphology of the deposits electroplated at current densities, varying from 0.083 to 0.3 A/cm<sup>2</sup>. The deposit morphology obtained is uniform, bright, and consists of well developed equiaxed grains with a gradual refinement in the grain size. This result is consistent with the previous findings which report that the nucleation rate increases with the current density resulting in a reduction in grain size (Paunovic and Schlesinger, 2006; Moon *et al.*, 2010). The current efficiency increases from 69.8 to 88.45% as the current density increases from 0.083 to 0.3 A/cm<sup>2</sup>.

When the current density is increased to 0.5 A/cm<sup>2</sup>, the equiaxed morphology of the grains changes to dendritic ones, as shown in Fig. 4.5 (f). This type of variation in morphology in response to the current density is due to the fact that if there is a significant increase in the current density, it increases the nucleation rate and is also associated with a higher rate of hydrogen evolution (Liu *Z et al.*, 2010). At this stage, due to high overpotential the flow rate of Sn<sup>2+</sup> ions towards cathode is very high causing heavy diffusion of Sn<sup>2+</sup> ions than its replenishment from solution. Thus, a gradient is created around solution/cathode interface and the deposition is taking place at certain

protrusions/nucleation sites on the cathode haphazardly. This results in the development of an unstable growth front giving dendritic structures in a random orientation. This type of unstable growth has also been observed in copper electrodeposition (Nikolic *et al.*, 2006). The current efficiency at this current density is poor. A poor current efficiency means an increase in hydrogen evolution and thus the concentration of depositing species falls. As a consequence, the solution conductivity drops, as shown in Table 4.3.

$J (A/cm^2)$	Conductivity	CCE (%)	Thickness (µm)	Roughness (µm)
	(mS/cm)			
0.083	46.2	69.86	0.49	2.18
0.1	47.0	75.13	4.06	2.62
0.2	46.5	85.07	8.84	2.30
0.3	45.9	88.45	8.36	2.35
0.5	45.3	65.03	10.88	3.13

Table 4.3: Various Properties of Plating Bath and Deposits Influenced by Current Density	

The roughness value also rises because of non uniform dendritic microstructures. It is generally believed that the surface roughness of plated films changes with current density (Watanabe, 2004). From these observations, it is inferred that an average current density of 0.2-0.3 A/cm<sup>2</sup> may be considered optimal as the deposit is smooth, i.e., without dendrites and the current efficiency is 85-88% which is quite good.

## 4.2.2 Effect of bath pH on Sn electrodeposition

### 4.2.2.1 XRD

Figure 4.6 shows the XRD patterns of Sn films plated at different pH of -0.1, 0.5, 1.0, 2.0 and 3.0. All the films are plated at a current density of 0.2 A/cm<sup>2</sup> so that the maximum cathode coverage is obtained. It is observed that the deposits consist of tetragonal structure ( $\beta$ -Sn) irrespective of the bath pH. It is interesting to note that at negative pH (~

-0.1), the (200) plane in the electrodeposits is the most intense (e.g., random orientation) while as pH increases upto 1.0, the (220) plane appears to be the most intense. At a very high pH (2 and 3), the (211), (101) becomes prominent along with (200). It is also observed that as pH approaches to 3,  $Sn_2O_3$  peak begins to develop as shown in Fig. 4.6(e).



Fig. 4.6: XRD Patterns of Tin Electrodeposited at Various pH (a) -0.1, (b) 0.5, (c) 1.0, (d) 2.0 and (e) 3.0

According to Kirby (1996), there is a possibility of the precipitation of  $Sn(OH)_4$  giving rise to a passivating film at higher solution pH. This  $Sn(OH)_4$  is usually insoluble and thus aids in lowering of current efficiency. The stability of the film increases with the dehydration reaction (Abdel Rehim *et al.*, 2003),

$$\operatorname{Sn}(\operatorname{OH})_4 \to \operatorname{SnO}_2 \cdot \operatorname{xH}_2 \operatorname{O} + (2 - \operatorname{x}) \operatorname{H}_2 \operatorname{O} \qquad \dots (4.3)$$

The  $\Delta G$  value for this dehydration reaction is highly negative, i.e., -42 kJ/ mol. Therefore, the formation of insoluble SnO<sub>2</sub> species is thermodynamically favoured.

#### Cathodic Polarisation

The effect of pH on the morphology of the tin electrodeposits can be explained by using cathodic polarization curves. Figure 4.7 presents the cathodic polarization curves obtained from the plating bath of different pH values.



Fig 4.7: Cathodic Polarization Behavior of Sn Plating Bath due to Different pH (a) -0.1, (b) 0.5, (c) 1.0, (d) 2.0 and (e) 3.0

It is observed that the formation of the isolated Sn nuclei takes place at around -500 mV, and the efficiency for metallic deposition is negligible. As the current increases further with the cathodic potential, a typical peak is observed and then a steady state region is reached where the significant deposition takes place. It is also observed that at lower pH values the peak height (i.e., current density) for curve a and b, is higher and the steady state mass transport region is minimum. This effect can be correlated with the higher consumption of current by discharge of hydrogen ions at lower pH values (Han *et al.*, 2008; Salles *et al.*, 2011; Kongstein *et al.*, 2007).

As the pH value increases, the peak height decreases and the steady state region increases. This increasing trend in the mass transport region with pH signifies a more efficient deposition, as shown in curve c where the steady state region is maximum. The similar trends as shown in Fig. 4.7, are also reported by previous study Salles *et al.* (2011) on pH effects for metal deposition. The mechanism of stannous reduction from sulphate solution for this region is given by Heusler as follows (Tunold and Broli, 1973):

$$Sn + H_2O --- Sn(OH)_{ads} + H^+$$
 ... (4.4)

$$Sn(OH)_{ads} - --- Sn(OH)_{ads} + e^{-1} \qquad \dots (4.5)$$

 $Sn + Sn(OH)_{ads} ----Sn_2OH \qquad \qquad \dots (4.6)$ 

 $\operatorname{Sn_2OH} + \operatorname{OH} - -- \operatorname{SnOH}^+ + \operatorname{SnOH}_{\operatorname{ads}} + 2e^- \dots (4.7)$ 

$$SnOH^+ + H^+ - Sn^{2+} + H_2O$$
 ... (4.8)

One more noteworthy point is the absence of steady state region in the polarization curves at higher pH (curve d and e), which indicates vigorous hydrogen evolution and a reduction in Sn deposition (i.e., a lowering in current efficiency). At a pH value of 3, there are two peaks observed which indicates the formation of a second compound (Stirrup and Hampson, 1977; Minzari *et al.*, 2011). The first peak at -550 mV signifies

deposition of Sn ions while the second peak at -820 mV indicates the precipitation of the insoluble hydroxides, i.e., the conversion of stannous  $(Sn^{2+})$  to stannic tin  $(Sn^{4+})$ , as shown by equations 4.4 to 4.8. This result is in agreement with that reported by Salles *et al.* (2011) for Zn electrodeposition from sulphate solutions.

### 4.2.2.2 SEM



Fig. 4.8: SEM micrographs showing different morphologies evolved due to different pH (a) -0.1, (b) 0.5, (c) 1.0, (d) 2.0 and (e) 3.0

The morphology of the deposited Sn coatings with different bath pH is shown in Fig. 4.8 It is observed that grain refinement continues to occur as the pH value increases from -0.1 to 1. It can also be confirmed from the polarisation behavior of the cathode. At a higher pH of 2 and 3, deposits are more irregular and porous. This can be correlated to hydrogen evolution reaction. At a very high pH (=3), powdery deposits are obtained, (Fig. 4.8(e)). This may be due to the precipitation of insoluble hydroxides according to equations (4.6 and 4.7) as described in previous section.

From Table 4.4, the current efficiency increases as the pH is increased from -0.1 to 1. The reason for this increase in current efficiency is that hydrogen evolution is suppressed with an increase in pH upto 1.0. This is already confirmed from the polarization curves, a, b

and c. However, the current efficiency drops at a pH of 2 and it is worse at a pH of 3, as shown in Table 3.1. The conductivity of the solution also drops, as shown in Table 4.4.

Table 4.4: Various Properties of Plating Bath and Deposits Influenced by pH

#### 4.2.3 Effect of concentration of additive (Triton X-100)

It is well known that additive concentration has a significant effect on the deposition rate and also on the morphology of the deposits. The effect of additive concentration on the cathodic polarization behavior and morphology of the deposit has been studied using Triton X-100 while keeping the other bath parameters constant. Triton X-100 is a nonionic surfactant, generally used as an organic additive in acidic tin baths.

## 4.2.3.1 XRD

Figure 4.9 shows the XRD patterns of Sn films plated with different concentration of surfactant Triton X-100 (0, 0.06, 0.1, 0.2, 0.5 and 1.0 g/L) at a current density of 0.2  $A/cm^2$ . It is observed that the deposits consist of tetragonal structure ( $\beta$ -Sn). It is also observed that in all the x-ray patterns obtained with Triton X-100 the (110) is the prominent texture, while in absence of Triton X-100 there is no presence of texture is noticed. This suggests that the adsorption of the additive on the cathode surface the orientation of the grains from a random to a preferred one.



Fig. 4.9: XRD Patterns of Tin Electrodeposited with Various Concentration of Triton X-100, (a) 0, (b) 0.06, (c) 0.1, (d) 0.2, (e) 0.5 and (f) 1.0 g/L.

It is already known that the surface energy of the crystallographic planes is modified by the selective adsorption of a molecule or ion and the growth rate of those planes thus gets slowed down. This phenomenon relatively promotes the growth on other planes along the substrate and induces textured deposits (Long, 2012). This type of (110) induced texture is beneficial in preventing tin whisker growth, already described in previous sections (Whitlaw *et al.*, 2004).

## Influence of additives on cathodic polarization

A preliminary study of cathodic polarization behavior is carried out in order to understand the deposition mechanism with different additive concentrations. Figure 4.10 shows the current potential curves recorded at a scan rate of 1 mV/s for the Sn plating with different amounts of additive. It is observed that initially a very small current flows, and nucleation and growth of isolated  $\beta$ -Sn crystals takes place at around -450 mV. There is a typical peak as observed in curve a, b, c and d, that indicates the adsorption of Sn atoms on the cathode surface (Survila *et al.*, 2000; Nakamura *et al.*, 1994).



Fig. 4.10: Cathodic Polarization Behavior for Acidic Tin Baths with Different Concentration of the Additive: (a) 0, (b) 0.05, (c) 0.1, (d) 0.2, (e) 0.5 and (f) 1.0 g/L

As the current flow increases, the curves enter the corresponding steady regions beyond the peaks, where the reduction of the  $Sn^{2+}$  ions to Sn occurs under a steady mass transport

control. The deposition mechanism as proposed by Ichino *et al.* (1996) in this region consists of various redox reactions at the cathode and anode, including the formation of active sites for the Sn deposition and enhancement of the Sn reduction in competition with the hydrogen evolution.

The mass transfer region corresponds to the useful region where significant deposition takes place. It is also observed that this steady mass transport region in the curve decreases drastically as the additive concentration (Triton X-100) increases beyond 0.2 g/L. There is also a substantial shift in the negative potential from -450 mV to -1200 mV as the additive concentration increases to 1 g/L. The negative shift in the reduction potential for tin, in the presence of Triton X-100, is reported to be due to its surface active property. Therefore, it is expected to be adsorbed at active sites, regions of high local current densities on the electrode surface (Vittal *et al.*, 2006; Joseph and Phatak, 2008). This kind of adsorption is potential dependent and there exists an optimum value beyond which the adsorption of Triton X-100 on cathode surface decreases. This is confirmed from the observation where with an increase in additive concentration to 0.5 and 1.0 g/L, a drastic shift in negative potential (curve e and f) occurs; this is associated with the desorption of the additive from the cathode surface. This causes an increase in the hydrogen evolution and a lowering in current efficiency from 82.2 to 75%, as shown in Table 4.5.

Triton X-100 (g/L)	Conductivity	CCE (%)	Thickness (µm)	Roughness (µm)
	(mS/cm)			
0.06	46.0	74.22	8.03	0.49
0.1	47.4	79.76	8.63	1.78
0.2	48.0	85.12	9.21	1.83
0.5	45.2	82.24	8.90	1.41
1.0	46.3	75.13	8.13	2.65

Table 4.5: Various Properties of Plating Bath and Deposits Influenced by Additive Concentration

The surface activity of Triton X-100 is due to its interesting chemical structure, as shown in Fig. 4.11. It has a hydrophilic polyethylene oxide group and a hydrocarbon lipophilic group.



Fig. 4.11: Chemical Structure of Triton X-100 (Mitsuda et al., 1989).

The linking oxygen in oxyethylene chain of this molecule provides a lone-pair of electrons that interacts with other molecules through hydrogen bonding. This helps in filling in the gaps/pores and thus provides a uniform coating around the cathode (Mitsuda *et al.*, 1989). In the present case, the negative shifts in reduction potentials and improvement in the bath stability due to Triton X-100 is attributed to such phenomena in the electrolyte.

## 4.2.3.3 SEM

The surface morphology of the developed coatings in response to different amount of the additive concentration is shown in Fig. 4.12. As discussed already, additives upto a certain concentration, are known to have a positive effect on the microstructure of the deposited films in terms of increasing the cathodic polarization.



Fig. 4.12: SEM Micrographs Showing Different Morphology Evolved due to Different concentrations of the Additive (a) 0, (b) 0.06, (c) 0.1, (d) 0.2, (e) 0.5 and (f) 1.0 g/L

It is observed from Fig. 4.12 that in the absence of an additive the cathode coverage is poor and copper substrate is quite visible, as shown in encircled regions (Fig. 4.12 (a)). From Fig. 4.12 (b-d), a sequential development of equiaxed grain structure is visible resulting in a slight variation in the deposit roughness, as inferred from Table 4.5. It is also observed that grain structure is deviated from its equiaxed nature when the additive concentration is 0.5 g/L (Fig. 4.12 (e)) and it becomes more irregular at 1 g/L (Fig. 4.12 (f)). This irregular shaped grain morphology is non adherent to the cathode surface and is porous. Therefore, it can be inferred that the additive has a beneficial effect on the morphology upto a certain concentration (i.e., 0.2 g/L). It has been discussed in the previous section that at higher concentration (> 0.2 g/L), the cathodic polarization increases (curve e and f). This is associated with progressive evolution of hydrogen gas leading to the development of non uniform powdery deposits may arise due to the adsorption and absorption phenomena of the evolved hydrogen gases according to the following reactions (Franklin, 1986):

$$2H_{ads} - H_2$$
 ... (4.9)

$$H^+ e^- --- H_{ads}$$
 ... (4.10)

$$H_{ads}$$
---- $H_{abs}$  ... (4.11)

The additive is expected to block the association of generated hydrogen atoms through equation (4.9). Thus, the concentrations of  $H_{ads}$  increase following equation (4.10). These adsorbed hydrogen atoms get absorbed in the deposits following equation (4.11). Thus powdery deposits are obtained. Consequently, the current efficiency decreases and the surface roughness jumps to a higher value, as seen in Table 4.5. A drop in bath conductivity is also noticed beyond a concentration of 0.2 g/L of Triton X-100. It is observed that bath conductivity is maximum (48 mS/cm) at 0.2 g/L concentration of additive, but after that the conductivity decreases. This can be correlated to the fact that this concentration is very near to the critical micelle concentration (i.e, CMC~ 2.4 mM (~0.2 g/L) for Triton X-100). Above this concentration the aggregation of additive molecules takes place on the cathode surface, thus blocking the deposition and increasing hydrogen evolution and hence, beyond this concentration, the surface morphology turns very poor (Vittal *et al.*, 2006; Koshy *et al.*, 1996).

## 4.2.4 Effect of duty cycle on Sn electrodeposition

The effect of duty cycle on the morphology of the deposits has been investigated while keeping the peak current density at 0.2 A/cm<sup>2</sup> and other parameters constant. The deposition rate in the pulse technique is governed by the pulse current density  $(J_p)$ , and on time  $(T_{on})$ , and off time  $(T_{off})$ . At a given peak current density, the duty cycle is given by:

Duty Cycle (%) = 
$$\frac{T_{on}}{T_{on} + T_{off}}$$
 ... (4.12)

The average current density  $(J_a)$  in a pulse electrodeposition is given by:

$$J_a = \text{Duty Cycle} \times J_p, \qquad \dots (4.13)$$

where  $J_p$  is the peak current density.

In the present investigation, duty cycle has been changed by varying the on time while keeping the off time constant. A 100% duty cycle means there is no pulse used. The duty cycle combinations are shown in Table 4.6, and the current efficiency, thickness, and roughness values are presented in Table 4.7.

Table 4.6: Pulse Parameters used for the Deposition of Sn Coatings at Various Duty Cycles

Duty Cycle (%)	$T_{on}(s)$	$T_{off}(s)$
4	0.00042	0.01
10	0.0011	0.01
20	0.0025	0.01
40	0.0067	0.01
60	0.0150	0.01

### 4.2.4.1 XRD

Figure 4.13 shows the XRD patterns of Sn films plated at different duty cycles keeping the current density constant at 0.2 A/cm<sup>2</sup>. The concentration of the surface active additive is maintained at the optimized value of 0.2 g/L. The pulse parameters are given in Table 4.6. It is observed that the deposits consist of tetragonal structure ( $\beta$ -Sn) with (110) prominent texture. It is also observed that the intensity of (220) peak decreases with an increase in duty cycle. This type of behavior is consistent with that obtained by Kim *et al.* (1996). He found that  $\beta$ -Sn deposited using pulsed current with low duty cycle and low frequency will exhibit {220} texture parallel to the {110} plane.



Fig. 4.13: XRD Patterns of Tin Plated Copper at Different Duty Cycles (a) 4, (b) 10, (c) 20, (d) 40, (e) 60 and (f) 100% (DC)

# Chapter 4

This influence of pulse parameters does not have a straightforward explanation. However, if we assume that the preferred orientation strictly depends on the additive (since with the addition of additive, from random to (110) texture change is already noticed already, section 4.2.3), then it can be speculated that a reduction in the duty cycle means a longer relaxation time, (e.g.,  $T_{off}$ ) for the growth interface, resulting in an effective stabilisation of the adsorbed film, hence the strengthening of the (110) growth texture at lower duty cycles.

#### 4.2.4.2 SEM

The SEM micrographs of the deposits plated with different duty cycles are given in Fig. 4.14. The microstructure of the electrodeposit shows a tendency to be finer as the duty cycle and/or  $T_{on}$  increase, as shown in Fig. 4.14 (a-e). However, at a duty cycle of 100% the grain size observed is much coarser, Fig. 4.14 (f). Thus, it is concluded that the grain size of the deposits decreases continously with the increasing on time (at constant  $T_{off}$  and  $J_p$ ) caused by higher overpotentials at longer current on times.



Fig. 4.14: SEM Micrographs Showing Different Morphology Evolved Due to Different Duty Cycles (a) 4, (b) 10, (c) 20, (d) 40, (e) 60, and (f) 100% (DC)

# Chapter 4

Youssef *et al.* (2004) have also found the similar behavior for zinc deposits. It is reported that grain size decreases upto 44% duty cycle; however, the grain size increases after that. He explained this fact as if the pulse electrodeposition is approaching towards the direct current electrodeposition.

It is also observed from Fig. 4.14 that the deposits are more uniform and less porous in case of the application of pulse current (PC) with lower duty cycles (< 20%) as compared to that of higher duty cycles (> 20%). In case of higher duty cycles (> 20%) and DC current, the porosity increase is due to the increase in average current flow time  $T_{on}$ , resulting in an increase in the amount of evolved hydrogen gases. Thus, the surface morphology is very porous and rough. This type of surface morphology can be explained in terms of the dissolved hydrogen and oxygen gases in the electrolyte. The solubility of hydrogen and oxygen in water at 25 °C and 1 bar is 1617 and 43.3 mg/L, respectively (Besra *et al.*, 2009). Therefore, the evolved hydrogen gas is more likely to get dissolved or trapped at the cathode surface as compared to oxygen released from the anode causing inhomogeneous/rough deposits.

The observed minimization of porosity in the case of PC electrodeposition with lower duty cycles can be attributed to the following factors: (i) the hydrogen and oxygen gas evolved at the cathode may get partly diffused away from the substrate during off time,  $T_{off}$  and get suppressed from being incorporated in the deposit during pulse electrodeposition (ii) the discrete amount of gas generated by electrolysis of water during each on time,  $T_{on}$  is expected to be significantly less compared to a single continuous DC. The gas evolution and dissipation in the case of pulse current electrolysis is a dynamic process and it may lead to the formation of micron to nano sized bubbles at different sites for each  $T_{on}$ . Incorporation of such small bubbles will not produce any macro-bubbles in the deposit. Thus, lower duty cycle (<20% in present case) results in a smooth morphology as compared to higher ones (Besra *et al.*, 2009).

D (%)	Conductivity	CCE (%)	Roughness (µm)	Thickness (µm)
	(mS/cm)			
4	45.2	67.42	0.93	3.28
10	45.6	81.74	0.69	8.85
20	46.9	88.5	1.52	21.3
40	45.8	76.24	1.68	36.6
60	46.1	69.13	3.71	49.9
DC	47.0	66.13	3.08	73.7

Table 4.7: Various Properties of Plating Bath and Deposits Influenced by Duty Cycle

The current efficiency increases upto 20% duty cycle and then it decreases with further increase in the duty cycle (Table 4.7). At higher duty cycles (> 20%), the hydrogen evolution increases and as a consequence a decrease in current efficiency is observed. The roughness is observed to be maximum ( $\sim 3.08 \mu m$ ) in case of 100% duty cycle.

# 4.2.5 Effect of pulse frequency on Sn electrodeposition

The morphology of an electrodeposit is also affected by the frequency of the pulse waveform. The pulse frequency parameters used in the present investigation are shown in Table 4.8. Frequency (f) of the pulse is described as follows:

$$f = \frac{1}{(T_{on} + T_{off})} ... (4.14)$$

-	10.11	50		100	TT	
	10 HZ	50	) HZ	100	HZ	

Table 4.8: Pulse Frequency Parameters

Frequency	10	Hz	50	) Hz	100	Hz	500	Hz
Duty Cycle	$T_{on}(\mathbf{s})$	$T_{off}(\mathbf{s})$	$T_{on}(\mathbf{s})$	$T_{off}(\mathbf{s})$	$T_{on}(\mathbf{s})$	$T_{off}(\mathbf{s})$	$T_{on}(\mathbf{s})$	$T_{off}(\mathbf{s})$
10%	0.01	0.09	0.002	0.018	0.001	0.009	.0002	.0018

Typical examples of the input PC waveforms at low and high frequencies recorded are presented in Fig 4.15.



Fig. 4.15: Typical Examples of the Waveforms at Various Frequencies (a) 10, (b) 50, (c) 100 and (d) 500 Hz

## 4.2.5.1 XRD

Figure 4.16 shows the XRD patterns of Sn coatings plated at different pulse frequency. The pulse frequency parameters are given in Table 4.8. It is observed that the deposits consist of tetragonal structure ( $\beta$ -Sn) and in all the x-ray patterns (110) is the prominent texture.



Fig 4.16: XRD Patterns of Tin Plated with Different Frequencies, (a) 10, (b) 50, (c) 100 and (d) 500 Hz

## 4.2.5.2 SEM

The morphology variation as a function of frequency is shown in Fig. 4.17. It is observed that at lower pulse frequency 10 Hz, large non uniform grains of tin have grown with porosity at their boundary edges and then with increasing frequency slowly the uniform grains start to develop resulting in a very good morphology at 500 Hz.

A lower pulse frequency (f) means a longer pulse cycle  $(T_{on}+T_{off})$  when the duty cycle (D) is kept constant, equation (4.12). Thus, at lower pulse frequencies the pulse duration is higher. This means that more time is available for the charging and discharging of the double layer during  $T_{on}$  and  $T_{off}$ , respectively.



Fig 4.17: SEM Micrographs Showing Different Morphologies Evolved Due to Different Frequencies, (a) 10, (b) 20, (c) 100 and (d) 500 Hz

Therefore, the Sn atoms can migrate to the most stable position and grain growth is favourable. As the pulse frequency increases, the pulses are much shorter, i.e., both  $T_{on}$  and  $T_{off}$  are of short duration as shown in Table 4.8. Shanthi *et al.* (2008) have observed grain refinement during pulse plating of silver alloy during short pulses at higher frequencies. At higher pulse frequencies the double layer does not have sufficient time to fully charge during  $T_{on}$  and to discharge during  $T_{off}$  time.

As soon as the one pulse cycle is completed, the next pulse arrives quickly. These phenomena produce very thin pulse diffusion layers which make the transport and diffusion of the migrating Sn ions from the solution to the cathode surface difficult. This leads to the enhanced nucleation rate with a limited growth rate resulting in a dense microstructure.

This type of behavior is also reported by Ibl (1980). The average roughness and thickness of Sn films decrease with the increase in frequency as shown in Table 4.9.

Frequency	Conductivity	CCE (%)	Thickness (µm)	Roughness (µm)
(Hz)	(mS/cm)			
10	45.3	99.63	10.78	2.81
50	47.3	98.41	10.65	0.65
100	47.1	93.70	10.14	0.76
500	46.8	70.2	7.6	0.46

Table 4.9: Various Properties of Plating Bath and Deposits Influenced by Frequency

The smoothest Sn surface with an average roughness of 0.46  $\mu$ m is achieved at the frequency of 500 Hz. Initially, the deposits are very thick due to the increased grain growth rate. The thickness drops from 10.78 to 7.6  $\mu$ m as the frequency changes from 10-500 Hz. The corresponding current efficiency also decreases from 99.6 to 70.2%.

## 4.2.6 Effect of bath temperature

It is well known that electrochemical processes are influenced by different diffusion processes: the diffusion of metal ions in the electrolyte, the movement of ad-atoms on the electrode surface, and also the mobility of grain refiners (Natter and Hempelmann, 1996). All of these processes depend on the bath temperature and therefore, should influence the structure of the deposits. It must be noted that in some cases, a deviation of more than 5°C from the optimum temperature is sufficient to harm the plating quality, deposition rate, and other properties of the coating (Paunovic and Schlesinger, 2006).

### 4.2.6.1 XRD

Figure 4.18 shows the XRD patterns of Sn films plated at different temperatures. The deposits consist of tetragonal structure ( $\beta$ -Sn). At room temperature, the (220) peak intensity is very strong which indicates a (110) texture. With increasing temperature (220) peak intensity goes down and other peaks (101) and (211) become stronger over rest of other peaks and peaks corresponding to the intermetallic compounds Cu<sub>6</sub>Sn<sub>5</sub> are

also found. This can happen because at elevated temperatures, breakdown of solution species occurs and therefore oxidation of  $\text{Sn}^{2+}$  to  $\text{Sn}^{4+}$  stannic tin is facilitated (Tan, 1993).



Fig. 4.18: XRD Patterns of the Coatings Plated at Different Temperatures (a) 28, (b) 35, (c) 40, (d) 50 and (e) 60 °C [((a) Cu-Target), ((b-e) Co-Target)]

## 4.2.6.2 SEM

Figure 4.19 shows the morphology of tin deposited at different bath temperatures. All the deposits have been deposited using the constant current density (0.2 A/cm<sup>2</sup>), duty cycle (10%) and other parameters so that the effect of temperature on the morphology can be analyzed. It is observed from Figure 4.19 (a) that the grains are finer when deposited at room temperature and with a rise in the temperature it increases, Fig. 4.19 (b-f). At a high temperature the mobility of metal ions and inhibiting species increases. Therefore, a higher supply of metal ions towards the cathode decreases the cathodic overpotential. This increases the energy barrier,  $\Delta G$ , for nucleation process according to the equation given by Glasstone (Natter and Hempelmann, 1996) resulting in coarser grain size at higher temperature:

$$\Delta G \propto \left\{ \frac{1}{\left( \eta + \left[ \frac{C'}{C} \right] \right)^2} \right\} \qquad \dots (4.15)$$

Where C' the activity of the  $Sn^{2+}$  on the electrode and C is the activity of  $Sn^{2+}$  in the bulk solution. Moreover, the adsorption rate of inhibitor molecules will decrease at high temperature due to the decrease in viscosity resulting in an increased grain growth.

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Fig. 4.19: SEM Micrographs Showing Different Morphology Evolved Due to Different Bath Temperature Kept During Deposition, (a) 28, (b) 35, (c) 40, (d) 50 and (e) 60 °C

The current efficiency is maximum at 40 °C, but then a slight drop is observed (Table 4.10). It is reported in the literature that in acidic aqueous solution, the solution may decompose at high temperature. As a result the solution bath color turns from light to dark yellow. This may be due to the decomposition of the sulfate entity or oxidation of Sn<sup>2+</sup> to Sn<sup>4+</sup> which affects the solution chemistry (Tan, 1993). In the present case, a drop in current efficiency is noticed above 40 °C but there is a little change in morphology of the deposits. A slight decrease in conductivity and thus current efficiency is observed due to the decomposition of chemical species at higher temperatures.

Temperature	Conductivity	CCE (%)	Thickness (µm)	Roughness (µm)
(°C)	(mS/cm)			
28	46.6	87	9.42	1.48
35	49.2	94	10.18	0.94
40	64.2	100.73	10.90	0.85
50	39.8	89	9.63	0.73
60	38.2	61	6.60	1.46

Table 4.10: Various Properties of Plating Bath and Deposits Influenced by Temperature

## 4.2.7 Effect of stirring rate (magnetic stirring)

It is interesting to note that the stirring rate of the bath has a significant effect on the deposit morphology. The deposition parameters except the stirring speed which controls the bath agitation are kept constant. The bath agitation has been varied from 0 to 700 rpm.

## 4.2.7.1 XRD

Figure 4.20 shows the XRD patterns of Sn films plated at different stirring rates while keeping the other deposition parameters constant.



Fig. 4.20: XRD Patterns of the Coatings due to Different Stirring Speed Kept While Deposition

It is observed that the deposits consist of tetragonal structure ( $\beta$ -Sn) and in all x-ray patterns the (110) is the prominent texture. There is not any noticeable change in texture with increasing stirring speed of the bath.

#### 4.2.7.2 SEM

Figure 4.21 shows the changes in the morphology of the deposits with the increase in the stirring speed. It is observed that during still deposition the cathode coverage is poor, and irregular and non uniform deposits are obtained. This can be explained as when no rotation is provided, the depositing ions come from the solution and get deposited preferentially on the substrate. Thus, a concentration gradient near the solution/cathode interface is developed. If the gradient becomes too high, the potential required for the deposition goes up and hence the deposition rate goes down significantly. Therefore, initially when no rotation is imparted in bath the deposition is uneven and thus giving rise to a very poor morphology, Fig. 4.21 (a).

As the stirring speed is increased slowly from 50 to 300 rpm, the concentration of ions while coming out from the anode starts to get distributed evenly in the electrolyte. This results in a uniform deposition on the cathodic surface (Fig. 4.21 (b-e)). When the stirring speed is increased the concentration gradient breaks down or minimized and hence both the deposition rate and morphology improve upto 300 rpm. The grain size also increases as a consequence (Wen and Szpunar, 2005). Further increase in the stirring speed (400-700 rpm) causes the ions to reach the electrode surface at a faster speed and decreases the mass transport influence in the process (Musa *et al.*, 2008). Whatever ions from solution coming towards cathode may come for a short span of time and easily fly away due to the turbulent flow of electrolyte. Thus, the deposition rate falls accordingly. This is evident from Table 4.11 which shows that the current efficiency is optimum at 300 rpm (93.2%) and it drops to 63.5% at 700 rpm. At a stirring speed of more than 300 rpm, an increase in grain size also occurs. This can be related to the Triton X-100 adsorption on the cathode surface which may get disrupted when the flow is turbulent. Agitation also decreases the deposit roughness to a certain extent.



Fig. 4.21: SEM Micrographs Showing the Different Morphology Evolved Due to Different Stirring Rates (a) 0, (b) 50, (c) 100, (d) 200, (e) 300, (f) 400, (g) 500 and (h) 700 rpm

Table 4.11: Various Properties of Plating Bath and Deposits Influenced by Stirring Rate

Stirring Rate	Conductivity	CCE (%)	Thickness (µm)	Roughness (µm)
(rpm)	(mS/cm)			
0	52.4	56.50	6.11	2.80
100	48.9	88.03	9.53	2.57
300	48.6	93.2	11.35	2.11
500	48.7	84.22	9.12	2.7
700	48.3	63.50	6.8	1.08

## 4.2.8 Sensitivity of the variables- Grain size distribution

Figure 4.22 shows the grain size distribution of the Sn coatings in response to the electrodeposition parameters. It is observed that the grain size decreases with the current density, surfactant concentration, duty cycle, pulse frequency, and pH while there is an increase in grain size is observed for temperature and rotation.



Fig. 4.22: The Grain Size Distribution Evolved Due to the Different Electrodeposition Parameters Investigated (a) Current Density, (b) Additive Concentration, (c) Duty Cycle, (d) Pulse Frequency, (e) Bath pH, (f) Bath Temperature, and (g) Stirring Rate.

## 4.2.9 Summary

The electrodeposition parameters considered in this investigation include current density, concentration of the additive, duty cycle, frequency, pH, temperature, and agitation. The
# Chapter 4

obtained results in this work indicate that the pulsed current electrodeposition can be an efficient method for the electrosynthesis of tin deposits.

The surface morphology evolution depends on the electrodeposition parameter that tries to modify the overpotential, direct or indirect way. The current density is found to be the most sensitive of all the parameters investigated that influences the morphology evolution drastically. The equiaxed grains which form at low current density ( $<0.3 \text{ A/cm}^2$ ) changes to dendritic form at 0.5 A/cm<sup>2</sup>.

It is found that by changing the duty cycle, the nucleation rate and growth kinetics can be controlled. Pulse current produces the compact and smooth morphology for duty cycles upto 20%, while the porosity rises and morphology turns poor when duty cycle exceeds 20%. Low pulse frequency gives bigger sized grains, about 8-12 micron at 10 Hz frequency which decreases to 700 nm at 500 Hz. Thus, we can find a combination of 10% duty cycle and 100 Hz frequency which gives optimum morphology and current efficiency for this acidic Sn bath. The additive (Triton X-100) concentration also affects the morphology. It mainly improves the cathode surface plated finish and also improves the morphology if it is added below its critical micelle concentration (i.e., 0.2 g/L). The current density decreases as pH increases. The grain size is found to decrease from 2560 to 1175 nm by increasing the cathodic polarization as the pH value increases from -0.1 to 2. However, as the pH increases to 3, powdery deposits with no proper grains are developed due to the precipitation of stannic hydroxide.

The effect of temperature is observed to increase the grain size continously from room temperature (1832 nm) to  $40^{\circ}$  C (5530 nm) as expected; beyond which there is no increase in grain size, however the solution conductivity and current efficiency decrease drastically due to the oxidation of Sn ions in solution bath. Agitation of the solution provides fresh solution of metal ions to cathode and thus increases the deposition rate upto 300 rpm and then decreases due to the turbulent flow of the solution where the metal ions fly away from the electrode. A drastic increase in grain size beyond 300 rpm is ascribed to the decrease in cathodic overpotential with rotation. These parameters are

optimised according to the maximum CCE which signifies an economic deposition process. From this investigation, a set of parameters are derived for pulse electrodeposition of pure tin coatings from aqueous sulfate bath. The optimized range of parameters can be summarized as current density =  $0.2-0.3 \text{ A/cm}^2$ , pH = 1, additive concentration (Triton X-100) = 0.1-0.2 g/L, duty cycle = 10-20%, frequency = 100 Hz, bath temperature = 28-35 °C, and stirring rate = 300 rpm.

4.3 Development of lead free pulse electrodeposited  $Sn/CeO_2$  and near eutectic  $Sn-Ag/CeO_2$  lead free solder nanocpmposites This section of Chapter 4 presents and discusses results of the investigated experiments on synthesis, microstructure, microhardness, density and porosity, wear and friction, electrochemical corrosion, melting point, electrical resistivity, and residual stress of the monolithic (Sn and Sn-Ag) and nanocomposite (Sn/CeO<sub>2</sub> and Sn-Ag/CeO<sub>2</sub>) solders.

This chapter is divided into the following sections and subsections:

In sections 4.3, the synthesis of the nano reinforcement (CeO<sub>2</sub>), and its microstructural characterisation, and synthesis of different composites and their microstructural characterization have been presented. The microhardness, density and porosity, melting point, and electrical resistivity, wear and friction behavior, corrosion behavior and residual stress measurement of the unreinforced and reinforced composites have been presented in section 4.4.

#### 4.3.1 Synthesis of the Ceria nanopowders

Cerium oxide based materials have been extensively studied for various electronic and photonic applications (Bedekar at al., 2008). There are various fabrication routes for producing the nanosized materials, for example, mechanical alloying, solution combustion synthesis, spray pyrolysis, sputter deposition, pulse electrodeposition, sol-gel process, hydrothermal routes, etc. Among these, high energy ball milling is the commonly used technique due to its simple nature and environmental friendliness (Sergeant and Bakhshai, 2006). High energy ball milling (HEBM) is one of the major techniques for producing powders with nanocrystalline structures. HEBM of the CeO<sub>2</sub> powder is carried out in a dual drive Fritsch Pulverisette - 4 planetary ball mill with variable  $\Omega$  (main disk speed) and  $\omega$  (planet speed).

According to  $\left(\frac{\Omega}{\omega}\right)$ , the rotation speed choice, one can have the shock mode process (SMP) when  $\Omega >> \omega$ , and the friction mode processes (FMP) when  $\Omega << \omega$  (Hamzaoui *et al.*, 2004).



Fig. 4.23: (a) Schematic Configuration of the Pulverisette-4 Planetary Ball Mill, (b) Model of Centrifugal Force Acting on a Ball, and (c) Difference in the Vector of Relative Velocity of Balls between Counter and Normal Directions (Mio *et al.*, 2002).

Figure 4.23 (a and b) shows the schematic diagram of the Pulverisette – 4 ball mill, and the various forces acting on a ball during milling, and Fig. 4.23 (c) shows the clock-wise and counter clock-wise rotation directions with respect to the direction of revolution of the main disk. Mio *et al.* (2002) have reported that in both rotation-revolution relationships, the specific impact energy increases with an increase in the rotation-to-revolution speed in the initial stage and then falls around the critical speed ratio due to rolling motion. The highest value in the specific impact energy of balls during milling can be achieved around this critical speed. The exact ratio can be calculated from the balanced equation, based on the centrifugal forces acting on a ball due to the combination of the rotation and revolution.

From figures 4.24 (a) and (b), the following equations can be derived:  $F_p = ml_c \omega^2$  ... (4.16)

$$F_r = m(R-l_c) \Omega^2 \qquad \dots (4.17)$$

And 
$$l_c = \left(\frac{d_v}{2}\right) - \left(\frac{d_b}{2}\right) \qquad \dots (4.18)$$

When,  $F_p = F_r$ ,

$$\left(\mathbf{r}_{c}\right)^{2} = \left[\left(\frac{R}{l_{c}}\right) - 1\right] \qquad \dots (4.19)$$

Where,  $F_p$  = rotation centrifugal force,

 $F_r$  = revolution centrifugal force,

 $l_c$  = distance from rotating shaft to the centroid of the ball that contacts the mill,

- R = revolution radius,
- $d_b$  = diameter of ball,

 $d_v =$  diameter of vial,

 $\omega$  = rotational speed of vial,

 $r_c = critical speed ratio,$ 

 $\left(\frac{\omega}{\Omega}\right)$  = transmission ratio

The values of the constants above are given in Table 3.3 in experimental procedure. In the present investigation, the theoretical critical ratio is calculated to be 1.687. Therefore, in the present investigation, the transmission ration is chosen to be around 1.8.

## 4.3.2 Characterization of ceria nanopowders

In the present investigation, the 20 hour ball milled  $CeO_2$  powders have been characterized for their microstructure, crystallite size, and lattice strain using the method given by Williamson and Hall (1953) and compared the obtained results with the TEM analysis.

# 4.3.2.1 XRD

Figure 4.24 shows the XRD patterns of the ceria powder milled for 0, 5, 10, 15 and 20 h. From XRD patterns, it is observed that the diffraction peaks are getting broadened as the milling time increases due to the reduction of the crystallite size and lattice strain increase. The inset clearly shows the broadening of the (111) peak confirming the nanocrystallite formation.



Fig. 4.24: XRD Patterns of  $CeO_2$  Powders Produced by (a) 0, (b) 5, (c) 10, (d) 15 and (e) 20 h Ball Milling

## Crystallite size and lattice strain

Figure 4.26 shows the Williamson hall plot of  $CeO_2$  powders prepared by ball milling. The crystallite size and lattice strain of  $CeO_2$  powders are calculated from the intercept and the slope of Williamson Hall plot, respectively.



Fig. 4.25: Williamson Hall Plot of  $CeO_2$  Powder Subjected to (a) 0 h, (b) 5 h, (c) 10 h, (d) 15 h and (e) 20 h Ball Milling

The crystallite size and lattice strain calculated from the Williamson Hall method for different ball milled  $CeO_2$  samples as shown in Table 4.12.

Samples	Crystallite size (nm)	Lattice Strain (x 10 <sup>-3</sup> )
0 h	191	0.49
5 h	69	0.65
10 h	43	0.79
15 h	39	1.06
20 h	32	1.34

Table 4.12: Crystallite Size and Lattice Strain of  $CeO_2$  Powders as Obtained from the Williamson-Hall method

It is revealed that the crystallite size decreases from 191 to 32 nm and the lattice strain increases from  $0.49 \times 10^{-3}$  to  $1.34 \times 10^{-3}$  with the increase in milling time.

## 4.3.2.2 Particle size distribution

Figure 4.26 shows the particle size distribution of the CeO<sub>2</sub> powders prepared by 0 and 20 h ball milling



Fig. 4.26: The Particle Size Distribution of the  $CeO_2$  Powder Ball Milled for (a) 0 and (b) 20 h.

It is observed that for 0 h powder, the average particle diameter of the distribution lies around 176 nm, while for 20 h the maximum amount of  $CeO_2$  particles lies in the interval 30-40 nm confirming the results obtained from the XRD analysis.

# 4.3.2.3 SEM

Figure 4.27 shows the SEM micrographs of  $CeO_2$  powders subjected to high energy ball milling. It is observed that as the milling time increases the morphology of particles changes from irregular and coarse particles to finer, homogeneous and granular shaped particles.



Fig. 4.27 SEM Micrographs of CeO<sub>2</sub> Powder Subjected to (a) 0, (b) 5, (c) 10, (d) 15 and (e) 20 h Ball Milling

## 4.3.2.4 TEM

Bright Field image of the  $CeO_2$  powder milled for 0 and 20 h are shown in Figure 4.28 (a and b). The particle size after milling for 20 h is clearly in nanometer range varying from 20-25 nm and also supports the measured value from both XRD and particle size distribution analysis. The presence of continuous rings in SAD pattern, as shown in Fig. 4.28 (c) further confirms the nanostructure formation in  $CeO_2$  powder.



Fig. 4.28: TEM Micrographs of  $CeO_2$  Powders Prepared by Ball Milling for (a) 0 h and (b) 20 h and (c) SAD Pattern of Figure (b)

# 4.3.2.5 Summary

The XRD analysis of as received  $CeO_2$  powder after ball milling for 20 h shows a particle size of ~30 nm. This has been verified by particle size analyser which shows that the crystallite size of maximum number of particle is approximately 30-40 nm. The TEM micrographs also confirm the nanocrystalline nature of the milled  $CeO_2$  and that the size of the particles lies in the range of 20-25 nm.

#### 4.3.3 Synthesis of Sn/CeO<sub>2</sub> nanocomposite

The Sn based monolithic as well as nanocomposites with different amounts of  $CeO_2$  have been produced by pulse co-electrodeposition. The as deposited monolithic and reinforced composites are characterised by XRD, SEM, and TEM, and have been evaluated for their microhardness, density, electrical resistivity, thermal, wear and friction, corrosion behavior, and residual stress measurement of the composites. The results obtained are reported in the following sections.

## (I): Sn/CeO<sub>2</sub> composite using sulfate bath (Bath 2)

For the production of Sn/CeO<sub>2</sub> composite coatings, the electrolyte containing stannous sulfate ( $SnSO_4.3H_2O$ ), sulfuric acid ( $H_2SO_4$ ) and Triton X-100 (Bath 2, Table 3.1) is utilized. The co-electrodeposition is performed by adding CeO<sub>2</sub> nanopowders to the electrolyte bath with varying concentration (5, 10, and 20 g/L) and the microstructures are examined. It is found from XRD measurements that there is no peak of CeO<sub>2</sub> in the diffractogram. On analysing the composite samples with EDS spectroscopy, the weight fraction of CeO<sub>2</sub> nanoparticles comes out to be lesser than 1 percent when the composite is prepared from the electrolyte containing in 5 and 10 g/L CeO<sub>2</sub>, while 1.5 wt% when it is deposited from the electrolyte containing 20 g/L CeO<sub>2</sub> with limited reproducibility. It is also observed that the codeposition of CeO<sub>2</sub> nanoparticles in these cases has a minor or no influence on the properties, such as microhardness and wear resistance of the pure tin matrix. The microhardness measurements and wear tests on these samples show negligible improvement. This created a great confusion with the co-electrodeposition process that why the nanocomposite coatings and pure tin deposited from sulfate baths are more or less similar. Also, the EDS analysis confirms that the atomic ratio Ce/O that corresponds to some of reduced species of CeO<sub>2</sub> i.e, Ce<sub>2</sub>O<sub>3</sub> and Ce<sub>6</sub>O<sub>11</sub>, but the reason is unclear since CeO<sub>2</sub> is stable at room temperature (Wang, 2003; Li et al., 2001). This made us to infer that the CeO<sub>2</sub> nanoparticles are highly unstable in the strongly acidic solution, and thus it is quite unlikely to get codeposited from sulfate electrolyte (Bath 2). It is also noticed that at the end of the experiment, the tin anode is completely covered by

the CeO<sub>2</sub> nanopowders. This can possibly be explained in a way that the nanoparticles are highly negative charged due to the very low pH environment of the plating bath (pH~1). It has been already reported that the ceramic nanoparticles are highly negative charged in such a strong acidic baths (Lekka, 2008). At very low pH, it is easier for the nanoparticles to get attracted towards anode rather than cathode. A more detailed study may be required to investigate the problem on the solution chemistry, which is outside the scope of the thesis. For this reason research regarding the development of the nanocomposite solders using the aqueous sulfate bath is not continued. Further, aqueous citrate bath (Bath 3) is having a weakly acidic pH value (~4.3) is tried and it is found that the CeO<sub>2</sub> can be successfully codeposited in the Sn matrix.

#### (II): Synthesis of Sn/CeO<sub>2</sub> composite using citrate bath using Bath A

Fig. 4.29 (a-i) shows the wave signals for the pulse co-electroplating of Sn/CeO<sub>2</sub> nanocomposite. The waveforms show a change in their peak amplitude with the addition of CeO<sub>2</sub> in the electrolyte. The corresponding variation in peak amplitude implies a change in the electrode potential with the change in CeO<sub>2</sub> concentration. From figure 4.29 (j), it is observed that initially as CeO<sub>2</sub> concentration increases upto 15 g/L there is a little change in the electrode potential from 2.75 to 3.75 V upto 15 g/L and then it increases significantly to 6 V with further addition of CeO<sub>2</sub> upto 30 g/L.



Fig. 4.29: Variation of Wave Signals for (a) C0, (b) C1, (c) C2, (d) C5, (e) C10, (f) C15, (g) C20, (h) C25, (i) C30, and (j) Corresponding Effect of CeO<sub>2</sub> Concentration on Electrode Potential

Since the electric current is being supplied over a fixed area of the deposit (~  $6 \text{ cm}^2$ ), the voltage will change due to the change in the solution resistance of the electrolyte upon addition of CeO<sub>2</sub> nanoparticles. Therefore, initially at a lower concentration of CeO<sub>2</sub>, the resistance increase is very small upto 15 g/L, but increases sharply with continuous increase in concentration of CeO<sub>2</sub> in the electrolyte upto 30 g/L. The total solution resistivity thus increases and the electrode potential varies accordingly (Venu, 2011).

#### 4.3.4 Characterisation of Sn/CeO<sub>2</sub> composite

## 4.3.4.1 XRD

Figure 4.30 shows the XRD patterns of pure monolithic Sn and Sn/CeO<sub>2</sub> nanocomposite coatings synthesized by the process of pulse co-electrodeposition. The XRD pattern shows the presence of (111) CeO<sub>2</sub> peak along with the peaks from Sn matrix. This confirms that the coelectrodeposition of CeO<sub>2</sub> particles in the matrix is successfully achieved.



Fig. 4.30: XRD Patterns of the  $Sn/CeO_2$  Composite Prepared from Electrolytes Containing Different Concentration of  $CeO_2$ 

Regardless of the other electrodeposition parameters, an increase in  $CeO_2$  concentration in the electrolyte will lead to an increased content of  $CeO_2$  in the matrix (Thiemig *et al.*, 2007). According to the co-electrodeposition theory, the process by which the codeposition takes place involves (1) electrolytic field assisted entrapment of particles under agitation near cathode, (2) electrophoresis, (3) adsorption, and (4) convective diffusion of particles on the cathode surface (Hovestad and Janssen, 2005). There are several mechanisms to understand the process of co-electrodeposition. One of the widely accepted mechanisms is given by Guglielmi to explain this co-electrodeposition behavior. The Guglielmi model involves two adsorption steps. First, is the loose physical adsorption of particles on the cathode with a high coverage area. Second adsorption step is thought to be field assisted, therefore substantial electrochemical adsorption of the particles onto the electrode. The strongly adsorbed particles are then progressively engulfed by the growing metal in due course of time (Hovestad and Janssen, 2005; Guglielmi, 1972; Thiemig *et al.*, 2007).

#### 4.3.4.2 SEM

The surface morphology of monolithic Sn and Sn/CeO<sub>2</sub> composites is shown in Fig. 4.31. The microstructure of the deposits consists of pyramid shaped grain clusters. It is observed that an increase in concentration of CeO<sub>2</sub> nanoparticles in electrolyte upto 15 g/L leads to fine grained and compact deposits. The particle incorporation limits the grain growth of the matrix and increases the number of nucleation sites resulting in a fine grained microstructure (Mangam, 2011). In present case, the grain size of Sn is reduced with an addition of CeO<sub>2</sub> but still it lies in micrometer range. The best morphology of the Sn/CeO<sub>2</sub> composite is obtained when it is deposited from the electrolyte containing 15 g/L CeO<sub>2</sub> as shown in Figs. 4.32 (f) and (j). The formation of cracks and pores can be seen on the composites when they are deposited from electrolyte containing more than 15 g/L CeO<sub>2</sub> as shown in figure 4.31 (g-i). Fig. 4.31 (k) shows the agglomerated CeO<sub>2</sub> particles and thus porosity is also noticed. Due to a high concentration of CeO<sub>2</sub> in electrolyte their interparticle distance decreases and the particles come closer to form agglomerates. As a result, they have difficulties in reaching towards the cathode and hence an agglomerated/non uniform deposit is observed.



Fig. 4.31: Surface Morphology of the  $Sn/CeO_2$  Nanocomposites with Different Concentrations of  $CeO_2$  (a) C0, (b) C1, (c) C2, (d) C5, (e) C10, (f) C15, (g) C20, (h) C25 and (i) C30; (j) High Magnification Picture of C15 Showing Uniform Distribution of  $CeO_2$ , (k) Magnified View of (i) Showing Agglomeration in Sample C30

SEM observation of the Sn matrix composite (C15) shows that the fine particles (ceria) are monodispersed and have a size distribution of about 30–40 nm. This is in good agreement with the XRD and particle size distribution results. The amount of the coelectrodeposited CeO<sub>2</sub> in the Sn matrix is analysed by EDS and is tabulated in Table 4.13. Figure 4.32 (a and b) shows the SE image and the corresponding EDS mapping of Ce of the sample deposited from the electrolyte containing 15 g/L CeO<sub>2</sub>. Figure 4.32 (c) shows the EDS spectrum of the composite, further confirming the codeposition of CeO<sub>2</sub>.



Fig. 4.32 (a) SE Image of the Sample C15, (b) Elemental X-ray Map for Ce (c) EDS Spectrum of the Sample Showing the Presence of Ce in the Sn Matrix

It is seen from Table 4.13 that as the concentration of  $CeO_2$  in the electrolyte increases, the wt% of co-electrodeposited  $CeO_2$  in the Sn matrix also increases upto C15 and then a decrease is observed. Initially as the particle concentration is less, the mobility of the particles in electrolyte is high. This results in uniformly codeposited  $CeO_2$  in the Sn matrix. But as the particle concentration increases beyond 15 g/L, their mobility decreases and the particles are attracted under weak Van der Waals interaction to form  $CeO_2$  agglomerates which are difficult to get codeposited and whatever is deposited is in agglomerated form. Thus, a drop in  $CeO_2$  content in matrix is observed. This results in the deposits with agglomerated  $CeO_2$  particles and development of cracks (sample C20) and formation of big pores (C25 and C30), as shown in Fig. 4.31.

Table 4.13: Amount of Codeposited  $CeO_2$  in the Nanocomposite Coatings Corresponding to Different Concentration of  $CeO_2$  in Electrolyte.

Sample	Wt % of CeO <sub>2</sub>
C0	0
C1	0.49
C2	1.81
C5	3.18
C10	5.38
C15	5.77
C20	4.84
C25	3.52
C30	3.01

## 4.3.4.3 TEM

Figure 4.33 (a and b) shows TEM bright field and dark field images of the as deposited nanocomposite coating. The corresponding SAD pattern, shown in Figure 4.33 (c), further confirms the presence of nanosized CeO<sub>2</sub> powder in the microcrystalline Sn matrix. The size of CeO<sub>2</sub> nano particles observed is about ~20 nm in size and are randomly oriented with no significant agglomeration.



Fig. 4.33: TEM Micrographs of Sn/CeO<sub>2</sub> Nanocomposite Showing (a) BF Image, (b) DF Image and (c) SAD Pattern of (a).

## 4.3.5 Synthesis of Sn-Ag/CeO<sub>2</sub> nanocomposite

The pulse electrodeposition of near eutectic  $Sn-Ag/CeO_2$  is performed from Bath B with an addition of silver nitrate,  $AgNO_3$  as a source of silver ions. In this bath, thiourea is also added which acts as a complexing agent. The addition of thiourea is necessary for the stabilization of the plating bath containing  $Ag^+$  and  $Sn^{2+}$ , because  $Ag^+$  precipitation occurs if it is not present. The effect of thiourea is ascribed to its complex formation behavior with  $Ag^+$  ions (Fukuda, *et al.*, 2002; Kim and Ritzdorf, 2003). Monolithic near eutectic Sn-Ag deposit is also prepared and its properties are compared with the coelectrodeposited Sn-Ag/CeO<sub>2</sub> composites. Plating parameters such as current density and AgNO<sub>3</sub> concentration are varied to obtain eutectic and near-eutectic Sn-Ag compositions. Triton X-100 is also added as a surfactant that helps in smoothening of the deposit and it also acts as a dispersing agent for CeO<sub>2</sub> nanoparticles. The as deposited coatings are cleaned ultrasonically and finally washed with alcohol before the characterization.

To obtain the near eutectic composition (Sn-3.5 wt% Ag), the variation of Ag concentration in the deposit with the AgNO<sub>3</sub> concentration in the electrolyte at a fixed current density of  $0.2 \text{ A/cm}^2$  has been investigated and plotted in Fig. 4.34 (a).



Fig. 4.34: The Ag Content in the Deposit as a Function of (a)  $AgNO_3$  Concentration in the Electrolyte, and (b) Current Density.

From Fig. 4.34 (a), it is clear that the eutectic composition is achieved at  $AgNO_3$  concentration of 0.24 g/L in the electrolyte and at a current density of 0.2 A/cm<sup>2</sup>. In an effort to investigate the effect of current density on the amount of Ag in the deposits, experiments are performed by varying the current density from 0.05 to 0.4 A/cm<sup>2</sup> while keeping the AgNO<sub>3</sub> concentration in the electrolyte constant at 0.24 g/L (Fig. 4.34(b)). The observed high amount of Ag in the low current density region (below 0.2 A/cm<sup>2</sup>) is

attributed to the relatively positive reduction potential of  $Ag^+$  (+0.799 V) as compared to that of  $Sn^{2+}$  (-0.134 V). The Ag concentration decreases at higher current density because at the higher overpotential, the reduction of  $Sn^{2+}$  becomes easier and it continues to be deposited but the supply of the Ag<sup>+</sup> ions in the electrolyte becomes limited (Chen HY *et al.*, 2008).

Fig. 4.35 (a-i) shows the wave signals for the pulse co-electroplating of Sn-Ag/CeO<sub>2</sub> nanocomposite. The electrode potential in this case is slightly higher as compared to the Sn/CeO<sub>2</sub> composite due to the complexation of ions coming from additives like thiourea and silver nitrate. The corresponding variation in the electrode potential, as shown by the peak amplitude in Fig. 4.35, varies with the change in CeO<sub>2</sub> concentration.



Fig. 4.35: Variation of Wave Signals for (a) D0, (b) D1, (c) D2, (d) D5, (e) D10, (f) D15, (g) D20, (h) D25, (i) D30, and (j) Corresponding Effect of CeO<sub>2</sub> Concentration on Electrode Potential

From the figure 4.35 (j), initially at a lower concentration of  $CeO_2$  upto 15 g/L in electrolyte there is a gradual change from 3.5 to 4.5 V in the electrode potential, but increases thereafter upto 8.5 V on the addition of  $CeO_2$  upto 30 g/L. As already discussed, the change in resistivity of the solution is higher when a greater amount of ceria is added in the electrolyte and therefore the electrode potential rises to a very high value.

## 4.3.6 Characterisation of Sn-Ag/CeO<sub>2</sub> composite

#### 4.3.6.1 XRD

Figure 4.36 shows the XRD patterns of monolithic Sn-Ag and Sn-Ag/CeO<sub>2</sub> nanocomposite coatings. The XRD pattern shows the presence of (111) CeO<sub>2</sub> peak in the nanocomposite. The peaks of Ag<sub>3</sub>Sn intermetallic compound are also observed in all the samples. Ahat *et al.* (2001) have demonstrated the formation of Ag<sub>3</sub>Sn in a Sn-3.5Ag solder alloy, which improves the mechanical properties.



Fig. 4.36: XRD Patterns of  $Sn-Ag/CeO_2$  Composite Prepared with Different Concentration of  $CeO_2$  in Electrolyte.

#### 4.3.6.2 SEM

The surface morphology of the monolithic Sn-Ag and Sn-Ag/CeO<sub>2</sub> composites is shown in Fig. 4.37. The microstructure of the deposits shows a tendency to be finer with the increase in CeO<sub>2</sub> nanoparticles. The sample deposited from electrolyte containing with 15 g/L CeO<sub>2</sub> (D15) exhibits best morphology among all the deposits. On addition of the CeO<sub>2</sub> nanoparticles, the grain size is reduced and adopts a more regular shape. This can be correlated to the two factors, (1) presence of more number of nucleation centres due to CeO<sub>2</sub> incorporation occurring during the co-electrodeposition and (2) the adsorption of CeO<sub>2</sub> on the cathode surface increases cathodic polarization and it results in finer grains. Figs. 4.37 (f) and (j) depicts an uniform distribution of ceria nanoparticles which are white in color and have a size range of about 20-30 nm. However, as noticed from the SEM micrographs the Ag<sub>3</sub>Sn compounds are not clearly visible. This type of observations on the morphology of deposits is consistent with earlier work on electrodeposited Sn-Ag solder by Chen HY *et al.* (2008).



Fig. 4.37: SEM Images of (a) D0, (b) D1, (c) D2, (d) D5, (e) D10, (f) D15, (g) D20, (h) D25, (i) D30 and (j) Magnified View of (f), (k) Magnified View of (i)

As the concentration of  $CeO_2$  in the electrolyte increases beyond 15 g/L,  $CeO_2$  nanoparticles form agglomerates. Due to such a high concentration of  $CeO_2$  in electrolyte their interparticle distance decreases forming lumps and they can not move easily towards the cathode, and hence an agglomerated/non uniform deposit is observed. As a result the porosities and cracks are formed in the microstructure, encircled in Fig. 4.37(g). The high magnification micrograph (Fig.4.37 (k)) confirms the formation of  $CeO_2$  agglomerates in the matrix.



Fig. 4.38: (a) SE Image of the Sample D15, (b) Elemental X-ray Map for Ag (c) Elemental X-ray Map for Ce, (d) EDS Spectrum of the Sample Showing the Presence of Ce in the Sn-Ag Matrix

Figure 4.38 (a) shows the SE image of the sample deposited from the electrolyte containing 15 g/L CeO<sub>2</sub>, and the corresponding EDS mapping of Ce and Ag in the sample is shown in Fig. 4.38 (b and c). Fig.4.38 (d) shows the EDS spectrum of the composite, further confirming the codeposition of CeO<sub>2</sub>.

The variation of the CeO<sub>2</sub> content in the deposits with CeO<sub>2</sub> concentration in the electrolyte is given in Table 4.14. It is clear that an addition of CeO<sub>2</sub> in the electrolyte upto 15 g/L increases the amount of CeO<sub>2</sub> in the deposit. However, as the CeO<sub>2</sub> content in the electrolyte is more than 15 g/L, the interparticle distance decreases as the amount of CeO<sub>2</sub> in bath is too high. This results in an increase in Van der Waals interaction eventually leading to the formation of agglomerates and lumps, which have difficulties in reaching the cathode and the amount of CeO<sub>2</sub> in the deposit decreases. The Ag concentration has been found to vary from 3-3.6% in the deposits confirming to a near eutectic composition of the composites produced.

Sample	Wt % of CeO <sub>2</sub>
D0	0
D1	2.4
D2	5.37
D5	7.82
D10	10.75
D15	11.52
D20	4.87
D25	4.26
D30	3.69

Table 4.14: Amount of Codeposited CeO<sub>2</sub> in the Sn-Ag Nanocomposite Coatings

The XRD analysis (Fig. 4.36) reveals the presence of Ag<sub>3</sub>Sn in all the composites as well as monolithic Sn-Ag alloy. However, as noticed from the SEM micrographs (Fig. 4.37), the Ag<sub>3</sub>Sn compounds are hardly observed. Therefore, the sample with the best morphology (D15) and monolithic Sn-Ag alloy (D0) are chosen for further study. The samples are mechanically polished with 1-µm diamond paste and etched with a solution of 5vol.% HNO<sub>3</sub> + 95vol.% C<sub>2</sub>H<sub>5</sub>OH. This type of electrolyte has been already employed in the past to visualise the eutectic microstructures of the Sn-Ag solders (Shen *et al.*, 2006). After the etching treatment, the soft phase Sn gets dissolved and  $Ag_3Sn$  is observed clearly in the microstructure as shown in Fig. 4.39. The point EDS analysis of these samples also confirms these particles to be  $Ag_3Sn$  compounds as shown in Fig. 4.39 (c and d).



Fig. 4.39: SEM Micrographs of Pulse Electrodeposited (a) Sn-Ag Alloy, (b) Sn-Ag/CeO<sub>2</sub> Nanocomposite, after Etching with the 5 vol.%  $HNO_3 + 95$  vol.%  $C_2H_5OH$ , (c) Point EDS analysis of (a), and (d) Point EDS analysis of (b)

The needle like particles in monolithic Sn-Ag alloy is confirmed to be  $Ag_3Sn$ . It is also observed that the size of  $Ag_3Sn$  in the composite is finer compared to the same in monolithic alloy and is visible only at very high magnification. This type of phenomena has been explained in terms of surface adsorption theory in the past by several authors (Shen *et al*, 2006; Shen and Chan, 2009; Gain *et al*, 2011). It states that the amount of surface absorption of active materials is different for different planes. The plane with maximum surface tension grows fastest and the adsorption amount of surface active material is maximized. However, an increase in amount of surface active material decreases its surface energy and therefore decreases the growth velocity of this plane. The surface energy of the whole crystalloid is given by,

$$\sum_{i} \gamma_{c}^{i} A_{i} = \sum_{i} \left( \gamma_{o}^{i} - RT \int_{o}^{c} \frac{\Gamma^{i}}{c} dc \right) A_{i} \qquad \dots (4.20)$$

Where,  $\Gamma^i$  is the adsorption coefficient of surface active materials at  $i^{th}$  plane, c is the concentration of surface active material, R is the ideal gas constant, and T is the absolute temperature.  $\gamma_c^i$  is the surface tension of the  $i^{th}$  plane with adsorption and  $\gamma_o^i$  is the initial surface tension of  $i^{th}$  plane without adsorption and A<sub>i</sub> is the area of the plane *i*.

For a constant volume,  $\sum_{i} \gamma_{o}^{i} A_{i}$  is constant, as it is independent of concentration, thus, for

a minimum surface energy, from equation we get,  $\operatorname{RT} \int_{o}^{c} \frac{\Gamma^{i}}{c} dc \rightarrow \max$ , which implies that

the plane where the nanoparticles are adsorbed with a maximum adsorption amount  $\Gamma^i$  is most effective. Since the ceria nanoparticles are smaller than Ag<sub>3</sub>Sn intermetallics, they can easily accumulate on these Ag<sub>3</sub>Sn particles and on the Sn matrix (Wu and Wong, 2007). Hence, adsorption of CeO<sub>2</sub> nanoparticles would refine the Sn grains and restrict the growth of Ag<sub>3</sub>Sn intermetallics.

# 4.3.6.3 TEM

Figure 4.40 (a) and (b) shows the bright and dark field image of the sample D15 confirming the presence of the  $CeO_2$  nanoparticles in the Sn-Ag matrix. Figure 4.40 (c)

shows the bright field image of the composite where few  $Ag_3Sn$  particles along with  $CeO_2$  nanoparticles are present in the microcrystalline Sn matrix.  $CeO_2$  nano particles are found to be about 20 nm in size and with a random orientation.



Fig. 4.40: TEM Micrographs of Sn-Ag/CeO<sub>2</sub> Nanocomposite Showing (a) BF image, (b) DF Image Showing the CeO<sub>2</sub> nanoparticles, (c) BF Image of the Matrix in a Region where few  $Ag_3Sn$  IMC are Clearly Shown as Needles.

### 4.3.6.4 Summary

The CeO<sub>2</sub> nanoparticles have been successfully incorporated in the Sn and Sn-Ag matrix from the electrolyte containing upto 30 g/L CeO<sub>2</sub>. The near eutectic Sn-Ag composites, are obtained at a current density of 0.2 A/cm<sup>2</sup> and 0.24 g/L AgNO<sub>3</sub> of in electrolyte. The maximum amount of CeO<sub>2</sub> in the deposits corresponds to the 15 g/L of CeO<sub>2</sub> in electrolyte. SEM micrograph reveals that presence of  $CeO_2$  in the Sn rich matrices. EDS result also confirms that the maximum amount of  $CeO_2$  occurs when the composite is deposited from the electrolyte containing 15 g/L  $CeO_2$ . It is also found that the  $CeO_2$  is adsorbed on the Sn and Sn-Ag matrices and refines their grain size. In Sn-Ag matrix, adsorption of  $CeO_2$  results in finer Ag<sub>3</sub>Sn particles in the matrix compared to the monolithic Sn-Ag alloy.



4.4 Property evaluation of the developed lead free pulse electrodeposited Sn/CeO<sub>2</sub> and near eutectic Sn-Ag/CeO<sub>2</sub> lead free solder nanocomposites

#### 4.4.1 Microhardness

The microhardness of nanocomposites, as measured using Vicker's microhardness tester, is shown in Fig. 4.41.



Fig. 4.41: Microhardness of (a) Pure Sn and Sn/CeO<sub>2</sub> Composite and (b) Sn-Ag alloy and Sn-Ag/CeO<sub>2</sub> Composite

It is observed from Figure 4.41 (a and b) that all the composites have a higher microhardness as compared to the monolithic materials. There are basically a number of causes for this enhancement in the microhardness of composite samples, such as (a) the higher hardness of  $CeO_2$  as compared to the matrix (b) the dispersion hardening effect of  $CeO_2$  particles in the Sn matrix, and (c) grain refinement of the matrix since  $CeO_2$  provides more nucleation centers during electrodeposition and also restricts the grain growth.

It is also noticed that the microhardness values of Sn-Ag/CeO<sub>2</sub> composites are much higher than that of Sn/CeO<sub>2</sub> composites. The XRD study reported in the previous section and also binary phase diagram of Sn-Ag system (Baker, 1992) suggest the formation of Ag<sub>3</sub>Sn compound in both the monolithic alloy and composites. The presence of this hard intermetallic compound ~ 300 Hv (Lucas *et al*, 2003), increases the hardness of the Sn-Ag/CeO<sub>2</sub> composite significantly. It also appears that the contribution of Ag<sub>3</sub>Sn in enhancing the hardness of Sn-Ag/CeO<sub>2</sub> composite increases as the amount of CeO<sub>2</sub> in the composite increases. Since the CeO<sub>2</sub> nanoparticles are smaller than Ag<sub>3</sub>Sn intermetallics, according to the adsorption theory described in section 4.3.6, they can easily accumulate on these Ag<sub>3</sub>Sn particles and on the Sn matrix. The adsorption of CeO<sub>2</sub> nanoparticles will refine the Sn grains and restrict the growth of Ag<sub>3</sub>Sn particles (Wu and Wong, 2007). Hence, a refined Ag<sub>3</sub>Sn is formed in presence of CeO<sub>2</sub> nanoparticles, resulting in an enhanced contribution to the microhardness.

It is also observed that the composite have lower hardness when they are deposited from the electrolyte containing more than 15 g/L CeO<sub>2</sub>. The microhardness of C20, C25 and C30 is lower than C15 and the microhardness of D20, D25 and D30 is also lower than D15. It is already mentioned that these samples, the total amount of CeO<sub>2</sub> particles incorporated is quite less compared to the corresponding composite samples C15 and D15. Moreover, the CeO<sub>2</sub> is present in the agglomerated form, as observed from the SEM micrographs (Fig. 4.31 and 4.37). These lead to a weakening in the described strengthening mechanisms and thus composite microhardness.

#### **4.4.2 Density Measurements**

The weight is of primary concern in smaller and portable electronic devices. Therefore, the density measurements are conducted by Archimedes principle for all the samples as shown in Fig. 4.42.



Fig. 4.42: Density of (a) pure Sn and Sn/CeO<sub>2</sub> Composites (b) Sn-Ag alloy and Sn-Ag/CeO<sub>2</sub> Composites

It is observed from Fig. 4.42 that the density of sample C0 and D0 is ~7.27 and 7.31 g/cm<sup>3</sup>, respectively. The reported values of density at room temperature for Sn, Sn-3.5Ag and CeO<sub>2</sub> are 7.28, 7.36 and 7.21 g/cm<sup>3</sup>, respectively (Song et al., 2004; Babaghorbani et al., 2009a; Kobayashi and Fujiwara, 2006). The measured density of the developed composite samples is lower as compared to the monolithic samples. With increasing concentration of reinforcements the density of all the investigated composite solders is found to decrease from 7.232 for C1 to 6.695 g/cm<sup>3</sup> for C30 and 7.302 for D1 to 6.898  $g/cm^3$  for D30. The apparent decrease is not due to the incorporation of CeO<sub>2</sub>, since CeO<sub>2</sub> has very similar density to pure Sn or Sn-3.5Ag alloy. This decrease is due to the increase in porosities in the coatings with an incorporation of CeO<sub>2</sub> in the coatings. Initially, the porosity increase is very slow due to a very small amount of CeO<sub>2</sub> in these composites and thus, a significant decrease in density is not observed upto C5 and D5. The observed density is minimum for both the composites when they are prepared from 30 g/L CeO<sub>2</sub> in electrolyte, (i.e., 6.695 g/cm<sup>3</sup> for C30 and 6.898 g/cm<sup>3</sup> for D30) which have not only a higher content of pores, but also cracks form in these coatings. It has been reported in the literatures that build up of porosities and cracks in the composite sample due to the addition of reinforcements can be detrimental to the mechanical properties (Mavoori and Jin, 1998; Zhong and Gupta, 2008; Nai et al., 2006b). Although the density is lesser for the composites developed from more than 15 g/L ceria in electrolyte, yet in view of the poor mechanical properties they are not suggested for light weight application. Therefore, an optimum amount of 15 g/L CeO<sub>2</sub> is suggested for a good combination of properties for light weight applications.

## 4.4.3 Melting behavior

Figure 4.43 shows the DSC curves of the different  $Sn/CeO_2$  composite solder specimens reinforced with different concentrations of  $CeO_2$  nanoparticles.



Fig. 4.43: DSC Curves of the Sn Composite Solder Specimens Reinforced with Different Concentrations of  $CeO_2$  Nanoparticles, a) C0, (b) C1, (c) C2, (d) C5, (e) C10, (f) C15, (g) C20, (h) C25 and (i) C30

It is observed that the melting temperature of the composite samples differ slightly from the monolithic sample, which agrees well with the results reported for other Sn based solders reinforced with nano ceramic particles (Nai *et al.*, 2006d; Tsao and Chang, 2010; Liu *et al.*, 2008). In the case of sample C0, the well-defined endothermic peak appears at a temperature of 235.18 °C, which decreases to 234.44 °C for sample C15. The melting point is minimum for the sample C15. This can be attributed to the decrease in grain size of the matrix with incorporation of CeO<sub>2</sub> in the matrix. The melting points of samples C20, C25 and C30 are 234.92, 235.28 and 236.32 °C, respectively, which are slightly higher than that of the melting point of C15. This slight increase in melting point is
attributed to the larger grain size caused by the presence of agglomerated  $CeO_2$  particles. This observation shows that the incorporation of  $CeO_2$  in the matrix causes hardly a maximum deviation of  $\sim 1^{\circ}$  C in the melting point. Thus, the developed composite samples can be applied to the soldering applications without much alteration in the operating conditions.

For the case of Sn-Ag composites (Figure 4.44), the eutectic peak for monolithic D0 sample is observed at 224.8 °C which decreases to ~222.19 °C for sample D15. This deviation in melting point compared to monolithic D0 is around  $\sim 2^{\circ}$  C. The decrement in melting point of a metal or alloy is an inherent physical property and depends on the material itself. According to the Lindemann criterion, a crystal will melt when the root mean-square displacement of the atoms in the crystal exceeds a certain fraction of the inter-atomic distance (Mei and Lu, 2007). Since the surface atoms of a crystal usually have low coordination numbers, they experience different bonding forces from that of atoms in the bulk. The combined effect of increasing the number of surface atoms and the surface phonon softening will significantly increase the atomic mean-square displacements, and then there will be very slight decrease in the melting temperature of the alloy. Therefore, when an alloy is on a nano-size scale or the refinement in grain occurs by the particle incorporation, the melting temperature of the composite may decrease. The grain refinement of Sn-Ag matrix in the composite brought about by the addition of CeO<sub>2</sub> nanoparticles and finer Ag<sub>3</sub>Sn particles compared to the same in the monolithic alloy depresses the melting point upto composite D15. However, the melting point increases slightly for the samples D20, D25 and D30 to 225.3, 225.28 and 225.8, respectively. This slight increase is due to the presence of agglomerated CeO<sub>2</sub> particles causing a reduction in grain refinement mechanism in these samples. Thus, D15 sample exhibits the best composition for existing soldering applications.



Fig. 4.44: DSC Curves of the Sn-Ag Composite Solder Specimens Reinforced with Different Concentrations of CeO<sub>2</sub> Nanoparticles, (a) D0, (b) D1, (c) D2, (d) D5, (e) D10, (f) D15, (g) D20, (h) D25 and (i) D30

From these DSC profiles, Fig. 4.43 and 4.44, it is confirmed that if  $CeO_2$  nanoparticles are incorporated in the Sn based matrices, it is not required to make any changes in the existing solder process parameters such as the reflow temperature when employing these developed composite solders.

#### **4.4.4 Resistivity Measurements**

The resistivity of the samples is measured using four-point probe method. The advantage of using four-point probe method is the possibility to measure the sample's resistance, without any interference from the contact resistance at the probe contacts. The resistivity

of a metal matrix composite is affected by the presence of a number of disturbances in the crystal structure such as solute elements, impurities, grain boundaries, dislocations, vacancies, etc. The general equation for the resistivity of a material is given by the Matthiessen's rule (Mayadas and Shatzkes, 1970) which states that the total resistivity of a material is the sum of three components: (i) foreign impurities ( $\rho_i$ ), (ii) thermal agitations of metal ions of lattice ( $\rho_i$ ), and (iii) presence of imperfections in the crystal, e.g., plastic deformation ( $\rho_d$ ) etc.

$$\rho_{\text{total}} = \rho_i + \rho_t + \rho_d \qquad \dots (4.21)$$

For composite solders, the total resistivity values are thus expected to increase due to the larger contributions of  $\rho_i$  and  $\rho_d$  when compared to that of monolithic solder samples. The value of  $\rho_d$  depends on several factors such as volume fraction of the pores  $(V_p)$ , plastic zone  $(V_{pz})$  and reinforcement  $(V_r)$ . The effective volume fraction of scattering centers,  $(V_T)$ , can now be represented as follows:

$$V_T = V_{pz} + V_r + V_p$$
 ... (4.22)

For a particulate reinforcement the volume fraction of the deformation region surrounding the reinforcement,  $V_{pz}$ , is expressed by

$$V_{pz} = (\alpha^3 - 1) V_r$$
 ... (4.23)

where  $\alpha$  is the ratio of the size of the heterogeneous nucleation zone to that of the reinforcement (Chang SY *et al.*, 2003).

Rearranging (4.19) and (4.20),

$$V_T = (\alpha^3 - 1) V_r + V_r + V_p = \alpha^3 V_r + V_p \qquad \dots (4.24)$$

The value of  $\alpha$  depends on the type of matrix and also the size, shape, and type of the reinforcement, but not on its volume fraction. Thus, according to equation (4.24) the effective volume fraction depends on the volume fraction of reinforcement and pores.

Figure 4.45 shows the electrical resistivity of the different samples under investigation. It is observed that the resistivity of the composite samples is always higher as compared to the monolithic materials, since in monolithic samples resistivity contribution of reinforcement is zero.



Fig. 4.45: Electrical Resistivity of the Composites (a) Pure Sn and Sn/CeO<sub>2</sub> Composite and (b) Sn-Ag alloy and Sn-Ag/CeO<sub>2</sub> Composite

It is noted from Fig. 4.45 (a and b) that the resistivity increase is very slow for the samples deposited from the electrolyte containing upto 15 g/L CeO<sub>2</sub> (i.e., C15 and D15). For example, from C0 to C15 there is a slow increase in resistivity from 12.16 to 13.08  $\mu\Omega$ .cm, while from D0 to D15, the resistivity increases from 12.2 to 13.5  $\mu\Omega$ .cm. This may be due to the fact that the porosity contribution,  $V_p$ , is not significant to cause much disturbance in electron path. Thus omitting the porosity ( $V_p$ ) term in equation 10, resistivity will increase with only the volume fraction of the ceria nanoparticles ( $V_r$ ). Hence, the total resistivity increases but the amount of increase is not so high. However, the resistivity increases at a considerable rate for those samples which are deposited from electrolytes containing more than 15 g/L CeO<sub>2</sub> and especially, it is very high for C30 and

D30. This can be expected since the resistivity is also getting affected by the presence of the significant amount of porosities and cracks in these samples. These porosities and cracks act as additional scattering centers to the path of the electron motion and increase resistivity. This type of increase in resistivity with ceramic reinforcements observed is consistent with a number of previous studies (Mangam, 2011; Sen, 2011). The electrical resistivity of Sn/CeO<sub>2</sub> and Sn-Ag/CeO<sub>2</sub> based nanocomposite solders measured are quite comparable with other composites like Sn-0.7Cu/Al<sub>2</sub>O<sub>3</sub>, Sn-Ag/SnO<sub>2</sub>, Sn-Ag/Y<sub>2</sub>O<sub>3</sub> etc. (Babaghorbani *et al.*, 2009b).

#### 4.4.5 Electrochemical Corrosion behavior

The quantitative information on corrosion currents and corrosion potentials can be extracted from the intersection of the slopes of the potentiodynamic linear polarization curves using the Stern-Geary equation (Stern, 1958) as follows:

$$I_{corr} = \frac{1}{2.303R_p} \left( \frac{b_a b_c}{b_a + b_c} \right) \qquad \dots (4.25)$$

where,  $I_{corr}$  is the corrosion current density in A/cm<sup>2</sup>,  $R_p$  is the corrosion resistance in ohms cm<sup>2</sup>,  $b_a$  and  $b_c$  are the anodic and cathodic Tafel slopes in V/decade of current density, respectively and  $\left(\frac{b_a b_c}{b_a + b_c}\right)$  is known as the Tafel constant. The corrosion rate

(CR) can be calculated by using equation (4.22):

$$CR (mm/year) = \left(\frac{I_{corr} (A/cm^2).M(g).C}{D(g/cm^3).V}\right) \qquad \dots (4.26)$$

where  $I_{corr}$  is the corrosion current density, *D* is the density, *M* is the atomic mass and *V* is the valence. The value of C can be calculated as  $C = 3270 = 0.01 \times [1 \text{ year} (in seconds)/96497.8]$  and 96497.8 = 1 Faraday in Coulombs (Ciubotariu *et al.*, 2008).

## 4.4.5.1 Potentiodynamic polarization behavior - Tafel plot

Depending on the application and the in-service environment, electronic components may be exposed to corrosion media. Thus, investigation of the corrosion resistance of the developed composites becomes important. The potentiodynamic polarization curves of pure Sn, Sn-Ag alloy and their composite coatings are shown in Fig. 4.46.

From these curves, the corrosion current  $(I_{corr})$ , corrosion potential  $(E_{corr})$ , polarization resistance  $(R_p)$  and corrosion rate (CR) of all the monolithic and reinforced composites are calculated through the Tafel extrapolation method and summarised in Table 4.15 and 4.16.



Fig. 4.46: Potentiodynamic Polarization Curves for (a)  $Sn/CeO_2$  and (b)  $Sn-Ag/CeO_2$  Composites.

Sample	E <sub>corr</sub> (V)	$I_{corr} (A/cm^2) x 10^{-7}$	$R_{p}\left(\Omega\right) x 10^{3}$	CR (mm/year) x $10^{-2}$
C0	-0.95	0.251	0.311	6.879
C1	-0.93	0.193	0.390	5.634
C2	-0.92	0.161	0.401	4.335
C5	-0.89	0.139	0.698	4.067
C10	-0.52	0.133	1.232	3.577
C15	-0.47	0.107	1.719	2.866
C20	-0.51	0.197	1.306	5.392
C25	-0.50	0.221	1.038	6.060
C30	-0.94	0.347	0.253	9.523

Table 4.15: The Electrochemical Corrosion Parameters of Sn/CeO<sub>2</sub> composites

Table 4.16: The Electrochemical Corrosion Parameters of Sn-Ag/CeO2 Composites

Sample	E <sub>corr</sub> (V)	$I_{corr} (A/cm^2) x 10^{-7}$	$R_{p}(\Omega) \times 10^{3}$	CR (mm/year) x $10^{-2}$
D0	-0.89	0.246	0.697	6.573
D1	-0.90	0.174	0.561	4.819
D2	-0.91	0.164	0.526	4.742
D5	-0.53	0.156	0.926	4.234
D10	-0.23	0.094	1.807	2.673
D15	-0.24	0.091	1.863	2.497
D20	-0.87	0.137	0.608	3.832
D25	-0.90	0.156	0.461	4.801
D30	-0.94	0.183	0.653	5.013

It is observed from Table 4.15 and 4.16 that the corrosion rate of composites is lower compared to the monolithic samples. This shows that the addition of  $CeO_2$  nanoparticles in the coating improves the corrosion resistance of the composites appreciably. The corrosion current ( $I_{corr}$ ) is found to decrease continously and the corrosion potential ( $E_{corr}$ )

gradually shifts to a less negative value up to the samples prepared from 15 g/L ceria in electrolyte. The polarization resistance  $(\mathbf{R}_{n})$  also increases as a consequence. This can be explained in view of two factors: (1) The chemical inertia of the composites is higher due to the low chemical reactivity of CeO<sub>2</sub> particles, which acts as a physical barrier. This increases the passivation and slows down the oxidation of anode, thus impairing the corrosion propagation. This results in a reduction of the corrosion rate of the composite. (2) The dispersed  $CeO_2$  nanoparticles within the matrix form various tiny micro corrosion cells which inhibits the localized corrosion attack. Since the standard potential of CeO2 is more positive than Sn, formation of an electrochemical cell is favourable with  $CeO_2$ acting as cathode and Sn as anode. Such corrosion micro cell facilitates the anodic polarization (Mangam, 2011; Sen, 2011). It accelerates the passivation process of the matrix and thus localized corrosion is inhibited and a homogeneous corrosion occurs throughout the matrix. This delays the corrosion crack propagation and improves the corrosion resistance. It is also observed that the composite sample prepared from the electrolyte containing 15 g/L CeO<sub>2</sub> (C15 in Sn/CeO<sub>2</sub> and D15 in Sn-Ag/CeO<sub>2</sub> system) exhibit the best corrosion resistance among all the samples tested. However, it is also noticed that the corrosion resistance is degraded in case of C20, C25 and it is worst for C30. A similar behavior is also seen in case of D20, D25 and D30. This may be due to the presence of significant amount of porosities and cracks in these samples which obstructs the formation of uniform micro corrosion cells, and localised corrosion is enhanced. Thus, the corrosive medium can pass more easily through the gaps to erode the sample and rapid dissolution of matrix occurs.

From the potentiodynamic polarization results, it is also observed that  $Sn-Ag/CeO_2$  solders exhibit somewhat better corrosion properties than that of the  $Sn/CeO_2$  solders. This can be due to the lower  $E_{corr}$  and  $I_{corr}$  as compared to  $Sn/CeO_2$  based composites. The addition of nanosized  $CeO_2$  in the Sn-Ag provides very fine Ag<sub>3</sub>Sn intermetallics. The presence of fine Ag<sub>3</sub>Sn compounds increases the passivation of the matrix which may act as an additional noble barrier against corrosion propagation. This result is consistent with the literature that a high content of noble and immune entities, and a stable structure

provides maximum corrosion protection (Tsao, 2012). Recent studies have also proved [(Li *et al.*, 2008; Osorio *et al.*, (2007, 2010, 2011); Pardo *et al.*, 2008)] that when the Ag<sub>3</sub>Sn, Al<sub>2</sub>Cu, Al<sub>3</sub>Ni, and Mg<sub>17</sub>Al<sub>12</sub> intermetallics of binary Sn-Ag, Al-Cu, Al-Ni and Mg-Al alloys, respectively, are finely and homogeneously distributed in a finer dendrite arrangement, they act as a protection against corrosion.

4.4.5.2 Microstructures of corroded samples

Figures 4.47 and 4.48 show the microstructures of corroded samples of Sn/CeO<sub>2</sub> and Sn-Ag/CeO<sub>2</sub> solders, respectively.

(I) Sn/CeO<sub>2</sub>



Fig. 4.47: Microstructures of Various Corroded Samples (a) C0, (b) C1, (c) C2, (d) C5, (e) C10, (f) C15, (g) C20, (h) C25 and (i) C30

## (II) Sn-Ag/CeO<sub>2</sub>



Fig. 4.48: Microstructures of Various Corroded Samples (a) D0, (b) D1, (c) D2, (d) D5, (e) D10, (f) D15, (g) D20, (h) D25 and (i) D30

It is observed that composites have a compact net/sheet like structure while monolithic samples have many micro gaps on the surface. As the ceria concentration increases upto 15 g/L in electrolyte, the shape of these sheet like structures becomes more regular. The composites with 15 g/L ceria in electrolyte, i.e., C15 and D15 show a compact microstructure with fine and uniform sheets showing a homogeneous corrosion of the matrix. A compact and uniform netlike structure is beneficial to prevent corrosive medium from eroding gradually. However, the SEM micrographs of the corroded surface of sample deposited from the electrolyte containing 20, 25 and 30 g/L ceria depict irregular sheet structures with full of pores showing pitting type corrosion. This can be attributed to the presence of porosity in these agglomerated deposits which enhances the matrix dissolution rate. The loose CeO<sub>2</sub> may come out of the surface as the corrosion is

progressed as their bonding with the matrix is poor in nature in these samples, thus forming pits along the surface (localized corrosion is enhanced) and a lower corrosion resistance is obtained.

After comparing Figs. 4.47 with 4.48, the results show that the microstructures of the corroded samples of Sn/CeO<sub>2</sub> and Sn-Ag/CeO<sub>2</sub> are more or less similar, except that the Sn-Ag/CeO<sub>2</sub> composites exhibit more compact and finer sheets/net like structures, which confirms better corrosion resistance. This type of sheet like structure is reported to be caused by the attack of Cl<sup>-</sup> ions in Sn based solders. The differences in corrosion resistance of Sn/CeO<sub>2</sub> and Sn-Ag/CeO<sub>2</sub> solders can also be investigated by the extent of corrosion damage due to Cl<sup>-</sup> ions. This is confirmed by the XRD (Fig. 4.49) and EDS (Fig. 4.50).



Fig. 4.49: XRD Patterns of the Corroded Samples (a) C0, (b) D0, (c) C15 and (d) D15

The XRD pattern shows the formation of  $\text{SnCl}_2$  as a major corrosion product in all the monolithic and composite samples consistent with the findings of other researchers [Mohanty and Lin, (2006, 2007)]. The Sn acts as anode in electrochemical reactions and thus reacts with Cl<sup>-</sup> ions to form  $\text{SnCl}_2$ , causing severe dissolution of Sn and thus the formation of pits. Hu *et al.* (2009) have reported that  $\text{SnCl}_2$  absorbs O<sub>2</sub> from air to form insoluble oxychloride. There is no oxychloride found unlike many in the past (Osorio *et al.*, 2011; Chang *et al.*, 2004). The XRD analysis also shows the presence of the Ag<sub>3</sub>Sn apart from CeO<sub>2</sub> nanoparticles along with SnCl<sub>2</sub> indicating its inertness to the corrosive medium. The Ag<sub>3</sub>Sn particles are not dissolved by this SnCl<sub>2</sub> and block the movement of Cl<sup>-</sup> ions and enhance the corrosion resistance. Therefore, corrosion resistance of Sn-Ag/CeO<sub>2</sub> composites is higher as compared to Sn/CeO<sub>2</sub> composites. The EDS analysis taken from some of the samples are presented in Table 4.17, and the EDS spectrum showing the presence of elements are shown in Fig. 4.50.

Sample	Atomic% of Cl	Sample	Atomic% of Cl
C0	43.93	D0	43.82
C2	45.02	D2	41.99
<b>C10</b>	43.24	D10	39.56
C15	26.47	D15	16.38
C25	42.26	D25	22.31
C30	43.34	D30	35.52

Table 4.17: EDS Analysis of the Corroded Surfaces of Sn and Sn-Ag Composites



Fig. 4.50: EDS Spectrum of the Corroded Samples (a) C15 and (b) D15.

It is known that the presence of Cl<sup>-</sup> ion initiates pitting and results in the breakdown of the passive film. It is observed from Table 4.17 that the atomic concentration of Cl<sup>-</sup> ion is higher in monolithic samples as compared to the composite samples. The atomic concentration of Cl<sup>-</sup> is found to be the highest at ~43 at%, in both C0 and D0 which progressively decreases with an increase in ceria concentration upto C15 (26 at%) and D15 (16 at%). The concentration of Cl<sup>-</sup> again increases for C30 (43 at%) and D30 (35 at%), suggesting the presence of higher concentration of chlorides on the surface, that results in pitting corrosion. However, in the present case, oxygen is present in very low concentration of oxychlorides in the samples.

#### 4.4.6 Wear

The tribological behavior of monolithic and composite samples has been evaluated. The samples selected for the study are C0, C15, D0 and D15. The samples C15 and D15 are selected since they have the maximum microhardness among all the composites studied in the present investigation. In the present investigation, ball on disc wear tester with a steel indenter ball of 2 mm diameter has been used to evaluate the wear resistance of the material.

## 4.4.6.1 Surface roughness and microhardness

The surface roughness and microhardness values have been measured, since these two parameters play an important role in determining the wear resistance of a material. The microhardness and average roughness of C0, C15, D0 and D15 are shown in Table 4.18.

Samples	Roughness (µm)	Microhardness (Hv)
CO	4.04	11
C15	9.4	78
D0	0.75	18
D15	2.53	138

Table 4.18: Roughness and Mi	crohardness Values	of the Selected	Samples fo	or Wear Test.
0			1	

# **Chapter 4**

From Table 4.18, it can be seen that the roughness values of the composites are higher as compared to the monolithic samples. The presence of reinforcement phases on the surface will act as a surface projection and thus increases the roughness. Figure 4.51 shows the surface profile of the selected samples.



Fig. 4.51: Roughness Profile (3D) of the Selected Samples, (a) C0, (b) C15, (c) D0 and (d) D15.

The 3D roughness profile shows that for composite samples C15 and D15, the surface is more uneven compared to the corresponding monolithic samples. This is in confirmation with earlier reports on electrodeposited metal matrix composites (Mangam *et al.*, 2010; Sen, 2011).

## 4.4.6.2 Wear Penetration depth

The variation of wear penetration depth of C0, D0, C15 and D15 with varying loads is shown in Table 4.19.

Load/	C0	C15	D0	D15
Samples				
4	4.93	2.25	3.26	1.63
6	9.1	3.91	6.09	3.20
8	10.7	6.09	9.69	5.60
10	18.4	16.33	14.77	7.59

Table 4.19: Wear Penetration Depth of the Selected Samples

It is observed that pure tin (C0) has the highest wear penetration depth due to its lowest microhardness (11 Hv) among all the samples under investigation. The penetration depth of monolithic samples is always higher as compared to the composites due to the lower microhardness.



Fig.4.52: The Wear Track Depth of the Different Samples as a Function of Load

The 2D mapping of the wear tracks at different loads for the selected samples is shown in Fig. 4.52 which also confirms that the penetration depth is directly proportional to the microhardness of the samples. It is also observed from Table 4.19 that the wear penetration depth increases with the increasing loads as expected.

#### 4.4.6.3 Volume loss and wear rate

The plots of volume loss and wear rate versus loads for the samples C0, D0, C15 and D15 are shown in Fig. 4.53, respectively. It is observed that the volume loss as well as the wear rate increases with the increase in applied load for all the samples as expected. From Fig. 4.53, it is observed that the composites C15 and D15 show a better wear resistance as compared to their monolithic counterparts C0 and D0 at all applied loads. This indicates the enhanced load-bearing ability of the composites relative to that of monolithic samples. The nanosized CeO<sub>2</sub> reinforcement increases the strengthening mechanisms of the composite matrix (as described in section 4.4.1) leading to an enhancement in wear resistance. The results are in good agreement with the Archard's relation which states that harder samples possess higher wear resistance (Archard, 1953).



Fig. 4.53: (a) Volume Loss and (b) Wear Rate of the Composites as a Function of Load

The wear rate of D0 and D15 is lower than that of C0 and C15, respectively. This is due to the presence of hard Ag<sub>3</sub>Sn compound in D0 and D15. The Ag<sub>3</sub>Sn compound has a

very high hardness, around 15 times the pure Sn and 12 times the eutectic Sn-Ag matrix (Deng *et al.*, 2004; Chromik *et al.*, 2003). Moreover, in D15 these Ag<sub>3</sub>Sn are present in much finer form. Their existence significantly contributes to the strain hardening of the matrix and thus lowers the wear rate. It is observed that when the applied load is increased from 4 to 8 N, the volume loss and wear rate increase slowly but increase at a higher rate when the load exceeds 8 N for C0 and C15.

At a load of 8 N, the wear rate of the sample C0 is about 7.66 x  $10^{-4}$  mm<sup>3</sup>/Nm which increases to 22.42 x  $10^{-4}$  mm<sup>3</sup>/Nm at 10 N while for C15 it is 2.27 x  $10^{-4}$  mm<sup>3</sup>/Nm at 8N and it increases to 11.41 x  $10^{-4}$  mm<sup>3</sup>/Nm at 10N (Fig. 4.53 (b)) indicating a severe wear when the load exceeds 8 N. The severity in wear at higher loads can be mainly attributed to the onset of delamination which in turn leads to the wear debris generation. This type of wear damage is resulting in a higher volume loss is consistent with the other reports in the past on copper matrix composites (Ramesh *et al.*, 2009; Zhan and Zhang, 2003). However, the Sn-Ag and Sn-Ag/CeO<sub>2</sub> show mild wear behavior at all loads tested in the present investigation. For instance, at a load of 8 N the wear rate of the sample D0 is about 3.07 x  $10^{-4}$  mm<sup>3</sup>/Nm at 8 N which increases to  $1.38 \times 10^{-4}$  mm<sup>3</sup>/Nm at 10 N (Fig. 4.53 (b)). This shows that the wear resistance of the Sn-Ag/CeO<sub>2</sub> system is better as compared to the Sn/CeO<sub>2</sub> system due to the presence of both CeO<sub>2</sub> and fine Ag<sub>3</sub>Sn particles.

## 4.4.6.4 COF

The variation of coefficient of friction (COF) with time for Sn and its composite is shown in Fig. 4.54. It is observed that the COF increases with time from a low value to a high value, and then arrives at a steady state.



Fig. 4.54: Variation of COF of Composites with Time for (a) C0, (b) C15, (c) D0 and (d) D15

The average values of COF for different samples as a function of loads are plotted in Fig. 4.55. The measured roughness for C0, C15, D0 and D15 are 4.04, 9.4, 0.75 and 2.53  $\mu$ m, respectively (Table 4.18). It is observed that the COF value of the composite samples is higher than that of the monolithic samples. It has been argued in the literature that wear rate depends on the value of microhardness but COF depends on the roughness values of the surface (Iwabuchi *et al.*, 1990). As load increases from 4 to 8N, the increase in COF is observed for the all the samples. In the case of the C15 composite sample, the COF increases at the highest rate due to its highest surface roughness. It is also noticed that for C15 there is a slight drop in the COF as the load exceeds 8 N.



Fig. 4.55: COF of the Different Samples as a Function of Load

This may be due to the fact that in case of C15, the soft Sn matrix and hard  $CeO_2$  particles from the coating easily may get easily mixed in due course of sliding and form mechanically mixed layer (MML). This type of MML formed at the wear surface will create a smoothening effect on the surface and decrease the friction. However, the COF of D0 and D15 is much lower than C15 and C0 due to their lower roughness and increases at all loads due to their better mechanical properties.

4.4.6.5 Worn Surface Morphology

(I) Sn/CeO<sub>2</sub> Samples

SEM micrographs of wear tracks of samples C0 and C15 at different loads are shown in Fig. 4.56. It is observed from Fig. 4.56 that in case of C0, the width of tracks increases with an increase in load. As the load increases from 4 to 6 N, the width of the wear track increases gradually and the wear track appears smooth due to the soft and ductile nature of Sn.



Fig. 4.56: SEM Micrographs Showing the Wear Track Morphology of C0 and C15 at Different Loads, (a) 4, (b) 6, (c) 8, (d) 10 N and (e) High Magnification Image of (d).

With further increase in load to 8 N, cracks nucleate on the subsurface, as shown in Fig. 4.56 (c). An excessive load of 10 N results in propagation of the nucleated cracks and ultimately chipping out of the tracks. The chipped regions get detached from the track which finally leads to the failure, as shown in Fig. 4.56 (d-e). This type of loose sheet or

flake like wear debris formation suggests the failure of coating by delamination wear (Park et al., 2007).

In case of C15, the width of the wear tracks is narrower than that of the same in C0. As the load is increased from 4 to 8 N, the wear track width increases but slowly as the CeO<sub>2</sub> particles present on the surface obstruct the plastic deformation of the matrix. When the load exceeds 8 N, it is noticed that loose CeO<sub>2</sub> particles are getting mixed with the matrix in due course of sliding (CeO<sub>2</sub> particles are shown in white color), as shown in Fig. 4.56 (d-e). This observation also supports the fact that the COF of sample C15 decreases at 10 N, as discussed in previous section 4.4.6.4.



Fig. 4.57: (a) High Magnification SEM Image of the Wear Track in C15 at 10 N, (b) Cross Sectional View of (a), and (c) the EDS Spectrum

To further confirm this phenomenon, a close examination of the plane and cross sectional view of the wear tracks is done in SEM (Fig. 4.57 (a-b)). The EDS analysis is also performed at the central region of wear track as shown in Fig. 4.57 (c). The plane view

SEM image shows that there is formation of a layer by layer structure in the wear track. The cross sectional SEM micrograph confirms the wavy pattern of this structure that is acquired during the mixing process. The EDS spectrum shows the presence of Sn, CeO<sub>2</sub>, and a little amount of Fe which is likely to come from the steel ball of the wear testing machine. The wear debris generated during sliding may go outside the wear track or be trapped by the two sliding surfaces and eventually undergo mechanical mixing process. Since this type of surface layer contains materials from both the counter surfaces, it is called mechanically mixed layer (Zhan *et al.*, 2004; Urena *et al.*, 2009).

#### (II) Sn-Ag/CeO<sub>2</sub> Samples

Figure 4.58 shows the SEM micrographs of wear tracks of samples D0 and D15 at different loads. It is observed that for sample D0, the width of the wear tracks increases with an increase in load. A closer look of the wear track of D0 shows that as the load increases from 4 to 8 N, the width of the tracks increases (Fig. 4.58 (a-c)). As the load is approached to 10 N, the matrix is enough strain hardened before the formation of cracks and ultimately failure occurs (Fig. 4.58 (d-e)). With an increase in the load, the sliding action causes the repetitive work-hardening, heavy plastic deformation, and shear strains in the worn surfaces giving rise to the formation of bigger cracks. This results in the spalling of the material in the surface layer as shown in Fig. 4.58 (e). The width of the tracks of D15 increases with loads. However, the tracks are much narrower as compared to the same in sample D0 as shown in Fig. 4.58. This shows that the presence of finer Ag<sub>3</sub>Sn and nano CeO<sub>2</sub> particle in this composite enhances the load bearing ability of the composite resulting in narrow wear tracks. It is also observed that during sliding, the composite sample D15 receives minor wear damage showing a mild wear upto 8N. However, with an increase in load to 10 N, very fine microcracks originate on the wear surface. These microcracks may further combine to form a bigger crack which eventually leads to failure.



Fig. 4.58: SEM Micrographs Showing the Wear Track Morphology of D0 and D15 at Different Loads, (a) 4, (b) 6, (c) 8, (d) 10 N and (e) High Magnification Image of (d).

This type of failure mechanism is a kind of fatigue failure mechanism and is dominant in Sn-Ag based solder (Sun *et al.*, 2006). It is noticed that unlike Sn/CeO<sub>2</sub> samples, there is a very small probability that the CeO<sub>2</sub> nanoparticles come out from the coating and take

part in mechanical mixing with a harder matrix and Fe from steel ball. Thus, formation of MML is not observed in case of sample D15.

## 4.4.7 Residual Stress Measurement

Pure Sn rich films deposited on copper substrate have a tendency to generate undesirable whiskers with time. These whiskers develop due to the build up of compressive stress in the coating caused by the formation of an intermetallic zone around Cu-Sn interface (Boettinger *et al.*, 2005). Therefore, the residual stresses of the selected composites electroplated on Cu substrates have been measured and plotted in Fig. 4.59.



Fig. 4.59: Residual Stress of Selected Samples

It is found that with an incorporation of  $CeO_2$  in the composites the distribution of stress occurs in such a way that the compressive stress gets minimized. The monolithic samples have negative residual stress, i.e., compressive stress while in case of composite samples the stresses are either less negative or positive (Fig. 4.59). The measured residual stress for C0 is -34.5 MPa which decreases to -2.7 MPa for C15, while for D0 the stress is -14.5 MPa which decreases to 4.5 MPa for D15. If we compare C15 and D15, it is observed that for C15 the stress is still compressive but with a lesser magnitude than C0 while for D15 the stress is tensile in nature. This may be explained in the following way. Nano  $CeO_2$  particles when incorporated inside the matrix, they create local stress fields around themselves.

This stress field distorts the lattice and this distortion perhaps hinders the free movement of copper atom inside tin matrix. Studies have shown that addition of hard ceramic particulates in a ductile matrix causes the formation of an annular plastic zone around the particulates because of high residual stresses around the particulates which affects the stresses present in the coatings (Lu et al., 2009). It has been reported in the literature that Ni-based coatings reinforced with Al<sub>2</sub>O<sub>3</sub> nanoparticles exhibit very high tensile stresses compared to monolithic matrix (Indyka et al., 2012). Recently, this kind of result has been verified by Bhattacharya and his co-workers, that the addition of an optimum amount of nano-ceramic particles inside the Sn matrix prevents the build up of compressive stresses in the coating (Bhattacharva et al., 2012). There is a clear indication that composite samples have a better resistance against the whisker growth. It is also noticed that the tensile zone is wider in case of Sn-Ag based solders. For samples C30 and D30, the stress completely lies in tensile region, which is obvious due to their porous microstructures that act as a channel through which the compressive stresses are dissipated quickly and tensile stress builds up. The CeO<sub>2</sub> particles also present in the agglomerated form in C30 and D30. It has been demonstrated in the past that highly agglomerated ceramic nanoparticles produce a significant increase in the residual stress (tensile state) of the coating (Ortolani et al., 2012). However, it is unclear why the sample D30 shows a dramatic increase in residual stress as compared to C30. A detailed characterization is needed to confirm this behavior.



Fig. 4.60: Line Scan Across the Substrate and Coating Interface for Selected Samples (a) C0, (b) C15, (c) D0 and (d) D15

Line scan analysis is further performed at the substrate and coating interfaces of the monolithic as well as selected composite samples (Fig. 4.60) which gives a clear understanding of the Cu-Sn diffusion in these samples. It is observed that the Cu-Sn interdiffusion region is quite wider in case of monolithic samples compared to the composite ones. For example, the interdiffusion distance in C0 is 50  $\mu$ m which decreases to 24  $\mu$ m in C15. While the interdiffusion distance in D0 is ~20  $\mu$ m which decreases to 4  $\mu$ m in D15. A large interdiffusion region in case of monolithic samples indicates a severe

diffusion of Cu in Sn while in composite samples, the nano  $CeO_2$  particles are hindering the diffusion of Cu and thus their interdiffusion zone gets narrowed. This observation indicates that the propensity for the growth of Cu-Sn intermetallic will be lesser in the composite samples compared to the monolithic samples. As a result, the residual compressive stress in the composite coating caused by the formation of intermetallics will be of lesser magnitude than that of the same in monolithic materials. This has been verified by the XRD stress analysis.

It is also noticed that the interdiffusion zone in D15 is narrower as compared to C15. This difference in behavior indicates that a large fraction of Sn in D15 is involved in the formation of Ag<sub>3</sub>Sn precipitates at the Cu<sub>6</sub>Sn<sub>5</sub> growth front and thus restricts the further growth of this compound. The result is consistent with the results of Ma *et al.* (2003). They have done thermodynamic calculation to determine the Gibbs free energy ( $\Delta$ G) of both Sn-Cu and Sn-Ag-Cu system. It is found from their calculation that the driving force for the formation of Cu<sub>6</sub>Sn<sub>5</sub> decreases with an addition of Ag in the Cu-Sn system. Therefore, the Cu<sub>6</sub>Sn<sub>5</sub> continues to grow at a faster rate in Sn/CeO<sub>2</sub> as compared to that in Sn-Ag/CeO<sub>2</sub> composites. The present investigation shows that the inclusion of nanoceramic particles can be a better option to mitigate the tin whisker growth in lead free solders and thus improving the coating life.

Chapter 5 – Summary and Conclusions

The present research work is divided into four parts, i.e., (i) synthesis of the pure tin coatings from different aqueous solutions and their microstructural characterization, (ii) effect of the pulse electrodeposition parameters, such as, current density, pH, amount of additive (Triton X-100), duty cycle, frequency, bath temperature, and stirring rate on the morphology evolution of tin coatings pulse electrodeposited from sulfate electrolytes, (iii) Synthesis of CeO<sub>2</sub> powders by high energy ball milling, and synthesis of Sn/CeO<sub>2</sub> and Sn-Ag/CeO<sub>2</sub> nanocomposite coatings containing different concentrations of CeO<sub>2</sub> by pulse electrodeposition, and subsequent microstructural characterization, and (iv) the investigation of different properties, such as, hardness, melting point, wear and corrosion resistance, electrical resistivity, and residual stress measurements of the coatings. Based on these studies, the following conclusions can be drawn:

## A study on pulse electrodeposition of pure tin from different aqueous solutions

(1) Pulse elctrodeposition of tin coatings on copper substrates is obtained from different aqueous baths, i.e., alkaline stannate bath (Bath 1), sulfate-based bath (Bath 2), stannous chloride-based bath (Bath 3), Methyl sulphonic acid bath (Bath 4) and pyrophosphate bath (Bath 5). Bath 3 has the highest current efficiency followed by Bath 2.

(2) The surface morphology of the coatings obtained from Bath 1 shows equiaxed grains, but at a very high current density  $(0.5 \text{ A/cm}^2)$  porous deposits are obtained. The deposits obtained from Bath 2 also show equiaxed grains and dendritic growth occurs at a current density of 0.5 A/cm<sup>2</sup>. The deposits obtained from Bath 3 show very big sized pyramid shaped grains due to its highest deposition rate among all the baths. Whereas, the deposits obtained from Bath 4 and 5 show non uniform and nodular grains.

(3) The microstructures of the coatings deposited from Bath 1, 2 and 3 show the presence of nodular and short length whiskers, while the deposited coating from Bath 4 and 5 show very thick and long whisker growth on the surface after ageing. The later observation can be related to the (211) and (321) texture responsible for the whisker growth in tin coatings.

## Pulse electrodeposition of pure tin from sulfate baths

(1) The surface morphology of the deposits depends on the electrodeposition parameters which modify the overpotential, directly or otherwise. The current density, which controls film nucleation and growth rate is found to be the most sensitive of all the investigated parameters which influences the morphology of the deposits drastically. The equiaxed grains which form at low current density ( $<0.3 \text{ A/cm}^2$ ) change to dendritic ones at 0.5 A/cm<sup>2</sup>.

(2) It is found that by changing the duty cycle, the nucleation rate and growth kinetics can be controlled. Pulse current produces the compact and uniform deposits with duty cycles upto 20%, while the porosity rises and the surface becomes rough when the duty cycle exceeds 20%.

(3) Low pulse frequency results in bigger sized grains, around 8-12 micron at 10 Hz frequency which decreases to 700 nm at 500 Hz. The current efficiency decreases with an increase in pulse frequency.

(4) The additive (Triton X-100) concentration also affects the morphology. It mainly improves the cathode surface plated finish and provides a uniform and equiaxed grain structure if it is added below its critical micelle concentration (i.e., 0.2 g/L).

(5) As the bath pH increases, the elctrodeposition current density is found to decrease. The grain size is found to decrease from 2560 to 1175 nm due to the increasing cathodic polarization as the pH value increases from -0.1 to 2. However, as the pH increases to 3, powdery deposits with irregular grains are developed due to the precipitation of stannic hydroxide.

(6) An increase in deposition temperature causes the grain size to increase continously from 1832 nm (room temperature) to 5530 nm ( $40^{\circ}$ C), as expected. Beyond which there

is no increase in grain size, however the solution conductivity and current efficiency decrease drastically due to the oxidation of Sn ions in solution bath.

(7) Agitation of the solution provides fresh solution containing metal ions to cathode and thus increases the deposition rate upto 300 rpm and then decreases due to the turbulent flow of the solution where the metal ions fly away from the electrode. A drastic increase in grain size beyond 300 rpm is caused by a decrease in cathodic overpotential with rotation.

### Development of lead free Sn/CeO<sub>2</sub> and Sn-Ag/CeO<sub>2</sub> composite solders

(1) The nanosized  $CeO_2$  particles are successfully produced using a high energy ball milling technique. The crystallite size of  $CeO_2$  particles calculated from the XRD pattern lies in the rage of 20-30 nm which agrees well with the TEM observation.

(2) Lead free Sn and near eutectic Sn-Ag composites reinforced with ball milled  $CeO_2$  nano particles have been successfully produced using pulse electrodeposition technique for the first time.

(3) The incorporation of CeO<sub>2</sub> particles in the matrix increases with an increasing CeO<sub>2</sub> concentration in the electrolyte upto 15 g/L, and then decreases due to the agglomeration of CeO<sub>2</sub> particles in the bath.

(4) The best morphology of the composites is realized with dispersing 15 g/L CeO<sub>2</sub> in the electrolytic solution that gives  $5.77 \text{ wt\% CeO}_2$  in Sn matrix and  $11.52 \text{ wt\% CeO}_2$  in Sn-Ag matrix.

## Property evaluation of developed composite solders

(1) The hardness of  $Sn/CeO_2$  and  $Sn-Ag/CeO_2$  composites with maximum amount of monodispersed CeO2 are 78 Hv and 138 Hv, respectively, indicating a tremendous

increase over the hardness of pure Sn (11 Hv) and Sn-Ag alloy (18 Hv) deposited under the same condition. The higher hardness of Sn/CeO<sub>2</sub> composites as compared to pure Sn can be attributed to the refinement of grain size and dispersion strengthening of the matrix by CeO<sub>2</sub> particles. The higher hardness of Sn-Ag/CeO<sub>2</sub> composite as compared to Sn-Ag alloy can be attributed not only to the grain size and dispersion strengthening effect, but also to the refinement of the Ag<sub>3</sub>Sn by CeO<sub>2</sub> particles.

(2) The density of  $Sn/CeO_2$  and  $Sn-Ag/CeO_2$  composites decreases with an increase in concentration of  $CeO_2$  in the electrolyte due to the formation of porosities in the composites. The observed density is minimum for both the composites when they are prepared from an electrolyte containing 30 g/L CeO<sub>2</sub>. A very low density of  $Sn/CeO_2$  composite when deposited from the electrolyte containing 30 g/L CeO<sub>2</sub> is due to the formation of both porosities and cracks.

(3) The melting point of the coating is minimum for both  $Sn/CeO_2$  and  $Sn-Ag/CeO_2$  composites when prepared from the electrolyte containing 15 g/L CeO<sub>2</sub>, and it is found to be lower than the monolithic alloy by ~2.6 °C for Sn-Ag/CeO<sub>2</sub> composites while there is a minor change of ~1 °C for Sn/CeO<sub>2</sub> composites, which indicates its possibility to use without any change in the existing soldering procedures.

(4) There is a rise in the resistivity of the composite matrix compared to the monolithic materials. However, the resistivity of the composites falls within the usable limits as reported for other Sn and Sn-Ag based composites, used for electrical contact applications.

(5) The addition of reinforcement in the Sn matrix also improves the wear resistance, which ultimately increases the coating life for application. The wear resistance of the composite coatings is better than that of the monolithic materials and it is associated with an enhancement in the microhardness of the composite. The wear resistance of the Sn-Ag/CeO<sub>2</sub> composites are far better than Sn/CeO<sub>2</sub> composites due to the presence of very fine Ag<sub>3</sub>Sn along with CeO<sub>2</sub> nanoparticles.

(6) At all loads studied here, monolithic materials exhibit the lower coefficient of friction compared to the composite coatings due to the higher roughness values of composites. The coefficient of friction is found to increase as loads are increased from 4 to 10 N for all the samples, except one Sn/CeO<sub>2</sub> composite This particular composite shows a reduction in coefficient of friction at a load of 10 N and this can be attributed to the formation of mechanically mixed layer in this system, while no such layer is observed for Sn-Ag/CeO<sub>2</sub> composite.

(7) The composite samples prepared from the electrolyte containing 15 g/L CeO<sub>2</sub> exhibit the best corrosion resistance among all the samples tested. However, it is also noticed that the corrosion resistance is degraded in case of the composite samples prepared from electrolyte containing more than 15 g/L CeO<sub>2</sub> due to the presence of significant amount of porosities and cracks in these samples, which increases the localized corrosion. It is also observed that Sn-Ag/CeO<sub>2</sub> composites posses the better corrosion resistance as compared to Sn/CeO<sub>2</sub> composites. The presence of fine Ag<sub>3</sub>Sn compounds in Sn-Ag/CeO<sub>2</sub> composite increases the passivation of the matrix which acts as a noble barrier in addition to CeO<sub>2</sub> against corrosion propagation.

(8) It is observed that an incorporation of CeO<sub>2</sub> nanoparticles in the composite matrix reduces the compressive stresses developed in the coatings. The residual stresses of monolithic materials are negative, i.e., compressive in nature. For Sn/CeO<sub>2</sub>, the residual stress is less negative for C15 (Sn/CeO<sub>2</sub> composite deposited from the electrolyte containing 15 g/L CeO<sub>2</sub>) compared to pure Sn, while in case of D15 (Sn-Ag/CeO<sub>2</sub> composite deposited from the electrolyte matrix is a whisker growth resistant behavior of these composite coatings. A decline in residual stress indicates that the driving force for whisker growth can be minimized by choosing an optimum concentration of ceria and thus, the coating life can be improved.