

CHARACTERIZATION OF ZINC BASED HIGH TEMPERATURE SOLDER ALLOYS WITH CHROMIUM AND MOLYBDENUM ADDITIONS

By

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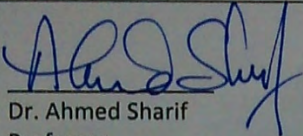
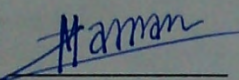
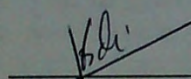
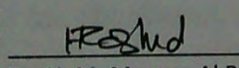
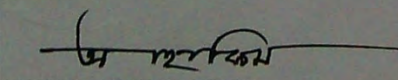
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Dedicated to My Parents

ABSTRACT

Initiative of development and characterization of Pb free high temperature solders was taken. Two systems such as Zn-xMo (x= 0.4, 0.6 and 0.8 wt% Mo) and Zn-xCr (x= 0.2, 0.4 and 0.6 wt% Cr) were chosen for this study. Samples of the selected compositions were fabricated through casting in a permanent metal mold. Their microstructural, thermal, mechanical and electrical characteristics were determined using several analytical techniques such as Scanning Electron Microscope (SEM), Differential Thermal Analyzer (DTA), X-Ray Diffractometer (XRD), Thermomechanical Analyzer (TMA), Universal Testing Machine (UTM), Hardness tester, Conductivity Meter etc.

Experimental findings revealed that with the addition of Mo and Cr particles grain refinement occurred in both Zn-xMo and Zn-xCr systems which was evident in the scanning electron micrographic images. Energy-dispersive X-ray spectroscopy (EDS) spots in several zones of the microstructure confirmed the presence of Mo and Cr particles throughout the respective structures. XRD analysis showed a very little or no shift in the peak pattern compared to standard Zn pattern indicating no new phase formation. However, crystallite size calculation using Scherrer equation showed that, average crystallite size decreases with increasing Mo content and it ranged from around 34.0-29.4 nm in case of Zn-xMo system, while the average crystallite size of Zn-xCr system ranged between 29.7 and 28.8 nm. Brinell hardness showed an incremental trend with increasing Mo content. Similar results were obtained in Zn-xCr system. Brinell hardness number of Zn-xCr increased from 33.98 in Zn-0.2 Cr to 42.74 in case of Zn-0.6 Cr alloy. Similarly, hardness increased from 29.71 to 41.28 in case of Zn-0.4 Mo to Zn-0.8 Mo respectively. Tensile strength of unalloyed zinc increased from 31.09 MPa to 33.04 MPa when alloyed by 0.8% Mo. In a similar manner, strength of Zn-Cr solders increased from 40.53 to 47.07 MPa due to an increase in 0.4% Cr than that of the former. Fractographic analysis of the tensile fracture surfaces with SEM indicated mixed (neither completely ductile nor completely brittle) fracture mode of both Zn-xMo and Zn-xCr systems. Coefficient of thermal expansion (CTE) of Zn-Cr system was found to vary from $4.5\text{--}5 \times 10^{-5}$ (1°C) while in Zn-Mo system it was $4.14\text{--}2.64 \times 10^{-5}$ (1°C). Electrical conductivity of both Zn-xMo and Zn-xCr decreased with increasing Mo and Cr contents respectively. The relative conductivity of Zn-xMo and Zn-xCr varied from 27.35 to 26.55 and 25.3 to 22.7 %IACS (International Annealed Copper Standard) respectively in the selected composition range. DTA results suggested that onset of melting started at temperature below the melting temperature of pure Zn. It was found that, the onset temperature of melting of all three compositions of the Zn-xMo system was around 416°C whereas, the finishing temperature of melting was around 423°C indicating a melting range of around 7°C . On the other hand, DTA graphs exhibited that, the onset of melting of the Zn-xCr alloys started at around 412°C and it finished near about at 418°C showing a melting/solidification range of about 6°C .

From the experimental findings it can be said that Zn-xMo as well as Zn-xCr systems might be promising candidate for high temperature solders in replacement of Pb based solders.

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List of Abbreviations

SEM	Scanning Electron Microscope
EDS	Energy-dispersive X-ray Spectroscopy
DTA	Differential Thermal Analyzer
XRD	X-Ray Diffractometer
TMA	Thermomechanical Analyzer
UTM	Universal Testing Machine
IACS	International Annealed Copper Standard
XRF	X-ray Fluorescence
CTE	Coefficient of Thermal Expansion
HB	Brinell Hardness
IC	Integrated Circuit
IMC	Intermetallic Compound
HCP	Hexagonal close-packed
BCC	Body-centred Cubic
FCC	Face-centred Cubic

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Chapter One

Introduction

The discovery of microelectronic devices revolutionized the world. However the performances of these devices are related to the generation of heat and associated with thermal degradation. So far, there are several systems developed to sustain a high temperature and to overcome the thermal degradation.

High temperature soldering has become a part and parcel for electronic industries. For various reasons, the high temperature solder have wide applications to the aircraft, space satellite, automotive, and oil/gas well exploration [1–4]. During the recent years scientists as well as technological researchers have been investigating to find a suitable Pb- free and Cd-free soldering alloy that could be used in high temperature soldering [5]. However, during solder design it is essential to choose proper melting temperature region since, the solder has to sustain higher temperature without melting until the last step of assembling process. Consequently, the solidus temperature of high temperature solder should be designed 20–25°K higher than the maximum operating temperature, and the liquidus line should be at least 20–40°K lower than the minimum temperature used in assembling process and service [6]. To meet the design requirements, the solidus temperature for the high temperature solder should be above 643°K and the liquidus temperature should be below 673°K. In this regard, Zn-based alloys are the reasonable candidates for the high temperature solder.

Lead containing solder alloys have been utilized for a very long time in microelectronic packaging applications due to their several advantages including good wettability, high ductility, and low shear modulus. Especially in high temperature applications, the most common solder alloys are Pb–Sn alloys containing 85–97%Pb because of several favorable characteristics such as melting temperature range (300–314°C), low cost, excellent wettability, and workability [7–8]. However, global concerns over the environmental impacts and human health issues due to toxicity of Pb bearing solder alloys [9–10], researchers are seeking for alternative Pb-free solder alloys which will fulfill the requirements of high temperature solder alloys and be environment friendly as well. Although with extensive research in the area of developing high temperature Pb-free solder thousands of paper have been published in literature, there is still no solder alloy which can completely replace Pb-based high temperature solders [11–12]. Consequently, finding a proper substitute for Pb-

based high temperature solders has become a major issue at present. Several prospective candidates, such as Au–Sn [13-17], Bi-based alloys [18-20], Sn–Sb-based alloys [21], and Zn-based alloys have been reported [22-28]. It has been proposed that Zn-based solder alloys may be a replacement of high Pb containing solders.

Solder alloys, used in high temperature applications such as die attachments, are regularly exposed to several thermal conditions. Incompatibility in coefficient of thermal expansion induces thermal stress which may lead to premature failure. In order to overcome these severities the high temperature solder alloys must have suitable thermal, mechanical, and electrical properties. High temperature solders which are used as die-attach materials, are required to be soft for the relaxation of thermal stress, and should be thermally conductive for effective heat dissipation [29]. Other typical requirements of high temperature solders are melting range in 270–350°C [30], good electrical conductivity, good mechanical properties, and fluxlessness. Among the high temperature Pb-free solder candidates gold-based alloys are highly expensive, while Au–Sn alloys form brittle intermetallic compounds and thus limit the use as high temperature solder [31-32]. Bismuth-based alloys, especially Bi–Ag-based alloys also become brittle due to the similar reason and exhibit relatively low electrical/thermal conductivities [33]. In contrast, Zn-based alloys, especially Zn–Sn and Zn–Al, are more ductile compared to others as no intermetallic compounds are formed in these alloys, have proper melting range, and good thermal/electrical conductivities [34-35]. Moreover, these alloys are comparatively inexpensive. Numerous research works have been accomplished on Zn-based high temperature solder alloys and published in literature.

There are some drawbacks for Zn based alloys used as high temperature solders. Firstly, Zn is a highly corrosive metal and secondly, it exhibits poor wetting behaviour due to the high oxygen affinity. Lastly, the microstructure of the Zn alloy is very sensitive to soldering temperature and relatively unstable compared with the high lead content solders [36]. The control of microstructure is the main highlighted area of future work which is required for a more comprehensive understanding of the lead-free Zn-based solders performance [37].

Pure Zn is proposed as alternative since it has excellent thermal shock resistance between –40°C and 300°C and low cost [38]. However, being hcp (hexagonal close-packed) metal Zn is brittle and possesses poor resistance to oxidation; hence caution must be taken in selecting pure Zn solder. As a result, addition of trace elements was proposed to enhance ductility and oxidation resistance of pure Zn solder for high temperature applications [39]. An

investigation was carried out by Park et al. [40] to elucidate the suppressing effect of trace elements on the reactions at interface of solder and Cu substrate by adding Ca, Mn, Cr, and Ti to Zn. It was revealed that thickness of IMC layer in the interface of Zn-0.1%X (X= Ca, Mn, Cr, or Ti) solder and Cu substrate was significantly smaller than that of pure Zn solder.

This study demonstrates the effect of small addition of Mo and Cr particles in the matrix of Zinc. As per our knowledge, no research work has been performed based on Zn-Mo solder till now. The addition of fine metallic powders is supposed to lead zinc towards superior microstructural and mechanical properties which may be a suitable alternative for Pb based high temperature solder alloys.

Chapter Two

Literature Review

Joining metals with tin-lead solders is a technology that has been in use since the early Bronze Age. Ancient cultures used these solders in the manufacture and repair of cooking utensils and metal tools. The Romans used an alloy of lead and tin for sealing their water pipes. Through the ages the process continued to be used primarily by craftsmen in the production of jewelry and artifacts. During the industrial revolution this use was greatly expanded with the development of portable torches and electricity to power tools facilitated soldering irons. These include applications such as plumbing connections, sealing of food and water containers and fabrication of heat exchangers such as automobile radiators.

While advances in transistors, resistors, capacitors, diodes, and especially integrated circuits (IC) have revolutionized the world, these devices are of very little value as individual components. For these devices to be of use, they must be electrically connected to each other and to mechanical devices. The invention of the transistor in 1947 revolutionized the semiconductor industry as it enabled the size of electronic products to decrease considerably. In order to achieve high functionality and high performance in products, the integrated circuit technology was developed in the early 1960's to integrate several transistors on a single semiconductor chip [41]. When the packaged ICs are interconnected to other electronic components, such as transistors and capacitors on a system board, it is called the assembly process. This is always involved at the system level during the packaging and assembly processes.

Various solder alloys have been used in soldering technology. Among them Sn-37Pb is widely used mainly because of its low melting temperature. This solder alloy provides many advantages over other solder alloys. But because of lead toxicity research has been made to develop lead free solder alloys.

As one of the primary components of eutectic solder, lead (Pb) provides many technical advantages of Sn-Pb solders. Pb reduces the surface tension of pure tin, which is 550 mN/m at 232°C, and the reduced surface tension of 63Sn-37 Pb solder (470 mN/m at 280°C) facilitates wetting [42]. As an impurity in tin, even at levels as low as 0.1 wt.%, Pb prevents the transformation of white or β -Sn phase (body-centered tetragonal structure) to grey or α -Sn

phase (face-centered cubic structure) upon cooling. The transformation, if it occurs, results in a 26% increase in volume and causes loss of structural integrity to the Sn [43].

Pure Sn is also prone to whisker growth. Sn whisker, β -Sn is a single crystal growth in form of fine wire [44]. Longer whiskers may cause shorts in circuits. Pb is able to suppress whisker growth in Sn so that no whisker growth is encountered in Sn-Pb solder [45]. Pb serves as a solvent metal, enabling the other joint constituents such as Sn and Cu to form intermetallic bonds rapidly by diffusing in the liquid state.

2.1 High Pb Solder

Conventionally, the most common high-temperature solders have been Pb-Sn alloys containing 85–97 wt.% Pb [46]. High-lead content solders are currently being used worldwide as high-temperature solders in power semiconductor packages [47]. Typical compositions of Pb-Sn solders are Pb-5Sn and Pb-10Sn, which have melting ranges of 300–314°C and 268–301°C, respectively [48-50]. Generally speaking, the microstructures of the high-lead content solders are quite stable and the microstructures do not obviously change during aging at elevated temperatures [51]. This stability, coupled with the lack of brittle intermetallic compounds (IMCs) in the matrix, makes high-lead content solders be used in a wide range of applications [50, 52-54]. Before introducing alternatives to leaded solders, it is believed useful to review research results on high lead Pb-Sn solder alloys, concentrating on two main issues: firstly, the effect of Sn concentration on the interfacial reaction between the solder and substrate and secondly the mechanical properties and reliability of the solder joint. The effect of Sn concentration on the interfacial reactions is one of the crucial aspects in high temperature soldering and mechanical performance of the joint [55]. In the case of high Pb solders, the concentration of Sn has a very strong influence on the formation and growth of interfacial intermetallics at the solder/substrate interface [56]. Wang et al. [56] previously reported that the concentration of Sn in Pb-xSn alloys greatly improved wettability on Cu substrates. These Pb-Sn alloys are also prone to massive spalling of Cu_3Sn , an IMC that forms in the soldering reaction between high-Pb solders and Cu substrates [57].

The spalling phenomenon was attributed to the high interfacial free energy between Cu and Cu_3Sn , which is a result of a loss of chemical adhesion at the interface [57]. Thermodynamic analysis of interfacial free energy with and without spalling after solid-state aging demonstrated that spalling is more stable, the spalling starts with the formation of small

isolated Pb-rich regions between the Cu_3Sn layer and the Cu [58]. These Pb-rich regions grow larger with increasing reaction times and connect with each other to form a continuous layer between the Cu_3Sn and Cu. A large amount of the Sn within the solder is consumed by the formation of intermetallic compounds very quickly. Due to a decrease in the Sn concentration, Cu_3Sn loses local thermodynamic equilibrium with Cu, and the Cu_3Sn is driven away allowing the high-lead solder phase to come into direct contact with Cu. The spalling progresses until the Pb-rich layer becomes continuous. The spalling process strongly depends on the Sn concentration in the solder. For low Sn concentrations (0.5 and 1 wt.%), the massive spalling occurred after 20 min, but for higher Sn (3 and 5 wt.%), the massive spalling was not completed even after 600 min [59]. It is proposed that the Pb atoms penetrating the Cu_3Sn layer through the grain boundary result in a slower spalling rate of Cu_3Sn [59].

As mentioned above, a sufficient supply of Sn in high-lead solder is required for the continuous chemical reaction during solid-state aging, and this is dependent on the solder composition. Besides Pb–Sn solder/Cu reactions, interfacial reactions will also occur between Pb–Sn solders when Ni or Ag is present in the substrate. The types of Ni–Sn intermetallic compounds formed in high-Pb/Ni soldering reactions are also closely related to the Sn concentration [58]. When the Sn concentration was 5 wt.%, Ni_3Sn_4 formed first, and then Ni_3Sn_2 formed between the Ni_3Sn_4 and Ni. When the Sn concentration decreased to 3 wt.%, the first compound formed was Ni_3Sn_2 , and then Ni_3Sn_4 was obtained between Ni_3Sn_2 and Ni as the interface reaction progressed. When the Sn concentration was 1 wt.%, only Ni_3Sn_2 formed. Similarly, as revealed by Chen et al. [59], the Sn concentration in Pb–Sn solder significantly affected the interfacial reactions between molten high-Pb solders and Ag at 350°C. Ag_3Sn phase is formed at the molten solder/Ag interface when the Sn concentration of the solder is 10 wt.%. When the Sn concentration decreases to 5 wt.% the reaction product changes to the Ag_4Sn phase. At a Sn concentration of only 3 wt.%, the Ag_4Sn phase is firstly produced, but disappears afterwards, with the entire layer converting to the Ag solid solution phase (94.7 at.% Ag– 5.3 at.% Sn) as the reaction progresses.

The intermixing phenomenon of Pb–5Sn solder bumps (95 μm in diameter) and Sn–37 Pb pre-solder on Ni metallization in flip– chip assembly after multiple reflows (up to 10) at 240°C has also been investigated [60]. The height to which the molten pre-solder climbed along the solid high-lead solder bump increased with an increasing number of reflows. The

molten pre-solder was able to reach the substrate/Pb–5Sn interface after 3–5 reflows. The molten solder also dewetted along the interface as the number of reflows increased, which can be attributed to volume shrinkage during solidification. This volumetric shrinkage occurs due to the significant density increase of the solder alloy during liquid cooling and solidification [61]. In addition, after being subjected to ten times reflow, the phase at the outer rim of the interface along the chip changed from Ni_3Sn_4 to $(\text{Cu}_{0.6}\text{Ni}_{0.4})_6\text{Sn}_5$ as enough Cu atoms diffused into the interface, while additional reflows did not change the interfacial reaction product on the substrate side [61].

2.2 Mechanical Properties and Reliability

As the trend for miniaturization in chip scale increases, the solder joints that connect the chip and the substrate can be expected to become smaller and smaller. The increasing electrical power density requires solder joints with excellent mechanical properties and high reliability, because higher electric power results in higher heat flux and, therefore, leads to a higher temperature for chip operation. As a result, the thermal expansion mismatch between the chip and the substrate grows larger due to differences in their coefficients of thermal expansion (CTE) and the accumulated strain become more severe [61]. Therefore, the development of new solder systems with generally reduced CTE is required to address serious reliability concerns.

A great number of failures of high temperature solders can be attributed either to creep or to a combination of creep and fatigue. Understanding the time-dependent plastic deformation of high temperature solders is one of the pre-requisites for employing these solders in the manufacture of electronic products. In the case of solders, the time-dependent deformation, i.e. creep mechanisms, play an important role because of the high homologous temperatures involved in the range of $0.5T_m < T < T_m$, where T_m is the melting point in Kelvin. The high temperature creep behavior of Pb–5In, Pb–5Sn–2.5Ag, Pb–3Sn–2Ag–2In was described by Schoeller et al. [62], and it was revealed that these are alloys located in the dislocation creep regime, where the stress exponent varies between 3 and 8. The variation of the stress exponent with temperature is remarkable. This plot is segmented into three regions based on the rate controlling mechanism for dislocation creep. A transition in the controlling climb mechanism from pipe diffusion to faster lattice diffusion was observed around $0.7T_m$. However, creep of Pb–10Sn was rate limited by viscous solute drag rather than dislocation climb due to the greater concentration of Sn in Pb.

In summary, high lead solders with a Pb content of more than 85 wt.% are still widely used for high-temperature applications. Comprehensive studies of the various properties of high lead solder have been reported, such as the stability of the microstructure and its impact on mechanical properties, and the effect of Sn concentration on interfacial reactions. Furthermore, Young's moduli, creep properties, plasticity, fatigue behavior, etc. have also been systematically studied and unified constitutive relationships developed by many researchers. Currently this quantity and quality of data is not present for high-temperature lead-free solder alloys, although, there are sufficient results to make some conclusions about the relevant properties of these alloys. The research on high-lead solders has evolved to address the issues relevant to the use of the solder during manufacture and service of assembled components. These issues include microstructure and strength characterization, interfacial behavior and reliability as well as the thermal-fatigue life.

2.3 Environmental and Health Perspectives

In addition to technology advances, another strong driving force affecting the industry is the environmental and health/safety issue [63]. Within the electronic packaging and assembly industry, the top four issues related to global environment and public health are:

- ✓ Ozone-depleting CFC elimination
- ✓ Wastewater handling
- ✓ Volatile Organic compound (VOC) control
- ✓ Pb control

Chlorofluorocarbons (CFCs) have been one of the most useful chemical groups serving several major industries effectively for many years. They are used as a coolant in refrigeration and air-conditioning, a foaming agent for plastic-foam metals, a propellant in aerosols, and a cleaning solvent for electronics and metal industry. Both government and industry have recognized the threat of ozone depletion and its relation to CFCs since the 1970s. Wastewater from the cleaning step of the electronic packaging and assembly process needs attention for not only the environmental effect but also for economic reasons. The concerns about contamination can be grouped into several areas [63]:

- PH
- Temperature
- Heavy metal
- Biological oxygen demand (BOD) and chemical oxygen demand (COD)

- Suspended solids
- Toxic chemicals or hazardous substances
- Pb content

The availability of a closed-loop water recycling system for a cleaning process makes in-process wastewater which needs disposal handling to a minimum. Most commercially available systems are capable of treating the bulk of in-process water for use as rinse supply and of removing waste without facing routine wastewater discharge problems. Solder reaction is one of the oldest metallurgical processes for joining metal parts. Today, the use of solder in modern microelectronic technology is ubiquitous [64]. Traditionally, binary Sn–Pb solders are extensively used in electronic packaging. With the advent of area array packaging concepts (flip chip and ball grid arrays); usage of solders in die attachment is increasing sharply. The solder ball melts and forms a joint between the solder ball pad of the substrate and the ball itself. The performance of solder alloys has become one of the crucial roles in die attach application.

2.4 Environmental and Health issues with Lead

Pb has been used in electronic applications for more than 50 years. In the U.S., consumer electronics account for roughly 40% of the Pb found in landfills. As 315 million computers became obsolete between 1997 and 2004, nearly 1.2 billion lbs. of Pb potentially entered the waste stream [65]. Pb is a highly toxic metal, particularly dangerous when ingested by inhaling fumes (while melting, working with, or recycling it) or through drinking water. Fig. 2.1 schematically represents the path of Pb from electronic scrap to the human body through drinking water [49]. The following reactions are the mechanisms for Pb dissolution into water [66]. Pb becomes a water soluble compound by acid rain. The solubility of some Pb compounds in water in g/l at different temperature is shown in table 2.1.

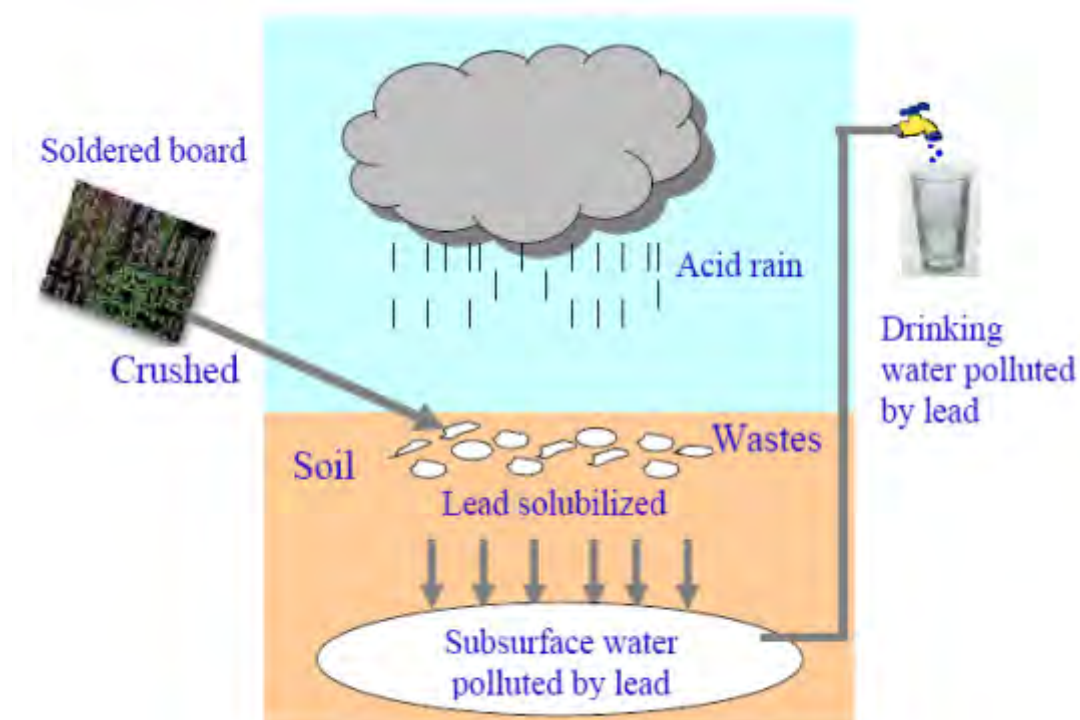


Fig. 2.1: The path of Pb from soldered board to the human body via drinking water

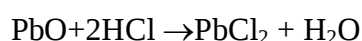
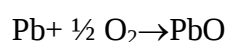


Table 2.1 Solubility of Pb compounds in water in g/l at different temperature

Compounds of Pb	Solubility in water (g/l) at temperature (°C)		
	10°C	20°C	30°C
PbSO ₄	0.035	0.041	
Pb(NO ₃) ₂	483	565	1150
PbCl ₂	6.7	9.9	26.2

When Pb accumulates in the body over time, it can have adverse health effects. Lead binds strongly to proteins in the body and inhibits normal processing and functions of the human body. Nervous and reproductive system disorders, delays in neurological and physical development, cognitive and behavioral changes, reduced production of hemoglobin resulting

in anemia and hypertension [67] are some of the adverse effects of lead on human health. When the level of lead in the blood exceeds 50 mg/dl of blood, lead poisoning is considered to have occurred [68]. 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. Besides the environmental and toxic issues, Pb poses a radioactivity problem. Conventional Pb-containing solder contains a certain amount of radioactive Pb [69]. Since the radioactive Pb possesses a long half-life, it produces a particle during decay series, which frequently causes the failure of functional devices, particularly in memory chips [70-71]. This is often called soft errors in DRAM and charge-coupled devices (CCDs). For example, a particle generates electron-hole pairs through elastic collisions during its penetration into Si. If the charge density in the capacitor of a memory cell changes, it results in a functional failure. Therefore, strict control of the amount of radioactive Pb or complete Pb removal is necessary especially for the application in high density memory chips.

2.5 Legislation and Directives

Due to environmental and health issues, the usage of Pb-bearing solders have been eliminated in the electronic industry. It is because Pb or Pb-bearing compound, as cited by the Environmental Protection Agency (EPA) of the US, is one of the top 17 chemicals posing the greatest threat to human beings and environment [72]. Some corresponding law or directive are planned in European Union (EU), such as WEEE (Waste Electrical and Electronic Equipment), which shall come into force at December 2008 and RoHS (Restriction of certain Hazardous Substances), which is effective since 1st July 2006 [73]. In addition, many companies have publicly announced their corporate policies on development and implementation of environmentally friendly technologies for a variety of reasons: to sustain resources, gain market-share, avoid trade barriers, or comply with potential legislation. In the electronic industry, the Pb generated by the disposal of electronic assemblies is considered as hazardous to the environment. In Japan, the legislation prohibiting Pb from being sent to landfills and other waste disposal sites is already in place. In the US, legislations in limiting the use of Pb have been introduced in both the Senate and the House of Representatives. The legislation includes (a) H. R. 2922, The Lead Based Paint Hazard Abatement Act of 1991, (b) S. 391, the Lead Exposure Reduction Act of 1991, and (c) H. R. 3554, the Lead Exposure Act of 1992 [74]. Although these bills have not been passed yet, it is likely that some form of bills will be passed in the future. However, due to environmental and health concerns about the toxicity of lead, using of lead-containing solders for soldering in electronics is likely to be prohibited in the future. By fulfillment of related directives, many lead-free solder techniques

are developed nowadays [75]. The lead-free solders have been developed so far in Sn rich binary and ternary alloy mainly. Binary alloys included Sn-Cu, Sn-Ag, Sn-Bi and Sn-Zn etc. Ternary alloys included Sn-Ag-Cu, Sn-Ag-Zn, etc.

2.6 The Role of Pb in Sn-Pb Solders

It is important to know the functions or properties of Pb in the Sn-Pb solder. Firstly, Pb provides the ductility in the Sn-Pb solder [76]. Secondly, Pb lowers the surface tension of pure Sn from a value of 550mN/m at 232°C to the value of 470 mN/m at 280°C for Sn- 37Pb [77]. Thirdly, Pb forms a eutectic alloy with the composition of 63wt%Sn- 37wt%Pb so that it has a low melting temperature at 183°C in the Sn-Pb phase diagram as shown in Figure 2.3 [78]. Finally, Pb prevents the transformation of white or β -Sn phase (body-centered tetragonal structure) to grey or α -Sn phase (face centered cubic structure), also referred as tin pest, upon cooling past 13°C. This transformation leads to 26% increase in volume and induce cracking in the Sn structure. Pure Sn is also prone to whisker growth. Sn whisker, β -Sn, is a single crystal growth in form of fine wire. Longer whiskers may cause shorts in PCBs. Pb is able to suppress whisker growth in Sn so that no whisker growth is encountered in Sn-Pb solder [74].

2.7 Required Characteristics for lead-free solders

Most Pb-free solders are Sn-based eutectic alloys of noble metals, such as Ag, Cu and Au. A eutectic alloy is used because it has a single and low melting point. Therefore, the entire solder joint will melt or solidify at eutectic temperature; otherwise, partial melting or solidification may occur. The main requirements for an alternative Pb-free solder alloy are:

- ❖ Low melting point: The melting point should be low enough to avoid thermal damage to the assembly being soldered and high enough for the solder joint to bear the operating temperatures. The solder should retain adequate mechanical properties at these temperatures.
- ❖ Wettability: Bonding between the solder and the metal surface is formed only when the solder wets the metal pad surface. As a result, a proper intermetallic compound layer (IML) is formed and acts metallic joining. Hence, this IML determines the solder joint strength.
- ❖ Availability: There should be adequate supplies or reserves available of candidate metals. Sn, zinc (Zn), copper (Cu) and antimony (Sb) are available whereas there is a limited supply of indium (In).

- ❖ Cost: Manufacturers of electronic systems are unlikely to change to an alternative solder with an increased cost unless it has demonstrated better properties or there is legislative pressure to do so.

Although several commercial and experimental Sn-based Pb-free solder alloys exist, none can meet all the above requirements, if the melting point of the candidate Pb free alloy is required to be very close to that of Sn-Pb. Third and fourth elements are added into the binary Pb-free solder to reduce the solidus temperature; however, most are not effective to reduce the liquidus temperature. Besides, a lot of brittle IMCs will form in the Sn matrix due to the variations of third and fourth additives. As a result, these Pb-free solders are more complicated system. Metallurgical alloying and microstructural evolution and their relationships to the soldering process and service conditions are critical scientific bases from which to develop new Pb-free solders. Although some Pb-free solders have been in use for years, there are no obvious replacements for the traditional Sn-Pb alloys. Still technical data as well as practical application information are continued to be generated at a reasonably rapid pace. It is anticipated that the implementation of the use of Pb-free solders in the electronic assembly is imminent. The selection of a Pb-free solder composition should be determined by the needs of the performance level of a specific application [79]. Under severe operational environments, such as under-the-hood automobile applications, require the Pb-free solder joints with a superior performance and high reliability [80]. As a result, composite solders have been developed with enhanced strength and desired properties. Apart from the development of proper alloy compositions for the new solder systems, suitable fluxes and assembly process for Pb-free solders are also needed and considered [81]. All alternatives to the standard eutectic Sn-Pb solder investigated so far are based on Sn alloys with a Sn content significantly over 90 weight percent in combination with Cu, Ag, Sb, Bi or Zn. Among the binary alloys, Sn/0.5-0.8% Cu and Sn/3-4%Ag play a dominant role. Some possible binary solders are shown in Table 2.2. The melting point of Sn-0.7%Cu is around 227°C. The eutectic Sn-Ag solders exhibit melting points in the range of 220-221°C, which is more than 30°C above the melting point of the standard eutectic Sn-Pb solder. At present, near-eutectic Sn-Ag-Cu alloys are leading candidate solders. The ternary-eutectic composition is now thought to be close to Sn-3.5Ag-0.9Cu (wt.%), with a melting point of 217°C. The Japan Electronics and Information Technology Industries Association (JEITA) recommended the Sn/3.0Ag/0.5Cu alloy [82]. The National Electronics Manufacturing Initiative (NEMI) Lead-free Assembly Project recommended the Sn/3.9Ag/0.6Cu ($\pm$ 0.2 per cent) alloy [26].

However, the high melting point of this alloy (217°C) as compared to the traditional Sn-37Pb solders (183°C) is still an issue in electronic packaging. Some other ternary alloys are shown in Table 2.3.

Table 2.2: some possible Pb-free binary candidates

System	Known composition	Alloy price (US\$/kg)	Melting temperature, °C	Remarks
Sn-Ag	96.5Sn/3.5Ag	13.90	221	Good thermal fatigue resistance
Sn-Sb	95Sn/5Sb	8.36	232-240	High melting point
Sn-Bi	58Bi/42Sn	7.79	138	Suitable for low temperature application
Sn-In	48Sn/52In	132.5	120	Expensive
Sn-Cu	99.3Sn/0.7Cu	7.66	227	Favorable price
Sn-Zn	91Sn/9Zn	7.99	199	Problem of oxidation, Strong dross formation

Table 2.3: Some possible Ternary Candidates

System	Known composition	Alloy price (US\$/kg)	Melting temperature, °C	Remarks
Sn-Bi-Ag	Sn/4.8Bi/3.4Ag	13.72	211	Sn/Bi melts at 138°C, obtained as a by-product of Pb extraction
	Sn/2Bi/3Ag	13.17	203.6-231.1	
	Sn/6Bi/1.5Ag		187.6-228.9	
Sn-Zn-In	Sn/9Zn/10In	51	178	Low melting point
Sn-In-Ag	Sn/20In/2.8Ag	58.1	138	Corrodes in combination with humidity, very soft, expansive
Sn-Ag-Cu	Sn/3.8Ag/0.7Cu	10.44	218.78	Good thermal fatigue properties at high temperature
	Sn/3Ag/0.5Cu	9.33	219.77	
	Sn/4Ag/0.5Cu	10.73	220.23	
Sn-Cu-Se (or Te)	95Sn/4.75Cu /0.25Se	53	210-217	Hardness, shear strength and % elongation are comparable with Sn-Ag-Cu

2.8 Some Lead-Free Solder Alloy Systems

Most of the lead-free solder developments for electronic applications are aimed at arriving at suitable alloy compositions. These lead-free solder alloys composition are based on four basic systems, there are Au-based, Sn-based, Zn-based and Bi-based. Many different lead free solder alloys have been investigated, such as Au-Sn, Sn-Zn, Sn-Zn-Ag, Sn-Ag, Sn-Ag-Cu, Au-Ge, Zn-Al, Zn-Sn, Bi-Ag and Sn-Sb. Among these, the Sn-9Zn eutectic alloy has been expected to be one of the best alternative choices for the Sn-37Pb eutectic solder because of its melting temperature close to that of a Sn-37Pb eutectic alloy [83]. Therefore, a lot of research works were performed on this system. Since Zn is very active, the Sn-Zn system solders show poor wetting during soldering to electrodes, poor oxidation resistance in reflow soldering and may cause soldering failures due to poor wetting and non-wetting. By adding Bi into Sn-Zn solders, the melting point can be decreased, and the greater the amount of Bi rendered, the lower the melting point. Bismuth also helps to improve the wettability and corrosion performance of Sn-Zn solders. Composite approaches have been developed in lead-free solder research in an effort to improve the service temperature capabilities and thermal stability of the solder joints. In order to improve the properties of Sn-Zn solders, a great deal of efforts were made. Alloying elements such as Fe, Ni, Bi, In, Al, Ag have been added into the binary system to improve its properties [84-86].

The development of lead-free solder alloys for high-temperature applications is required to meet increasing demands for reliable replacements of lead-containing alloys. In here a discussion on the review of recent research on suitable replacement alloys, as well as traditional Pb-Sn alloys, collating relevant properties and identifying areas where further development is required. The main candidate alloys covered are derived from the Au-Sn, Au-Ge, Zn-Al, Zn-Sn, Bi-Ag and Sn-Sb alloy systems. Each of these systems is discussed with respect to the advantages and disadvantages associated with their use in soldering applications. It is concluded that further development of alloys suitable for high-temperature lead-free soldering applications is required.

Recently, lead-free solders have received considerable attention in the field of high temperature applications, particularly step soldering technology, flip-chip connections, solder ball connections and the bonding of semiconductor devices onto substrates, and the need for lead-free higher-temperature solder alloys has increased for a variety of reasons . Despite significant research into lead-free solders and thousands of paper published in recent years,

only a small proportion of these specifically relate to high temperature lead-free solders. High-temperature solder alloys are however, a key structural material for various industrial components and assemblies which require a high level of quality and reliability and also to be free from lead. As such, there is a need to review the literature to identify the relative strengths and weaknesses of the current generation of lead-free solder alloys suitable for high-temperature applications and identify opportunities for further developments.

The current options for high temperature solders, typically designed to withstand temperatures between 150 and 200°C, are derived from Pb–Sn, Au–Sn, Au–Ge, Zn–Al, Zn–Sn, Bi–Ag and Sn–Sb alloys, as well as some other alloy systems. These solders have been the subject of research on properties such as the melting and solidification behaviour, microstructure, interfacial compounds and structures, mechanical properties and reliability issues [84-88]. One of the basic criteria a high-temperature solder should satisfy is having an appropriate melting range that allows for manufacture and assembly of the soldered components. This melting range has been defined by industry as 270–350°C in order to ensure efficient process control [89].

Selection of the appropriate solder alloy must guarantee that its melting temperature is significantly higher than the service temperature. At the same time, the solder alloy should possess a solidus temperature higher than 270°C in order to withstand peak temperatures of second level soldering. The liquidus temperature of solder alloy should be below 350°C to avoid thermal degradation of polymers commonly used in the substrate. These temperature criteria are fundamental considerations in the selection of high temperature solders, however reasonable consideration must be given to alloys that fall outside of the temperature guidelines if properties are not adversely affected. Table 2.4 summarizes the melting temperature (including solidus and liquidus temperatures) of typical high temperature solder alloys.

Table 2.4: Melting behavior of typical Pb-free solders

Alloys	Composition (wt.%)	Solidus temperature (°C)	Liquidus temperature (°C)	Reference
Pb-Sn	Pb-20-35Sn	183	248-279	[49-50,62] [26-27, 39]
	Pb-10Sn	268	301	
	Pb-5Sn	300	314	
	Pb-2Sn	316	322	
Au-Sn	Au-20Sn	280	280	[54] [32]
	Au-5Sn	215	215	
Au-Ge	Au-0.3Ge	360	360	[54] [32]
Bi-Ag	Bi-2.5Ag	262.5	262.5	[90, 91][47, 48]
	Bi-10Ag	261.4	380.6	
Zn-Al	Zn-5Al	381	381	[24]
Zn-Sn	Zn-20Sn	198	383	[8, 9]
	Zn-30Sn	198	374	
	Zn-40Sn	198	365	
Sn-Sb	Sn-5Sb	245	245	[49] [92]

Attempts at improving solder alloy performance typically involve making alterations to the microstructure by manipulating phase transformations to change the number and/or character of the phases. To do this, researchers have applied the basic principles of diffusion and phase transformations to high temperature solder alloys [44, 92-97], with a particular focus on the kinetics of interfacial growth and nucleation/growth during solidification. The relationships between the microstructure and its response to heat treatment and the resulting mechanical properties are critical to the evaluation of solder joint performance. Due to the relatively high service temperature, it is necessary to characterize the strength and reliability of solder alloys at elevated temperatures. The mechanical properties of high-temperature lead-free solders are mainly characterized by conventional tensile tests and shear testing of the substrate/solder/substrate joints at room temperature, although nano-indentation is also commonly used.

Because of the increasing demand to reduce the amount of lead used in high-temperature solder applications, a brief on the recent advances in this field is enlisted here. The discussion critically examines the available literature and outlines potential candidate lead-free alloys that could substitute for high-lead alloys. It is clear from the review that advances are still required to satisfy the demands of high temperature solder applications and areas requiring further research are emphasized.

2.8.1 Bi–Ag

In the case of high temperature lead-free solders, the Bi–Ag eutectic system exhibits an acceptable melting point (the eutectic temperature is 262.5°C at the eutectic composition, Bi–2.5 wt.% Ag) shown in Fig. 2.2 , a comparable hardness to that of Pb–5Sn, and affordable cost. Therefore, it has been developed as a die attach solder for power devices and light-emitting diodes (LEDs). With the addition of Ag, the ductility of the brittle Bi phase could be drastically improved [98]. Meanwhile, Bi–Ag alloys exhibited a non-equilibrium solidification feature and have a considerably large undercooling when compared to Pure Bi [99]. Microstudy of the gravity-cast Bi–2.5Ag and Bi–11Ag alloys was conducted by Song et al. [100]. Eutectic grains comprising extremely fine Ag-rich phases can be observed in Bi–2.5Ag. In contrast, in Bi–11Ag alloys, irregular primary Ag and Bi phases increased, as the area fraction of eutectic structure was dramatically reduced. The author concluded that the massive primary Ag in Bi–11Ag, which has the ability to retard strain localization and inhibit crack growth, is probably responsible for the superior ductility of the Bi–11Ag at high deformation rates [101].

Development of this solder alloy system is still under way mainly due to its inferior thermal and electrical conductivity as well as poor workability. It has been demonstrated that raising the Ag concentration of Bi–Ag to 11 wt.% promotes an increase in thermal conductivity. A recent study revealed that the electrical resistivity of the Bi–11 wt.% Ag alloy is 86.5 $\mu\Omega/\text{cm}$, which is much lower than that of the Bi–2.5 wt.% Ag eutectic specimen at 116.5 $\mu\Omega/\text{cm}$ [82,-102]. Shi et al. [49] dealt with rare earth Ce-doped Bi– Ag solders with various Ag concentrations. The author suggested that the microstructure and properties of the solders can be modified due to the unique properties of rare earth elements. Small amounts of rare earth addition may enhance the wettability of Bi–Ag solder on Cu substrates, and result in an increase of the shear strength of the solder joints. In addition, the rare earth elements may not

adversely affect the melting temperature and the electrical conductivity. Overall however, there is much more work required to understand the effects of Ce on the Bi–Ag solder.

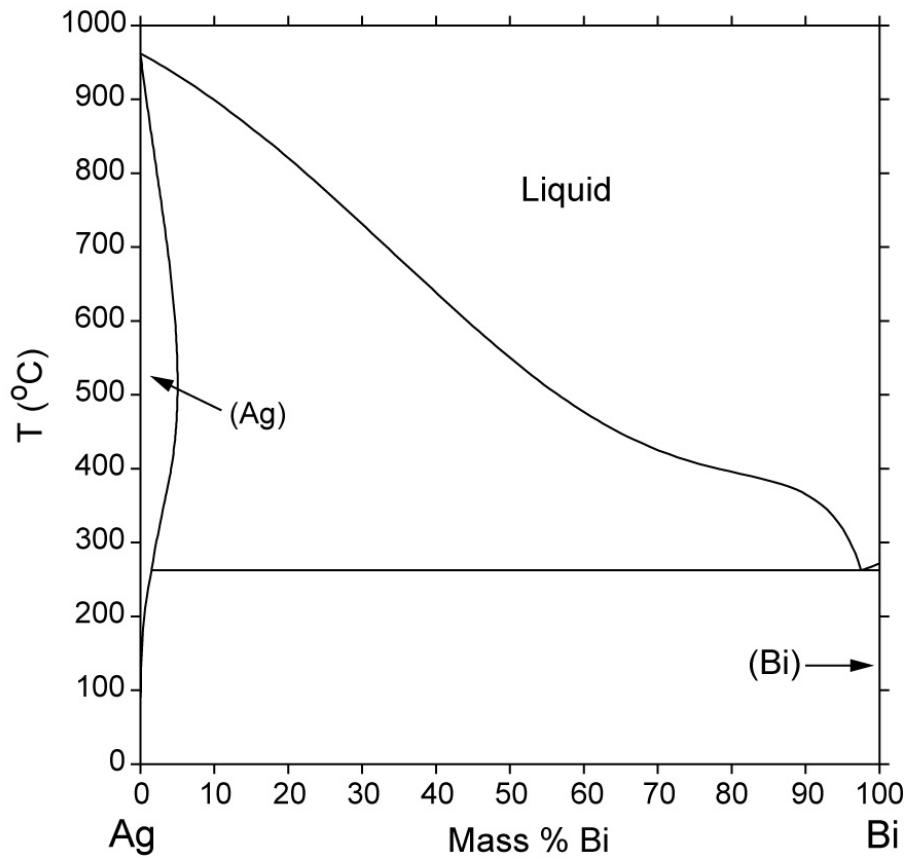


Fig. 2.2: Binary Ag-Bi phase diagram [103]

2.8.2 Sn–Sb

Sn–Sb solders are also considered to have great potential to replace high lead solder in applications involving high temperatures due to better microstructure stability and mechanical properties. Recently, numerous studies of Sn–Sb solder alloys have been reported, covering their solidification behaviour, interfacial reactions on substrates [104-105], and mechanical properties. The near-peritectic composition, Sn–5Sb, with a melting point of 245°C and a solder-substrate contact angle of about 43°, was investigated widely. The melting temperature of Sn–10Sb is around 270°C, and it may also be suitable as a substitute for high Pb content, high-temperature solders.

2.9 Stability in Sn–Sb Solders

Interfacial reactions between the Sn–Sb alloys and Cu substrates were investigated at 260°C by Lee et al. [106], by means of electron probe microscopy analysis (EPMA), Sb was observed to be present in the Cu_6Sn_5 and δ phases, and Sb did not form SnSb IMCs in the interfacial reactions. Moreover, the addition of up to 7wt.% of Sb into Sn does not significantly affect the total thickness of IMC layers. It is stated by the authors that the phase formations in the SnSb/Cu couples are very similar to those in the Sn/Cu couples.

The deformation behaviour of the Sn–5Sb solder during high temperature exposure (from 298 to 473°K) is very interesting. It is concluded by Schoeller et al. [107] that the deformation under high temperature is greatly influenced by the presence of the second phase (Sn–Sb) distributed within the Sn-rich matrix, and the precipitates appeared to be dissolved into the Sn-rich phase above 453°K, which converts the solder into a single-phase alloy and results in a change in its deformation mechanism. There is no grain growth in this alloy between room temperature and 433°K due to pinning of the grain boundaries by the intermediate phase. After crossing the solidus line for Sn–Sb, there is an immediate jump in the average grain size, and as a result, Sn–5Sb may be more reliable below 433°K due to the more stable microstructure.

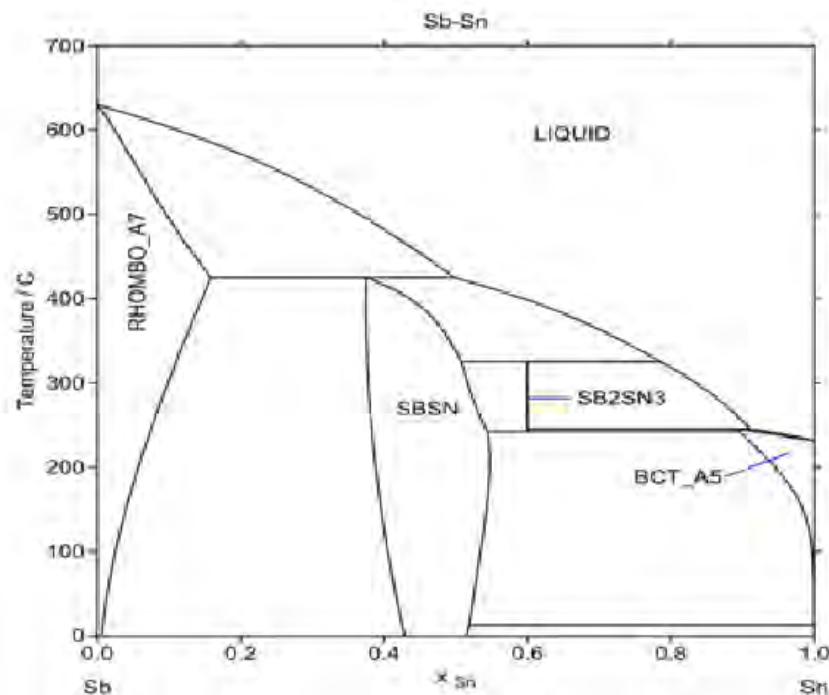


Fig. 2.3: Binary Sb-Sn phase diagram [54]

The author also reported that the elastic modulus and strength (YS and UTS) were found to be significantly higher in 95Sn–5Sb at temperatures below $0.7T_m$. Sn–5Sb showed nearly constant strain hardening in the temperature range of 298–398°K, because of the limited solubility of Sb in the Sn matrix. Beyond 398°K, the strain hardening exponent increased linearly with temperature, due to the dissolution of SnSb into the matrix coupled with limited grain mobility due to boundary pinning. As SnSb dissolved, the concentration of Sb in the matrix increased, leading to greater solid solution strengthening and thus, a higher strain hardening exponent. At temperatures greater than 473°K, the strain hardening exponent is expected to decrease due to accelerated grain growth and a decrease in dislocation density [41].

In the application of high temperature soldering, creep is an important deformation mechanism. To guarantee solder joint reliability, the creep study of Sn–Sb alloys has received a great deal of attention [103]. It has been shown that while antimony atoms in solution have only a minor effect on the creep resistance, alloys with higher concentrations of antimony contain Sn–Sb precipitates, which provide a significant strengthening effect that reduces the creep rate. It is suggested that with a rather coarse grain size and a low volume fraction of second-phase particles, dislocation creep is the dominant creep mechanism.

2.10 The Element Zinc

Zinc, also referred to in nonscientific contexts as spelter, is a bluish-white, lustrous, diamagnetic metal, though most common commercial grades of the metal have a dull finish. It is somewhat less dense than iron and has a hexagonal crystal structure.

The metal is hard and brittle at most temperatures but becomes malleable between 100 and 150°C [44]. Above 210°C, the metal becomes brittle again and can be pulverized by beating. Zn is a fair conductor of electricity. For a metal, zinc has relatively low melting (419.5°C) and boiling points (907°C). Its melting point is the lowest of all the transition metals aside from mercury and cadmium.

Many alloys contain zinc, including brass, an alloy of copper and zinc. Other metals long known to form binary alloys with zinc are aluminum, antimony, bismuth, gold, iron, lead,

mercury, silver, tin, magnesium, cobalt nickel, tellurium and sodium. While neither Zn nor zirconium is ferromagnetic, their alloy $ZrZn_2$ exhibits ferromagnetism below 35°K [107].

Zn based solders are used for structural materials joining purpose for a long period. Zn-2Al alloy is used for centuries as a means of joining metals together, these types of solders are ideal for lower temperature applications. Zn-Al alloys are successfully used for joining Al and Al-based alloys.

2.11 Zinc Based Solders

Soldering aluminum has never been a mainstream process for industries and manufacturers. The main reasons are: tenacious aluminum oxide which foils most attempts to solder using conventional means; its dissimilarity with many solders and base metals for potential galvanic corrosion consequences; the varieties of Al alloys, grades and tempers with varying soldering results; and the most often misunderstood and overlooked factor of how Al accepts or rejects heat during soldering. Through a collaborative project between Oak Ridge National Laboratory, Ford Motor Company, and Johnson Manufacturing Company, a high density infrared source of 300 kW plasma lamp has been demonstrated to have successful results with Zn-20 wt%Al and flux at a soldering temperature of 490°C. Mechanical tests showed that the joint area is stronger than the parent material with minimum softening. Detailed process parameters have been studied to provide a basis for future mass production.

In an investigation the movement of [liquid/(solid + liquid)] interphases $L/(S + L)$, [(solid + liquid)/(eutectic+solid+liquid)] interphases $[(S+L)/(E+L)]$, [(eutectic+solid+liquid)/solid] interphases $[(E+L)/S]$, and [(solid+liquid)/solid] interphases $[(S+L)/S]$, running in a binary Zn-Al alloy system from the chilled ends of a hemicylindrical sample was studied. It is found that under specific solidification conditions, new $[(S+L)/(E+L)]$ and $[(S+L)/S]$ interphases can be created in the centre of the sample, and then move toward the ends of the probe and collide with the solidification advancing fronts. In a horizontal setup with chilled ends they determined the speeds and accelerations of the four imposed interphases, two of which moved from left to right and two of which moved from right to left. They were also able to detect the creation of new $[(S+L)/(E+L)]$ and $[(E+L)/S]$ or $[(S+L)/S]$ interphases created near the centre of the sample, and to calculate their speeds and accelerations from the near

beginning of the creation to the instant in which they collided with the imposed solidification fronts [108].

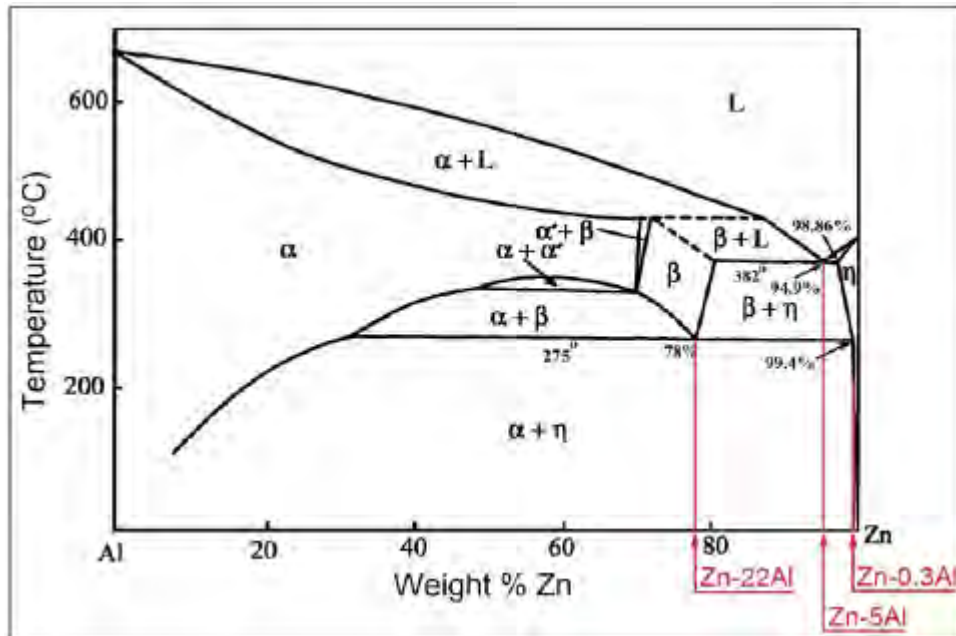


Fig. 2.4: Binary Zn-Al phase diagram [109].

Zn–Al based alloys have proper melting range and excellent thermal/electrical properties. In this study, Zn–Al–Mg–Ga solder wire was used to attach Ti/Ni/Ag metallized Si die on Cu lead frame in an automatic die attach machine [52]. Die attachment was performed in a forming gas environment at temperature ranging from 370 to 400°C [79]. At the interface with Cu lead frame, CuZn_4 , Cu_5Zn_8 and CuZn intermetallic compound (IMC) layers were formed. At the interface with Si, Al_3Ni_2 IMC formed when 200 nm Ag layer was used at the die back and AgZn and AgZn_3 IMC layers when the Ag layer was 2,000 nm thick [110]. Microstructure of the bulk solder consists of mainly two phases: one with a brighter contrast (about 80.9 wt% Zn) and another is a mixture of light (about 73.7 wt% Zn) and dark phases (about 45 wt% Al). Die shear strength was found within the acceptable limit (21.8–29.4 MPa) for the entire die attach temperatures. In electrical test, maximum deviation of output voltage after 1,000 thermal cycles was found 12.1% [111].

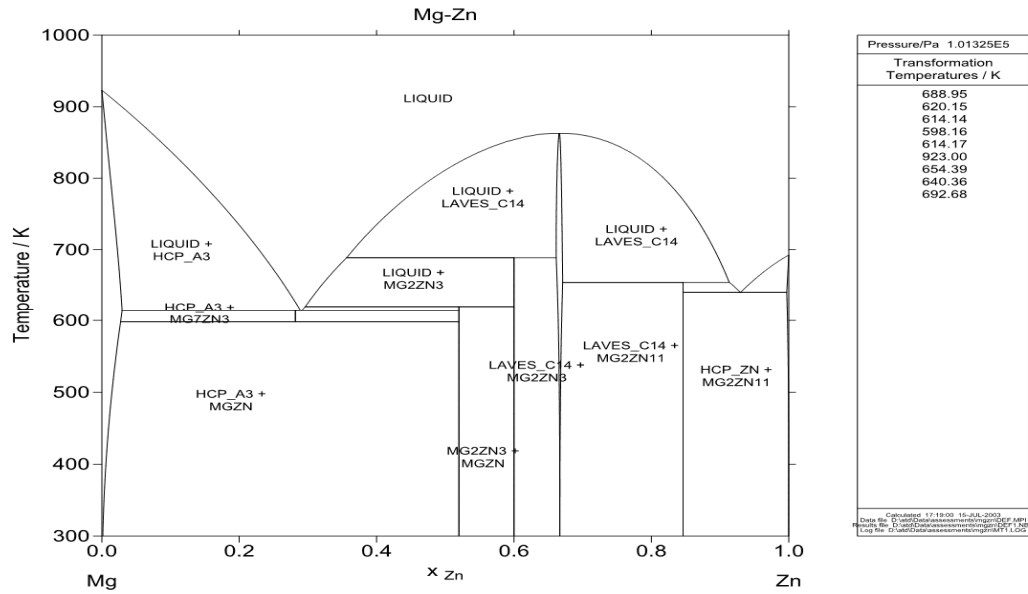


Fig. 2.5: Binary Zn-Mg phase diagram [54].

Interfacial reactions during Si die attachment with Zn-Al-Mg-Ga high-temperature lead (Pb)-free solder on bare Cu frame and Ni metallized Cu lead-frame were investigated. Cross sectional microstructural investigation revealed that as many as three intermetallic compound (TMCs) layers form at the solder/lead-frame interface for bare Cu lead-frame. Wetting on Ni metallized Cu lead-frame was found to be lower as compared to that at bare Cu lead-frame. Die shear strength was found to be higher on bare Cu lead-frame (24.2 MPa) as compared to Ni metallized Cu lead-frame (20.5 MPa).

The Zn-Al(-Cu) eutectic alloys (melting point 381°C) are candidates for use as Pb-free high-temperature solders as a substitute for Pb-based solders, which are suitable for severe working environments such as the engine room of hybrid vehicles equipped with an inverter system as well as a heat engine [101]. Interfacial reactions between Cu/Zn-4Al and Cu/Zn-4Al-1Cu with regard to the consumption of the Cu substrate, and the growth of the IMPs during soldering and aging treatments were investigated. The consumption of the Cu substrate and the growth of IMPs during soldering were found to be controlled by the volume diffusion of constituent elements. In view of the aging process, the growth of IMPs is considered to be controlled by the volume diffusion. In particular, the layer thickness of β rapidly grows over 200°C, although the thickness of β layer grows quite slowly. With the addition of 1 mass% Cu in Zn-4Al solder, the suppression of the consumption of Cu substrate was confirmed.

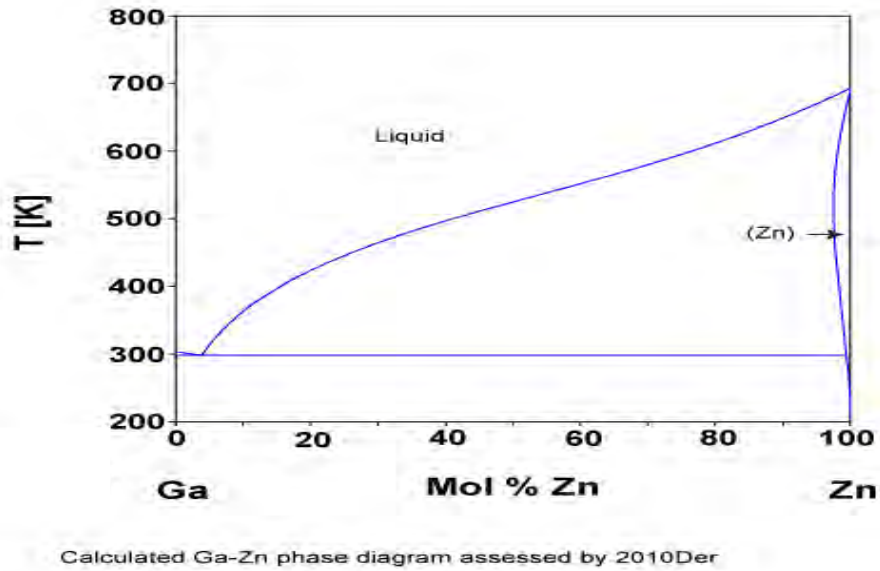


Fig. 2.6: Binary Zn-Ga phase diagram [54]

In another study, the interfacial reaction between Zn-Al (-Cu) alloys and the Ni substrate during soldering, aging, and thermal cycling was investigated. During 420°C soldering, the Al_3Ni_2 IMC phase formed between the Ni substrate and the Zn-Al solder, the growth rate of which was very small [100]. The soldered assemblies were then heat-treated at 200°C and 300°C, where the growth of the Al_3Ni_2 remains slow. During 450°C soldering, the interfacial reaction between Ni and Zn-4Al solder proceeded continuously.

The measurements of wettability of eutectic Sn-Zn and Zn-Al alloys on the surfaces of copper and Al pads were conducted. The wettability problems discussed in other studies, resulting from the presence of ZnO or Al_2O_3 at the solder/pad interface, were eliminated by the appropriate preparation of substrates, using an appropriate flux and atmosphere, as well as the proper choice of soldering temperature. These alloys can be used for soldering both Cu and Al. Spreading tests indicated that the wetting properties of eutectic solders based on Sn-Zn on copper pads do not depend on temperature (up to 400°C), but in the lack of protective atmosphere, the solder does not wet pads. At the interface of Sn-Zn/Cu joints obtained at 250°C, there is Cu_5Zn_8 phase layer as observed in other studies, and a thin strip of CuZn phase from the side of pad, and another thin strip of CuZn_4 on the side of solder.

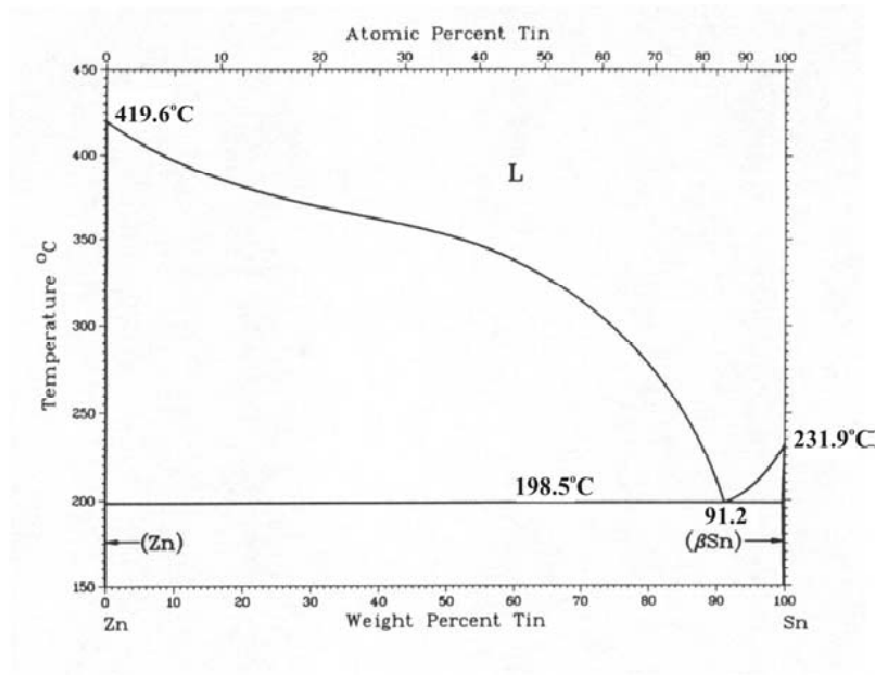


Fig. 2.7: Binary Zn-Sn phase diagram [112]

Zn-based solders were developed for ultra high temperature applications with the alloying elements: (4–6) wt.% Al and (1–5) wt.% Cu. The solder was designed to have a liquidus temperature between 655°K and 675°K. The Al content improved the spreadability and electrical resistivity, but the Cu content had insignificant influence on the characteristics. The alloying contents increased hardness and tensile strength with the α - η eutectic/eutectoid phases. The multiple regression analysis on the measured characteristics was conducted for the alloy design of the Zn–Al–Cu solder [6].

Interfacial reaction and die attach properties of Zn-xSn solders on an aluminum nitride–direct bonded copper substrate were investigated [113]. At the interface with Si die coated with Au/TiN thin layers, the TiN layer did not react with the solder and worked as a good protective layer. At the interface with Cu, CuZn_5 , and Cu_5Zn_8 IMC layers were formed, the thicknesses of which can be controlled by joining conditions such as peak temperature and holding time. During multiple reflow treatments at 260°C, the die attach structure was quite stable. The shear strength of the Cu/solder/Cu joint with Zn-Sn solder was about 30 MPa to 34 MPa, which was higher than that of Pb-5Sn solder (26 MPa) [46]. The thermal conductivity of Zn-Sn alloys of 100 W/m K to 106 W/m K was sufficiently high and superior to those of Au-20Sn (59 W/m K) and Pb-5Sn (35 W/m K) [79].

The Sn-Zn-Al alloys are one of the significant alternatives for the Pb-based alloys. It is found that increasing the Zn above 10-15 wt% causes to the decrease of corrosion resistance of the alloys [111].

Recently, a new Cu-Zn alloy solder wetting layer for the Pb-free solders has been developed to reduce the IMC growth rate. The IMC growth rate on Cu-Zn layers during aging was much slower than that on Cu layers, because the Zn in the layer depressed the interdiffusion of Cu and Sn atom. The initial shear force of as-reflowed Cu specimens was slightly higher than that of Cu-Zn specimen. After aging, the shear force of SAC solder bumps on Cu pads was shown to be slightly lower than that on Cu-Zn pads at the same aging time. The failure mode was ductile mode. The drop reliability test showed that the mean number of drops to failure of Cu-Zn specimens was higher than that of Cu specimens both before and after aging. The enhancement of drop reliability is ascribed to the delayed growth of IMC and no microvoid formation at the interfaces.

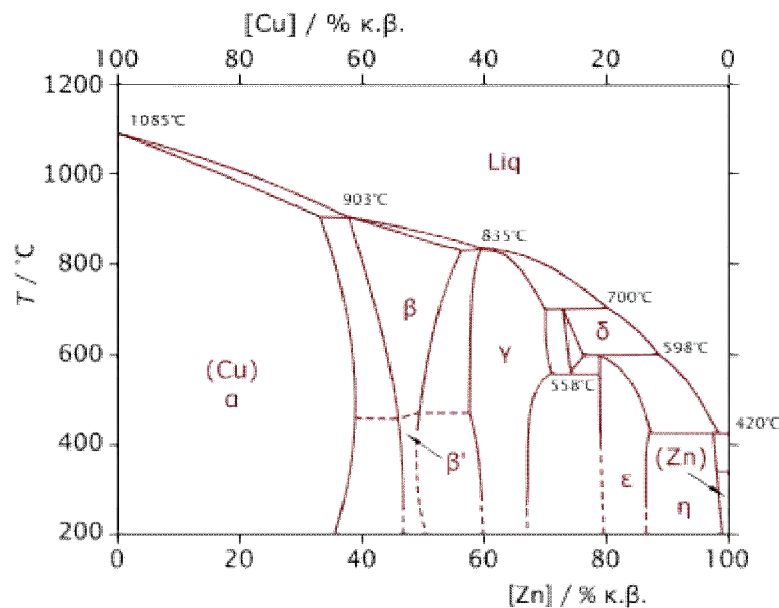


Fig. 2.8: Binary Zn-Cu phase diagram [113].

Pure Zn is one of the best die-attachment candidates for use in next-generation wide-gap semiconductor power devices operating at temperatures up to 300°C. However, it has certain drawbacks when used at high operating temperatures: poor ductility and limited oxidation resistance. S. W. Park et. al. investigated the effect of adding minor elements, Ca, Mn, Cr, and Ti in improving Zn ductility and oxidation resistance. This addition significantly reduced the grain size of the microstructure, thus improving the tensile strength and elongation of

pure Zn. In addition, the minor elements addition significantly improved oxidation resistance of pure Zn. Consequently, because of higher ductility and oxidation resistance, the interconnection ability of Zn alloys as die-attachment candidates was significantly enhanced.

2.12 Some well known lead-free solder alloys

2.12.1 Eutectic Sn-3.5 Ag Alloy

The eutectic composition of Sn-Ag binary system is 96.5wt%Sn-3.5wt%Ag (Sn- 3.5Ag) with melting temperature of 221°C. The microstructure consists of β -Sn phase with dendritic structure and intermetallic Ag_3Sn in form of thin platelets. Intermetallic compound (IMC) is a compound of two metals that has a distinct chemical formula. In the Ag-Sn phase diagram as shown in Figure 2.9 [114], ϵ phase, Ag_3Sn , belongs to one kind of IMCs of Sn-Ag alloy and exists in a very narrow range of compositions. Because of the high concentration of Sn in this alloy, it may have Sn whisker growth.

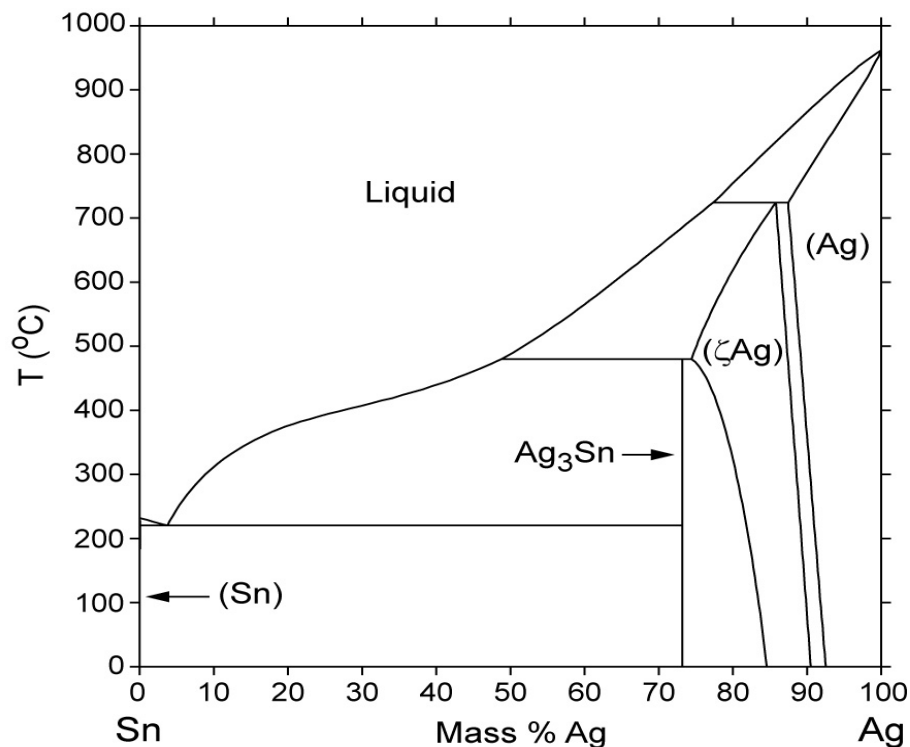


Fig. 2.9: Ag-Sn binary phase diagram

2.12.2 Eutectic Sn-0.7Cu Alloy

The Sn-Cu binary alloy has a eutectic composition of 99.3wt%Sn-0.7wt%Cu (Sn- 0.7Cu) with melting temperature of 227°C. The microstructure consists of β -Sn phase with dendritic structure and intermetallic Cu_6Sn_5 as hexagonal rods. In the Cu-Sn phase diagram as depicted in Figure 2.10 [115], two kinds of IMCs are commonly formed at the interface when the Pb-free solders are applied on Cu substrate. The η phase, Cu_6Sn_5 , is always found inside the bulk solder as large facet and at the interface as IML in scalloped structure. The IML acts as a metallic joining layer to provide the necessary bonding strength between the solder and the substrate. Another IMC, ϵ phase Cu_3Sn , usually appears between Cu_6Sn_5 and Cu substrate during thermal aging. The growth of these phases are reported to follow an Arrhenius relationship, with the activation energy for Cu_6Sn_5 being between 0.41 and 0.5 eV and for Cu_3Sn being between 1.06 and 1.27 eV, in the 90-170°C range [116]. Similar to the Sn-3.5Ag solder alloy, this solder may favor to Sn whisker growth due to its high Sn composition.

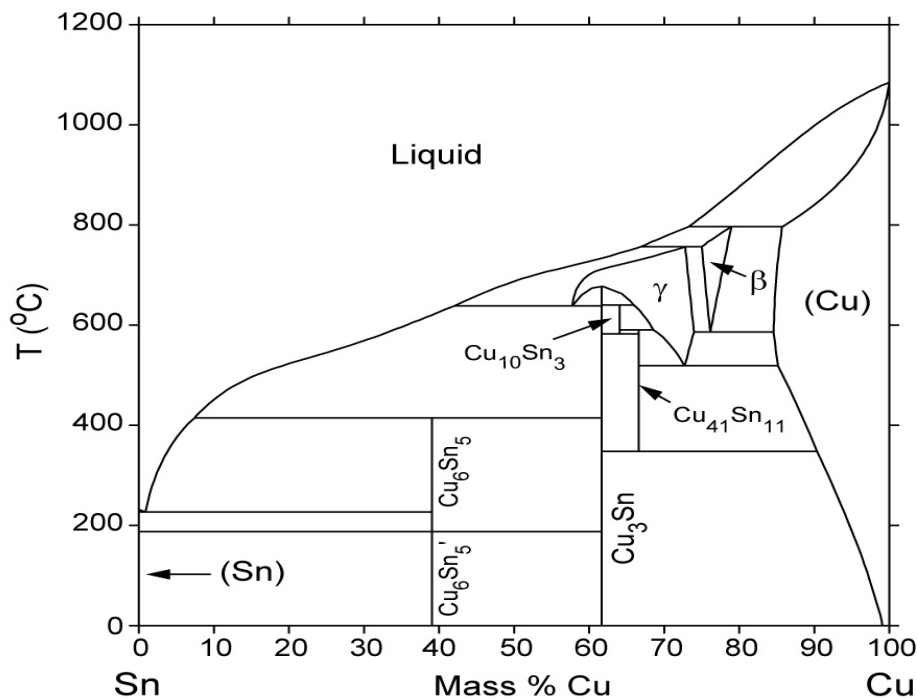


Fig. 2.10: Cu-Sn binary phase diagram.

2.12.3 Eutectic Sn-52In Alloy

The eutectic composition of Sn-In binary system is 48.3wt%Sn-51.7wt%In (Sn- 52In) with melting temperature of 120°C. The eutectic microstructure consists of β - In, γ -Sn phase with dendritic structure and intermetallic In_3Sn in form of thin platelets. In the In-Sn phase diagram as shown in Figure 2.11 [117], β phase, In_3Sn , belongs to one kind of IMCs of Sn-In alloy and exists in a very wide range of compositions. Diffraction data show that In_3Sn (β) disproportionates to tetragonal (In) and hexagonal γ phase below about 140°K and reverses upon warming to room temperature. γ phase has been found at room temperature at the surface of solid β -phase samples [118]. Here less chance to Sn whisker growth due to presence of low Sn composition compared to Sn-3.5Ag and Sn-0.7Cu solder alloys.

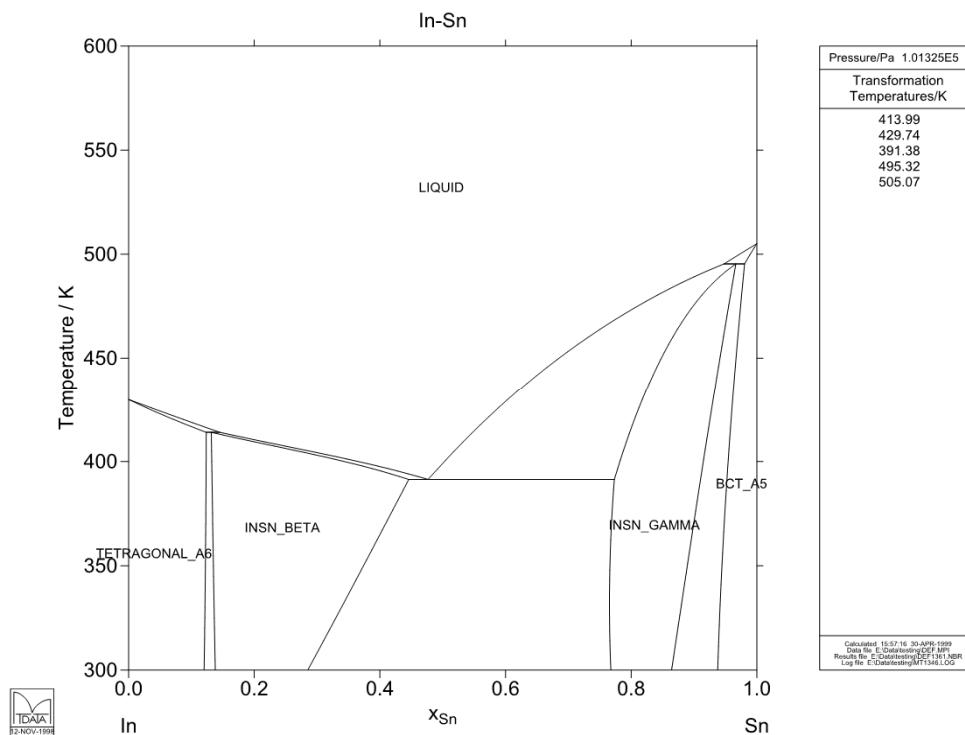


Fig. 2.11: In-Sn phase diagram.

2.12.4 Eutectic Sn-9Zn alloy

The eutectic composition of Sn-Zn is 91wt%Sn-9wt%Zn (Sn-9Zn) with a melting temperature of 198°C, as shown in Figure 2.6 [119]. Its eutectic microstructure consists of two phases: (1) a body-centered tetragonal β -Sn phase, and (2) a hexagonal Zn with less than 1wt% of Sn in solid solution [120]. The microstructure can be expected to be lamellar, alternating of Sn-rich (β -Sn) and Zn-rich (Zn), under equilibrium solidification. Zn is very inexpensive and readily available. Also, Zn is extremely effective in reducing the melting point of Sn alloys. However, Zn reacts rapidly with oxygen. It forms excessive oxide or dross quickly during the wave soldering. More problematic is the very poor wetting properties due to the oxide formation. This technical problem can be overcome by using a special flux [121]. For this reason, Sn-Zn alloy is an attractive alternative to Pb-free solder.

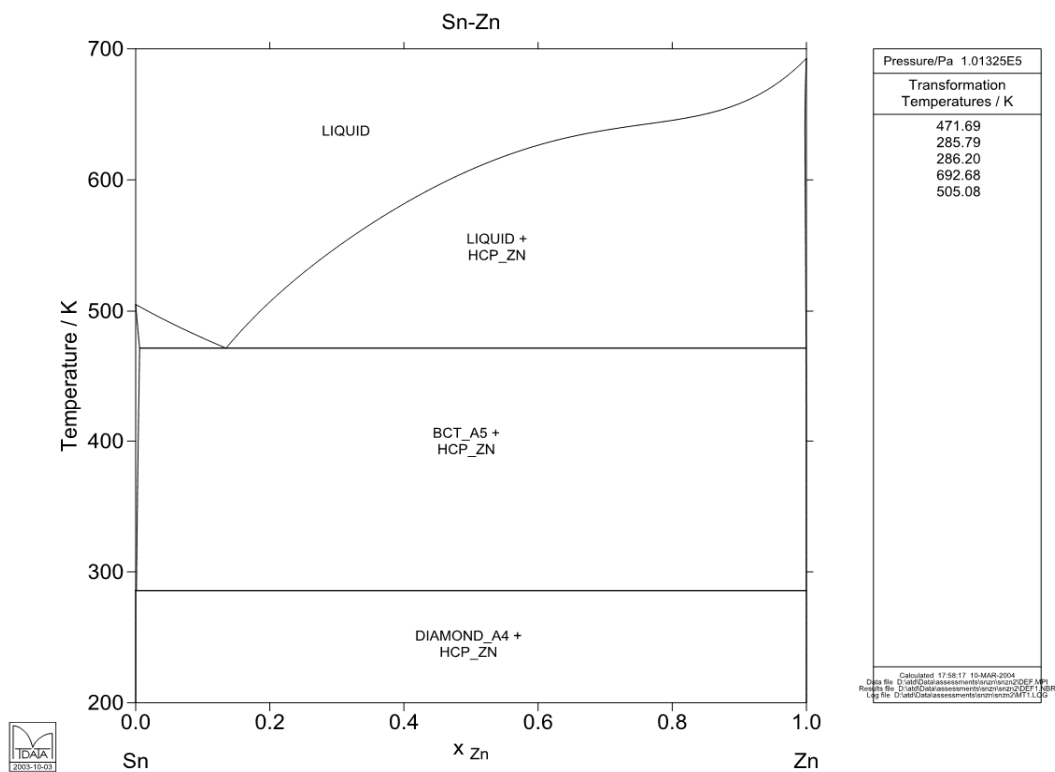


Fig. 2.12: Sn-Zn phase diagram.

2.13 The Physical Forms of Solder

The common forms of solder are: paste, preforms, spheres, wire, ribbon and foil, shot and ingot (bar) [122].

Paste: Solder paste is a mixture of a pre-alloyed solder powder and flux-vehicle that has a creamy peanut butter-like consistency. The flux-vehicle portion of the paste is made with rosin or resin, activators, viscosity control additives, flux chemicals, stabilizers and solvents. The ratio of powder to flux (referred to as ‘metal load %’) will vary slightly with different alloys and different applications. Solder pastes are commonly used in electronics assembly for printed circuit PCB assembly in surface mount technology applications. An example of a typical use would be in the assembly of PCB used in computers and cellular (mobile) phones. Pastes can be “printed” through a stencil onto the circuitry. After printing, components are placed onto the bonding pad areas of the printed circuit and are held temporarily by the tackiness of the paste. Boards are then sent through a reflow oven where a specific temperature profile is used to evaporate the solvent, activate the flux, and melt the solder alloy. The type of flux used is dependent on the desired activity and whether or not cleaning is an option.

The three basic flux formulations are: No-clean, RMA and Water-Washable. No-clean – are mild activity fluxes which produce post-soldering residue which is both non-conductive and non-corrosive. Therefore, the residue can be safely left on the assembly with no corrosion concern, and cleaning is not required. No-clean flux residues can be removed after soldering if desired. Cleaning procedures are generally similar to RMA flux residue removal.

RMA Rosin –are also mild activity fluxes (Rosin Mildly Activated). RMA fluxes were the precursor to No-Clean formulations. However, the RMA flux residues may be conductive and/or corrosive after soldering. Removal of the flux residue is recommended. RMA flux residues, being rosin-based and organic in nature, are generally removed with a solvent/saponifier.

Water-Washable (Soluble) – are higher activity fluxes designed for removal after soldering. The flux residue is cleanable using water. The water is typically heated and used in a pressurized spray. Water-washable flux residues are corrosive and conductive after soldering, therefore removal is mandatory. Specific flux residue cleaning procedures and products (saponifiers and solvents) can be recommended by the solder provider.

Preforms: Preforms are generally flat, manufactured solder shapes. Solder preforms come in standard shapes such as squares, rectangles, washers, frames and discs manufactured to custom geometries. Preforms can be coated with a flux (by the solder provider) to eliminate an assembly steps or a liquid or paste flux can be applied separately during assembly. In certain circumstances flux is not required. However, certain parameters must be met for fluxless soldering. Preforms are used in a wide range of applications.

Spheres: Spheres are precise spherical shapes of solder with diameters ranging from 100 μ m to 2375 μ m. The most common use of spheres is for BGA (Ball Grid Array) package and flip-chip assembly. Spheres are typically used with a tacky flux which holds the spheres in place until soldering occurs. Spheres can be placed manually or, more commonly, using commercially available automated equipment. Like solder paste, the flux can be stencil printed onto an assembly substrate, and spheres manually or automatically placed on the flux-coated bonding pad.

Wire: Wire solder can be solid or, in the case of commonly used solder alloys, cored with a flux. Typical diameters are 150 μ m and up. Solder wire is typically used in manual soldering operations but, with the appropriate equipment can be automated. In the case of solid core wire, a liquid or paste flux can be applied separately.

Ribbon and Foil: Ribbon and Foil are long strips (typically spooled) and sheets, respectively. Ribbon widths range from 0.10" to 2+". Ribbon thicknesses range from .0005" and up. Foil is similar to ribbon, with both the X and Y dimensions being greater than 2.375" (maximum limit of the X or Y dimensions is less than or equal to 12". Examples: 12" x 12", 11" x 18", 6" x 6", 4" x 8" and 4" x 16"). The dimensions available (particularly the thickness) will be heavily dependent on the alloy. Ribbon and foil are used in any application where a somewhat large, flat piece of solder is needed. Simple preforms can be manually cut from both. Liquid fluxes are applied in a separate operation.

Shot and Ingot (Bar): Shot and Ingot (Bar) are the most basic forms of solder available. Shot is teardrop shaped solder that allows for convenient weighing. Ingot or bar, a simple three-dimensional block of solder is cast in a mold. These forms are generally used to fill solder pots for manual lead pre-tinning or to fill the solder holding reservoir of conveyORIZED wave soldering machines. Parts to be pre-tinned are first dipped in a liquid flux then dipped into a heated pot containing molten solder. Wave soldering is a printed circuit assembly process that utilizes PCBs with plated through-holes for attaching leaded components. The

process is less costly than the surface mount assembly described above, but can only be used for PCBs with substantially less circuit density. In this process, components are inserted into the holes in the centre of the bonding pads of the boards and placed on the wave-soldering conveyor. The conveyor passes through a flux sprayer where liquid flux is applied to the bottom side of the board. The board continues through a molten wave of solder which bonds the component leading to the PC board metallization pads.

2.14 Selection of lead-free solder

Starting with the above list, we began to search for the best alloy, the choices of acceptable elements dwindle rapidly. Silver is in adequate supply but has a cost disadvantage. Bismuth poses a potential supply problem since it is a by-product of lead mining, and also has embrittlement problems. Bismuth is also a poor conductor, both thermally and electrically. Concerning cadmium, toxicity is the leading reason not to use this element. With copper, there is plenty of supply, and it is soluble in tin. In low percentages, copper works well. There is a long history of tin alloys containing copper. Gallium supply and costs are the main reason not to use it, as well as its brittleness. The cost, inadequate supply, poor resistance to corrosion and rapid oxide formation during melting all eliminate the element indium.

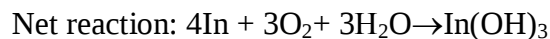
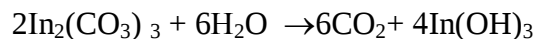
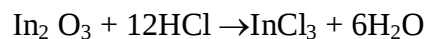
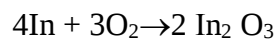




Fig. 2.13: Corrosion of Sn-In eutectic solder and corrosion reaction of Indium

Figure 2.13 shows a solder fillet formed with an indium eutectic, aged at 90°C and 93% relative humidity. The corrosion of indium can be seen as the dark areas on the solder joint. The remaining area is the tin. The reaction that has occurred is also seen in Figure 2.13. For the most part, indium is safe if kept in low humidity conditions, or if it is conformally coated. Antimony has an adequate history and supply to be a viable solder additive. Tin is the base of solders, toxicity is low and supply is adequate. Zinc is in adequate supply, but has oxidation problems and also causes solder to become brittle. This oxidation problem creates an issue with existing automatic soldering equipment [57].

Chapter Three

Experimental

3.1 Raw materials

This study was accomplished using several raw materials to manufacture solders of desired compositions. Among them the key materials are Zinc (Zn), Molybdenum (Mo) and Chromium (Cr). Zinc was purchased from the local market of which purity was 99.95 %, Mo powder (99.99%, particle size $\leq 10\mu\text{m}$, Merck, Germany), Cr powder (99.9%, Loba Chemie, India).

3.2 Development of the solders

Six different compositions of composite solders were chosen for casting as well as characterization. Since the melting point of both Chromium ($1,907^{\circ}\text{C}$) and Molybdenum ($2,623^{\circ}\text{C}$) is much higher compared to Zinc (419.5°C), the composition of the solders has been selected in the higher Zinc region with very small amount of Chromium and Molybdenum with a view to keeping the melting of the solders in lower temperature region. The composition of the selected solders has been mentioned in Table 3. 1:

Table 3.1: Composition of the selected solders

Alloy Identification	wt.%Cr	wt.%Mo	wt.%Zn
Zn-0.2 Cr	0.2%	0	99.8%
Zn-0.4 Cr	0.4%	0	99.6%
Zn-0.6 Cr	0.6%	0	99.4%
Zn-0.4 Mo	0	0.4%	99.6%
Zn-0.6 Mo	0	0.6%	99.4%
Zn-0.8 Mo	0	0.8%	99.2%

The phase diagrams of Zn-Mo and Zn-Cr are shown in Fig. 3.1 & Fig.3. 2 respectively.

For each selected composition, the required amount of Zinc and Mo or Cr was weighed in precision balance. The zinc was put into a graphite crucible which was placed into a gas fired pit furnace for melting. At the same time, the weighed Mo or Cr was also preheated to 200-

250°C temperature. When the whole zinc ingot was molten completely, the crucible containing molten Zn was taken out of the furnace, wait until the temperature fall down to 600°C. The preheated Mo or Cr was added into the liquid Zn and then stirred with mechanical stirring set up in order to homogenize the mixing of the added metal powders. The temperature of the molten pool was measured by a k-type thermocouple. The molten metal was poured into a preheated metal mould keeping the pouring temperature at 550°C. The mould along with the cast solder was allowed to cool to near room temperature and then this was separated from the mould. The same method was followed during casting of every composition. The steps followed in the casting are shown in Fig.3.3.

The rectangular plates of the solders were machined in the machine shop to prepare tensile testing specimen. Other specimens for various testing and characterization were prepared from cutting the respective plate of solders.

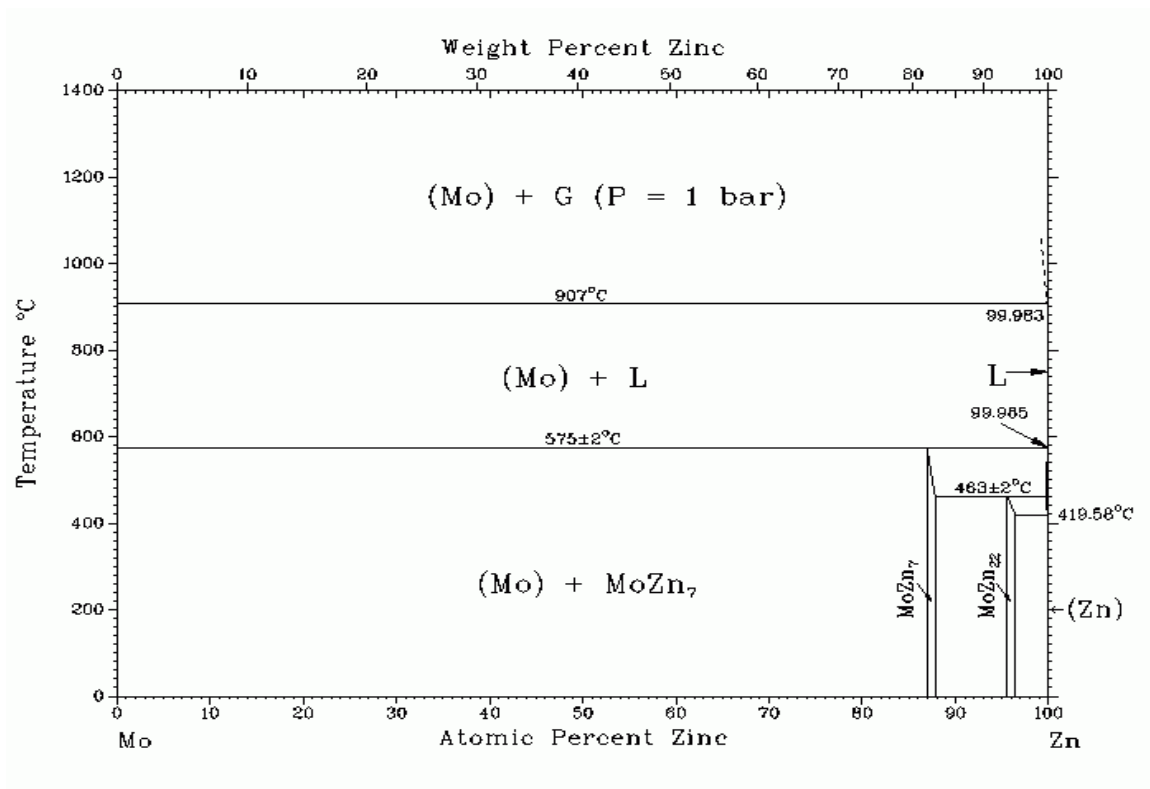


Fig. 3.1: Binary Phase diagram of Zn-Mo

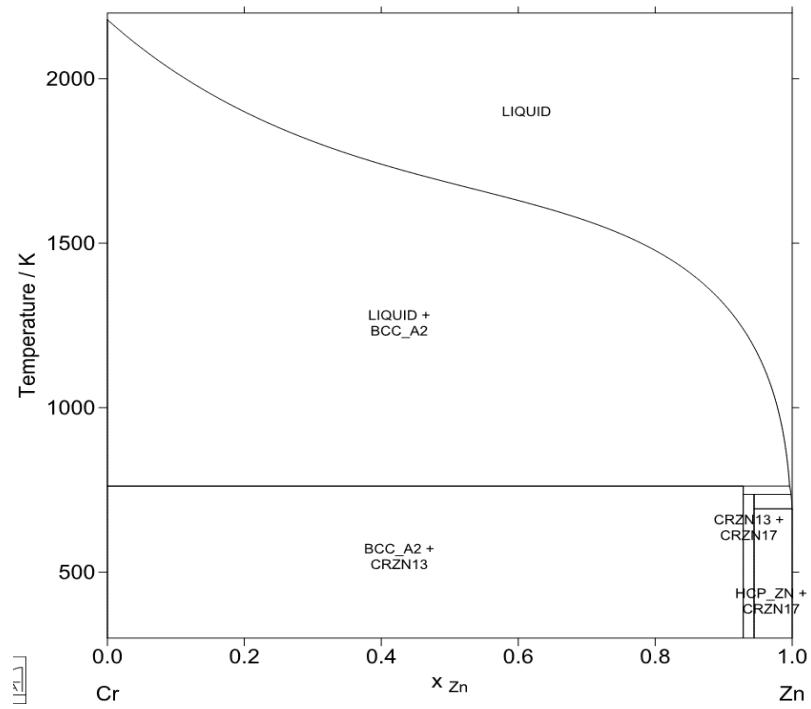


Fig 3.2: Binary Phase diagram of Zn-Cr

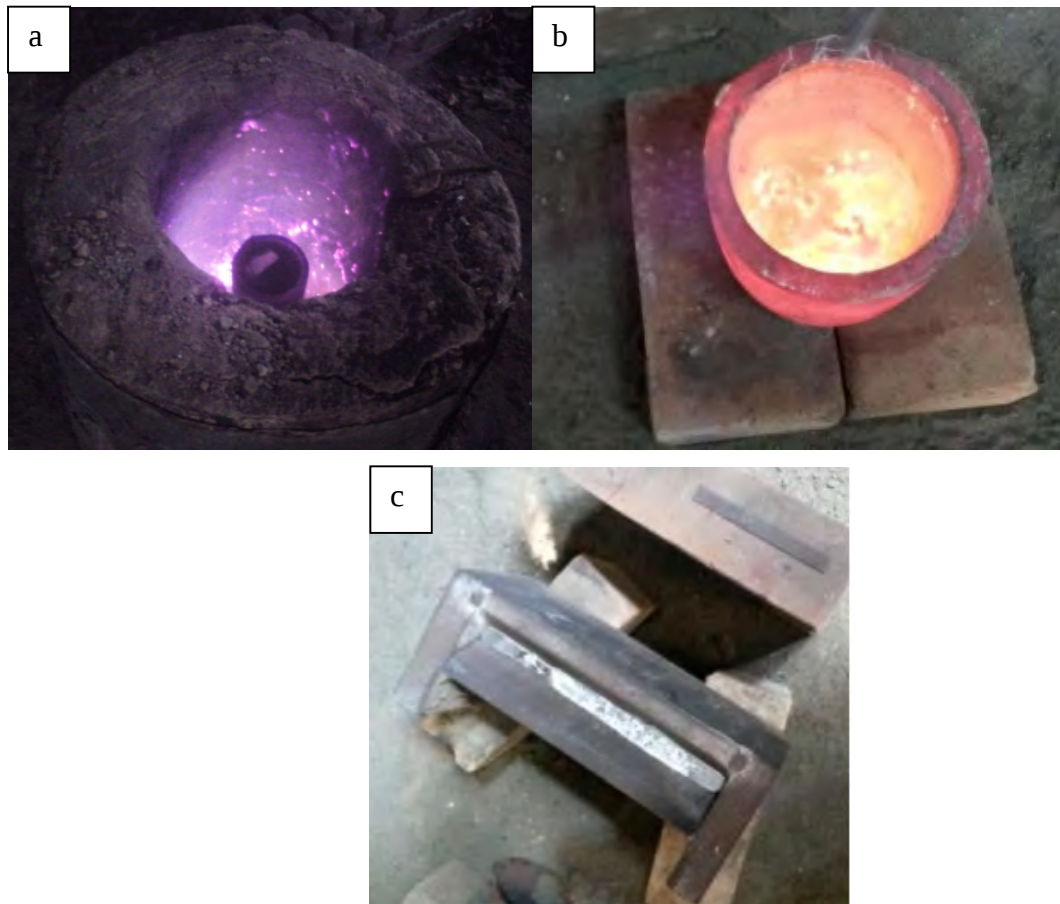


Fig. 3.3: Images showing the casting steps (a) Crucible in pit furnace with solid metal (b) Crucible containing molten metal and (c) molten metal poured into mold

3.3 Characterization of the Solders

To know whether the properties of the developed solders are suitable for using as solder alloys for high temperature applications the developed solders were characterized using the available facilities. Following tests were carried out to characterize the solder alloys:

1. Differential Thermal Analysis (DTA)
2. Structural analysis by Scanning Electron Microscope
3. Elemental analysis of phases by EDX
4. X-Ray Diffraction analysis (XRD)
5. Brinell hardness test
6. Tensile Test
7. Thermomechanical Analysis (TMA)
8. Electrical Conductivity Analysis

3.3.1 Differential Thermal Analysis (DTA)

The melting temperature and solidification range of the solders were measured with SII EXSTAR TG/DTA 6300. Powdered sample of each composition was collected separately from cutting off the as cast solders by a hacksaw blade. For DTA analysis, powdered sample of about 20 mg of each solder was placed into a platinum pan. To obtain the melting properties data, the samples were scanned from 25 to 450°C at a rate of 10°C min⁻¹ under the inert atmosphere of nitrogen gas.

3.3.2 Microstructural Analysis

The as-cast solders were sectioned and from there samples measuring 10mm×10mm were prepared for microstructural analysis. After progressive grinding on grit papers, samples were brought for fine polishing on a wheel, where gamma alumina powder was used as polishing media. Non-ferrous metallographic fine polishing standard technique was carried out with 0.05 µm Al₂O₃ particles in order to make a mirror polish in the surface and observe the microstructure. Then samples were cleaned with distilled water and finally cleaned and dried with acetone. After drying, the samples were etched in an etching solution containing 100 ml ethanol (96%) and 1-5 ml hydrochloric acid (32%). These etched metallographic samples were analyzed by a field emission scanning electron microscope (FESEM) [JEOL JSM

7600F, Japan] equipped with Energy-dispersive X-ray spectroscopy (EDX). Samples were loaded in the chamber and then images were taken in different mode and magnification focusing on various spot of the specimen. EDX spot was taken in different phases to know the chemical composition where contrast was observed. In addition, the tensile fracture surfaces of the selected alloys were analyzed in a similar fashion in the Scanning Electron Microscope.

3.3.4 X-Ray Diffraction Analysis (XRD)

X-ray diffraction technique was used to determine the phases present in the samples and also to confirm that whether any intermetallic had formed. XRD analysis was carried out using a Bruker D8 advance (USA) X-ray diffractometer. Cylindrical samples of 5mm diameter and 8mm height were used for XRD analysis. Cu-K α radiation with wavelength of 0.15418 nm was used for the inspection. Line counts were plotted against the diffraction angle 2θ starting from 10° to 90° with an increment of 0.02° . The obtained peaks in different 2θ position were analyzed with the standard available for the same experimental condition.

3.3.5 Hardness Test

Grinding and polishing were necessary to obtain polished, smooth and flat parallel surface before indentation. Thus, the polished samples were placed in the Brinell hardness tester machine to make the indentations. At least five indentations were taken for each composition at room temperature to obtain the mean value. The diameter of the indentation marks were measured under an optical system. Hardness was calculated using the following formula:

$$HB = 0.102 \times \frac{2F}{\pi D (D - \sqrt{D^2 - d^2})}$$

where:

F = applied load (Newtons)

D = diameter of indenter (mm)

d = diameter of indentation (mm)

3.3.6 Tensile Testing

The tensile specimens were prepared by machining of the as cast ingots. The dimension of the tensile sample is shown in Fig. 3.4. Tensile tests were carried out in an Instron testing machine (Instron 3369 Universal Testing Machine, UK) at a rate of 3.00 mm/min at 25°C to obtain data on the stress-strain curves which contain information of elongation and the ultimate tensile strength (UTS). Four samples of each composition were tested to get an average value of tensile strength. The fracture samples were preserved in a desiccator to investigate under SEM to find the fracture mode.

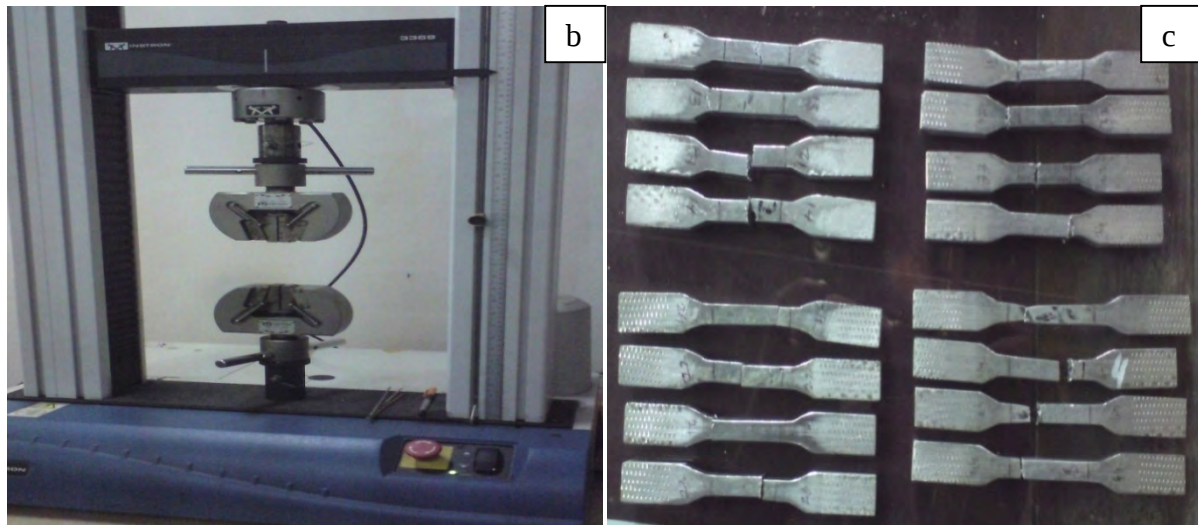
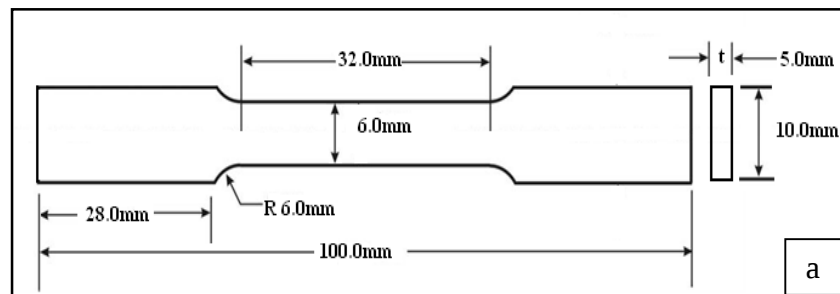


Fig 3.4: (a) Tensile specimen (b) Universal Testing Machine and (c) Fractured sample after tensile test

3.3.7 Thermomechanical Analysis (TMA)

Thermomechanical analysis (TMA) is a technique used in thermal analysis, a branch of materials science, studies the properties of materials as they change with temperature. Thermo mechanical analysis is a sub-discipline of the thermo mechanometry (TM). Thermo

mechanometry is the measurement of a change of a dimension or a mechanical property of a sample while it is subjected to a temperature regime. An associated thermo analytical method is thermo mechanical analysis. A special related technique is thermo dilatometry (TD), the measurement of a change of a dimension of the sample with negligible force acting on the sample while it is subjected to a temperature regime. The associated thermo analytical method is thermo dilatometric analysis (TDA).

The co-efficient of thermal expansion (CTE) of the solders was measured with a SII EXSTAR TMA SS6300, SII Nanotechnology, Japan. For thermomechanical analysis (TMA), cylindrical piece of the solder samples of about 5 mm diameter and 5 mm height were prepared and then placed into the sample chamber. TMA of the samples was done up to a temperature of 310°C at a heating rate of 5°C/min in a nitrogen atmosphere.

3.3.8 Electrical Conductivity Analysis

Electrical conductivity or specific conductance is the reciprocal of electrical resistivity, and measures a material's ability to conduct an electric current. A high conductivity value indicates a material that readily allows the movement of electric charge. In order to reveal the electrical conductivity of the solders, solid blocks of 30 mm x 30 mm x 6 mm were prepared. The surfaces of the blocks were then grinded and polished. The electrical conductivity of the samples was measured by Electric Conductivity Meter (type 979, Technofour, India). In case of every specimen 6-7 readings were taken and their average value was reported as the electrical conductivity of that particular solder.

Chapter Four

Results and Discussion

Zn-xMo System

4.1 Differential Thermal Analysis (DTA)

Differential Thermal Analysis (DTA) test was conducted at a heating rate of 10°C/min in the temperature ranging from room temperature to around 550°C to determine the melting temperature and solidification range of the solders. Lower melting temperature and smaller solidification range are required for quality soldering, because both of these reduce the oxidation of the solder alloys and improve the wettability. DTA curves of the alloys showed only a single peak in the mentioned temperature range indicating the transformation of these from solid to liquid state during heating. Since, these are not pure metal a range of melting temperature is obtained instead of a single melting temperature like pure metals. Experimental results revealed that, the temperature, where the melting started, decreased in comparison with the melting temperature of the pure Zn. It is clear from the Fig. 4.1 and Table 4.1 that the onset temperature of melting of all three compositions of the Zn-xMo system was around 416°C whereas, the finishing temperature of melting was around 423°C indicating a melting range of around 7°C. The onset, finishing temperature and melting range changed very slightly with the change in Mo content. The melting temperature of Zn decreased due to the presence of intended impurity in the system which was in agreement with the basic theory of materials science.

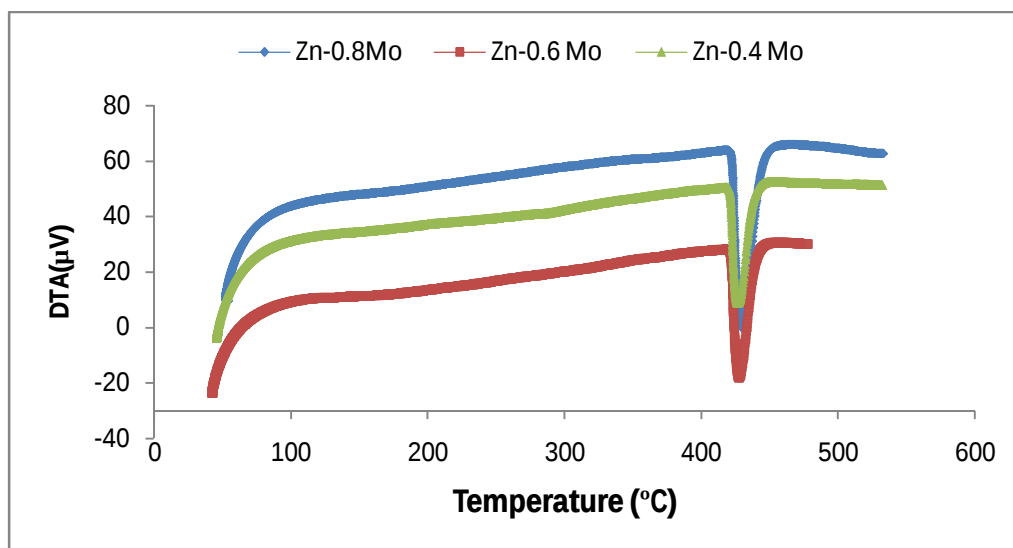


Fig. 4.1: DTA curves for Zn-xMo system.

Table 4.1: Melting properties of Zn-xMo system

Sample ID	Melting start (°C)	Melting finish (°C)	Melting range (°C)
Zn-0.4 Mo	415.2	423.3	8.1
Zn-0.6 Mo	416.1	423.2	7.1
Zn-0.8 Mo	417.8	422.0	4.2

4.2 Microstructure of Zn-xMo system

The microstructural features of the solders selected for study in this research were analyzed with field emission scanning electron microscope (FESEM). Figure 4.2-4.4 shows the microstructure of Zn-xMo system with grain size measurement. The structure clearly revealed the grains and grain boundary constituting the bulk structure. It was observed that, with increasing amount of Mo content the grain size of the solders decreased. This grain refining behavior due to addition of Mo had a significant effect on the mechanical, electrical and other characteristics of the solders. From figure 4.2 (b) the average grain size of Zn-0.4 Mo alloy was seen to be 16.43 micron, whereas this was 7.41 micron in case of Zn-0.6 Mo (Fig. 4.3b) and becomes 4.8 micron in Zn-0.8 Mo alloy (Fig. 4.4b). Mo particles were found to be dispersed in the whole structure not forming any intermetallic compounds with the base metal Zn, which was evident in the microstructure and EDX analysis in different zone of the structure. Since, the addition of Mo was very minute, the particles were not abundant through the whole structure. However, addition of Mo reduced the grain size of the Mo-Zn solder system by acting as nucleating agent during solidification of the solders. As the number of these particles increased, due to increase in total Mo content, the number of nucleating sites increased. Therefore, crystallization starts at many more sites simultaneously compared to that containing lower Mo content and thus providing relatively lower number of nucleation sites. Hence, the grain size decreased with increasing Mo content.

Such grain refinement by fine metallic powder addition guided to superior mechanical properties (i.e. tensile strength, hardness etc.) of the developed solders. Moreover, a previous study reported that the addition of such minor elements also increased the ductility, oxidation

resistance, shear strength and retards the formation of IMC in between the interface of solder and Cu substrates as well [123].

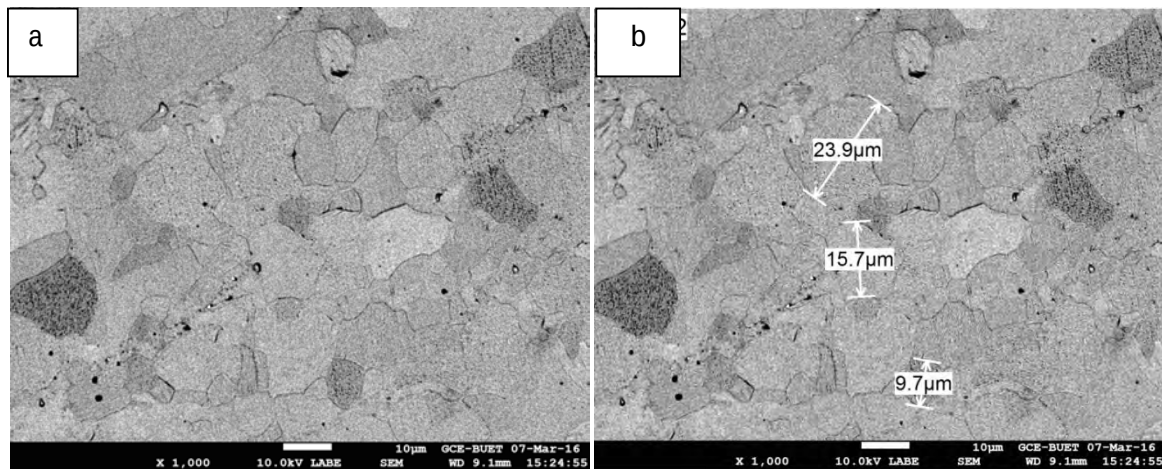


Fig. 4.2: (a) Scanning electron micrograph of Zn-0.4 Mo (b) showing grain size measurement

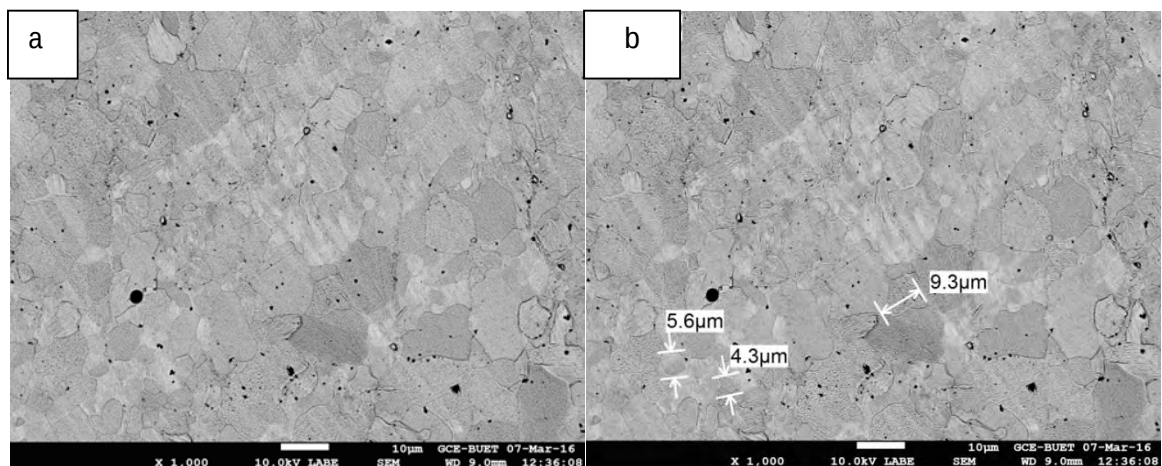


Fig. 4.3: (a) Scanning electron micrograph of Zn-0.6 Mo (b) showing grain size measurement

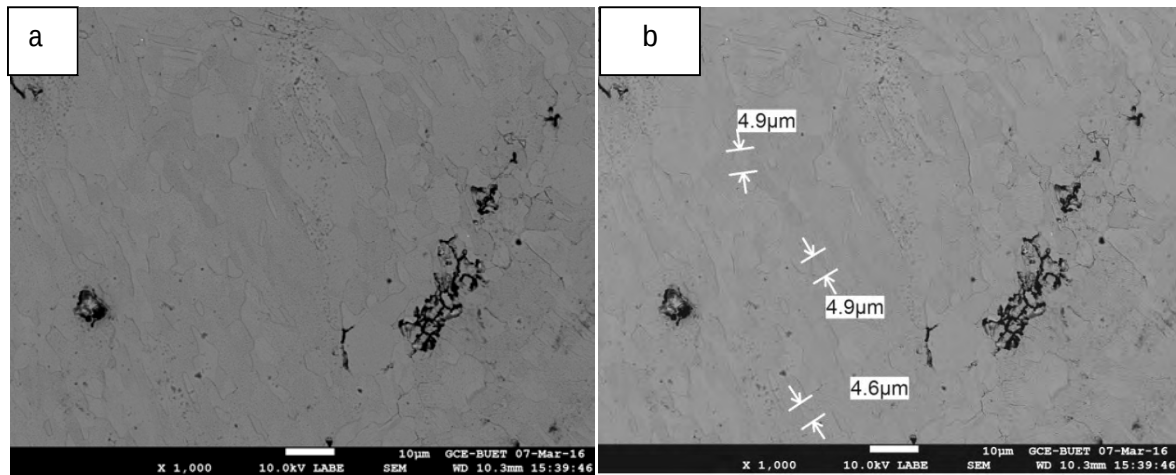
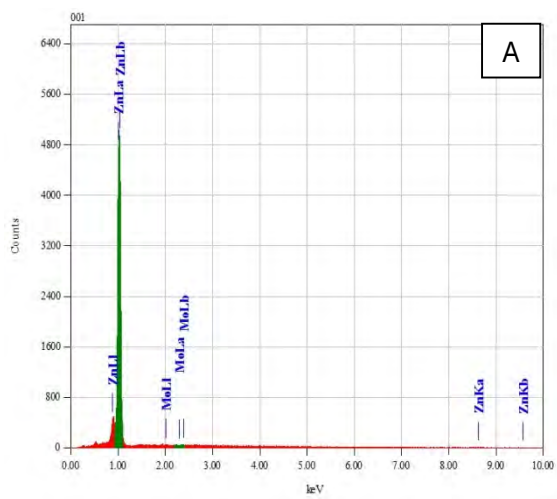
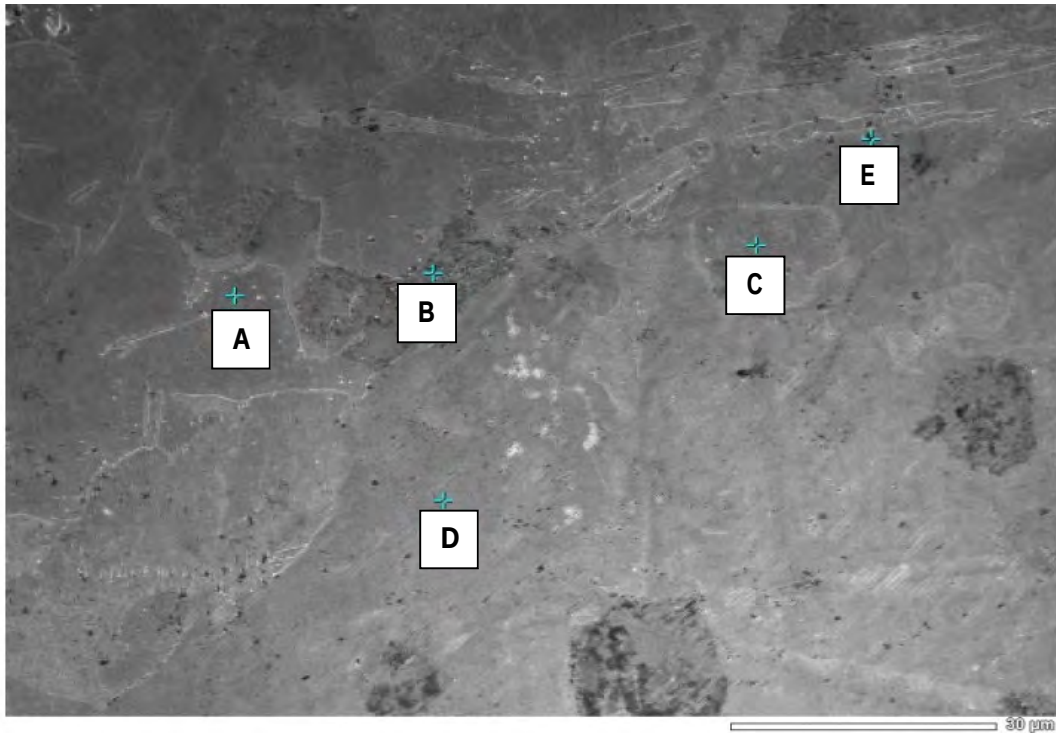


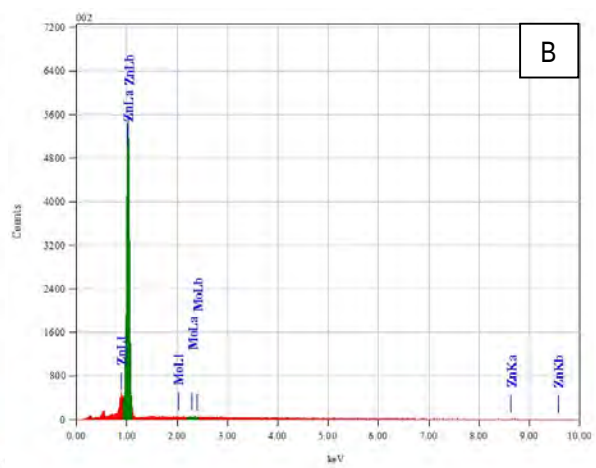
Fig. 4.4: (a) Scanning electron micrograph of Zn-0.8 Mo (b) showing grain size measurement

4.3 EDS Analysis

Several EDS spots were marked in different zones of the microstructure during scanning electron microscopy in order to reveal the chemical composition in different zones of the structure. Figure 4.5 exhibits some such EDS spots in several zones of Zn-0.4 Mo alloy. From the elemental analysis of these spots it was observed that, in the spot A, which was taken inside the grain, there was 100 percent Zn. The same thing was noticed in case of spot C, D and E. However, in spot B, there was found 0.10 percent Mo while the rest is Zn.



Element	(keV)	Mass%	Sigma	Atom%	Compo
Zn L	1.012	100.00	0.59	100.00	
Mo L					
Total		100.00		100.00	



Element	(keV)	Mass%	Sigma	Atom%	Compo
Zn L	1.012	99.90	699816105315705820000.		
Mo L	2.293	0.10	32559371640400511000.0		
Total		100.00		100.00	

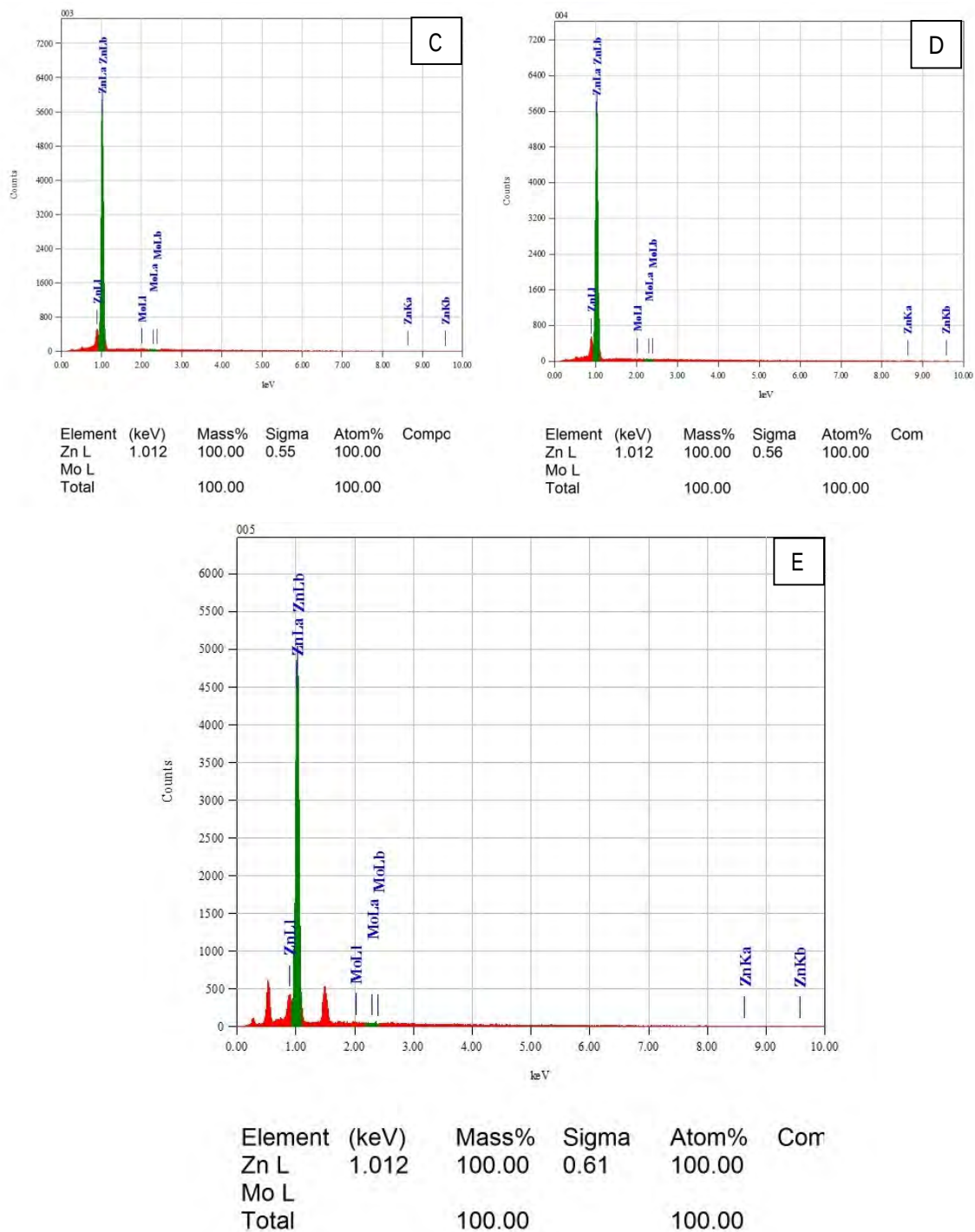


Fig.4.5: EDS analysis of Zn-Mo system

4.4 X-Ray Diffraction (XRD)

The XRD pattern of the Zn-xMo solders is depicted in Fig 4.6. The peaks pattern obtained here in case of both type of alloys almost matched with the standard pattern of pure Zn. The whole pattern was analyzed by PDF 2 software and searched for any intermetallics or any other phases comprising of Zn/Mo. Since, the amount of Mo was very minute, the formation

of intermetallics or other phases was not found from XRD analysis. Furthermore, with the increasing of Mo content in the solders there was no shifting in the peak position. However, there was difference in the peak intensity and hence in full width at half maxima (FWHM) values which is related to the crystallite size of the respective alloys. The average crystallite size of all these alloys was calculated using **Scherrer equation**.

$$\tau = \frac{k\lambda}{\beta \cos \theta}$$

where,

τ is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size;

k is a dimensionless **shape factor**, with a value close to unity. The shape factor has a typical value of about 0.9, but varies with the actual shape of the crystallite;

λ is the X-ray wavelength; here used Cu k-alpha, $\lambda=0.15406$ nm

β is the line broadening at half the maximum intensity (FWHM), after subtracting the instrumental line broadening, in radians. This quantity is also sometimes denoted as $\Delta(2\theta)$;

θ is the Bragg angle.

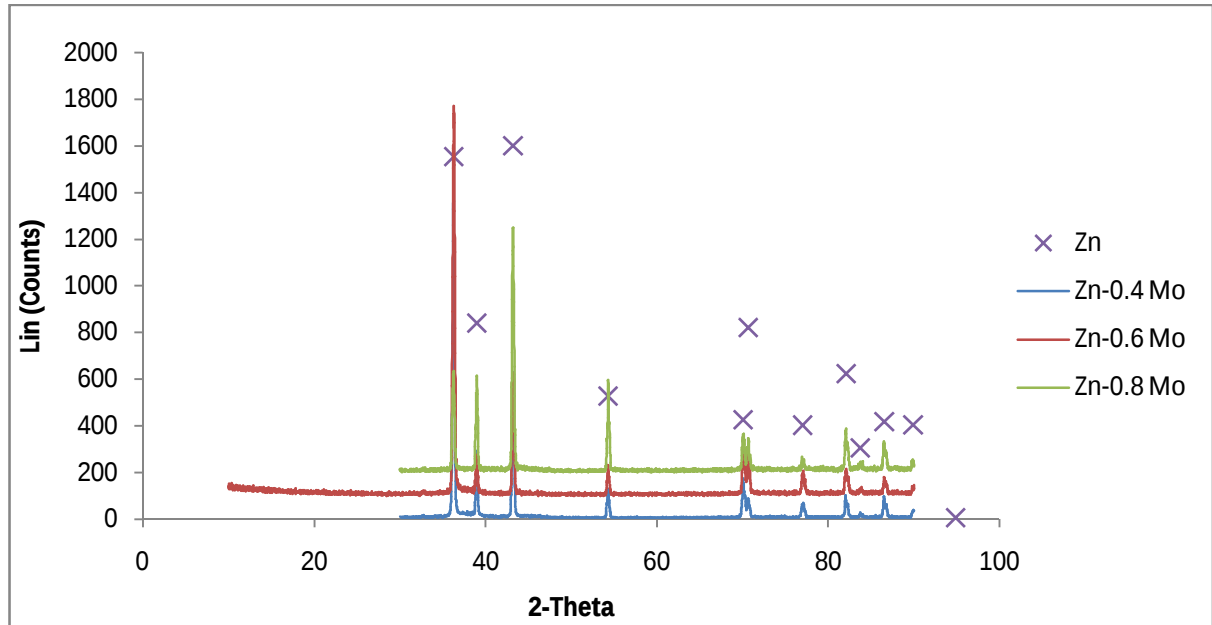


Fig.4.6: XRD peaks of Zn-xMo system with standard Zn.

Table 4.2: Calculation of Crystallite size of Zn-xMo using **Scherer equation**

Sample ID	FWHM (degree)	2 Theta	Crystallite size (nm)	Average (nm)
Zn-0.4 Mo	0.2422	36.2630	34.5	34.1±3.3
	0.2266	38.9696	37.2	
	0.2794	43.2248	30.6	
Zn-0.6 Mo	0.2874	36.2947	29.1	30.0±1.3
	0.2853	38.9782	29.5	
	0.2711	43.2273	31.5	
Zn-0.8 Mo	0.300	36.2464	27.9	30.4±2.2
	0.2611	38.9793	32.3	
	0.2759	43.2003	30.9	

The calculation of crystallite size of the solders has been shown in Table 4.2. The effect of increasing Mo content on the crystallite size can be easily visualized from the presented data. It is evident that, with increasing the percentage of fine particles of Mo in Zn the resulted

crystallite size decreases. This phenomenon of grain refining with addition of fine particles is also proved by the scanning electron microscopy, where the grain size was found to be decreased with increasing Mo content. It is to be noted that, grain, we observe in microscopy, is nothing but a single crystal or a summation of some crystallites.

4.5 Hardness

Brinell Hardness

Brinell Hardness Number (BHN) of the Zn-Mo solders is depicted in the Fig. 4.7. This clearly revealed that hardness of the solders increased with increasing Mo content in the solder. Experimental results revealed that, BHN of Zn-Mo alloy was 29.71 in case of Zn-0.4 Mo while, BHN was found to be 41.28 in Zn-0.8 Mo. The mechanism of such hardening can be easily understood from the microstructural characteristics of the solders. As discussed earlier that, grain refinement of Zn-Mo as well as Zn-Cr solders was evident due to the addition of Mo and Cr particles. With increasing percentage of Mo particles grain size of the solders decreases gradually, this was confirmed by both scanning electron microscopy and X-ray diffraction analysis. In general, fine grained structure exhibits superior hardness compared to coarse one. Moreover, the dispersion of small metallic particles throughout the structure adds value to the mechanical properties by dispersion strengthening mechanism.

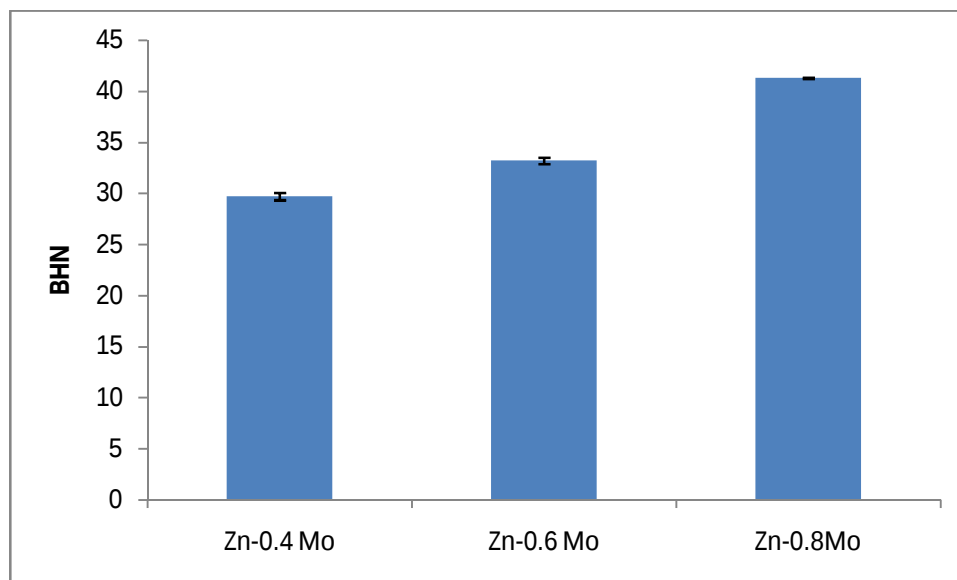


Fig.4.7: Column chart showing Brinell hardness of Zn-xMo system

4.6 Tensile Testing

4.6.1 Tensile Strength

Tensile strength of the proposed Zn-xMo solders has been depicted graphically in the Fig.4.8. From the figure it is clear that, as the Mo content increased strength of the solders also increased. One way of increasing tensile strength is strengthening by metal particles. During solidification after pouring the molten alloy in the mould, impurity particles, here Mo, act as nucleating sites assisting crystallization and result in grain refining. According to Hall-Petch relationship it is evident that tensile strength is inversely proportional to the grain size. Therefore, small grains produced by heterogeneous nucleation are supposed to increase strength of the Zn-xMo solders. This experimental study also supports the theory given by Hall-Petch. Strength of unalloyed zinc increased from 31.09 MPa to 33.04 MPa when alloyed by 0.8% Mo. One of the major outcomes of this study is that zinc can be strengthened by Mo particles.

Apart from grain refining, Mo particles obstruct the movement of dislocations. Dislocation needs to move from one grain to another to reach in rupture. Easy movement of dislocations consequently leads to relatively lower strength and hardness. In this experiment strength was found to be increased when Mo was added to Zn. One reason for this is, during the period of loading dislocation was not able to move easily from one grain to another. This means, dislocation needed two forces, one to move from grain to grain, another to bypass the hindrance of metallic particles. As a result, total force for fracture increases because of Mo addition.

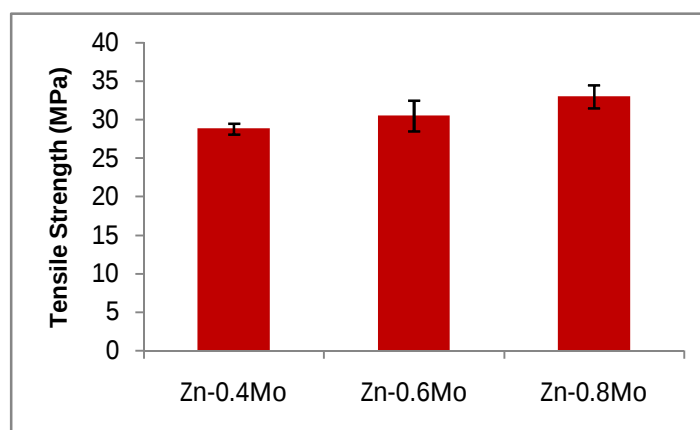
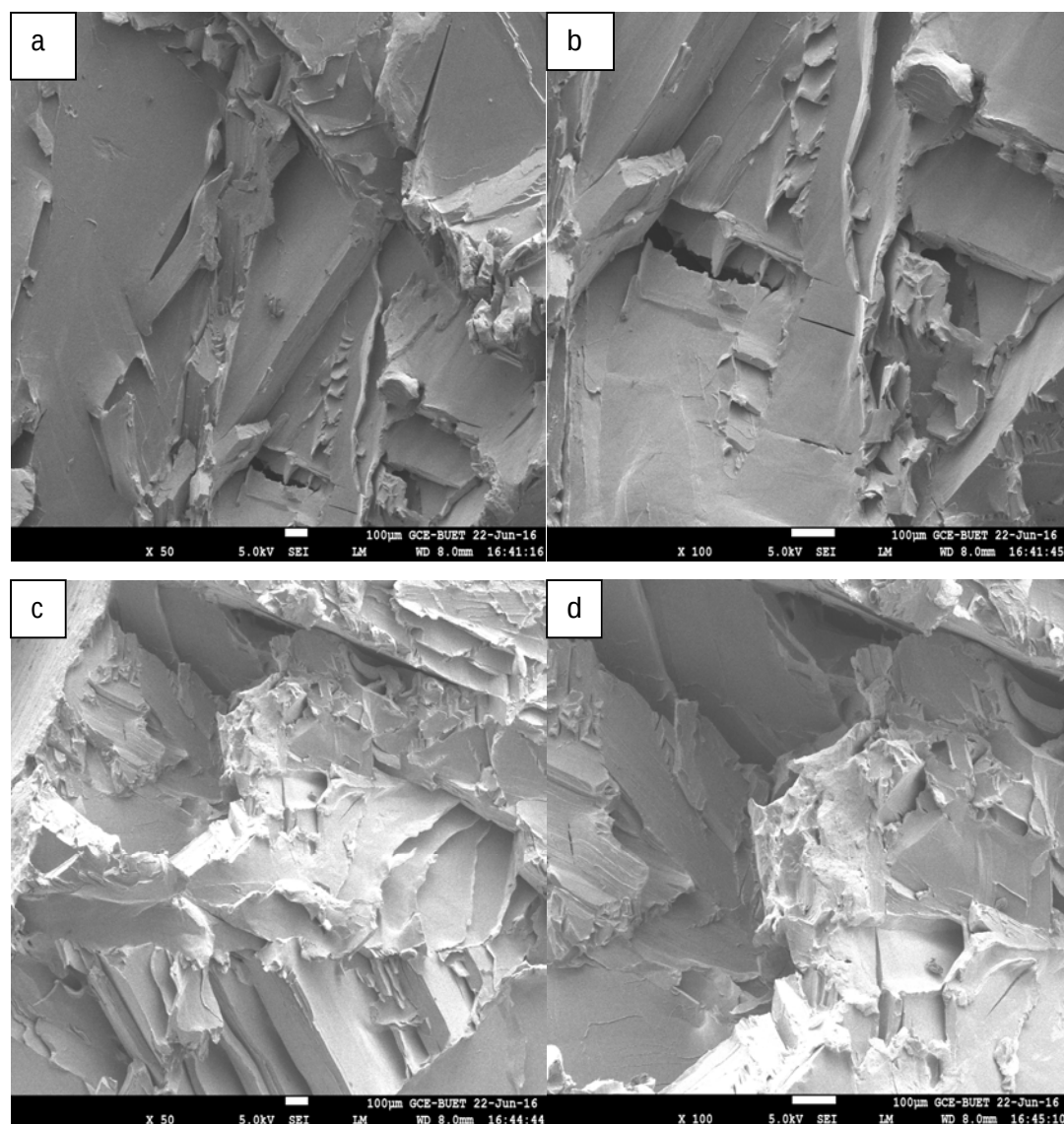


Fig. 4.8: Column Chart Showing tensile strength of Zn-xMo system

4.6.2 Fracture Surface Analysis

Fracture surface produced after tensile tearing of the specimens from the Zn-xMo alloys. The Scanning electron microscopic analysis of these fracture surfaces revealed the fracture mode. The fracture surfaces of the Zn-xMo captured in scanning electron microscope in 50X and 100X magnification are shown in Fig.4.9. All the images are almost similar showing similar fracture behavior. It was observed that, there was only slight difference in the size of the area of the cleavage faces due to a change in the chemical composition of the alloys. However, this is not uniform to indicate a trend in the transition of properties with a gradual change in composition. The fracture plane is smooth enough, showing no cup and cone structure, not shiny, but having some small ridges which indicates that the fracture was neither completely ductile nor completely brittle. It was a mixed fracture mode.



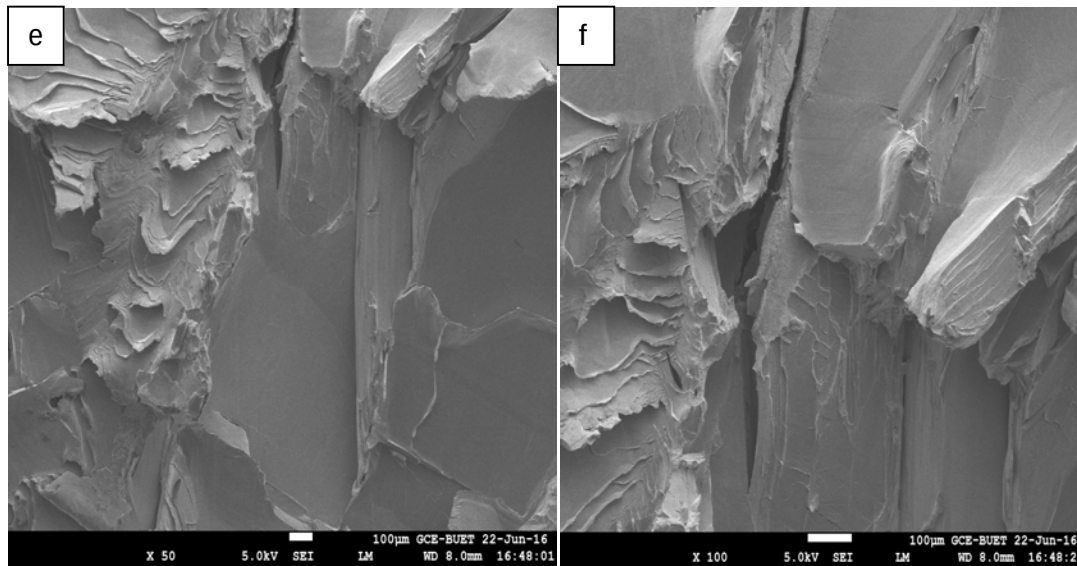


Fig. 4.9: Tensile fracture surface of (a) and (b) Zn-0.4 Mo; (c) and (d) Zn-0.6 Mo; (e) and (f) Zn-0.8 Mo. Here (a), (c) and (e) in 50X whereas (b), (d) and (f) are in 100X magnification.

4.7 Thermomechanical Analysis (TMA)

Figure 4.10 shows the TMA plot of the samples on heating in the temperature range of 30-320°C. From the TMA analysis the linear average co-efficient of thermal expansion (CTE) is found. Since there is no eutectic, eutectoid or peritectic transformation in the selected composition and temperature condition, there found no transition in the plot of TMA graphs. Therefore, linear TMA plots for these Zn-Mo samples are found. The summary of the TMA plots are shown in the Table 4.3. It was observed that, CTE of Zn-xMo decreases with increasing Mo content in the solders. From a previous study, it was found that, CTE of Zn was 34.0×10^{-6} in the temperature range of 30-270°C [124]. Here, CTE of Zn-0.4 Mo was higher but the other two Zn-0.6 Mo and Zn-0.8 Mo was lower than that of virgin Zn.

Table 4.3: CTE of Zn-xMo alloy

Sample	CTE ($1/^{\circ}\text{C}$)
Zn-0.4 Mo	41.5×10^{-6}
Zn-0.6Mo	28.1×10^{-6}
Zn-0.8Mo	26.4×10^{-6}

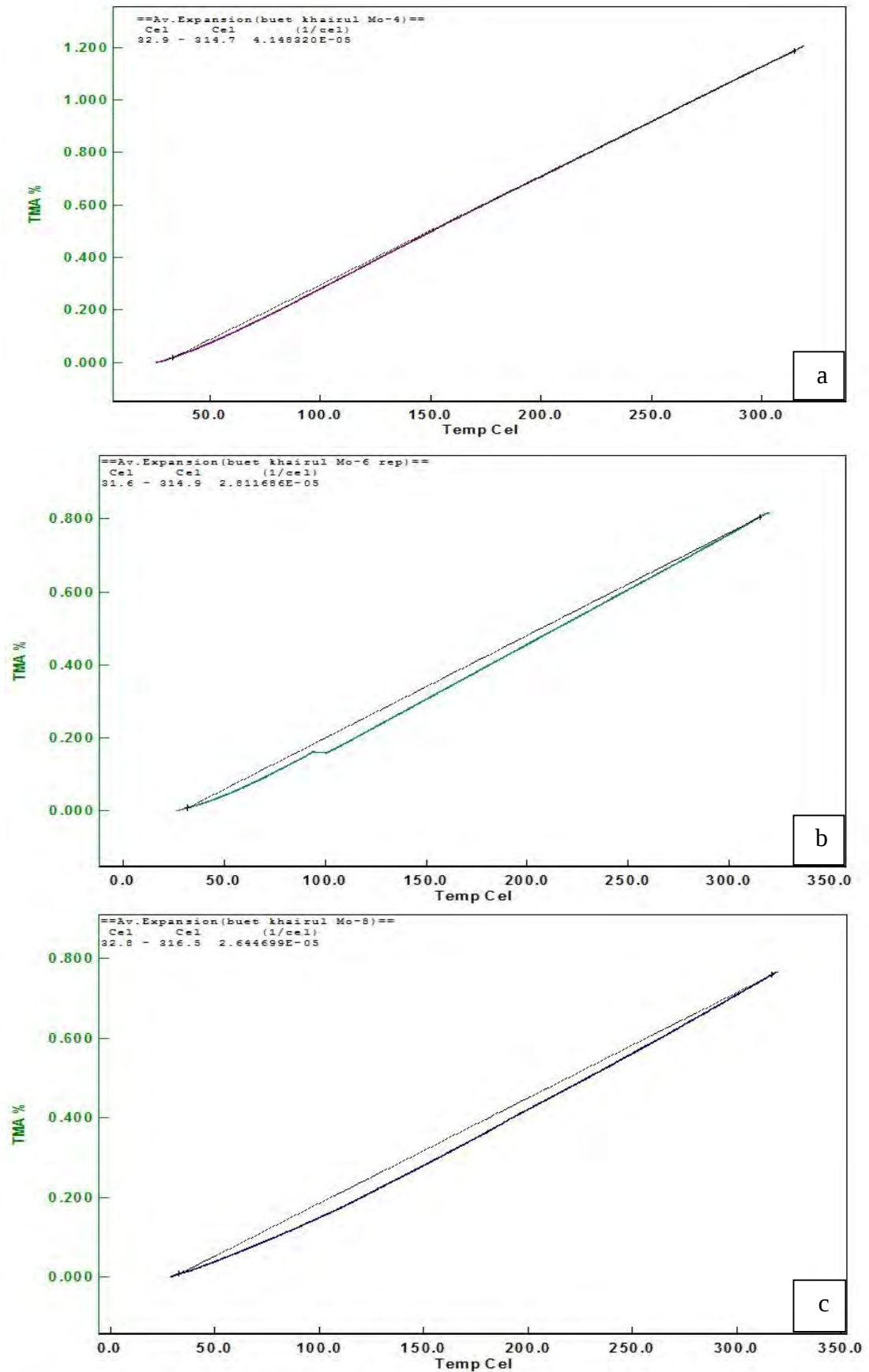


Fig 4.10: TMA plots of (a) Zn-0.4 Mo (b) Zn-0.6 Mo and (c) Zn-0.8 Mo

4.8 Electrical Conductivity Analysis

Electrical conductivity of the solder alloys was determined in %IACS. The experimental results revealed that, conductivity of the alloys decreased with increasing Mo content in the alloys. From %IACS data the resistivity and conductivity can be calculated from the following formulae: $\text{Resistivity} = 172.41 / \% \text{IACS}$ and $\text{Conductivity} = 1 / \text{Resistivity}$ [125,126]. Pure metal is a very good conductor of electricity, where there comes the presence of impurity, the conductivity of the metal falls. Same thing is found now-a-days in case of copper. Now it is found that some specially formed copper shows conductivity of around 103% IACS, which is more than the standard copper. This occurs due to the enhanced purity of copper by sophisticated techniques in the present period. When the standard was formulated the level of purity of copper available at present, was not possible that time. It is evident that, in this study the conductivity of the developed alloys follows the basic theory of electrical conductivity. The obtained result of electrical conductivity of the Zn-Mo solders is graphically represented in Fig. 4.11.

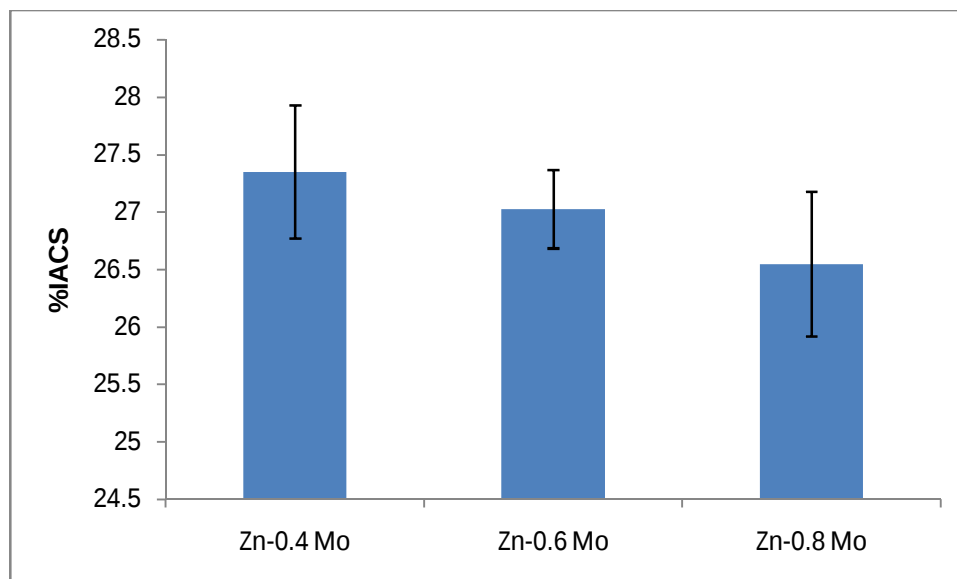


Fig. 4.11: Column chart showing %IACS of Zn-xMo alloys

Zn-xCr System

4.9 Differential Thermal Analysis

Differential Thermal Analysis (DTA) test was conducted at a heating rate of 10°C/min. ranging from room temperature to around 550°C to determine the melting temperature and solidification range of the solders. Lower melting temperature and smaller solidification range are required for quality soldering, because both of these reduce the oxidation of the solder alloys and improve the wettability. DTA curves of the composite solders showed only a single peak in the mentioned temperature range indicating the transformation of these from solid to liquid state during heating. Since, these are not pure metals a range of melting temperature is obtained instead of a single melting temperature like pure metals. Fig. 4.12 shows the DTA graph of the Zn-xCr solders. The graphical data is also presented in table 4.4. DTA graphs exhibited that, the onset of melting started at around 412°C and it finished near about at 418°C showing a melting range of about 6°C. The temperature of melting onset and finish very slightly varied with the small increase in the Cr contents. The similar thing happened in case of melting range (solidification range) of the solders. It is to be noted that, minor addition of Cr contents in the Zn matrix reduces the melting temperature of the pure Zn (419.5°C)

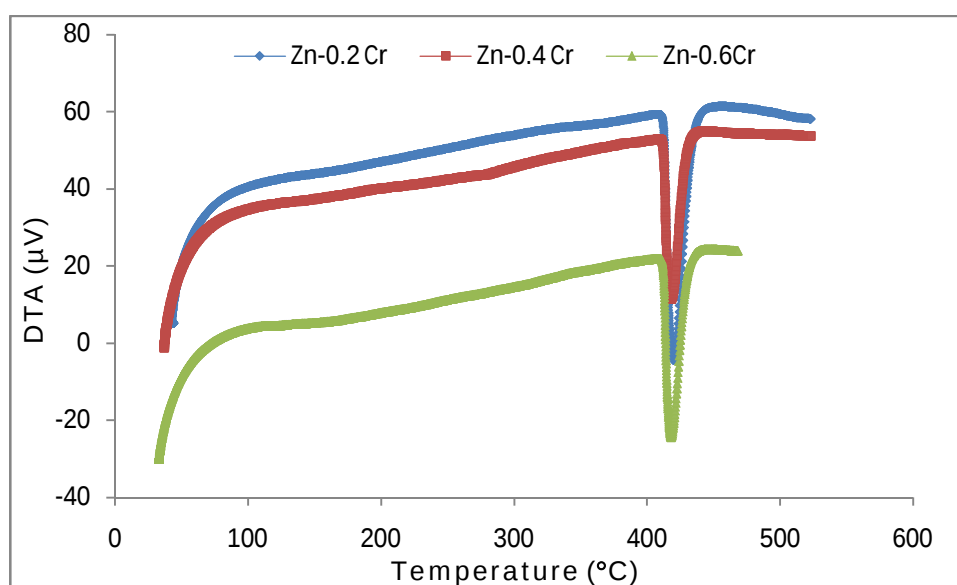


Fig. 4.12: DTA graph of the Zn-xCr system

Table 4.4: Melting properties of Zn-xCr system

Sample ID	Melting start (°C)	Melting finish (°C)	Melting range (°C)
Zn-0.2 Cr	412.8	420.2	7.4
Zn-0.4 Cr	412.3	418.2	5.9
Zn-0.6 Cr	411.6	418.3	6.7

4.10 Microstructure of Zn-xCr system

The microstructure of the Zn-xCr alloys was also analyzed in a similar fashion of Zn-xMo alloys. However, the grain size and shape is not regular like what observed in Zn-Mo system. The microstructures with grain size measurement of the Zn-Cr solders are shown in Fig.4.13 and 4.14. According to literature, due to addition of Cr particles in Zn matrix grain refining should occur. Although it is not evident from the SEM micrographs, grain refining during crystallization is confirmed by calculating crystallite size using the X-ray diffraction data with the help of Scherer equation, which will be discussed in the following sections.

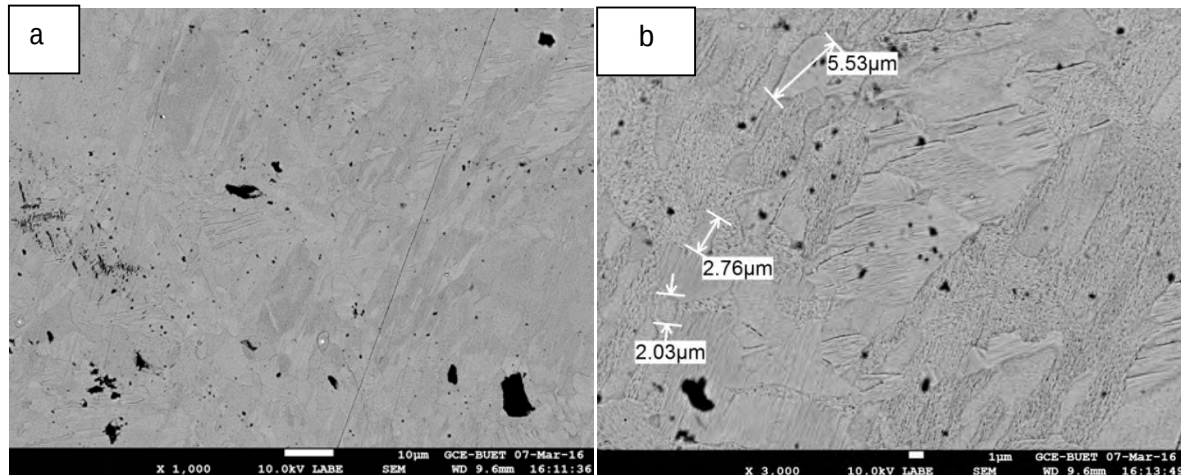


Fig. 4.13: (a) Scanning electron micrograph of Zn-0.2 Cr (b) showing grain size measurement

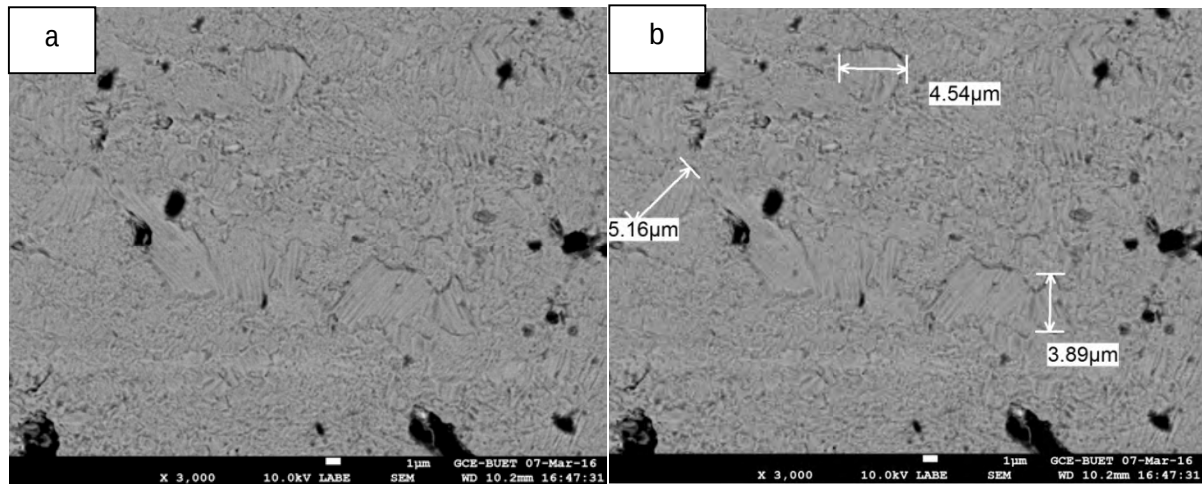
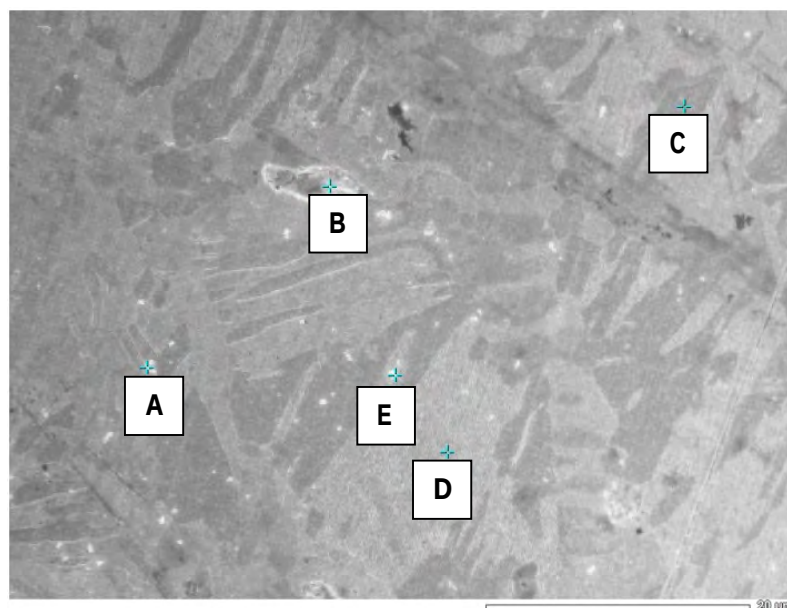
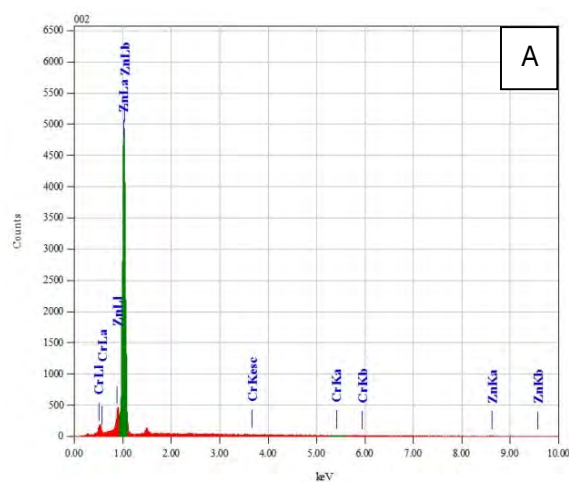


Fig. 4.14: (a) Scanning electron micrograph of Zn-0.4 Cr (b) showing grain size measurement

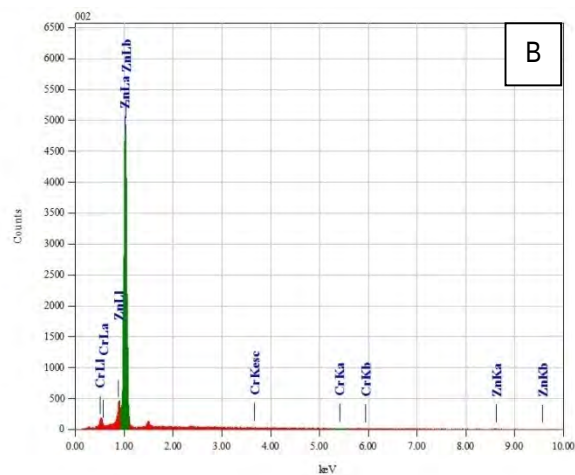
4.11 EDS Analysis of Zn-Cr system

Several EDS spots were also marked in different zones of the microstructure of Zn-Cr solders. Figure 4.15 exhibits some such EDS spots in Zn-0.2 Cr solder. From the elemental analysis of these spots it was observed that, in the spot A, which was taken inside the grain, there was 100 percent Zn. The same thing was found in case of spot B and C. On the other hand, in spot D and E, there was found 0.33 and 0.30 percent Cr respectively, while the rest was Zn

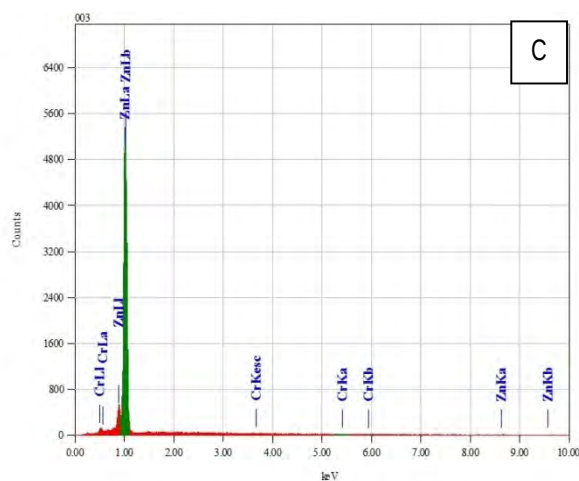




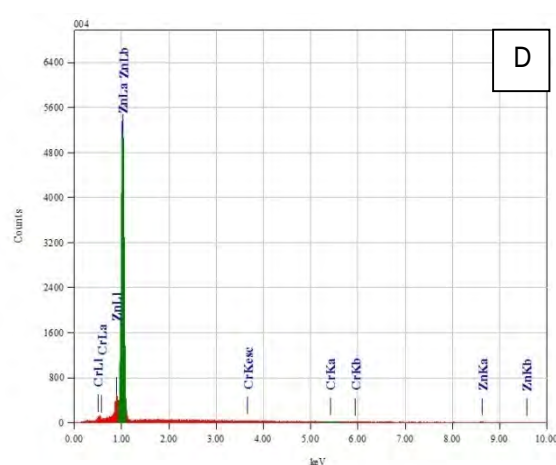
Element	(keV)	Mass%	Sigma	Atom%	Cc
Cr K	*				
Zn L	1.012	100.00	0.60	100.00	
Total		100.00		100.00	



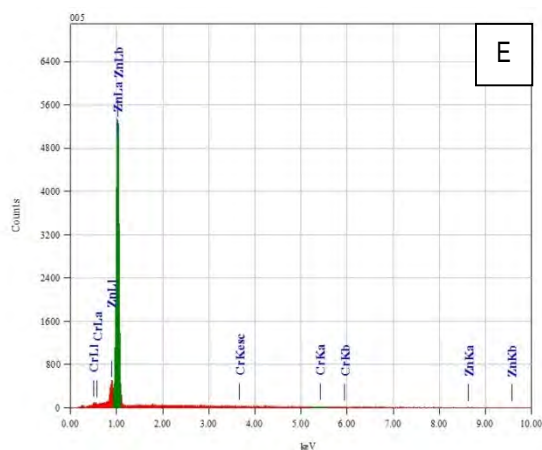
Element	(keV)	Mass%	Sigma	Atom%	Cc
Cr K	*				
Zn L	1.012	100.00	0.60	100.00	
Total		100.00		100.00	



Element	(keV)	Mass%	Sigma	Atom%
Cr K	*			
Zn L	1.012	100.00	0.57	100.00
Total		100.00		100.00



Element	(keV)	Mass%	Sigma	Atom%
Cr K	*	5.411	0.33	0.22
Zn L	1.012	99.67	0.58	99.59
Total		100.00		100.00



Element	(keV)	Mass%	Sigma	Atom%	C
Cr K	*	5.411	0.30	0.21	0.38
Zn L	1.012	99.70	0.57	99.62	
Total		100.00		100.00	

Fig. 4.15: EDS analysis of Zn-Cr solders

4.12 X-Ray Diffraction (XRD) Analysis

The XRD pattern of Zn-xCr solders is depicted in Fig 4.16. The peaks pattern obtained here in case of these compositions almost match with the standard pattern of pure Zinc. The whole pattern was analyzed by PDF 2 software and searched for whether any intermetallics or any other phases comprising of Zn/Cr present in the structure. Since, the amount of Cr was very minute and XRD can hardly detect any 2nd/3rd component comprising less than 5% of the total elements, the formation of intermetallics or other phases was not found from XRD analysis. With the increasing of Cr content in the solders there was no shifting in the peak position except in the case of Zn-0.6Cr. However, there was difference in the peak intensity and hence in full width at half maxima (FWHM) values which is related to the crystallite size of the respective solders. The average crystallite size of all these compositions was calculated using **Scherer equation**.

$$\tau = \frac{k\lambda}{\beta \cos \theta}$$

Where,

τ is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size;

k is a dimensionless **shape factor**, with a value close to unity. The shape factor has a typical value of about 0.9, but varies with the actual shape of the crystallite;

λ is the X-ray wavelength; here used Cu k-alpha, $\lambda=0.15406$ nm

β is the line broadening at half the maximum intensity (FWHM), after subtracting the instrumental line broadening, in radians. This quantity is also sometimes denoted as $\Delta(2\theta)$;

θ is the Bragg angle.

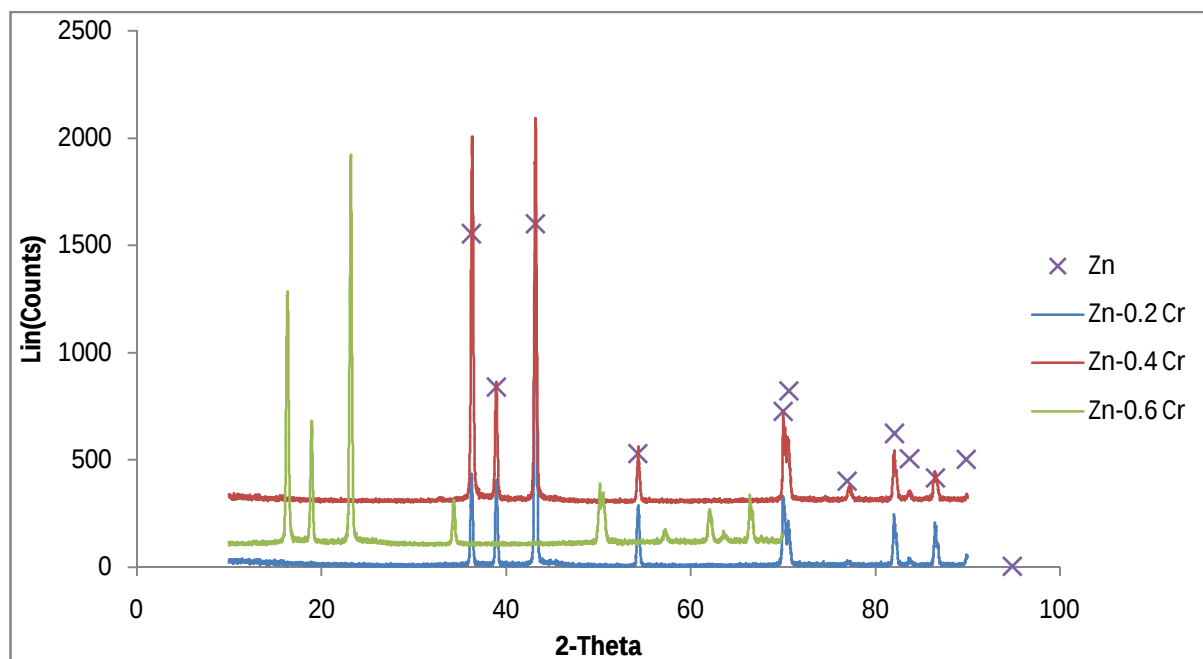


Fig. 4.16: XRD peaks of Zn-xCr system with standard Zn.

Table 4.5: Calculation of Crystallite size of Zn-xCr using **Scherer equation**

Sample ID	FWHM (degree)	2 Theta	Crystallite size (nm)	Average (nm)
Zn-0.2 Cr	0.2882	36.2958	29.0	29.7±0.8
	0.2853	38.9794	29.5	
	0.2798	43.2229	30.5	
Zn-0.4 Cr	0.2975	36.3468	28.1	29.0±1.3
	0.2799	43.2101	30.5	
	0.2959	38.9624	28.5	
Zn-0.6 Cr	0.3041	36.3344	27.5	28.8±1.3
	0.2928	38.9563	28.8	
	0.2847	43.1998	30.0	

The calculation of crystallite size of the Zn-xCr alloys has been shown in Table 4.5. The effect of increasing Cr on the crystallite size can be easily visualized from the presented data.

It is evident that, with increasing the percentage of fine particles of Cr in Zn the resulted crystallite size decreases. This phenomenon of grain refining with addition of fine particles is also proved by the scanning electron microscopy, where the grain size was found to be decreased with increasing Cr content. Grain, we observe in microscopy, is nothing but a single crystal or a sum of some crystallites.

4.13 Hardness of Zn-xCr system

Brinell Hardness

Brinell hardness number of the Zn-Cr solders is depicted in the Fig. 4.17. This clearly revealed that hardness of the solders increased with increasing Cr content in the Zn matrix. Experimental results revealed that, Brinell hardness number of Zn-xCr increased from 33.98 in Zn-0.2 Cr to 42.74 in case of Zn-0.6 Cr solder. The mechanism of such hardening can be easily understood from the microstructural characteristics of the solders. As discussed earlier, grain refinement of Zn-Cr solders was evident due to the addition of Cr particles. With increasing percentage of Cr particles grain size of the solders decreased gradually, which was not only confirmed by scanning electron microscopy but also by X- ray diffraction analysis. In general, finer grained structure exhibits superior hardness compared to coarser one. Moreover, the dispersion of small metallic particles throughout the structure adds value to the mechanical properties by dispersion strengthening mechanism.

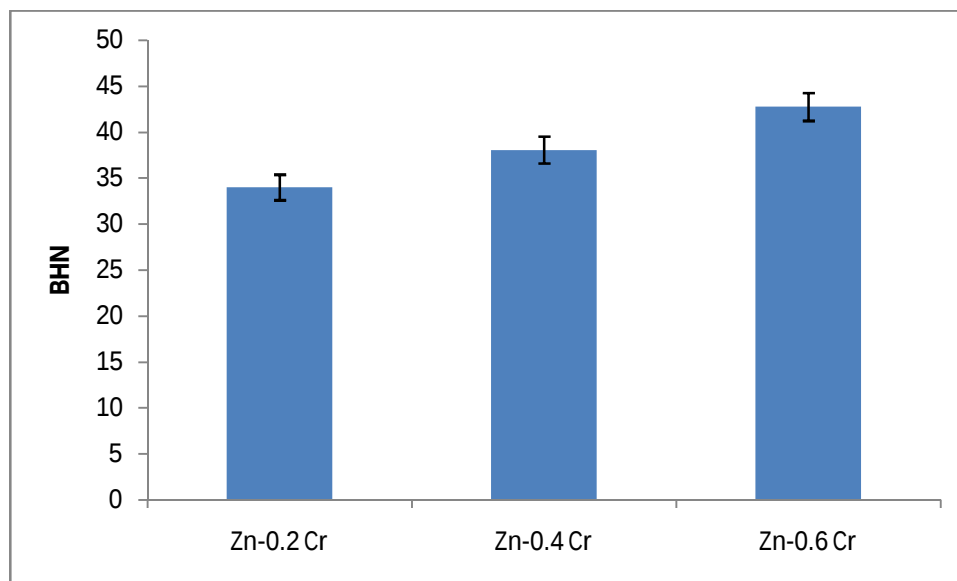


Fig. 4.17: Column chart showing Brinell hardness of Zn-xCr system

4.14 Tensile Testing

4.14.1 Tensile Strength

Tensile strength of the proposed Zn-xCr solders has been depicted graphically in the Fig. 4.18. From these figures it is clear that, as the Cr content increased strength of the solders also increased. One way of increasing strength is strengthening by metallic particles. During solidification after pouring the molten alloy in the mould, impurity particles, here Cr, act as nucleating sites assisting crystallization and result in grain refining. According to Hall-Petch relationship it is evident that tensile strength is inversely proportional to the grain size. Therefore, small grains produced by heterogeneous nucleation are supposed to increase strength of the Zn-xCr solders. This experimental study also supports the theory of strengthening by Hall-Petch. In a similar manner of Zn-Mo alloys, strength of Zn-Cr alloys increased from 40.53 to 47.07 MPa due to an increase in 0.4% Cr than that of the former. One of the major outcomes of this study is that zinc can be strengthened by Mo and Cr particles addition which is proved by both theory and experiment.

Apart from this, Cr particles obstruct the movement of dislocations. Dislocation needs to move from one grain to another to reach in the rupture point. Easy movement of dislocations leads to relatively lower strength and hardness of the respective alloys. In this experiment, strength was found to be increased when Cr was added to Zinc. One reason for this is, during the period of loading dislocation was not able to move easily from one grain to another. This means, dislocation needed two forces, one to move from grain to grain, another to bypass the hindrance of dispersed precipitations. As a result, total force for fracture increases because of Cr addition.

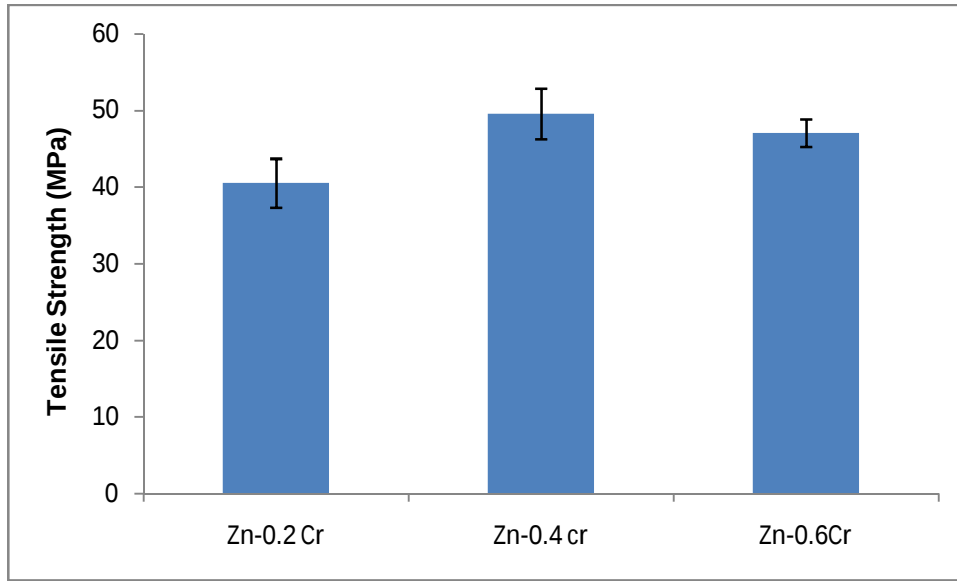


Fig. 4.18: Column Chart Showing tensile strength of Zn-xCr system

4.14.2 Fracture Surface Analysis

Fracture surface produced after tensile tearing of the specimens from the Zn-xCr systems. The scanning electron microscopic analysis of these fracture surfaces revealed the fracture mode during tensile loading. The fracture surfaces of the Zn-xCr captured in scanning electron microscope in 50X and 100X magnification are shown in Fig. 4.19. All the images are more or less similar showing similar fracture behavior. It is observed that, there is only slight difference in the size of the area of the cleavage faces due to a change in the chemical composition of the alloys. However, this was not uniform to indicate a trend in the transition of properties with a gradual change in composition. The fracture plane was smooth enough, showing no cup and cone structure, not very shiny, showing some ridges in different zone which was indicative that the fracture mode was neither completely brittle nor completely ductile. The Zn-Cr solders experienced a mixed fracture mode in tensile load.

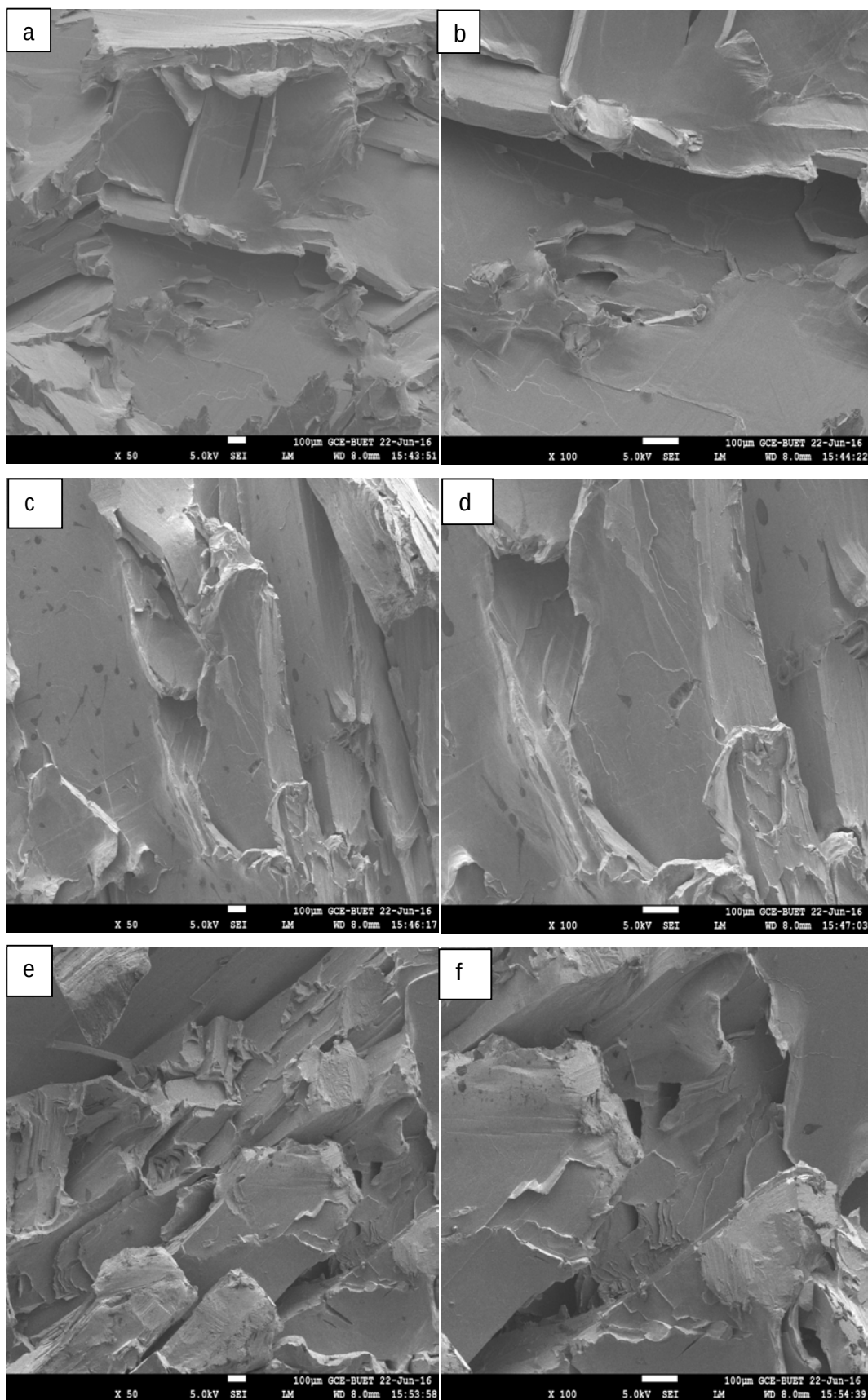


Fig. 4.19: Tensile fracture surface of (a) and (b) Zn-0.2 Cr; (c) and (d) Zn-0.4 Cr; (e) and (f) Zn-0.6 Cr. Here (a), (c) and (e) in 50X whereas (b), (d) and (f) are in 100X magnification.

4.15 Thermomechanical Analysis (TMA)

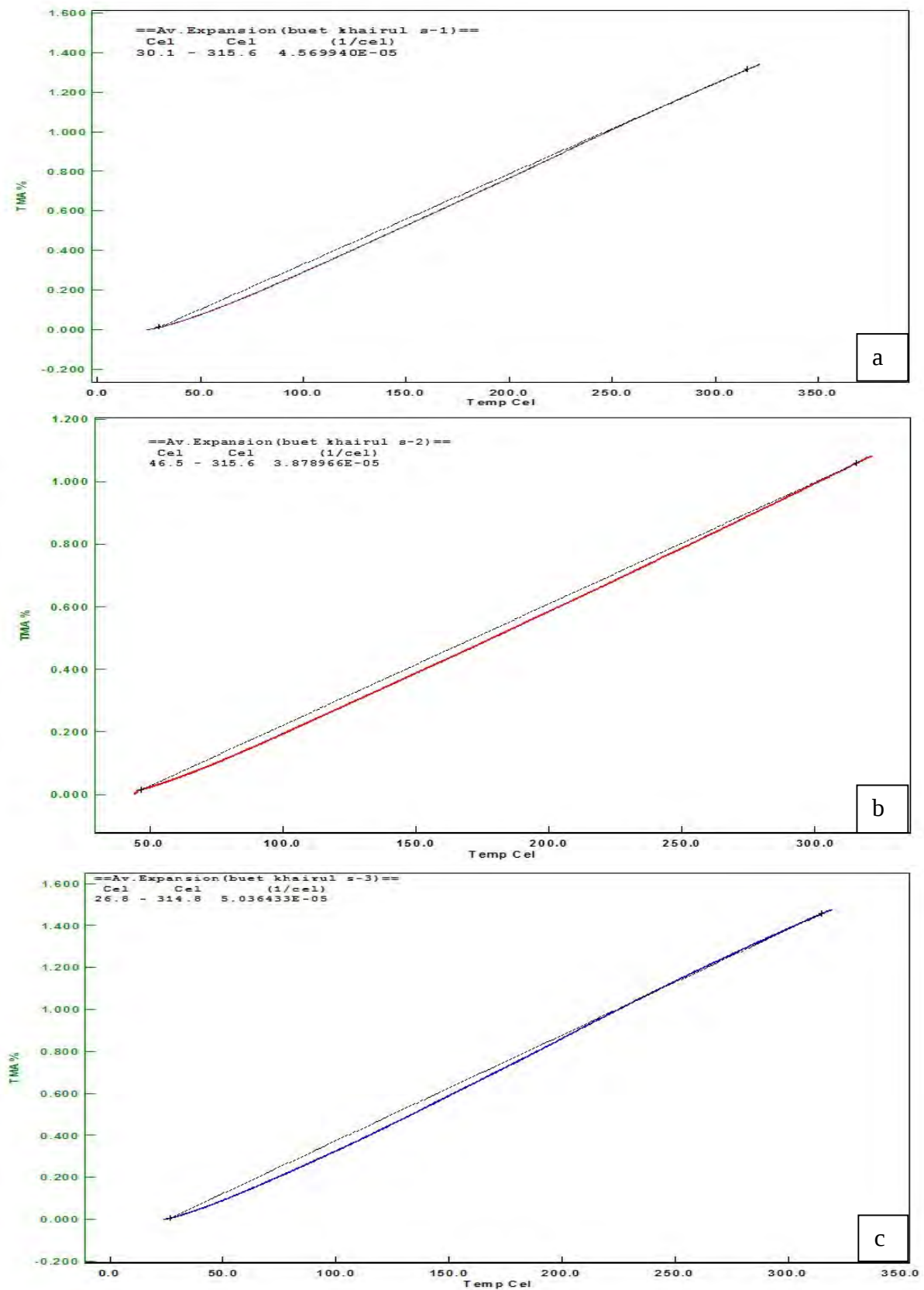


Fig. 4.20: TMA plots of (a) Zn-0.2Cr (b) Zn-0.4Cr and (c) Zn-0.6 Cr

Table 4.6: CTE of Zn-xCr system

Sample	CTE (1/°C)
Zn-0.2 Cr	45.7×10^{-6}
Zn-0.4 Cr	38.8×10^{-6}
Zn-0.6 Cr	50.4×10^{-6}

Figure 4.20 shows the TMA plot of the samples on heating in the temperature range of 30-320°C. From the TMA analysis the linear average co-efficient of thermal expansion (CTE) is found. Since there was no eutectic, eutectoid or peritectic transformation in the selected composition and temperature condition, there was no transition observed in the plot of TMA graphs. Therefore, linear TMA plots for these Zn-Cr samples were found. The summary of the TMA plots are shown in the Table 4.6. Interestingly, in case of Zn-xCr system, CTE decreased first in Zn-0.4 Cr and then increased again for Zn-0.6 Cr. From a previous study, it was found that, CTE of Zn was 34.0×10^{-6} in the temperature range of 30-270°C [124]. Here, all the Zn-Cr based systems exhibited higher CTE compared to pure Zn, whereas CTE of Zn-0.4 Mo was higher but the other two Zn-0.6 Mo and Zn-0.8 Mo was lower than that of Zn.

4.16 Electrical Conductivity Analysis

Electrical conductivity of the solders has been determined in %IACS. IACS is an acronym for International Annealed Copper Standard. The conductivity of the annealed copper (5.8001×10^7 S/m) is defined to be 100% IACS at 20°C [125]. All other conductivity values are related back to this conductivity of annealed copper. The experimental results revealed that, conductivity of the solders decreases with increasing Cr content. The result is shown graphically in fig. 4.21. From % IACS data the resistivity and conductivity can be calculated from the following formulae: Resistivity= $172.41 / \% \text{IACS}$ and Conductivity= $1/\text{Resistivity}$ [126]

Pure metal is a very good conductor of electricity, where there comes the presence of impurity, the conductivity of the metal falls. Same thing is found now-a-days in case of copper. Now it is found that some specially formed copper shows conductivity of around 103% IACS, which is more than the standard copper. This occurs due to the enhanced purity of copper by sophisticated techniques in the present period. When the standard was formulated the level of purity of copper available at present, was not possible that time. It is evident that, in this study the conductivity of the developed alloys follows the basic theory of electrical conductivity.

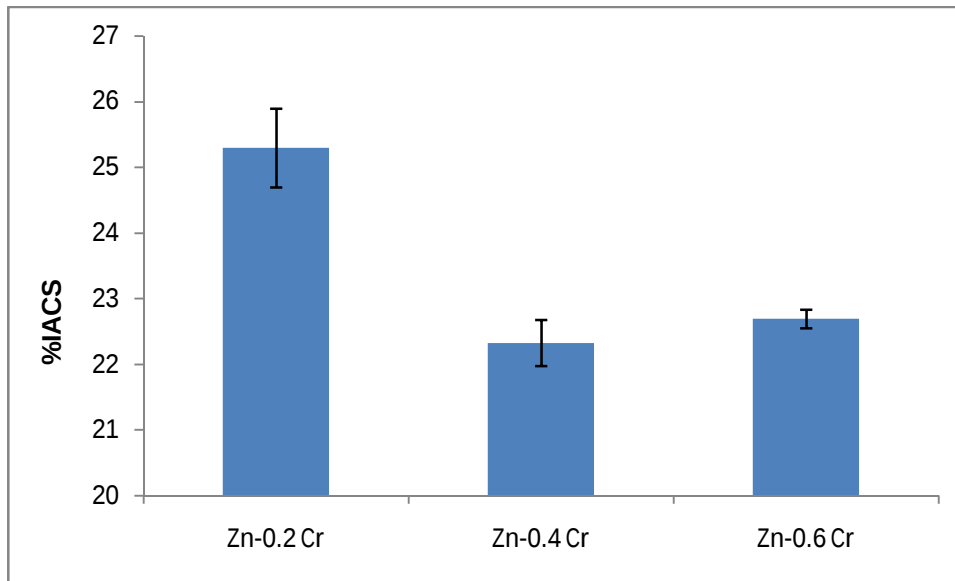


Fig.4.21: Column chart showing %IACS of Zn-xCr system

4.17 Comparison of Zn-xMo and Zn-xCr solders with conventional solders

Table 4.7 shows a comparative analysis of some properties such as tensile strength, hardness, co-efficient of thermal expansion, melting temperature and electrical conductivity of some high temperature solder alloys, eutectic Sn-Pb solder with Zn-xMo and Zn-xCr solders of this study. It is observed that, tensile strength of Pb based solders as well as Sn-Pb eutectic solder is very closer to the strength of Zn-xMo while, Zn-xCr has a higher tensile strength compared to them. Both Zn-xMo and Zn-xCr solders have much higher hardness than that of Pb based high temperature solders. Zn-xMo solders have a comparable coefficient of thermal expansion with that of Pb-5Sn as well as Pb-10Sn, while Zn-xCr solders have much higher value of CTE which might play negative role in the application of this as solders. Melting temperature of the Zn based solders of this study is much higher compared to the Pb based and Sn-Pb eutectic solders. The higher melting temperature requires higher energy intensive processes and may cause thermal damage if the soldering is not properly designed. Superior electrical conductivity of the Zn based solders compared to the others adds further value towards the applicability of the proposed Zn based high temperature solders.

Table 4.7: Comparison of some properties of high temperature Pb based solders, eutectic Sn-Pb with Zn-xMo and Zn-xCr solders

Composition	Properties					References
	Tensile Strength (MPa)	Hardness (HB)	CTE (1/K) $\times 10^{-6}$	Melting Temperature (°C)	Electrical Conductivity (% IACS)	
Sn-37 Pb	30.6	17	24	183	11.9	[127],[128]
Pb-5Sn	28	8	28.4	300-314	8.79	[127],[128]
Pb-10Sn	30	10	27.9	268-301	8.88	[127],[128]
Zn-xMo	31-33	29-41	26-28	412-438	26-27	
Zn-xCr	40-47	34-43	38-50	409-434	22-25	

Chapter Five

Conclusion

- ✓ The microstructure of the solders developed in this study showed grain refinement with the addition of Mo and Cr particles in Zn. With increasing percentage of these metal powders the grain size of the solders decreased.
- ✓ Differential Thermal analysis of the specimens showed that, melting of the Zn-Cr system started at around 412°C and finishes at 418°C showing about 6°C of melting/solidification range. It is also indicative that, melting temperature was reduced from that of pure zinc (419.5°C) due to the addition of Cr. In case of Zn-xMo system the similar phenomenon was also found. Melting temperature of Zn decreased due to the addition of Mo with a solidification range of around 7°C.
- ✓ X-ray diffraction pattern confirmed that there was no evidence of formation of any intermetallics between Zn and Mo/Cr. However, crystallite size of the solders was decreased with increasing Mo and Cr powders confirmed by the crystallite size calculation using Scherer equation.
- ✓ Experimental results of Brinell hardness test revealed that, the hardness of the Zn-Mo as well as Zn-Cr alloys increased due to an increase in Cr and Mo content in the solders.
- ✓ With increase in Cr and Mo content in the proposed solders grain refinement was evident both from scanning electron microscopy and X ray diffraction analysis. This grain refinement, in effect, improved the tensile properties of the solders which were in agreement with Hall-Petch relationship, although there was found a slight fall of strength in Zn-0.6Cr solder. Fracture surface analysis showed the fracture mode to be mixed (not fully ductile or brittle) in both the type of solder systems.
- ✓ Thermomechanical analysis of the solders provided the data of the coefficient of thermal expansion (CTE). The conclusion might be drawn as CTE of Zn-xMo decreased with increasing Mo content in the solders. But interestingly, in case of Zn-xCr system, CTE decreased first in Zn-0.4 Cr and then increased again for Zn-0.6 Cr.
- ✓ The electrical conductivity of the solders decreased with increasing both Mo and Cr content in the Zn based systems. Both Zn-xMo and Zn-xCr solders exhibited lower electrical conductivity compared to pure Zn.

- ✓ The proposed Zn based solders have some comparable properties with conventional Pb based high temperature solders as well as eutectic Sn-Pb solder. In some cases, Zn based solders exhibited superior properties compared to that of conventional Pb based solders.

Chapter Six

Recommendation for future works

6.1 Investigation of the interconnecting properties

As the use of solder alloys is to join metals on PCB, it is obvious to study the interconnecting properties of the solder alloys to evaluate the performance in a long run. Specifically, the bath soldering in PCB may be performed to join the circuit's electronic components on it.

6.2 Investigation of hot/cold working properties

Since solder alloys are found in market in different forms such as wire, bar, paste, shot and ingot, the workability of the solder proposed solders should be investigated to make the product marketable and consequently usable in the final application.

6.3 Investigation of the Interface of Solder Joint

During studying the interconnecting properties of the solders for different base metals, the formation and growth of IMCs are required to be studied along with the evaluation of microstructure and mechanical properties.

6.4 Determination of the Performance in Aggressive Environment

As the oxidation resistance of the Zn-based alloys is questionable, the oxidation and corrosion properties at various atmospheres are needed to be evaluated.

6.5 Spalling and Creep Resistance

During the performance of the solder temperature is associated, so it is required to study the mechanical properties at higher temperature and the spalling resistance of the solder and its joints are also required.

6.6 Wetting Properties

It is needed to reveal the wetting behavior of the solder alloys to evaluate the performance of solders. In this case, copper substrate can be used to know the spreadability and wettability.

6.7 Study the Other Zn based Alloys

As Zn based solders provide comparable mechanical properties at a reasonable price it is required to study the other binary, ternary and quaternary Zn-based alloys to find the most economical alloy with the superior solder properties.

6.8 Study of the thermal conductivity

Almost many times in service the solder alloy has to dissipate heat to work properly. Hence, thermal conductivity of the solder alloys is a crucial parameter. Thermal conductivity of Zn based solders may be further studied.

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