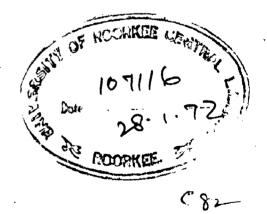
# EFFECT OF TERNARY ADDITIONS ON THE AGEING CHARACTERISTICS OF SOME ALUMINIUM-ZINC ALLOYS

A Dissertation submitted in partial fulfilment of the requirements for the degree of MASTER OF ENGINEERING in METALLURGICAL ENGINEERING [PHYSICAL METALLURGY]

BY



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## CERTIFICATE

Certified that the Dissertation entitled, "EFFECT OF TERNARY ADDITIONS ÔN THE AGEING CHARAC-Al-Zn ALLOYS, which is being sub-SOME TERISTICS OF mitted by Mr. VINAY KUMAR GARG in partial fulfilment for the award of the Degree of Master of Engineering in Metallurgical Engineering [Physical Metallurgy] of the University of Roorkee, Roorkee(India), is a record of his own work carried out by him under my supervision and guidance, from 2nd January 1971 to October 11, 1971.

The matter embodied in this dissertation has not been submitted for the award of any other degree.

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#### ABSTRACT

The influence of homogenisation temperature, ageing temperature and solute concentration on the rate of pre-precipitation has been studied employing resis tivity and hardness measurements. Whereas hardness measurement was restricted only to binary Al-Zn alloys, resistivity measurements were extended to two ternary additions of In also.

It has been found that both resistivity and hardness increase with ageing time and that the hardness curves are characterized by a well-defined incubation period while resistivity starts increasing almost instantaneously. Time taken to reach the resistivity maxima and "flat hardness" are strongly dependent of the homogenisation and ageing temperatures. Homogenisation temperature is found to have no influence on the resistivity peak and "flat hardness" while these are strongly dependent on the ageing temperature.

It is observed that addition of In to the binary alloys lowers the rate of pre-precipitation and higher the In content, slower is the ageing process.

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#### CHAPTER - I

#### LITERATURE REVIEW

#### 1.1 INTRODUCTION :

The phenomenon of age hardening, as is understood in its present form, is known to involve a precipitation reaction leading to the formation of a fully or partially coherent phase from a supersaturated solid solution and thus resulting in net increase in hardness. This technique has acquired a conspicuous position as one of the modern strengthening techniques because of the obvious advantage of possibility of heat-treating after the alloy has been worked to its final shape. Most important age hardenable alloys include Al-Zn, Al-Cu, Al-Mg and Cu-Be. The strength of such alloys can be increased by ageing to as much as five times.

Al-Zn system was chosen to be studied in the present investigation since it offers a wide range of solid solubility and hence constitutes one of the best alloy systems suited for age hardening.

#### 1.2 HISTORICAL SURVEY :

Alfred Wilm<sup>1,2</sup> a German Scientist, in the years 1903-1911, discovered that Duralumin (an aluminium alloy) when quenched from high temperature below its melting point to low temperature and then allowed to stand at room temperature the hardness increased with time. It was later on found that the change in hardness could occur even at other temperatures but the course of hardening differed at different temperatures. This process has come to be known as "Ageing" and the change in hardness as Age Hardening.

Subsequently, some alloys other than duralumin were found to exhibit ageing and hence the phenomenon attracted the attention of many workers<sup>3-7</sup> due primarily to the fact that super high strength light alloys needed for many industrial applications could be developed. Since ageing is undoubtably followed by precipitation of a second phase from the parent matrix of supersaturated  $\alpha$ , it came to be known as "Precipitation Hardening" also.

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Age hardening consists of :

- Homogenisation ; i.e., heating the alloy to a temperature where homogeneous solid solution is obtained.
- 2. quenching the alloy from solutionizing temperature to lower temperatures so that supersaturated solid solution is obtained, and
- 3. ageing ; holding the quenched specimen at a definite temperature for various lengths of time.

Prerequisits of age hardening :

Following are the prerequisits for an alloy system to be precipitation hardened :

- The solubility of the solute must decrease with decreasing temperature in the solid solution or, in other words, the phase diagram of the alloy system should have a sloping solvus,
- 2. on quenching from solutionising temperature a supersaturated solid solution must form, and

3. on heating, this supersaturated solid solution must decompose into a non-equilibrium or intermetallic phase which is fully or partially coherent with the matrix.

#### 1.3 STRUCTURAL CHANGES DURING AGEING :

Complex structure changes occur in age hardening alloys during the process of ageing. A typical sequence of structural changes can be represented as :

> Solid solution(at homogenisation temperature) Quench : supersaturated solid solution Excess vacancies  $\longrightarrow$  Loops, Helics, Stacking faults Solute atoms  $\longrightarrow$  clusters  $\longrightarrow$  zones Intermediate precipitate Equilibrium precipitate

1.3.1 Defect structure :

At the homogenisation temperature, solute atoms and vacancies are randomly distributed in the substitutional solid solution. On quenching, the alloy becomes supersaturated with vacancies and solute atoms. These excess vacancies give rise to various structural defects which act as potential sites for nucleation of metastable precipitate.

The defect structure introduced by quenching 8-10 has been studied in Al and Al-alloys by various authors. In aluminium, the microstructure consists of prismatic dislocation loops about 500  $A^{0}$  in diameter which are formed by the collapse and shear of discs of vacancies in the manner predicted by Kuhlman-Wilsdorf<sup>11</sup> In dilute aluminium alloys excess vacancies are generally precipitated as prismatic dislocation loops while in concentrated alloys they form helical dislocations.

According to Kuhlman-Wilsdorf,<sup>11</sup> the excess retained vacancies first form clusters or discs. Prismatic dislocation loops are then formed by collapse and shear of these vacancy clusters or discs. The mechanism of formation of helical dislocations has been suggested by Cottrell<sup>12</sup> which is based on the absorption of vacancies

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on a screw dislocation. Thomas and Whelan<sup>13</sup> have investigated the mode of formation of helical dislocations in quenched alloys and have suggested a mechanism to explain the large number of helical dislocations found in these alloys. According to them, a prismatic dislocation loop may elongate along its glide cylinder to produce two long screw dislocations. These screw dislocations then transform to helical ones by the mechanism suggested by Cottrell<sup>12</sup>

Kelly and Nicholson<sup>14</sup> concluded that the defect structure of a quenched dilute supersaturated alloy is generally similar to that of pure metals although the number of excess vacancies is higher due to the binding energy between a solute atom and a vacancy. In concentrated supersaturated alloys, formation of defects is difficult, and no defects other than helical dislocations and a few isolated dislocation lines and prismatic loops have yet been observed.

Rajan and Saxena<sup>15</sup> studied the effect of cold working on precipitation hardening. They concluded that the effect of cold working on precipitation, hardening is a complex phenomenon involving interaction between vacancies, dislocations, solute atoms, zones, intermediate phases and the equilibrium precipitate.

#### 1.3.2. Pre-precipitation :

During the early stage of ageing, solute atoms segregate on certain preferential crystallographic planes thus leading to the formation of solute rich clusters. These clusters are mobile and grow at the expense of each other forming G.P. zones. The clusters are completely homogeneous with the matrix and so also the zones and do not possess structures of their own. Zones, however, have a definite shape depending upon the degree of mismatch between the atomic diameters of solute and solvent. Strictly speaking, if zones are left to itself, they have their lattice parameter different from that of the parent But since zones are homogeneous or, in other matrix. words, have one to one correspondence with the matrix, the overall zone: is either compressed or expanded to match its lattice parameter with that of the parent matrix.

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Elastic strains are thus set up and there is an elastic interaction of the field due to dislocations and elastic strain set up due to the formation of zones. This offers resistance to the movement of dislocations and hence the hardness increases. The change in hardness eventually depends upon the difference in atomic diameter of solute and solvent. There is no nucleation barrier for clustering and zone formation. Guinier termed this phenomenon as pre-precipitation, to distinguish it from the true precipitation.

Kinetics of pre-precipitation :

Jagodzinski and Laves<sup>16</sup> first pointed out that Guinier's model<sup>6</sup> of G.P. zones in Al - Cu alloys required a very high diffusion coefficient, at least  $10^7$ times greater than normal diffusion coefficient obtained by extrapolation of high temperature measurements to room temperature. Two attempts have been made to explain this anomalously high solute diffusion coefficient in quenched alloys.

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The first explanation proposed by Turnbull<sup>17</sup> assumed the diffusion of solute atoms to take place via dislocations. A large number of dislocations may act as channels for easier diffusion, but this theory failed to explain why the diffusion coefficient was so sensitive to quenching rate, homogenisation temperature etc.

Another plausible explanation proposed by Zener<sup>18</sup> and later developed by Federighi<sup>19</sup> and De Sorbo <u>et al.</u><sup>20</sup>, attributes this anomaly to quenched-in vacancies. The theory, came to be known as 'Excess Vacancy Theory', is widely accepted and assumes that high rate of diffusion is due to higher concentration of quenched-in vacancies.

The diffusion coefficient of Cu in Al at an ageing temperature  $T_A$  is given by:

$$D_{Cu} = A \exp \left[-\frac{E_F + E_M}{k T_A}\right] ...[1.1]$$

where  $E_F$  and  $E_M$  are the activation energies for the formation and migration of vacancies respectively, and A is a constant. At 20°C, assuming  $E_F + E_M = 1.4 \text{ eV}$ ,  $D_{Cu}$  was calculated to be  $10^{-24} \text{ cm}^*/\text{sec.}$  But De Sorbo et al<sup>20</sup> calculated  $D_{Cu} \sim 10^{-16} \text{ cm}^*/\text{sec}$  by assuming

that Cu atoms move three or four atom diameters during clustering. Thus there is a discrepancy of  $\sim 10^8$  between experimental and theoretical values. The excess vacancy theory attributes this discrepancy to the fact that diffusion is governed by a concentration of vacancies which would be in equilibrium at the homogenisation temperature  $T_H$  rather than at ageing temperature  $T_A$ . Thus :

$$D_{Cu} = A \exp \left[-\frac{E_F}{k T_H}\right] \exp \left[-\frac{E_M}{k T_A}\right]$$
... [1.2]

Assuming  $E_F = 0.76 \text{ eV}$ ,  $E_M = 0.58 \text{ eV}$ ,  $T_H = 550^{\circ}\text{C}$ and  $T_A = 20^{\circ}\text{C}$ , the value of  $D_{Cu}$  was calculated to be  $5 \times 10^{-16} \text{ cm}^2/\text{sec.}$  which is in good agreement with the value estimated from experimental data. If the quenching is slow, some vacancies have time to migrate to sinks during quenching itself and thus the retained vacancy concentration will not be associated with  $T_H$  but with some lower temperature  $T'_H$ . The equation [1.2] can thus be modified as :

$$D_{Cu} = A \exp \left[-\frac{E_F}{k T_H^{\dagger}}\right] \exp \left[-\frac{E_M}{k T_A}\right]$$
+. [1.3]

where  $T'_H$  is the effective homogenisation temperature.

The excess vacancy theory is confirmed by the following experimental observations employing resistivity measurement :

- 1. With increase in  $T_{H}$ , the initial resistivity and also the initial rise in resistivity increases.
- 2. Ageing temperature remaining constant, time taken to reach peak is lesser for higher  $T_{H}$ .

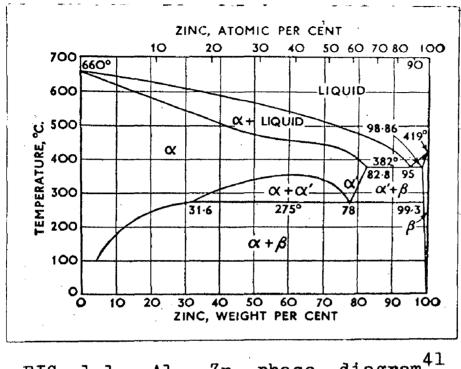
1.3.3 Precipitation : Intermediate and Equilibrium :

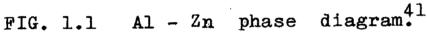
On continued ageing the G.P. zones are gradually replaced by a metastable phase having definite crystal structure and lattice parameter. This phase termed as intermediate precipitate is partially or fully coherent with the matrix.

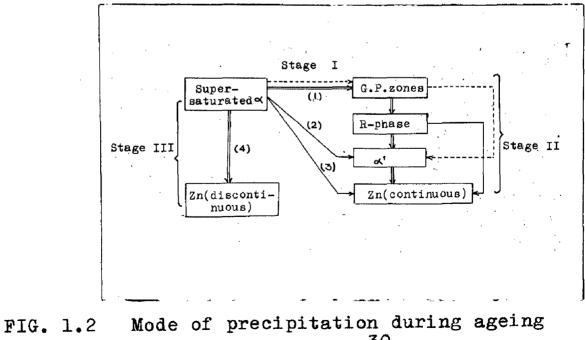
As the intermediate precipitate grows, the strain fields enlarge till they overlap. Now on further growth of precipitate, the strains become too great to be accommodated merely by bending the lattice planes. At this stage coherency breaks down and the strains at the interface are now accommodated by the formation of structural dislocations. This is the stage where intermediate precipitate transforms to the equilibrium precipitate and since it is followed by disappearance of the coherency strain, softening results. Hence we get a peak after the hardness maxima in the hardness vs. ageing time curve.

1.4 Al-Zn SYSTEM :

In has an extensive solid solubility in Al which ranges from 16 at. pct. In at  $275^{\circ}$ C to 1.5 at. pct. at  $100^{\circ}$ C. Thus, Al-Zn alloys are very favourable for the study of precipitation reaction over a wide range of compositions. The Al-Zn alloy system has attracted considerable attention in recent years as precipitation sequence has been found to be more complicated than thought of earlier. Existence of spinodal transformation has also been reported in some alloys.<sup>21-24</sup> The Al-Zn phase diagram is shown in Fig.1.1. A short account of the ageing characteristics of Al-Zn alloys is being given in the following sections :







in Al - Zn alloys<sup>30</sup>

1.4.1 Sequence of precipitation :

Till recently the precipitation sequence in Al-Zn alloys was accepted to be quite simple :

Supersaturated solid solution — spherical G.P. zones — equilibrium precipitate. Garwood <u>et al</u><sup>25</sup> for the first time detected a face-centred cubic transition precipitate in an Al-12.5 at. per cent Zn alloy aged at 200°C. Since then, investigations by various workers<sup>22,26-29</sup> have established the existence of another phase (called R phase) in the precipitation sequence of Al-Zn alloys.

The effect of solute concentration and ageing temperature on the sequence of precipitation is, however, not still clearly known. Reviewing various experimental data, Krishna Rao <u>et al.<sup>30</sup></u> have summarised the mode of precipitation in Al-2n alloys as indicated in Fig. 1.2. According to them.

 zones form by normal solute clustering or by spinodal decomposition. These zones are homogeneously distributed. Zone composition is controlled by metastable miscibility gap in two phase region, but its size and thus volume increases which introduces a large

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amount of strain, which leads to the formation of R-phase and then following sequence takes place :

R-phase  $\rightarrow \alpha' \rightarrow Zn$  (continuous),

- heterogeneous formation of α' takes place in small amounts. It probably occurs within the grains at dislocations, normally present or arising due to vacancy aggregates,
- 3) continuous Zn precipitation by heterogeneous nucleation on structural defects is not very significant as it will require a great deal of solute to be localised and again surmounting of a large free energy barrier for nucleation,
- 4) discontinuous precipitation of Zn is the common mechanism for high Zn alloys. It becomes more prominent with decreasing ageing temperature and increasing solute concentration.

1.4.2 Effect of ternary addition :

Since binding energy between a Zn atom and vacancy is small, Al-Zn system happens to be most suitable one for studying effect of trace additions of a third element.<sup>31,32</sup>

As has already been pointed out in this section, the clustering rate in Al-Zn system is very fast. clustering rate, however, can be hampered appreciably by

This

trace additions of a third element. Noting this decreased clustering rate, the binding energy of the third element with vacancies can be evaluated.

Silcock<sup>33</sup> and Kimura and Hasiguti<sup>34</sup> have made an alternative explanation for this decreased clustering rate that the trace element atoms might get paired-off with the excess vacancies and thereby reduce the rate of clustering and zone formation. This explanation seems to be quantitatively plausible since the concentrations of vacancies and trace element atoms are similar. Kimura and Hasiguti conducted resistivity measurements on Al-1.7 pct. Cu - 0.006 pct. Sn alloy and found that binding energy of a Sn atom is 0.2 eV greater than between a Cu atom and a vacancy. Hence majority of vacancies are bound to Sn atoms and the rate of diffusion of Cu atoms to form G.P. zones is rather slow.

1.5 SCOPE OF THE PRESENT INVESTIGATION :

The present work was undertaken to study the effect of Indium additions on the kinetics of pre-precipitation of Al-Zn binary alloys and thereby calculate the energies of formation and migration between a Zn atom and a vacancy and that between an In atom and a vacancy. It was therefore decided to take three compositions of the binary alloy and subsequently two additions of In were added to the same binary alloys. Values of  $E_{\rm F}$  and  $E_{\rm M}$  were calculated for the binary and ternary alloys using electrical resistivity measurements.

Efforts have been made to explain the change in kinetics of pre-precipitation brought about by the additions of In, in terms of the positive binding energy between an In atom and a vacancy.

Hardness measurement was also employed for the binary alloys to make the resistivity results more authentic.

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#### CHAPTER - II

#### EXPERIMENTAL PART

2.1 ALLOY PREPARATION :

The binary and ternary alloys were prepared from high purity aluminium (99.99 pct. purity) supplied by Riedel-De Haen, Germany, zinc of 99.9 pct. purity and indium of 99.999 pct. purity.

Weighed amount of aluminium was melted in a clean graphite crucible in a muffle furnace and zinc in required quantity was added to the molten aluminium. To account for the loss of zinc during melting, 15 pct. excess zinc was taken. The melt was thoroughly stirred to ensure complete homogenisation of the melt and hexachloroethane was used as degasant before pouring the melt into cylindrical mild steel moulds and allowed to cool. The alloy ingots thus obtained were 7/8 in. in diameter and 6 in. long. The ingots were then hot forged at  $450^{\circ}$ C to break up the cast structure. Ternary alloys were made by remelting the scrap of the binary ones and adding to that the required quantity of pure indium. Two ternary compositions corresponding to each binary alloys were made.

•

Binary alloys were chemically analysed for zinc content. Aluminium content of the alloys was determined by difference. The table 2.1 gives the final composition of the various alloys .

#### 2.2 SAMPLE PREPARATION :

Wire samples of 0.63 mm diameter for the binary and 0.67 mm diameter for the ternary alloys were made use of in the resistivity measure-ment. Wires, three meters in length, for the binary and one meter for that of ternary alloys, were wound like a lamp coil filament.

The samples employed for hardness measurement were cylindrical type, 20 mm in diameter and 8 mm in height. They were cut from the cast and hot forged cylindrical ingot (7/8" x 6"). The specimens were ground and polished, and used for hardness measurement.

Alloy	¦ Zn wt.	pct. ;	In wt. pct.	Al wt. pct.
linary				
D	8.1		_	Rest
E	9.5		-	**
F	12.1			**
fernary - 1				
Dl	8.1		0.05	••
E 1	9.5		0.05	••
Fl	12.1		0.05	••
lernary - 2				
D2	8.1		0.15	**
<b>E</b> 2	9.5		0.15	••
F 2	12.1		0.15	••

<u>TABLE 2.1</u>: Compositions of the various binary and ternary alloys.

#### 2.3 HEAT TREATMENT :

Initial homogenisation treatment was given to all the samples so as to give a single phase supersaturated  $\alpha$  at room temperature on quenching from the homogenisation temperature. Wire samples were homogenised for 8 hours at 480°C in a muffle furnace and quenched down to room temperature. Hardness specimens were homogenised for 60 hours at 500°C in a muffle furnace. The specimens were then quenched down to room temperature and were ensured to be homogeneous as revealed by optical microscopy as well as by hardness measurement.

### 2.4 RESISTIVITY MEASUREMENT :

Resistivity of the wire samples was measured potentiometrically with a least count of 0.01 mV. Specimens were homogenised in a muffle furnace, the temperature of which was controlled within  $\pm 2^{\circ}$ C. Quenching operations were carried out by manual extraction of samples from the furnace and by rapid immersion in the quenching media (ice water at  $0^{\circ}$ C); then samples were immediately transferred to the ageing bath.

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Resistivity measurements carried out for Binary, Ternary-1 and Ternary-2 alloys were made in two ways :

1. Varying  $T_{\rm H}$  from 280°C to 500°C in steps of 20 degrees and keeping  $T_{\rm A}$  constant ( 0°C).

2. Varying  $T_A$  from 0°C to 55°C in steps of 5 degrees and keeping  $T_H$  constant (300°C).

The variations in resistivity were computed by the relation :

$$\triangle ? = \triangle R \cdot \frac{A}{L}$$

where  $\triangle R = R - R_0$  is the variation in resistance of the sample, with reference to  $R_0$ , when it has reached by ageing - the value R, A is the area of cross section of the wire sample and L is the length of the sample employed.

#### 2.5 HARDNESS MEASUREMENT :

It was confined only to the Binary alloys. Homogenisation was done in a vertical tube furnace fitted with a Mahindra Electroflo temperature controller having a sensitivity of  $\pm 2^{\circ}$ C. The samples were rapidly quenched in the cooling medium ( ice water at  $0^{\circ}$ C ) and then immediately transferred to the ageing bath. The temperature of the ageing bath was controlled by means of a thermostat within an accuracy of  $\pm$  0.2°C. All the hardness measurements were done on a Vicker's hardness tester employing a load of 5 kgs.

Similar to resistivity, hardness measurements were done in two ways :

- 1. Varying  $T_{\rm H}$  from 280°C to 500°C in steps of 20 degrees and keeping  $T_{\rm A}$  constant (50°C).
- 2. Varying  $T_A$  from 30°C to 85°C in steps of 5 degrees and keeping  $T_H$  constant (300°C).

# 2.6 CALCULATION OF $E_F$ AND $E_M$ :

Arrhenius equation governing the rate of diffusion of Zn atoms in Al is given by :

$$D_{Zn} = D_0 \exp \left[-\frac{E_F}{k T_H}\right] \exp \left[-\frac{E_M}{k T_A}\right] \dots [2.1]$$

where,  $D_{Zn}$  is the diffusion coefficient of Zn,  $D_0$  is a constant,  $E_F$  and  $E_M$  are the activation energies of formation and migration of vacancies and  $T_H$  and  $T_A$  are the homogenisation and ageing temperatures respectively. At constant ageing temperature :

$$\ln D_{zn} = C_{1} - \frac{E_{F}}{k T_{H}} \qquad .. [2.2]$$

Now, since D<sub>Zn</sub> is proportional to the diffusion rate which inturn is inversely proportional to the ageing time, t, the equation [2.2] may be written as :

$$\ln \frac{1}{t} = C_2 - \frac{E_F}{k T_H} .. [2.3]$$

Thus, for a temperature  $T_{H_1}$  and time  $t_1$ ,

$$\ln \frac{1}{t_1} = C_2 - \frac{E_F}{k T_{H_1}} \qquad .. [2.4]$$

and at a temperature  $T_{H_2}$  and time  $t_2$ ,

or

$$\ln \frac{1}{t_2} = C_2 - \frac{E_F}{k T_{H_2}} \qquad .. [2.5]$$

Substracting equations [2.4] and [2.5] we get

$$\ln \frac{t_2}{t_1} = \frac{E_F}{k} \left[ \frac{1}{T_{H_2}} - \frac{1}{T_{H_1}} \right] \qquad .. [2.6]$$

$$\log \frac{t_2}{t_1} = \frac{E_F}{2.303 \text{ k}} \left[ \frac{1}{T_{H_2}} - \frac{1}{T_{H_1}} \right] \qquad \dots [2.7]$$

Thus, slope of the line plotted between log t and  $\frac{1}{F_H}$  and equating it to  $\frac{E_F}{2.303 \text{ k}}$ , the value of  $E_F$ can be evaluated. Similarly, at constant  $T_H$ , values of  $E_M$ can be evaluated by equating the slope of the line drawn between log t and  $\frac{1}{T_A}$  to  $\frac{E_M}{2.303 \text{ k}}$ .

In the present investigation, values of  $E_F$ and  $E_M$  have been calculated for binary and ternary alloys by means of various Arrhenius plots. Slope of the lines was calculated by Least Square Method. All the calculations were done on an IBM 1620 computer. Listing of the computer programs calculating various variables are given in the appendix.

#### CHAPTER - III

#### RESULTS AND DISCUSSION

3.1 RESULTS :

The variation in resistivity and hardness as a function of ageing time for binary andternary alloys at different  $T_H$  and  $T_A$  have been shown from fig.3.1 to 3.72. Figs. 3.1 to 3.27 indicate resistivity change with ageing time for the Binary, Ternary-1 and Ternary-2 alloys with varying  $T_H$  while those from fig.3.29 to 3.54 for the corresponding alloys with  $T_A$  varying. Hardness plots for the Binary alloys with  $T_H$  and  $T_A$ varying are shown in Figs. 3.55 to 3.72.

On the basis of these graphs, Arrhenius plots as shown in figs. 3.73 to 3.108 have been derived. Values of  $E_F$  and  $E_M$  for the binary and ternary alloys have been calculated and also the values of binding energy between a Zn atom and a vacancy and that between an In atom and a vacancy arrived at. All these results are discussed later in this chapter.

