ROLE OF DEFECT STRUCTURE ON PRECIPITATION HARDENING

A DISSERTATION
submitted in partial fulfilment
of the requirements for the
award of the Degree of
MASTER OF ENGINEERING
in
METALLURGICAL ENGINEERING
(PHYSICAL METALLURGY)

By

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ROORKEE, U. P.
1972

CERTIFICATE

Certified that the dissertation entitled " ROLE OF DEFECT STRUCTURE ON PRECIPITATION HARDENING ", which is being submitted by Mr. Param Ajit Singh in partial fulfilment for the award of Degree of Master of Engineering (Physical Metallurgy) of University of Roorkee, Roorkee is a record of his own work carried out by him under my supervision and guidance. The matter embodied in this dissertation has not been submitted for award of any degree or diploma.

This is further to certify that he has worked for a period of eight months from January 1972 to August 1972 for preparing this dissertation at this University.

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Roorkee September 7
Dated : ~~August~~ , 1972.

ABSTRACT

Role of vacancies and varying amount of cadmium addition on the pre-precipitation stage of ageing in aluminium - zinc alloy was studied with the help of resistivity measurements. Activation energies associated with formation and migration of vacancies in three ternary alloys were evaluated. The binding energy between cadmium atom and vacancy has also been estimated. The values are compared with those reported in literature.

It has been found that resistivity increases with ageing time and starts increasing almost instantaneously.

It has also been observed that addition of cadmium to the aluminium - zinc alloy lowers the rate of pre-precipitation and higher the cadmium content, slower is the ageing process.

ACKNOWLEDGEMENTS

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(P. A. SINGH)

CONTENTS

CHAPTER - I

LITERATURE REVIEW

1.1 INTRODUCTION

To meet the evergrowing demand of high-strength aluminium-base alloys, many of which are age-hardenable, in the field of defence, aviation, automobile and other related industries it has become necessary to study the phenomenon of age hardening.

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 super saturated 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 these alloys can be increased by ageing to as much as five times.

As Al-Zn alloys form the base for an important series of commercial age-hardenable alloys, a thorough understanding of ageing behaviour of these alloys will be of considerable value in the development of high-strength aluminium alloys.

1.2 HISTORICAL SURVEY

Alfred Wilm[1, 2], 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 was 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 due primarily to the fact that super high strength light alloys needed for many industrial applications could be developed. Since ageing is undoubtedly followed by precipitation of a second phase fromthe parent matrix of supersaturated α , it came to be known as " Precipitation Hardening " also.

Age Hardening consists of :

1. Homogenisation; i.e., heating the alloy to a temperature where homogenous 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.

Pre-requisits of age hardening :

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

1. The solubility of the solute must decrease with decreasing temperature in the solid solu-

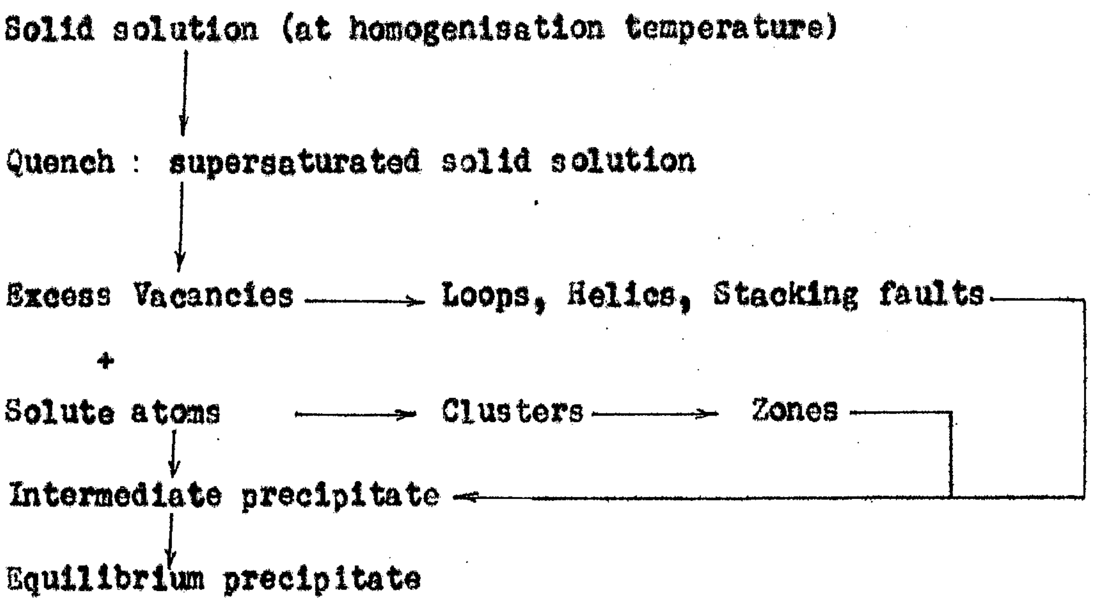
tion or, in other words, the phase diagram of the alloy system should have a sloping solvus,

2. on quenching from solutionising temperature a super saturated solid solution must form, and

3. on heating, this super saturated 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 :



1.3.1 Role of 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 has been studied in Al and Al-alloys by various authors[3-5]. In aluminium, the microstructure consists of prismatic dislocation loops about 500 Å in diameter which are formed by the collapse and shear of discs of vacancies in the manner predicted by Kuhlman-Wilsdorf[6]. 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[6], 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[7] which is based on the absorption of vacancies on a screw dislocation. Thomas and Whelan[8] 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[7].

Kelly and Nicholson[9] 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[10] 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 homogenous 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 matrix. But since zones are homogenous or, in other words, have one toono correspondence with the matrix, the overall zone is either compressed or expanded to match its lattice parameter with that of the parent matrix. 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 :

Jagodinski and Laves[11] first pointed out that Guinier's model[12] 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.

The first explanation proposed by Turnbull assumed the diffusion of solute atoms to take place via dislocations.

A large number of dislocations may act as channels for easy 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[14] and later developed by Federighi[15] and De Sorbo et.al.[16], attributes this anomaly to quenched-in vacancies. The theory, came to known as 'Excess Vacancy Theory', is widely accepted and assumes that high rate of diffusion is due to high concentration of quenched-in vacancies.

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

$$DCu = A \exp \left[- \frac{E_F + E_M}{k\, T_A} \right] \quad \ldots \quad (1.1)$$

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 $E_M + E_F = 1.4$ eV, DCu was calculated to be 10^{-24} cm^2/sec. But De Sorbo et al[16] calculated DCu $\sim 10^{-16}$ cm^2/sec by assuming that Cu atoms move three or four atom diameters during clustering. Thus there is a discrepancy of 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 :

$$DCu = A \exp \left[- \frac{E_F}{k\,T_H} \right] \exp \left[- \frac{E_M}{k\,T_A} \right] \;.. (1.2)$$

Assuming $E_F = 0.76$ eV, $E_M = 0.58$ eV, $T_H = 550^\circ$C and $T_A = 20^\circ$ C, the value of DCu was calculated to be 5×10^{-16} cm^2/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 :

$$DCu = A \exp \left[- \frac{E_F}{k\,T_H'} \right] \exp \left[- \frac{E_M}{k\,T_A} \right] \;..(1.3)$$

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 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

Zn has an extensive solid solubility in Al which ranges from 16 at. pct. Zn at 275° C to 1.5 at. pct. at 100° 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[17-20].

The Al-Zn phase diagram is shown in Figure 1.1 A short account of the ageing characteristics of Al-Zn alloys is being given in the following sections.

1.4.1 Sequence of precipitation :

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

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 et al.[21] 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[18, 22-24] 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,

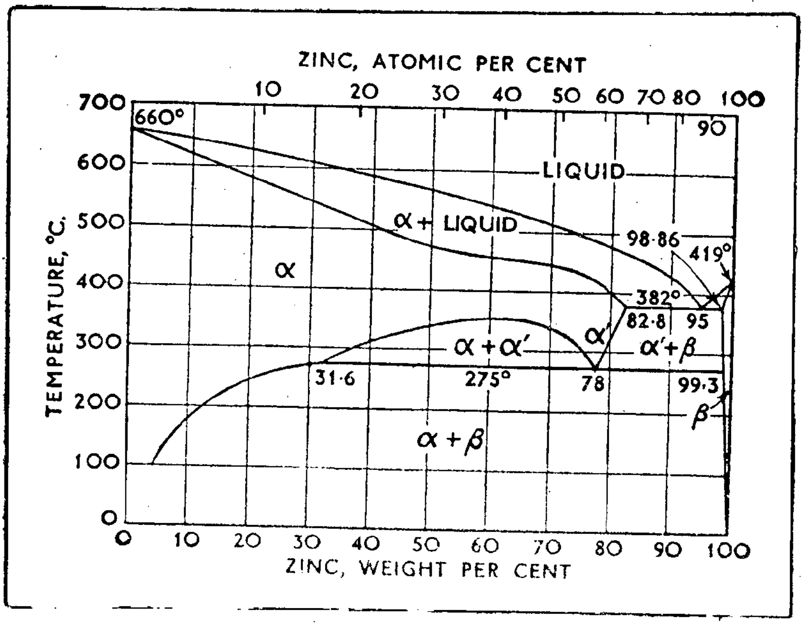


Fig. 1.1 Equilibrium Diagram of Al-Zn System

not still clearly known. Reviewing various experimental data, Krishna Rao et al.[25] have summarised the mode of precipitation in Al-Zn alloys as indicated in Fig. 12. According to them,

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

$$\text{R-phase} \longrightarrow \alpha' \longrightarrow \text{Zn} \quad \text{(continuous)},$$

(2) heterogenous 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

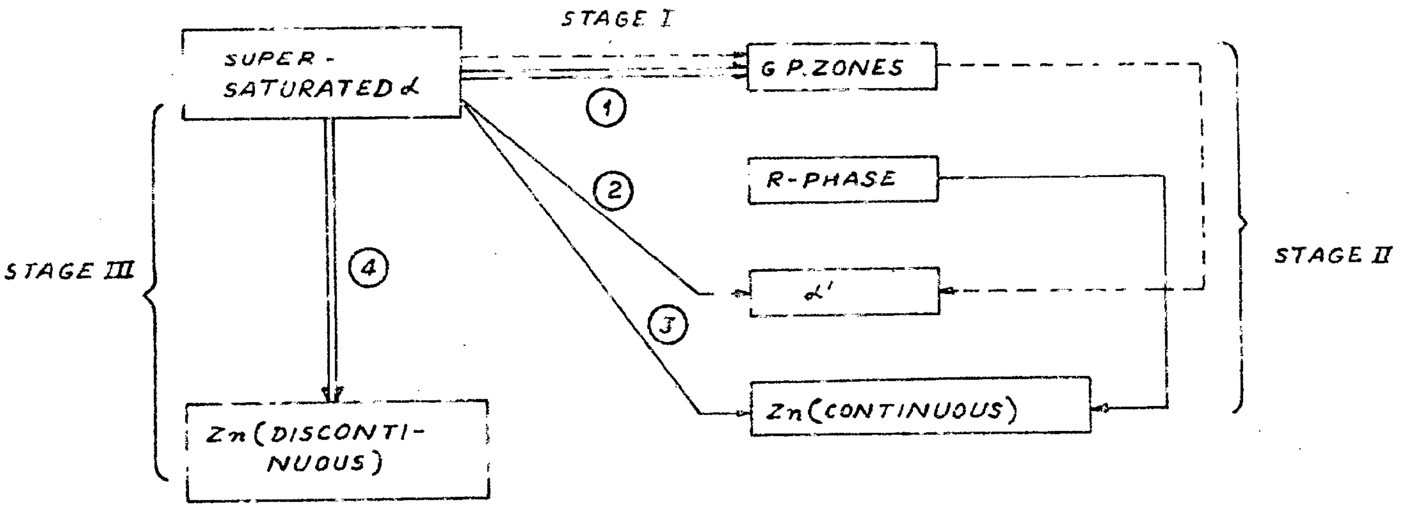


FIG. MODE OF PRECIPITATION DURING AGEING IN AL-Zn ALLOYS[30] to be localised and again surmounting of a large free energy barrier for nucleation,

(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[26, 27].

As has already been pointed out in this section, the clustering rate in Al-Zn system is very fast. This clustering rate, however, can be hampered appreciably by trace additions of a third element. Noting this decreased clustering rate, the binding energy of the third element with vacancies can be evaluated.

Silcock[28] and Kimura and Hasiguti[29] 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[29] 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 Cd additions on the kinetics of pre-precipitation of Al-Zn binary alloy and thereby calculate the energies of formation and migration between a Zn atom and a vacancy and that between Cd atom and a vacancy. It was therefore decided to add Cd in Al-Zn alloy in three varying quantities. Values of E_F and E_M were calculated for 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 Cd, in terms of positive binding energy between Cd atom and a vacancy.

CHAPTER - II

EXPERIMENTAL PART

2.1 ALLOY PREPARATION :

The ternary alloys were prepared from high purity aluminium (99.99 per cent purity), Zinc of 99.9 per cent purity and Cadmium(99.9 per cent pure).

Three ternary alloys were made by remelting the scrap of binary alloys of required Zn amount and adding to that the required quantity of pure Cadmium. The alloys were made in a clean graphi to crucible in a muffle furnace. To account for the loss of cadmium during melting, 10 per cent excess cadmium was taken in each case. 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 were then hot forged at 450° C to break up the cast structure.

Ternary alloys were analysed polographically for Zn and Cd content. Aluminium content of the alloys was determined by difference

The table 2.1 gives the final composition of the various alloys.

TABLE 2.1 : Compositions of the various ternary alloys

Alloy	Zn at per cent	Cd at per cent	Al at per cent
A	4.18	.04	Rest
B	4.18	.072	---
C	4.20	.126	---

2.2 SAMPLE PREPARATION :

The alloy ingots were drawn into wire samples of .75 mm diameter. The net specimen length was taken to be 50 cms. in each case. The overall length of specimen in each case was taken as 60 cms.

2.3 HEAT TREATMENT :

Initial homogenisation treatment was given to all the samples so as to give a single phase supersaturated at room temperature on quenching from the homogenisation temperature. Wire samples were homogenised for 12 hours at 400° C in a muffle furnace and quenched down to room temperature and were ensured to be homogenous as revealed by optical microscopy.

2.4 RESISTIVITY MEASUREMENT :

Resistivity of wire samples was measured with the help of portable potentiometer with a least count of 0.01 mV. Specimens were homogenised in a muffle furnace, the temperature of which was controlled within ± 2° 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° C), then samples were immediately transferred to the ageing bath.

Resistivity measurements for Ternary A, B and ternary C alloys were made in two ways :

1. Varying T_H from 280° C to 500° C in steps of 20 degrees and keeping T_A constant(20°C).

2. Varying T_A from 0° C to 55° C in steps of 5 degrees and keeping T_H constant(400°C).

The variations in resistivity were computed by the relation.

$$\Delta\rho = \Delta R \frac{A}{L}$$

where $\Delta R = R - R_o$ is the variation in resistance of the sample, with reference to Ro, 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 CALCULATION OF E_F AND E_M :

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

$$DZn = Do \exp\left[-\frac{E_F}{k\,T_H}\right] \exp\left[-\frac{E_M}{k\,T_A}\right] \quad \ldots \quad (2.1)$$

where, DZn is the diffusion coefficient of Zn, Do 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 :

$$\ln DZn = C_1 - \frac{E_F}{k\,T_H} \qquad \ldots \quad (2.2)$$

Now, since DZn is the proportional to the diffusion rate which in turn is inversely proportional to the ageing time, t, the equation (2.2) may be written as :

$$\ln \frac{1}{t} = C_2 - \frac{E_F}{k\,T_H} \qquad \ldots \quad (2.3)$$

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

$$\ln \frac{1}{t_1} = C_2 - \frac{E_F}{k\,T_{H_1}} \qquad \ldots \quad (2.4)$$

and at a temperature TH_2 and time t_2,

$$\ln \frac{1}{t_2} = C_2 - \frac{E_F}{k\,T_{H_2}} \qquad \ldots. \quad (2.5)$$

Subtracting equations (2.4) and (2.5) we get

$$\ln \frac{t_2}{t_1} = \frac{E_F}{k}\left[\frac{1}{T_{H_2}} - \frac{1}{T_{H_1}}\right] \ldots \quad (2.6)$$

or $$\log \frac{t_2}{t_1} = \frac{E_F}{2.303\ k}\left[\frac{1}{t_{H_2}} - \frac{1}{t_{H_1}}\right] \quad \ldots (2.7)$$

Thus, slope of the line plotted between log t and $\frac{1}{T_H}$ and equating it to $\frac{E_F}{2.303\ k}$, 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 $1/T_A$ to $\frac{E_M}{2.303\ k}$.

In the present investigation, values of E_F and E_M have been calculated for ternary alloys by means of various Arrhenius plots.

CHAPTER - III

RESULTS AND DISCUSSION

3.1 RESULTS :

The variation in resistivity as a function of ageing time for three different ternary alloys at different homogenization and ageing temperatures i.e. T_H and T_A have been shown from figure 3.1 to 3.18. Figs. 3.1 to 3.9 indicate resistivity change with ageing time for the Ternary - 1, Ternary - 2 and Ternary - 3 alloys with varying T_A while those from figure 3.10 to 3.18 for the corresponding alloys with T_H varying.

On the basis of these graphs, Arrhenivs plots as shown in figs. 3.19 to 3.24 have been drawn and values of E_M and E_F for three alloys have been calculated. Also the value of binding energy between a Zn atom and a vacancy and that between Cd atom and a vacancy have been estimated. All these results are discussed below.

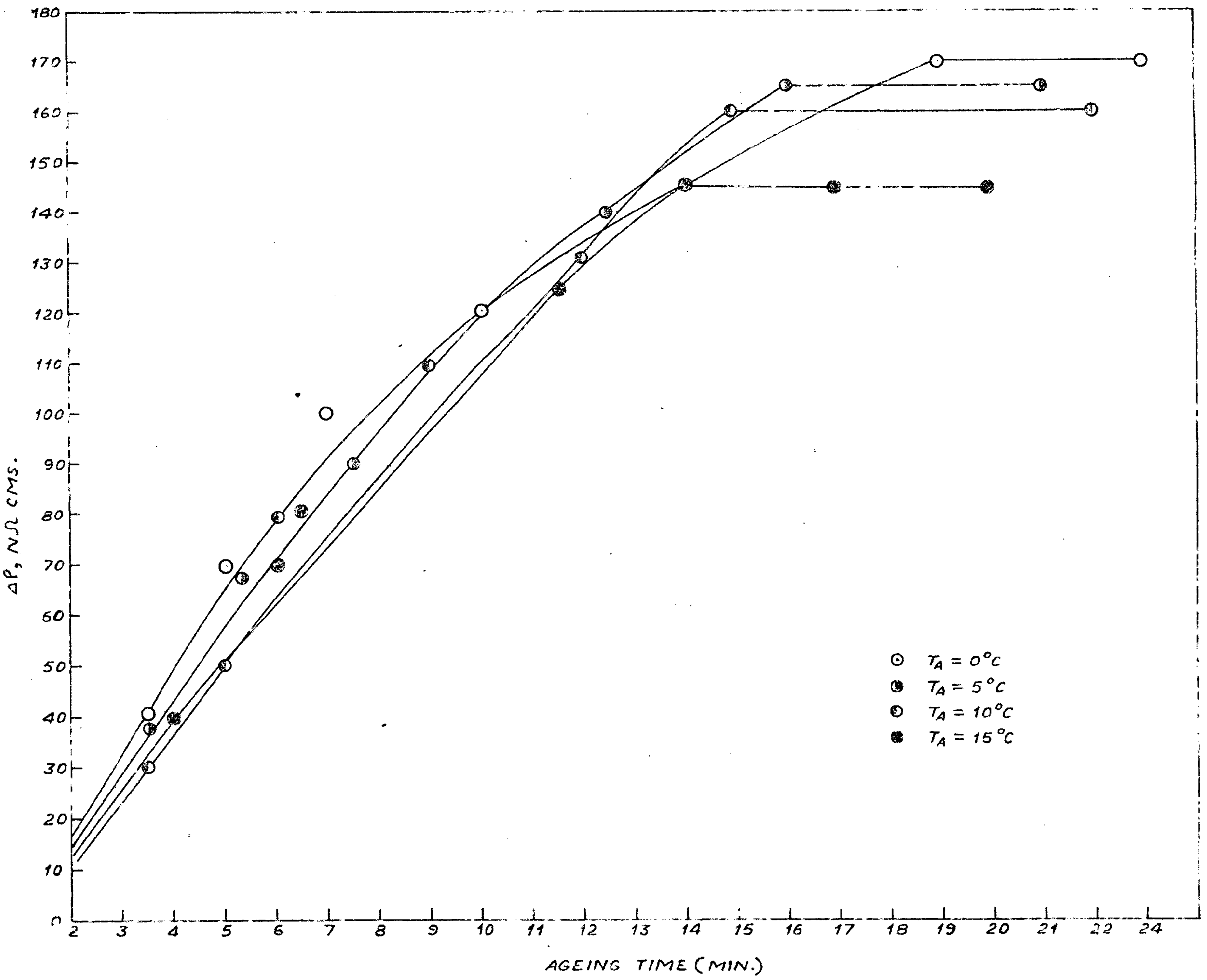
3.2 DISCUSSION :

On the basis of the results obtained in the present investigation, it is possible to present a general picture of pre-precipitation and role of vacancies. The discussion is based on the basis of electrical resistivity measurement which has a special application on the early stage of precipitation hardening i.e. during the pre-precipitation stage when clustering takes place.

3.2.1 Resistivity Measurement :

General Nature :

The curves showing the variation in resistivity with ageing time are shown in figs. 3.1 to 3.18. Value of has been plotted in N Ω CMS. (IN Ω CM = 10^{-9} Ω CMS). It is seen that resistivity starts increasing with time and reaches a constant value, the resistance did not attain a maximum value in a reasonable length of time, which is in accordance with the work of Perryman and Blade[30] and Panseri and Federighi[31]. The absence of incubation period is in good agreement with the earlier work of Panseri and Federighi[31]. Since the resistance attain a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AGEING TIME (MIN.)
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T_A = 10°C
T_A = 15°C

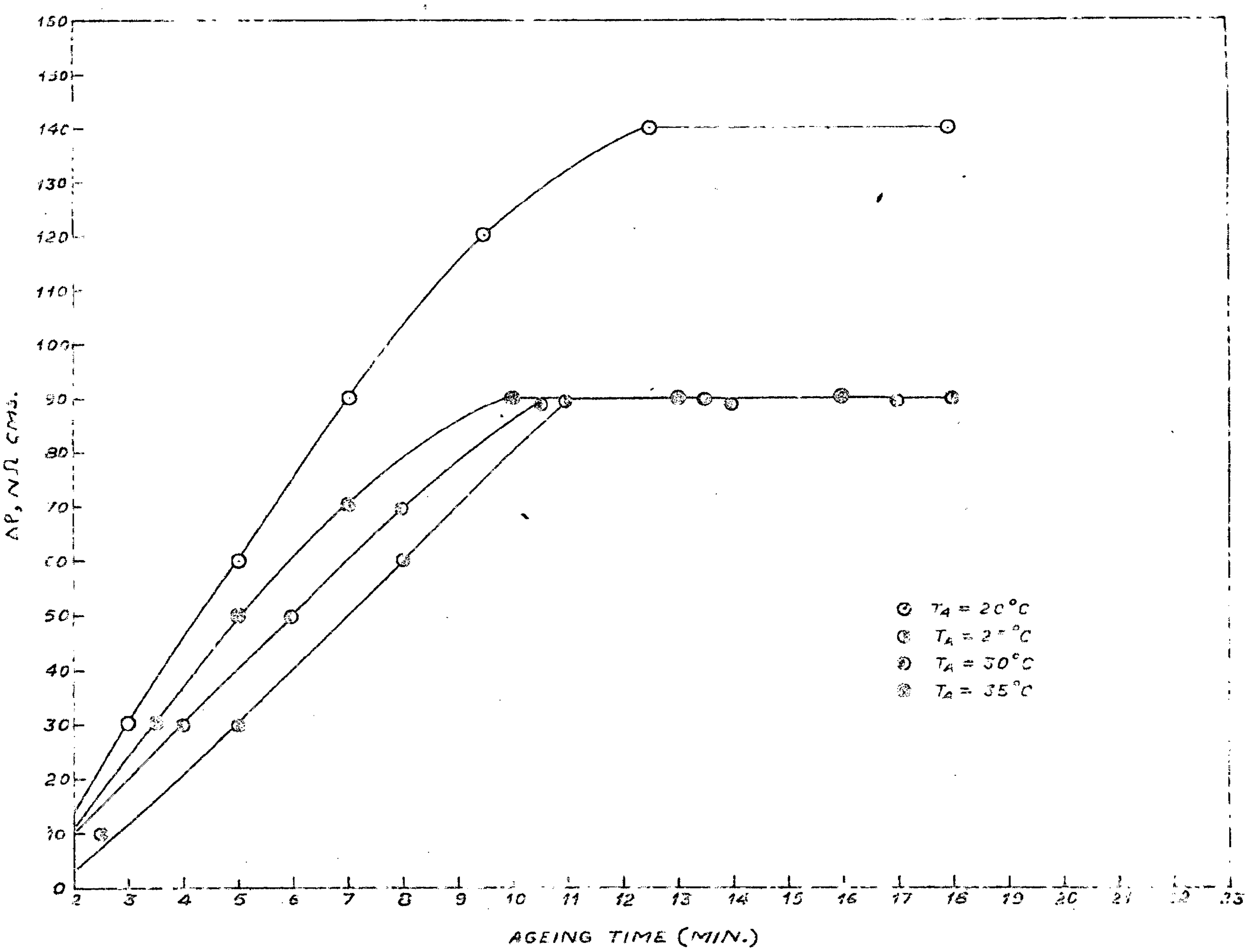
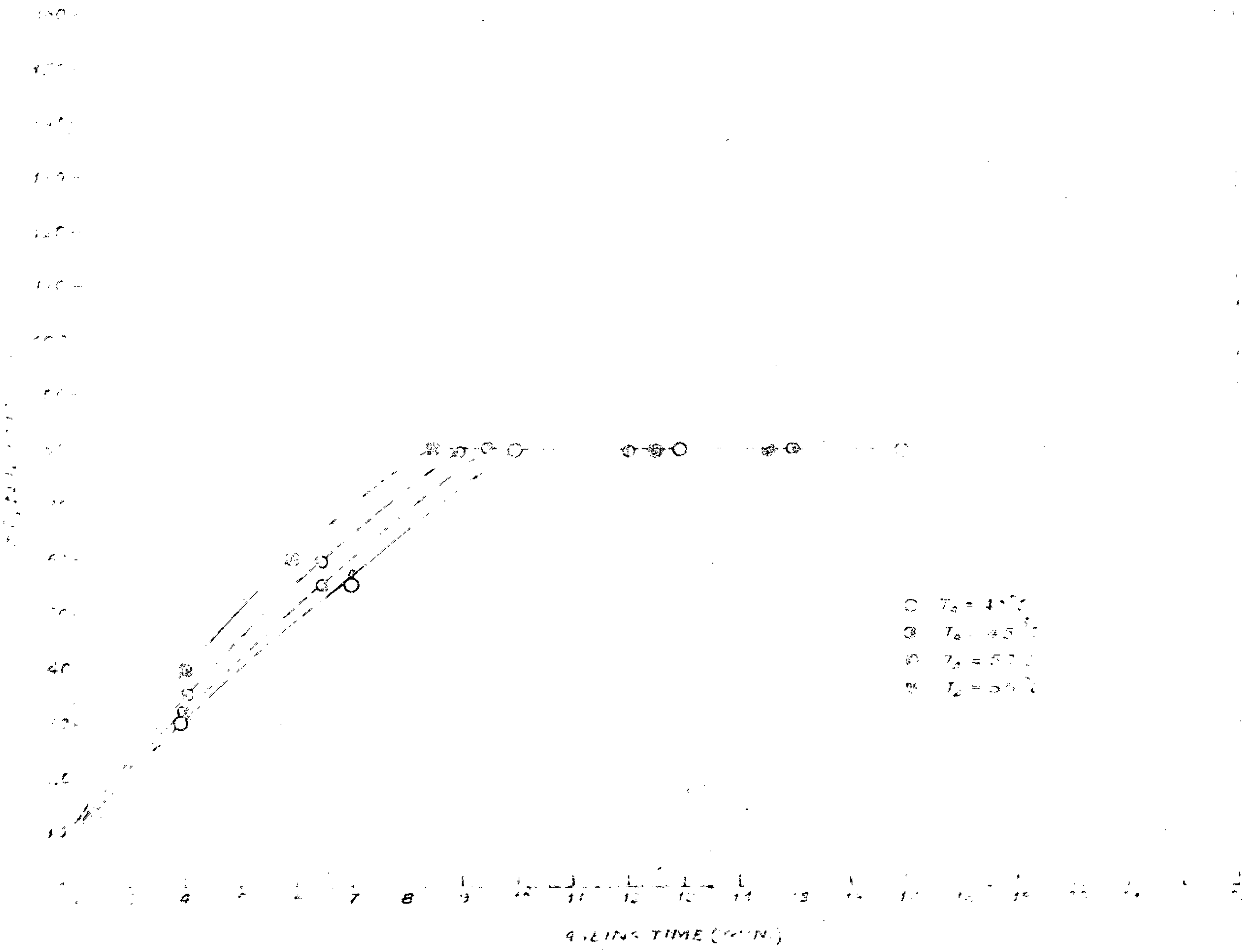


FIG. 3.2

ALLOY (A)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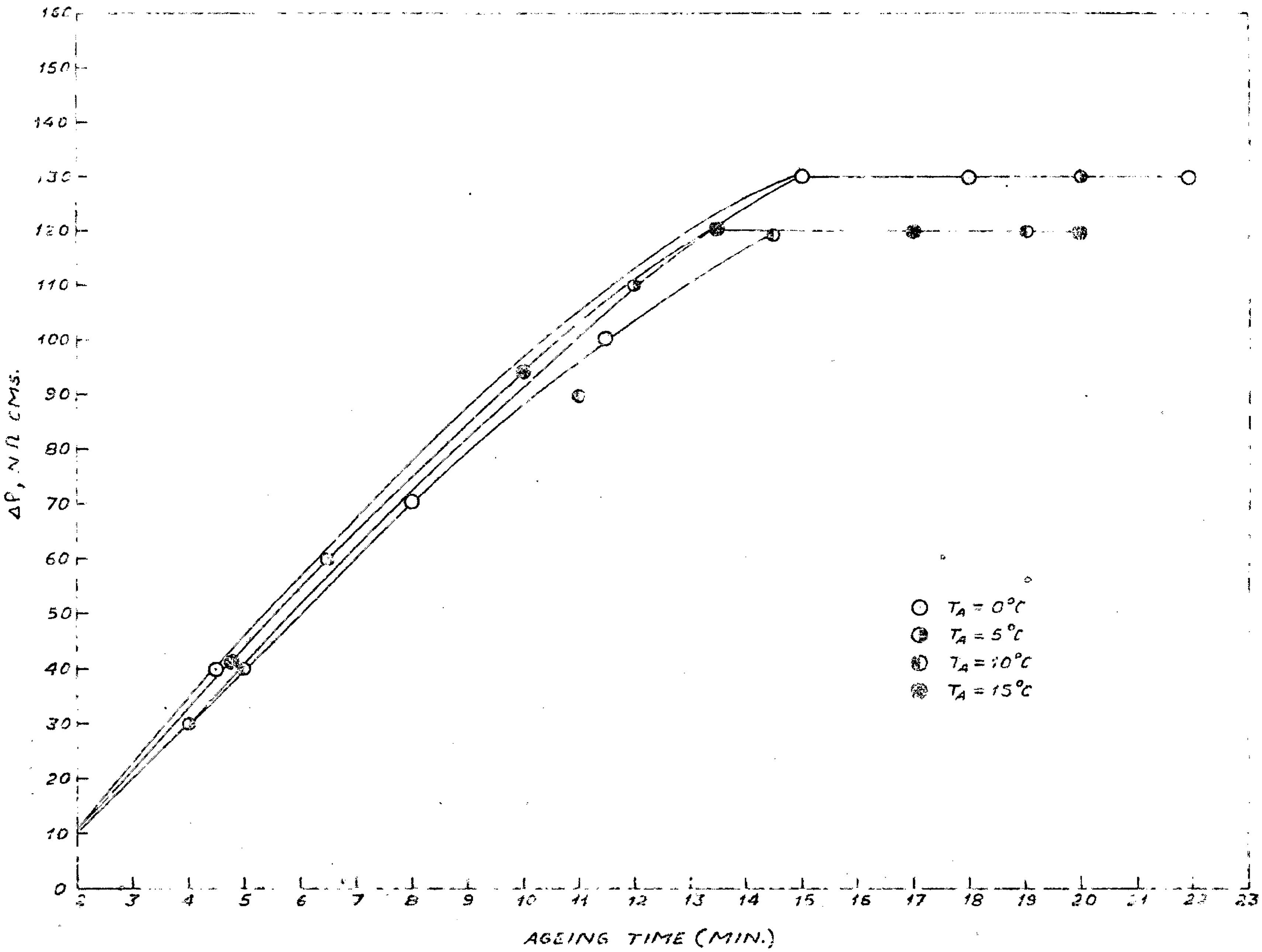
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AGEING TIME (MIN.)
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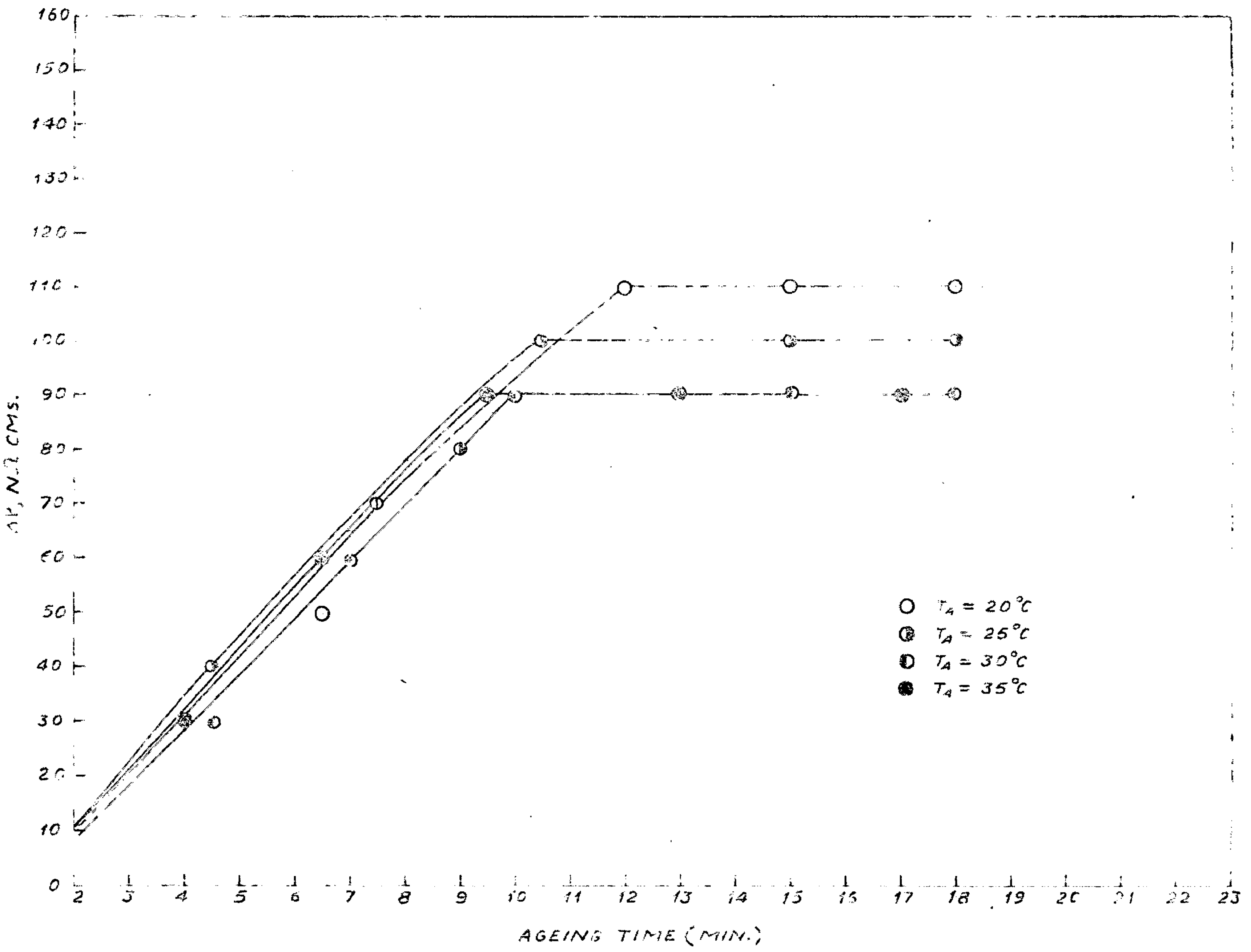ΔP, N.T. CMS.
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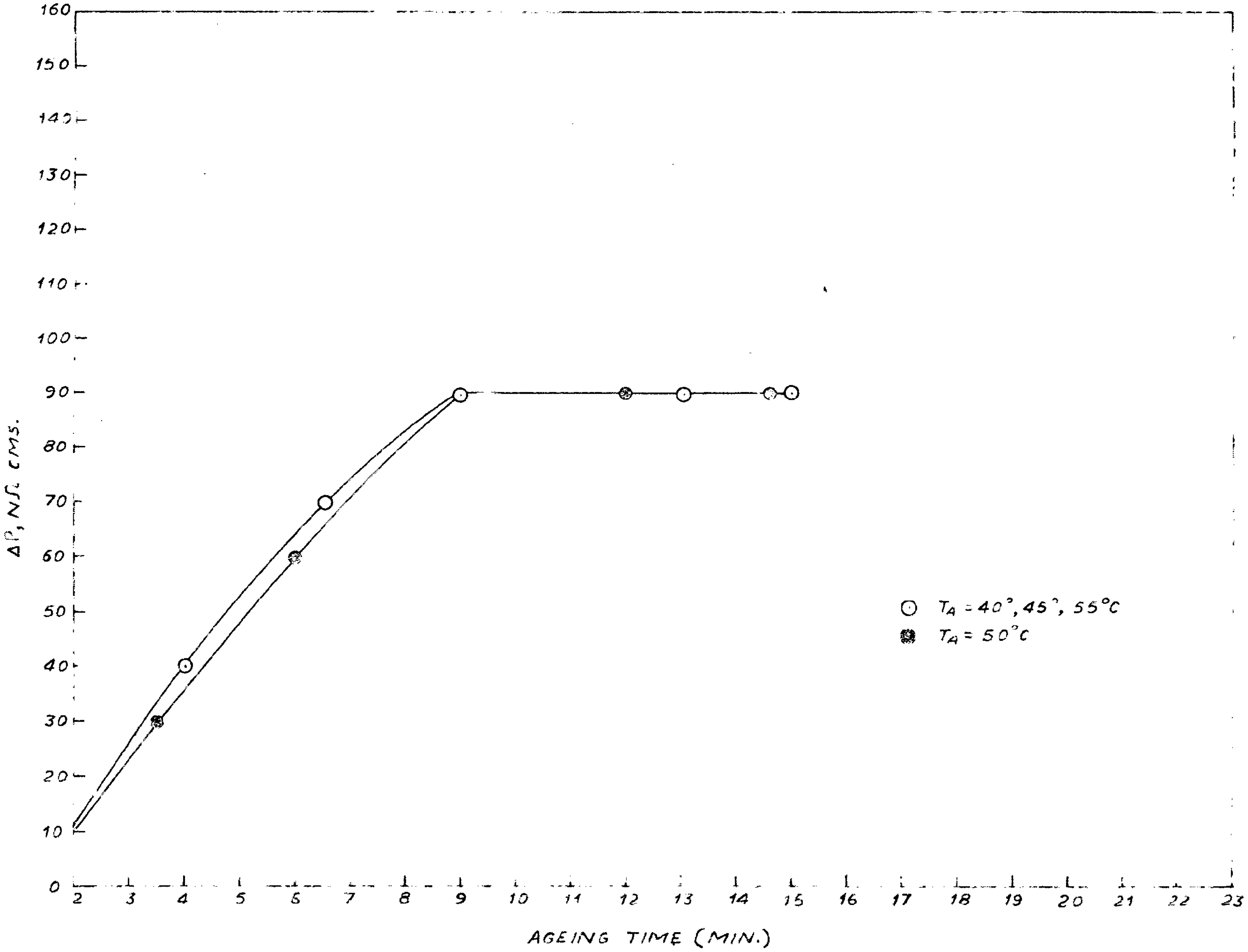
AGEING TIME (MIN.)
○ T_A = 20°C
◐ T_A = 25°C
◐ T_A = 30°C
● T_A = 35°C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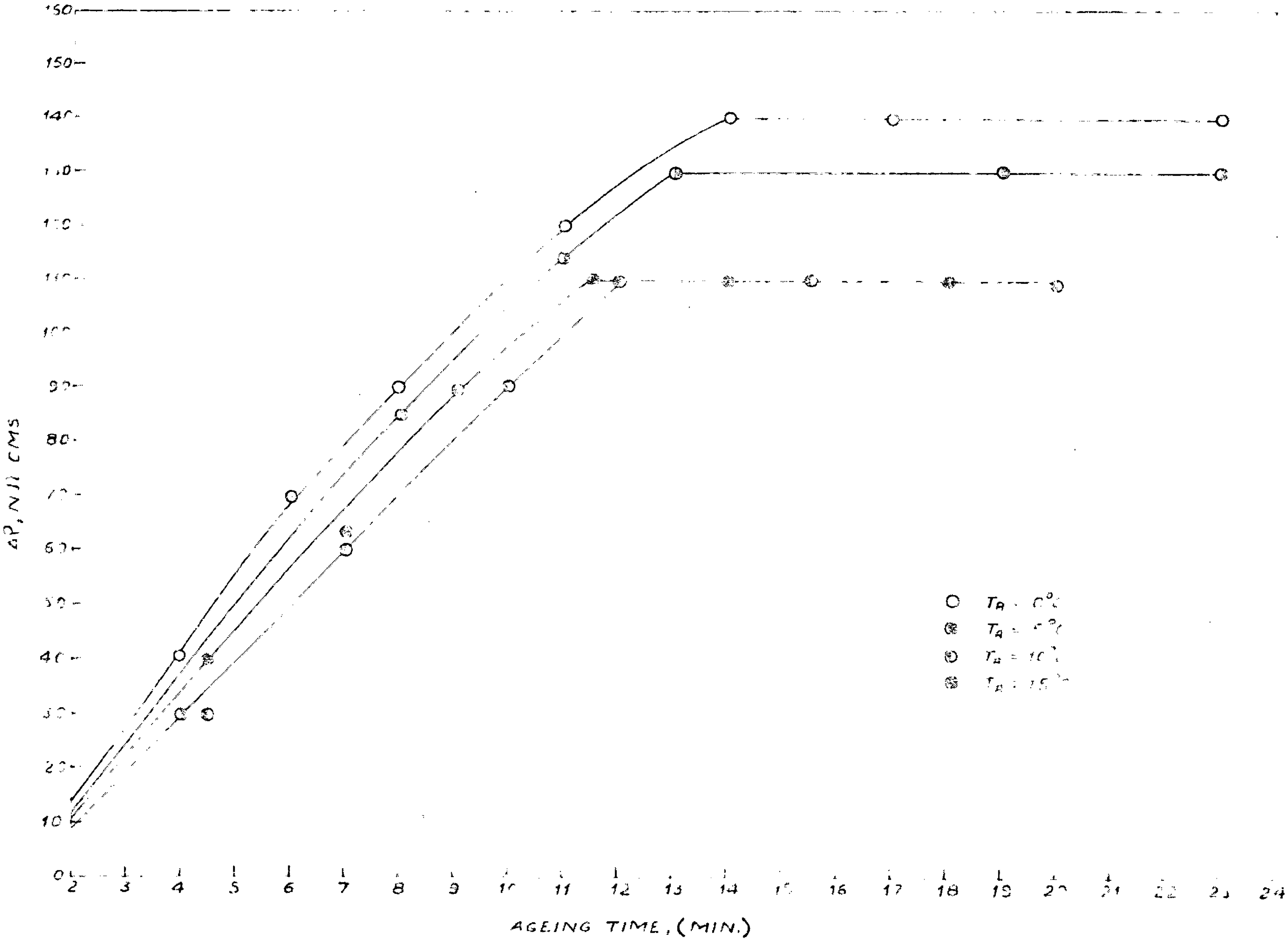
AGEING TIME (MIN.)
○ T_A = 40°, 45°, 55°C
● T_A = 50°C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AGEING TIME, (MIN.)
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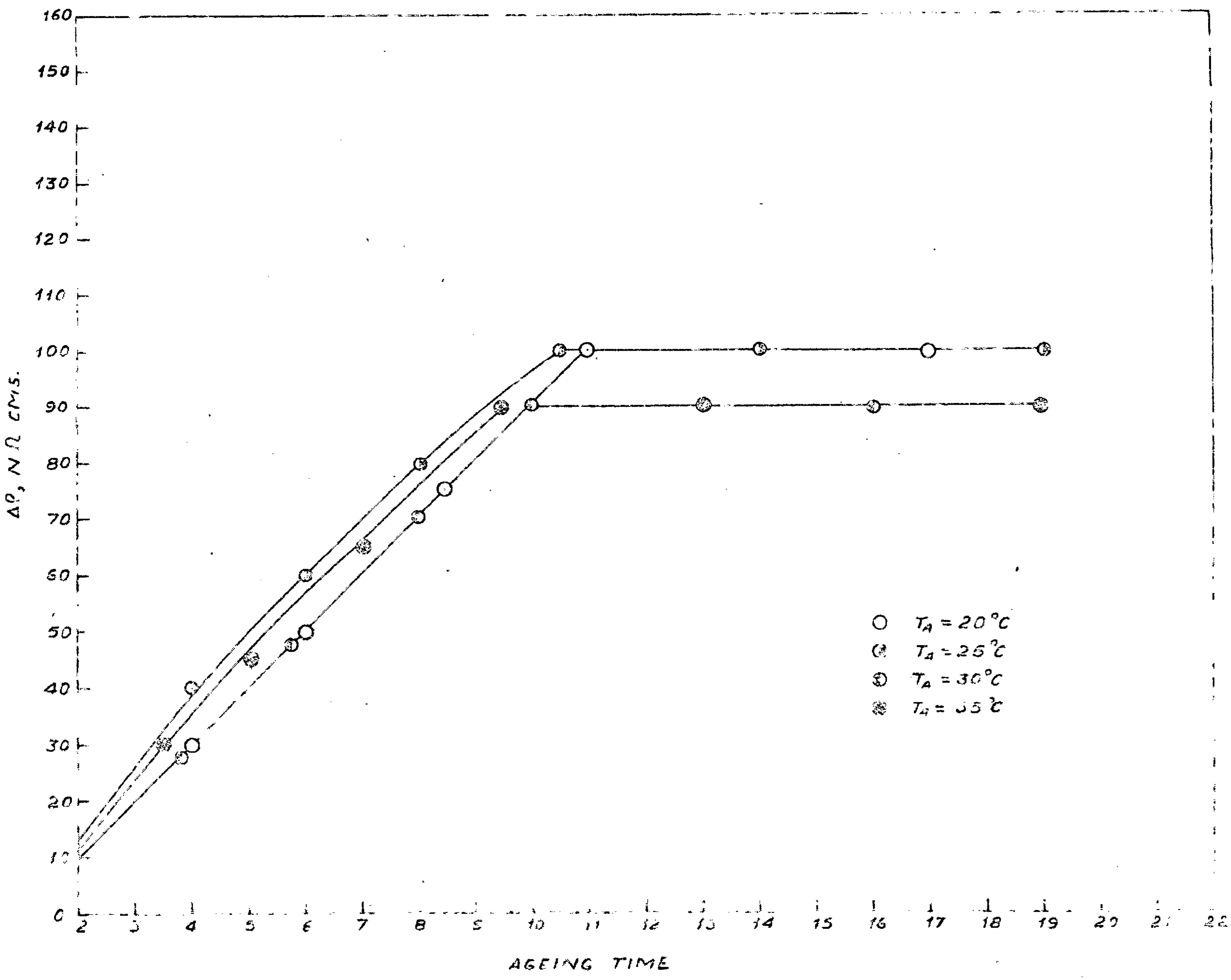
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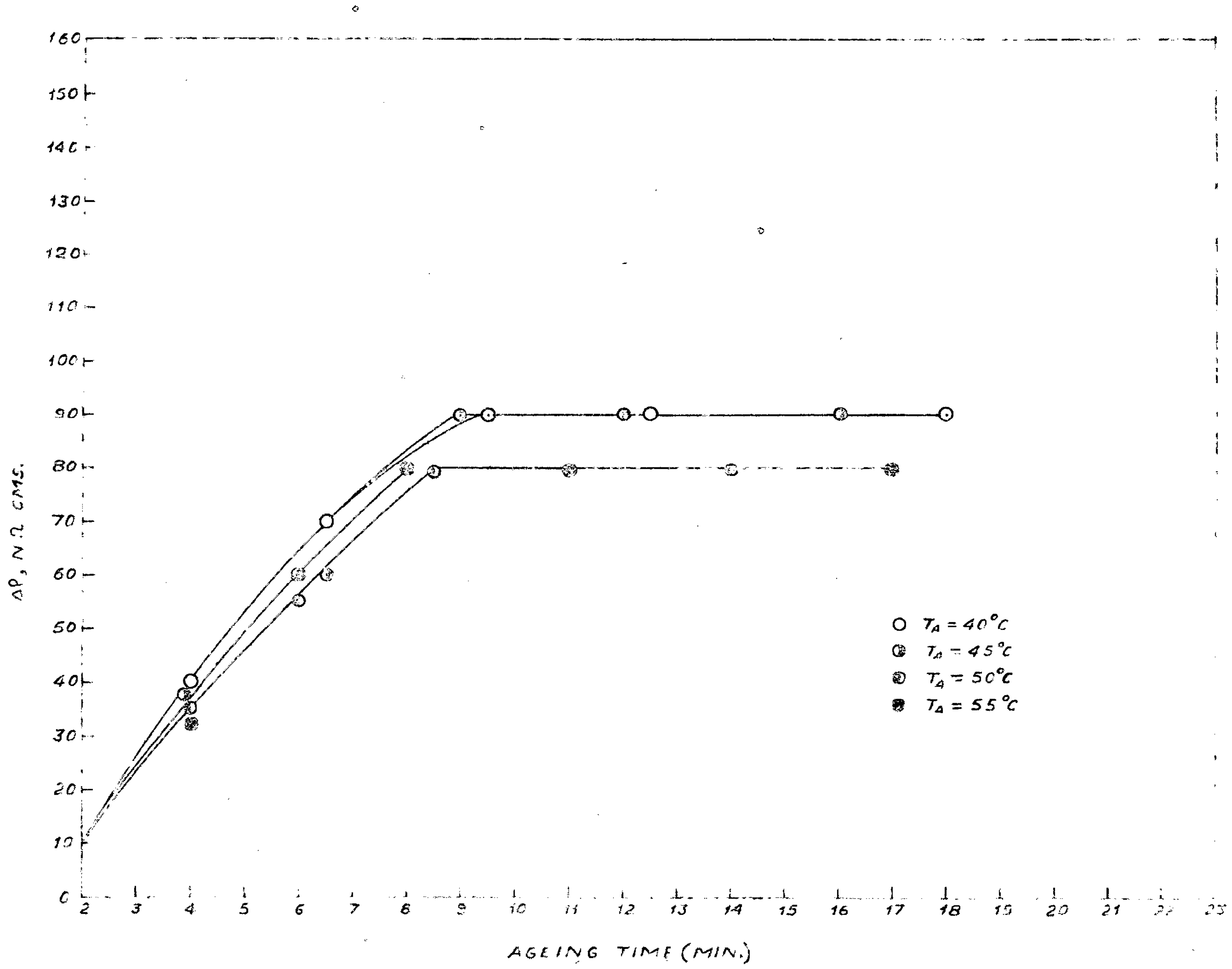
14
15
16
17
18
19
20
21
22
AGEING TIME
○ $T_A = 20°C$
◐ $T_A = 25°C$
⊖ $T_A = 30°C$
● $T_A = 35°C$


ΔP, N Ω CMS.
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
AGEING TIME (MIN.)
○ T_A = 40°C
◍ T_A = 45°C
◍ T_A = 50°C
● T_A = 55°C

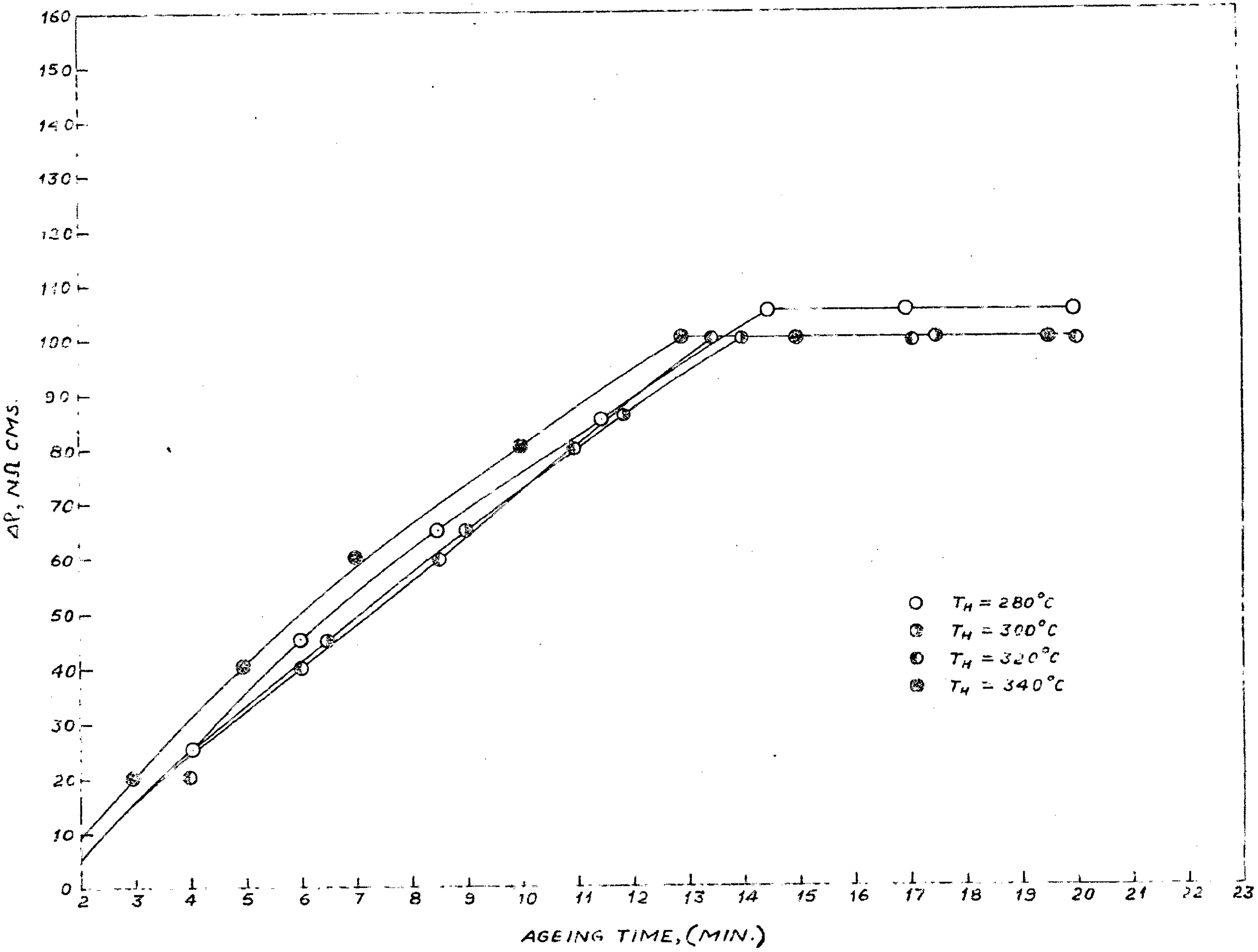
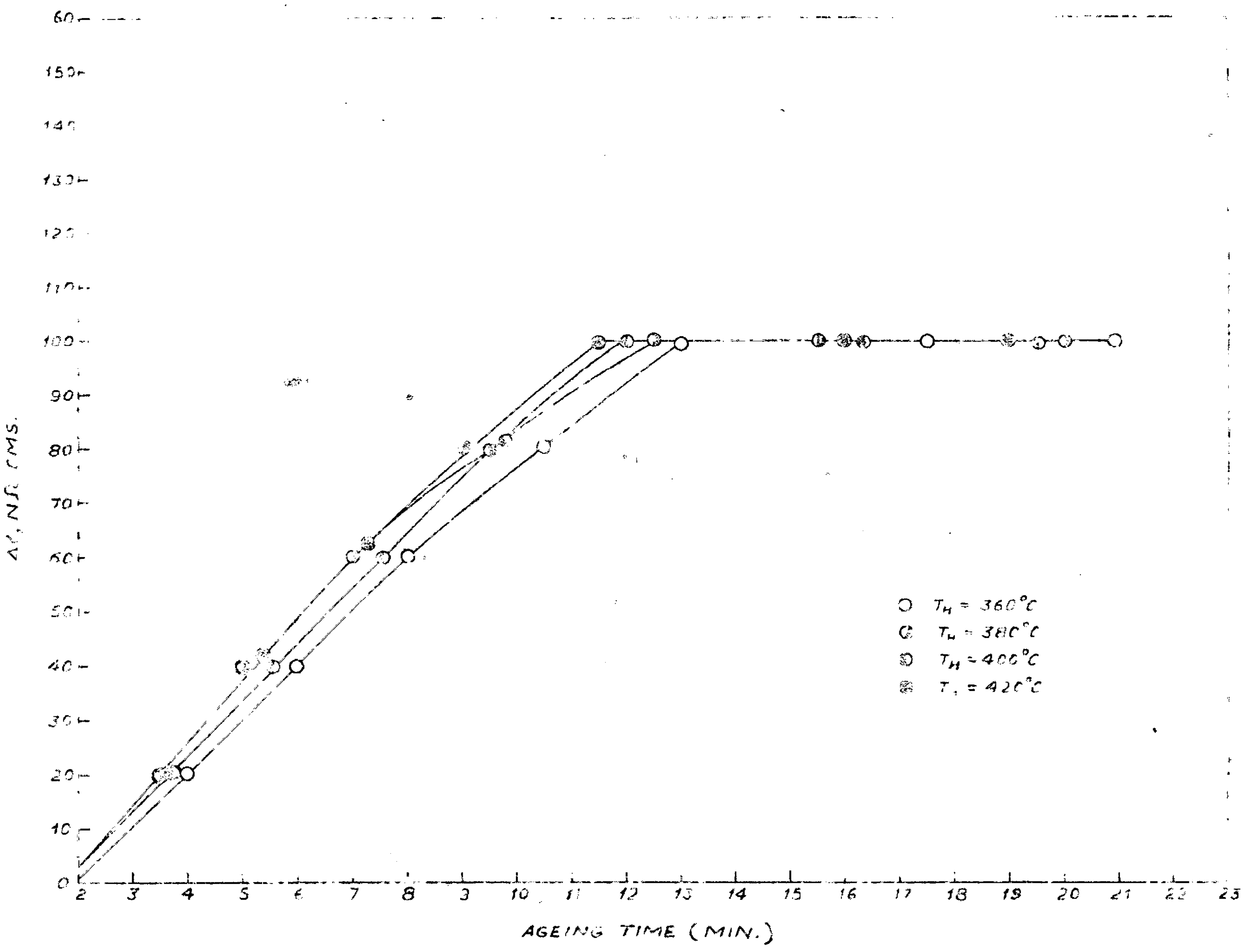
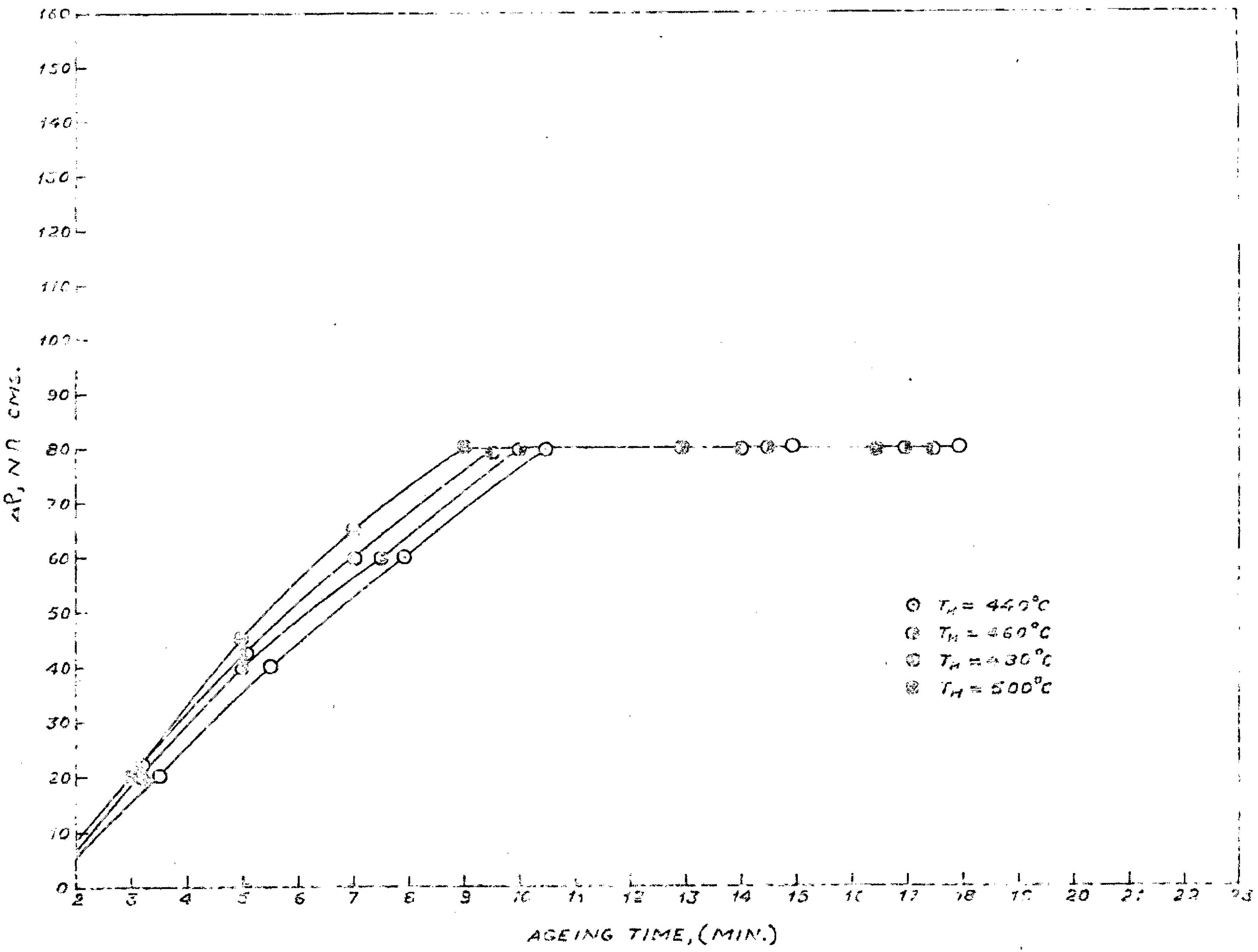
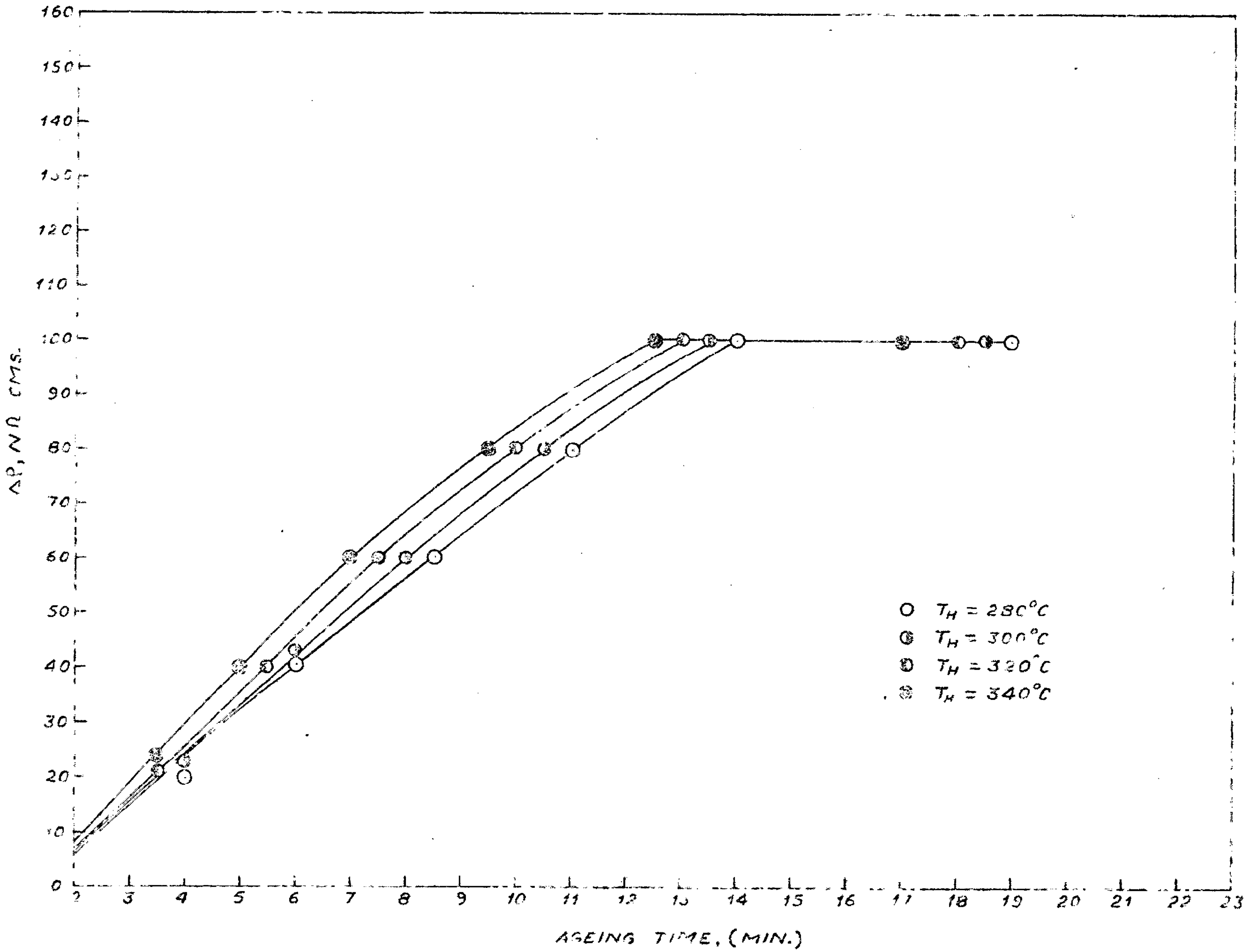


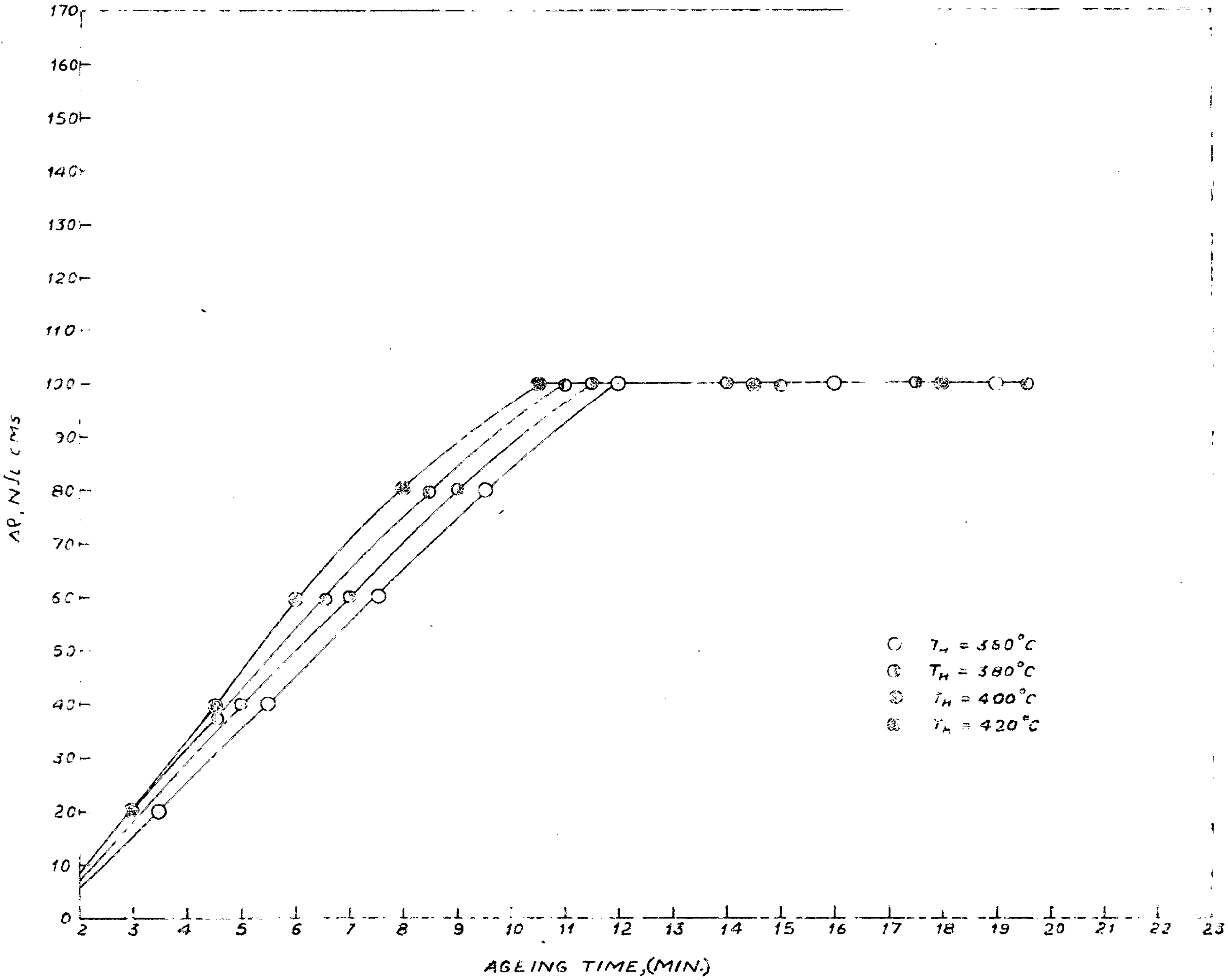
FIG. 3.10

ALLOY (A)


Δρ, nΩ cms.
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
60
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
AGEING TIME (MIN.)
○ T_H = 360°C
T_H = 380°C
T_H = 400°C
T_H = 420°C


ΔP, N.D. CMS.
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
AGEING TIME, (MIN.)
⊙ T_H = 440°C
◐ T_H = 460°C
○ T_H = 480°C
● T_H = 500°C


ΔP, NΩ CMS.
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
AGEING TIME, (MIN.)
○ T_H = 280°C
◐ T_H = 300°C
◑ T_H = 320°C
● T_H = 340°C


170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ΔP, N/L cms
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
AGEING TIME,(MIN.)
○ T_H = 360°C
◐ T_H = 380°C
◍ T_H = 400°C
● T_H = 420°C

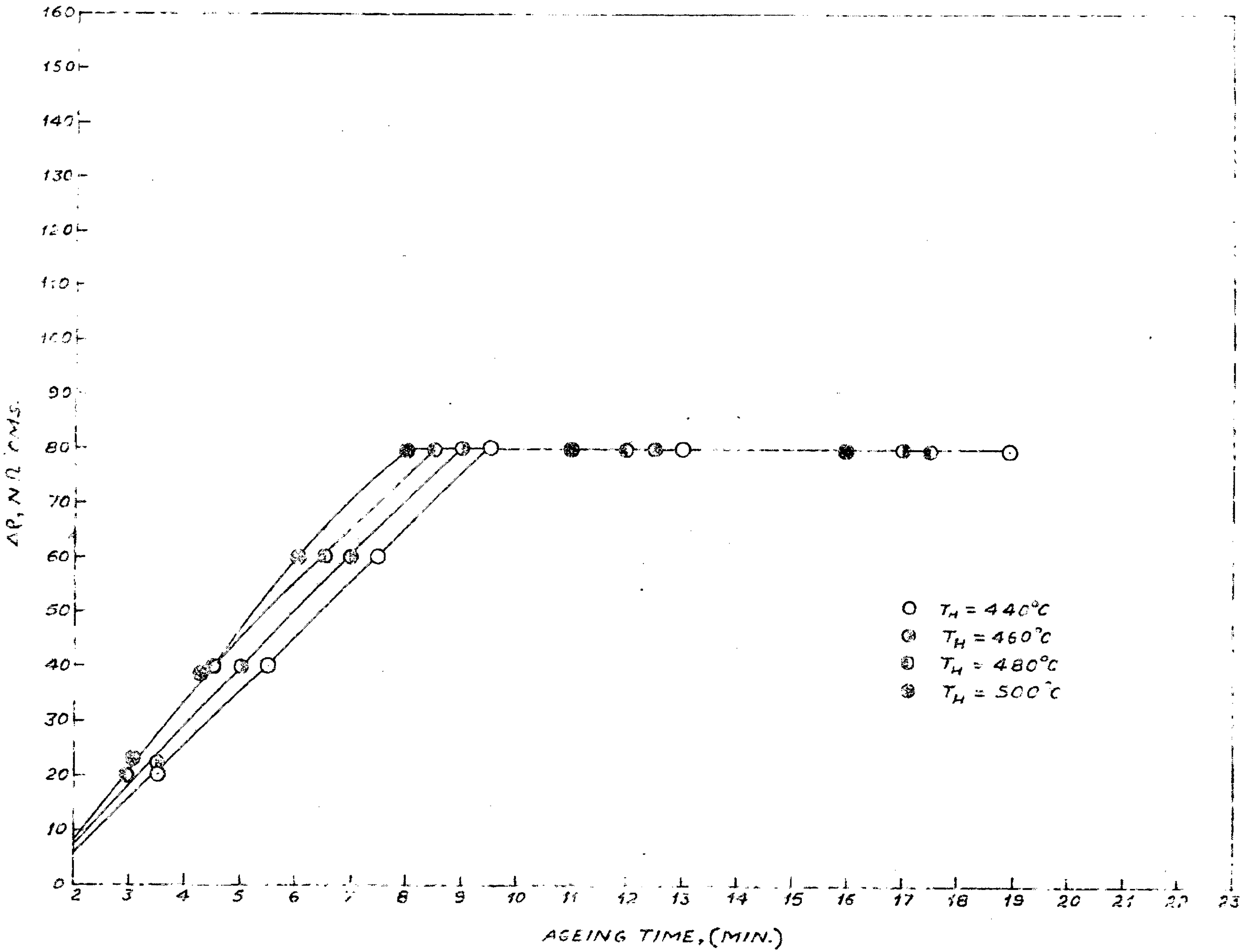


FIG. 3.15

ALLOY ③

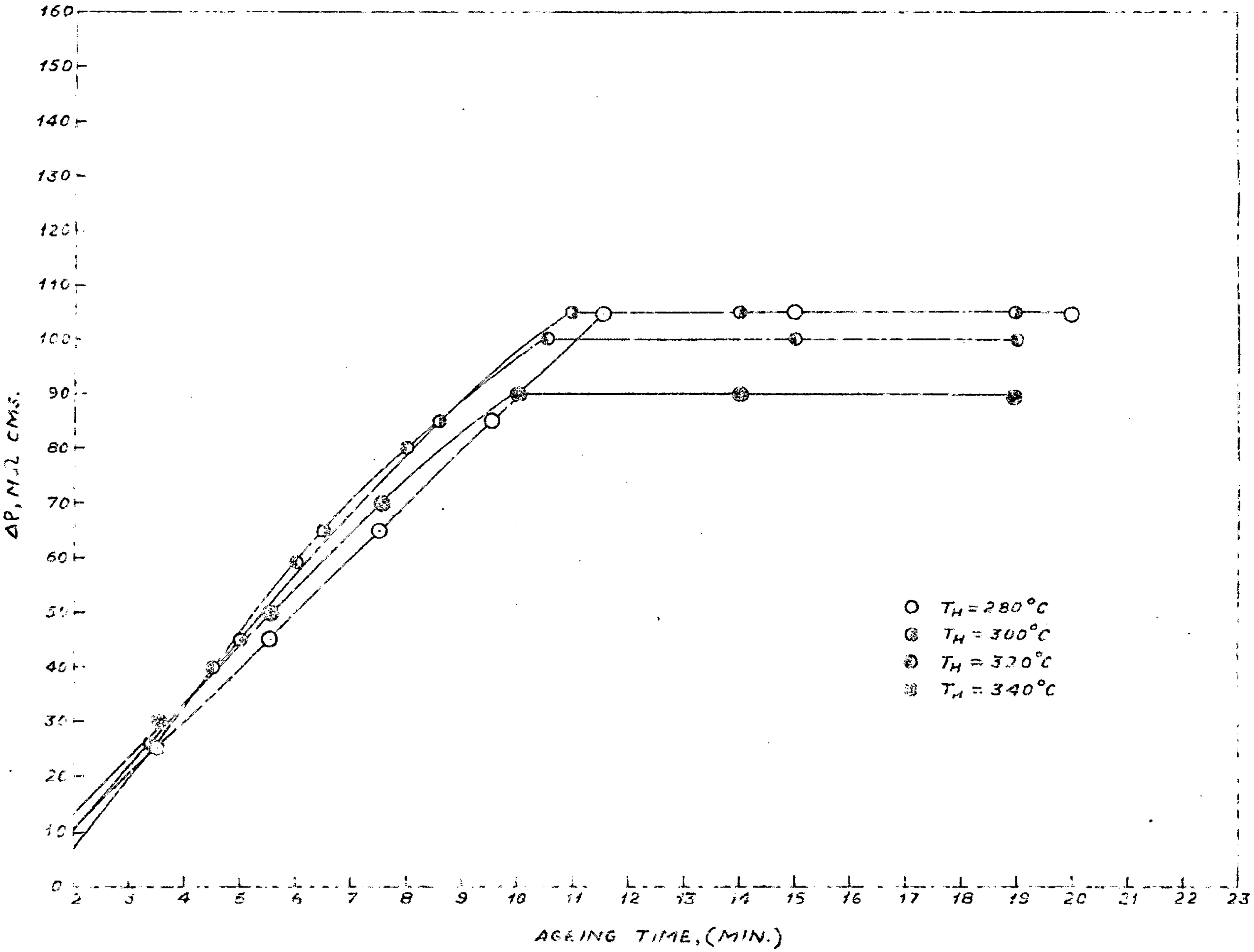
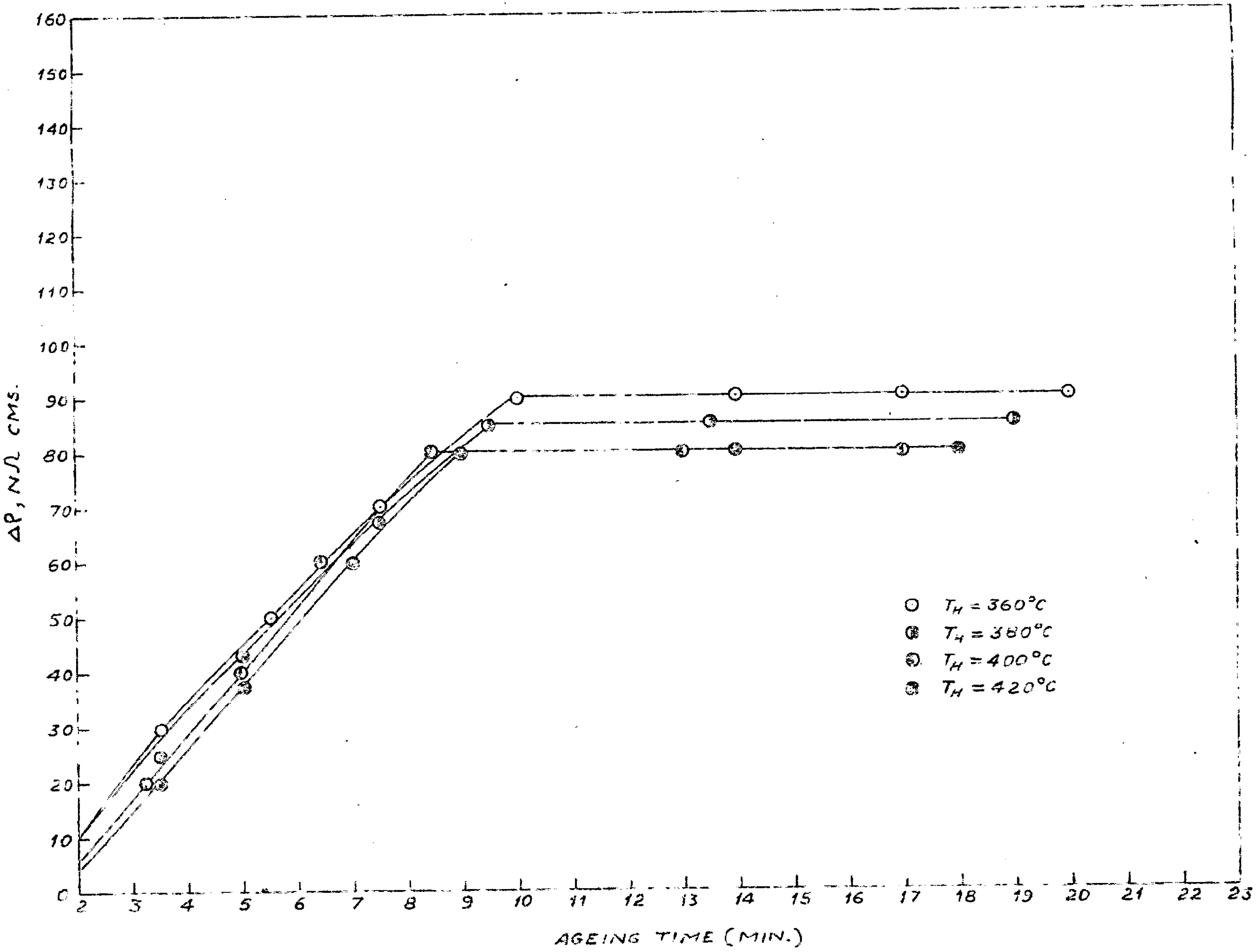


FIG. 3.16

ALLOY Ⓒ


160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ΔP, NΩ CMS.
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
AGEING TIME (MIN.)
○ T_H = 360°C
● T_H = 380°C
◉ T_H = 400°C
● T_H = 420°C

[illegible]

ALLOY (C)

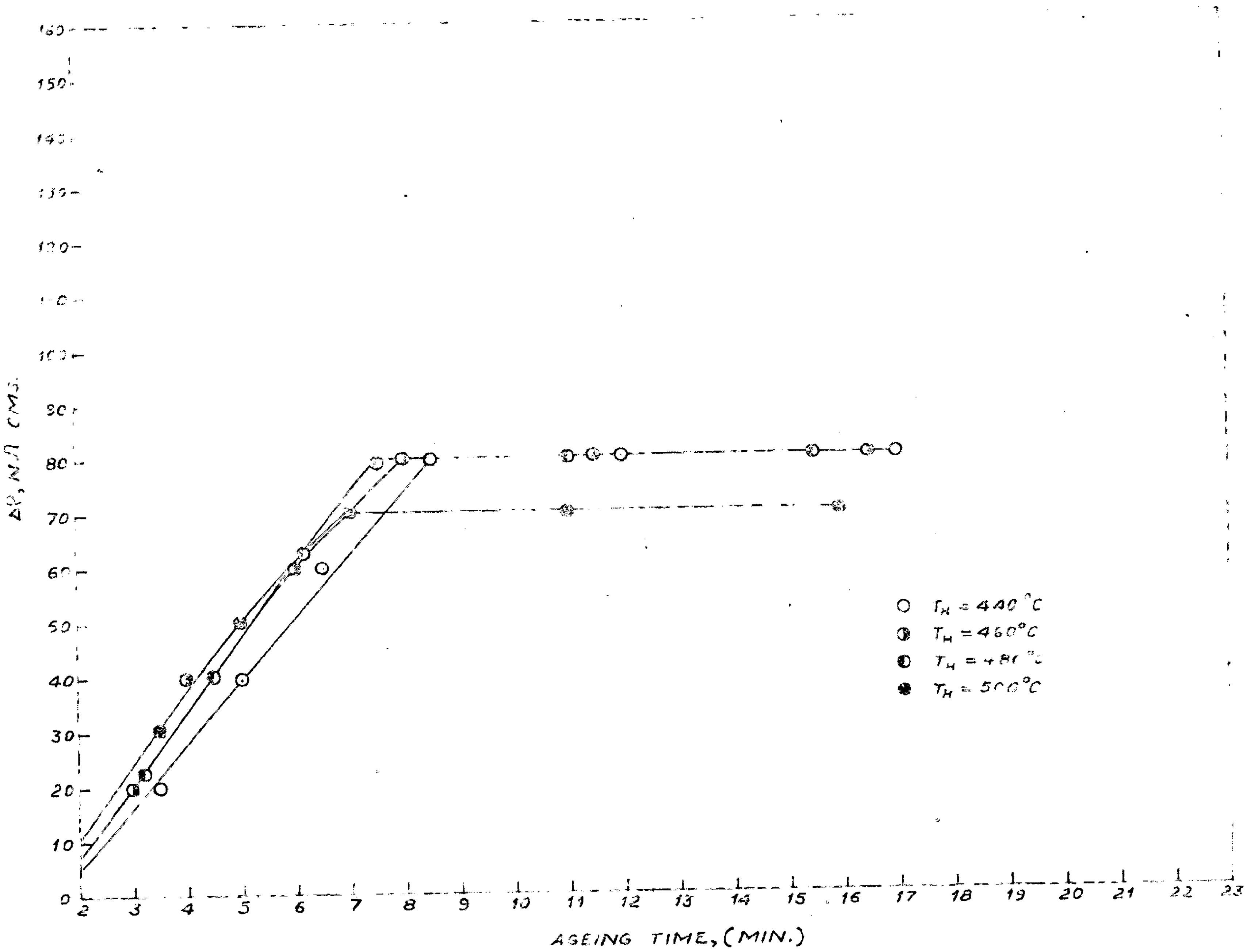


FIG. 7.48

ALLOY Ⓒ

constant value for an appreciable length of time, it is termed as 'slow reaction'. In the present work this may be due to three reasons :

(i) rapid decay of excess vacancies in less concentrated alloys,

(ii) depletion of the matrix of solute atoms after a certain degree of clustering,

(iii) Cd atoms are trapped in vacancies and forms strông bonding resulting in low mobility and less number of mono vacancies.

3.2.2 Effect of Homogenisation Temperature

Higher the T_H, higher will be the amount of gene quenched in vacancies, quicker the formation and growth of zones and lesser the time required to reach the resistivity maximum or a constant value as observed in present investigation.

3.2.3 Effect of Ageing Temperature

Concerning the influence of ageing temperature, it has been found that the amount of increase in resistivity decreases greatly by increasing the ageing temperature. This is due to less number of zones formed. Higher ageing temperature results in early migration of vacancies to the sink.

3.2.4 Effect of Varying Cadmium Percentage :

By comparing the isothermal ageing curves for the binary Al-Zn alloys and the corresponding Al-Zn-Cd alloys, it is very much evident that the rate of clustering is decreased appreciably by Cd addition. This is in accordance with the earlier published work of Perry and Entuistle[32] on other ternary alloys. The ageing is further delayed by higher amount of Cd addition. The delay in the ageing sequence can be interpreted due to a high positive binding energy between Cd atom and a vacancy Cd atoms get paired-off with excess vacancies thus vacancy migration becomes sluggish leading to decreased clustering rate. This is one of the reasons which has resulted 'slow reaction' in the present work.

3.3 ROLE OF VACANCIES IN THE PRESENT ALLOYS

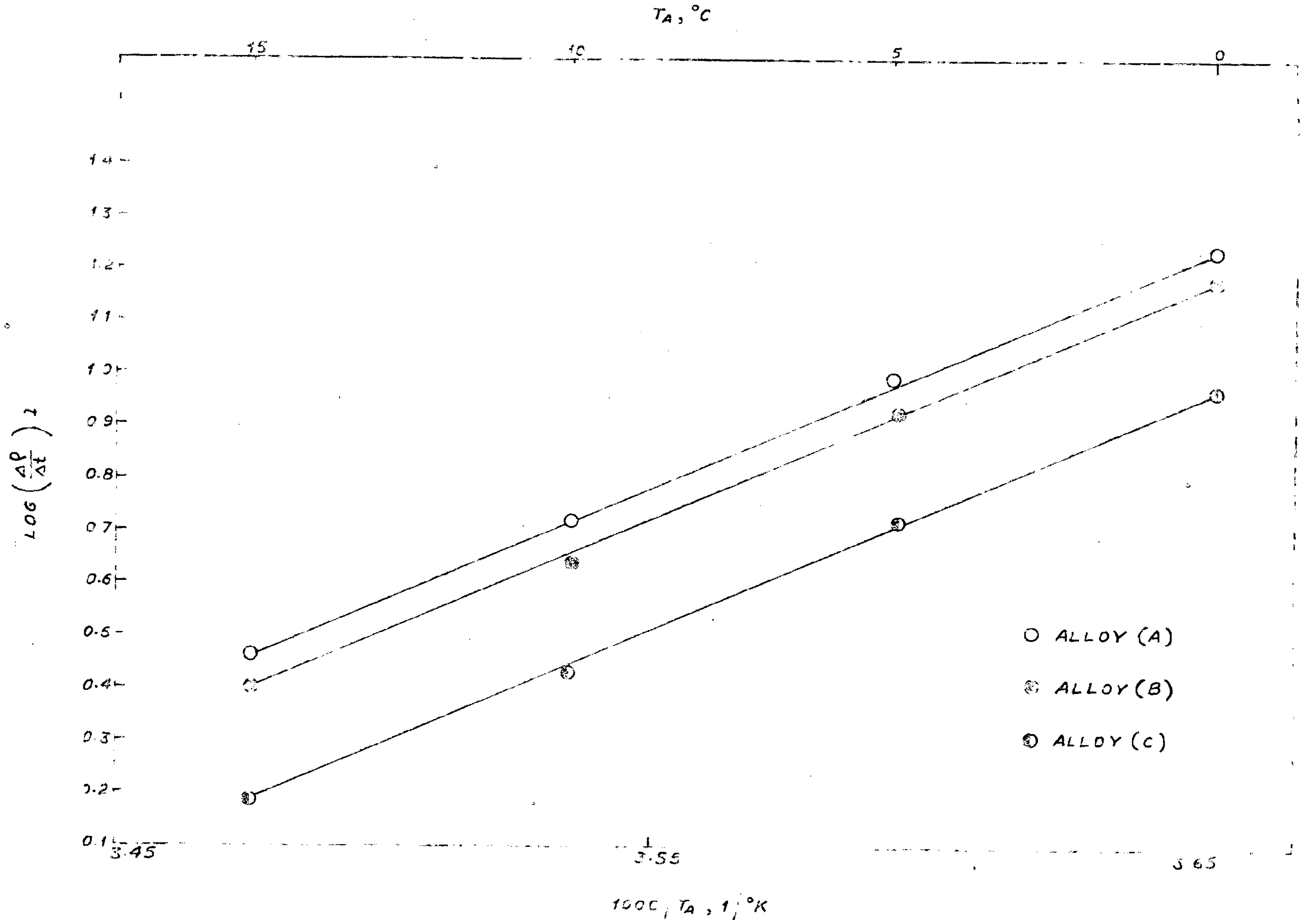
3.3.1 Formation Energy of Vacancies (E_F) :

Figs. 3.22, 3.23 and 3.24 show the plots between logarithm of initial rate of change in resistivity ($\Delta\rho/\Delta t$), and reciprocal of homogenization temperature ($\frac{1}{T_H}$) for all the three alloys.

Summarising the table 3.1, it is evident that E_F values for ternary alloys lie in the range 0.25 to 0.28 eV which is low as compared with binary Al-Zn alloy (0.65 eV). The lower value of E_F for ternary alloys suggests a positive binding energy between Cd atom and a vacancy.

3.3.2 Migration energy of Vacancies (E_M)

From the slope of logarithmic plot between initial rate of change in resistivity ($\Delta\rho/\Delta t$)$_I$ and reciprocal of ageing temperature ($1/T_A$), activation energy of migration of vacancy/solute atom (E_M) can be evaluated. Figs. 3.19, 3.20 and 3.21 show a set of such plots for all the three alloys.


T_A , °C
15
10
5
0
LOG $\left(\frac{\Delta\rho}{\Delta t}\right)_1$
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
3.45
3.55
3.65
1000 / T_A , 1/°K
○ ALLOY (A)
ALLOY (B)
ALLOY (C)

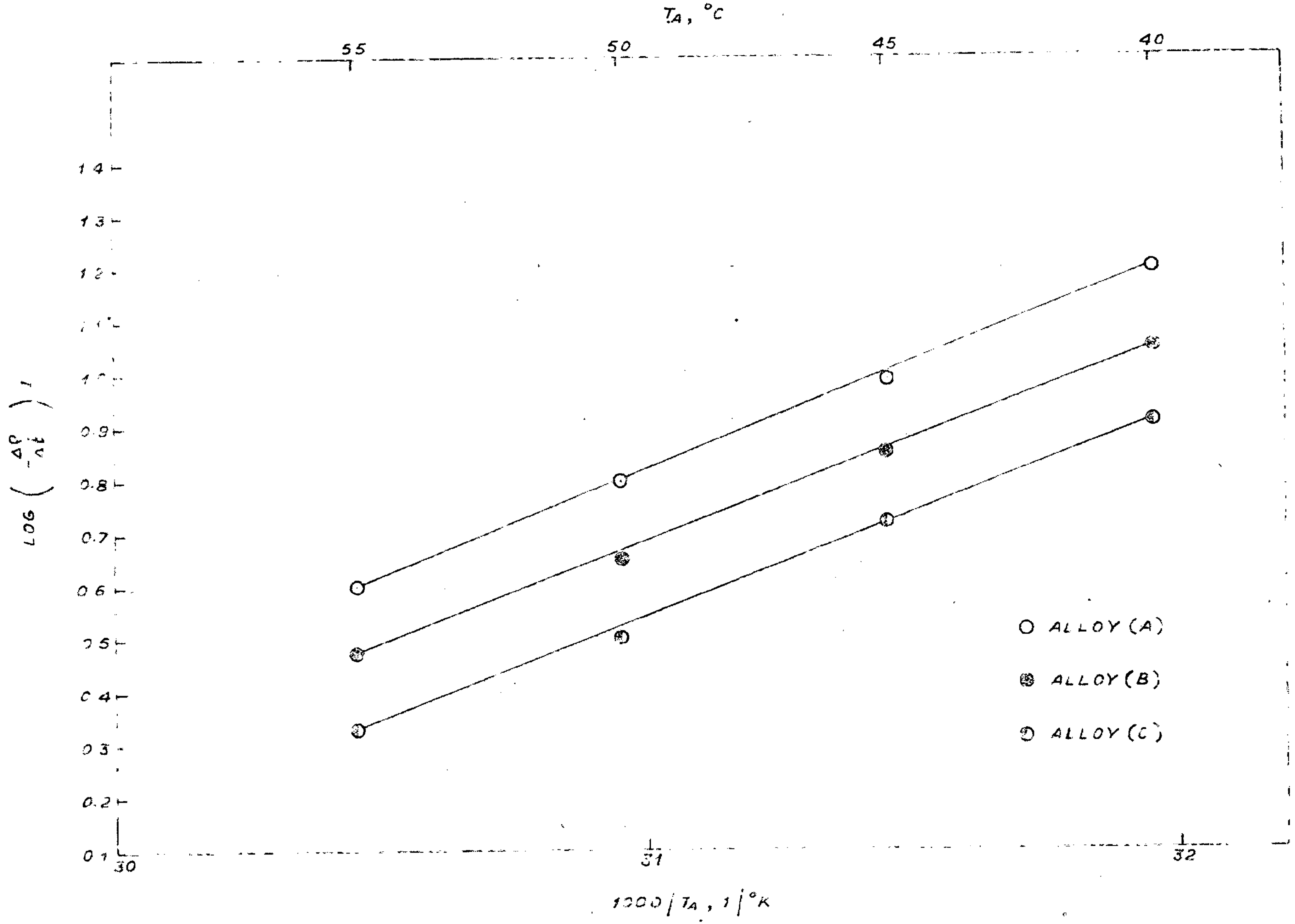

T_A, °C
55
50
45
40
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
LOG $\left(-\frac{\Delta \rho}{\Delta t} \right)_I$
30
31
32
$1000/T_A$, 1/°K
○ ALLOY (A)
● ALLOY (B)
◐ ALLOY (C)

FIG. 3.21

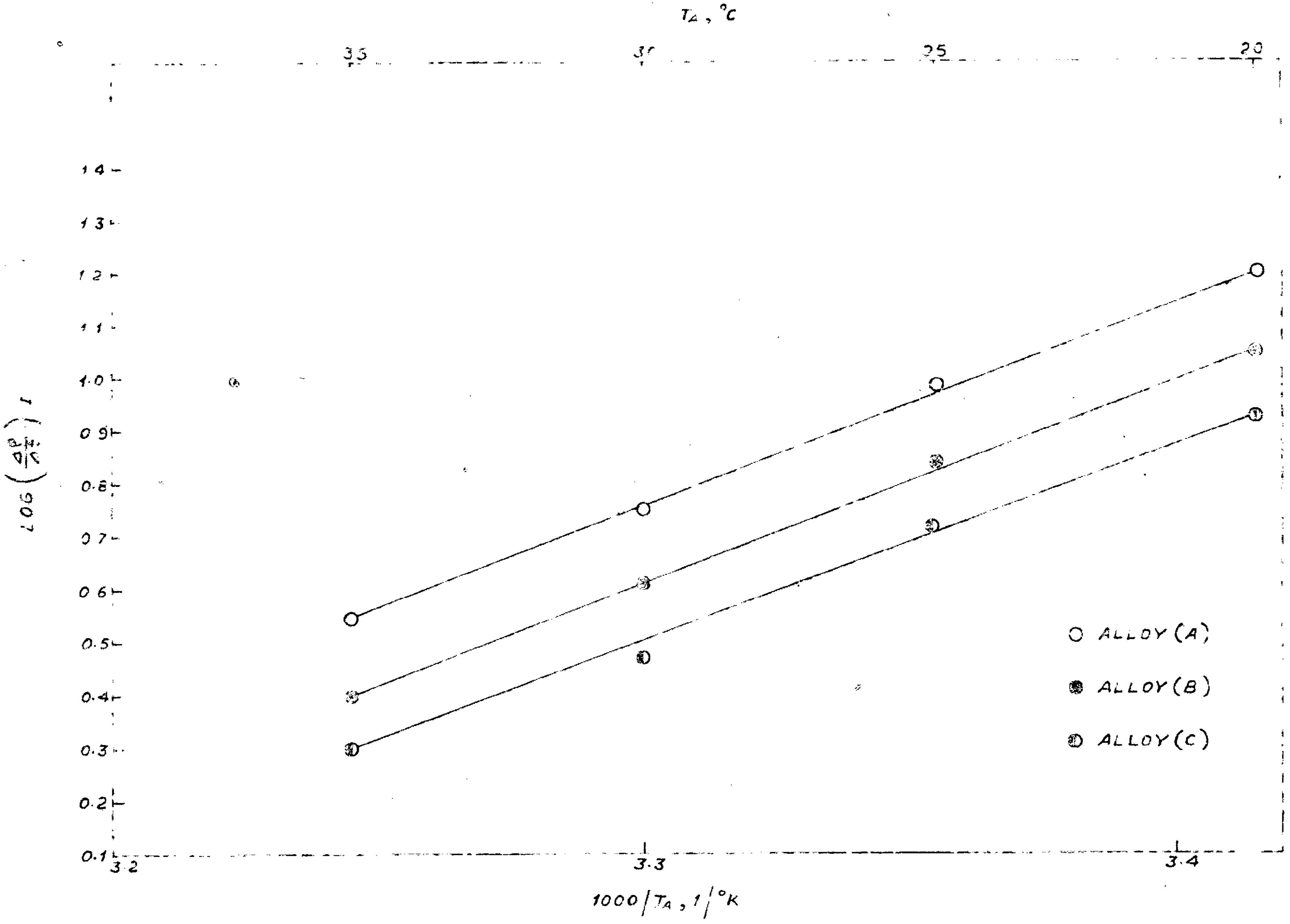
TA, °C
35
30
25
20
LOG (dP/dt)
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
3.2
3.3
3.4
1000/TA, 1/°K
○ ALLOY (A)
● ALLOY (B)
◐ ALLOY (C)

FIG. 3.20

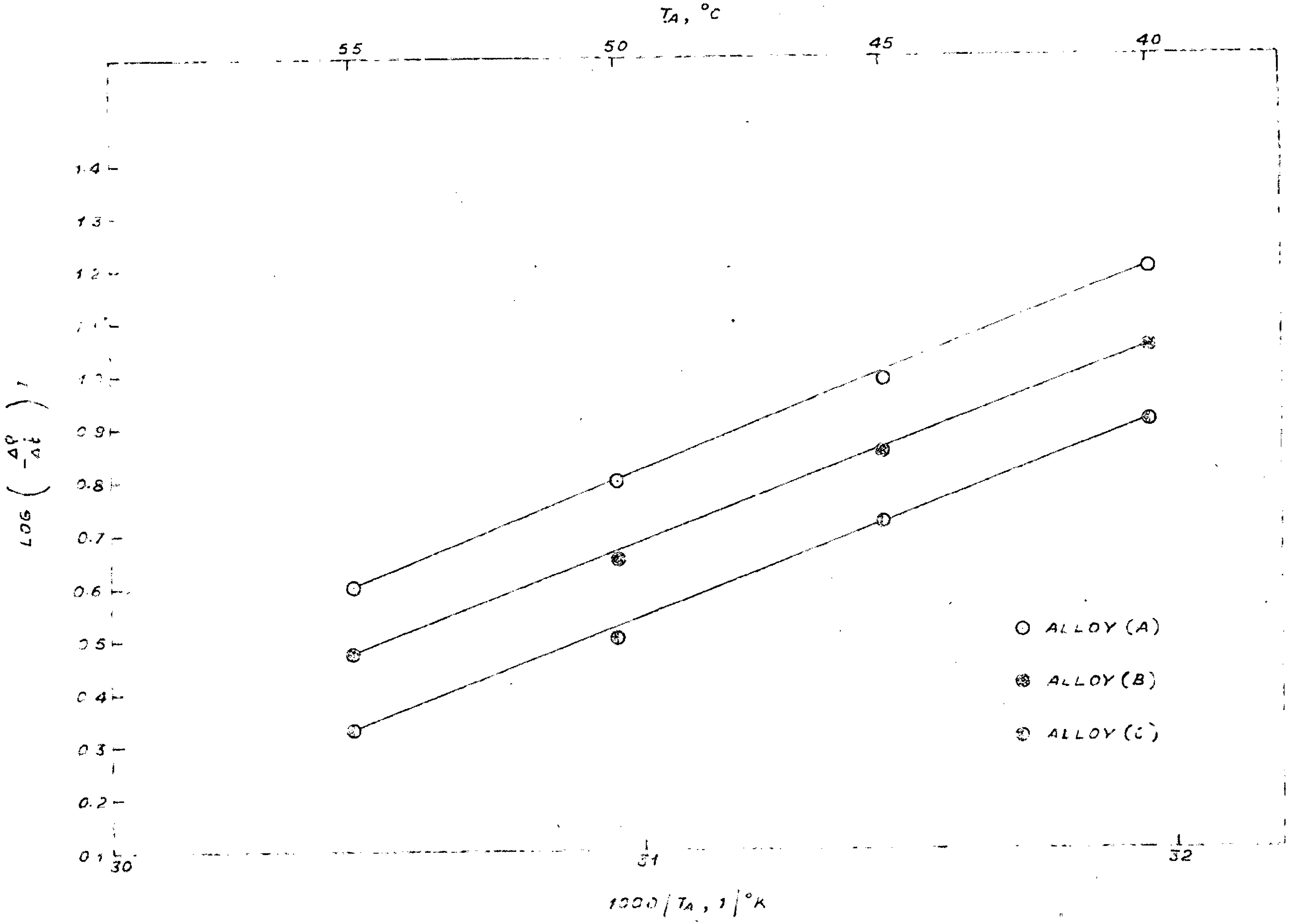

T_A, °C
55
50
45
40
$LOG \left(-\frac{\Delta\rho}{\Delta t} \right)$
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
30
31
32
$1000 / T_A$, 1/°K
○ ALLOY (A)
● ALLOY (B)
● ALLOY (C)

FIG. 3.21

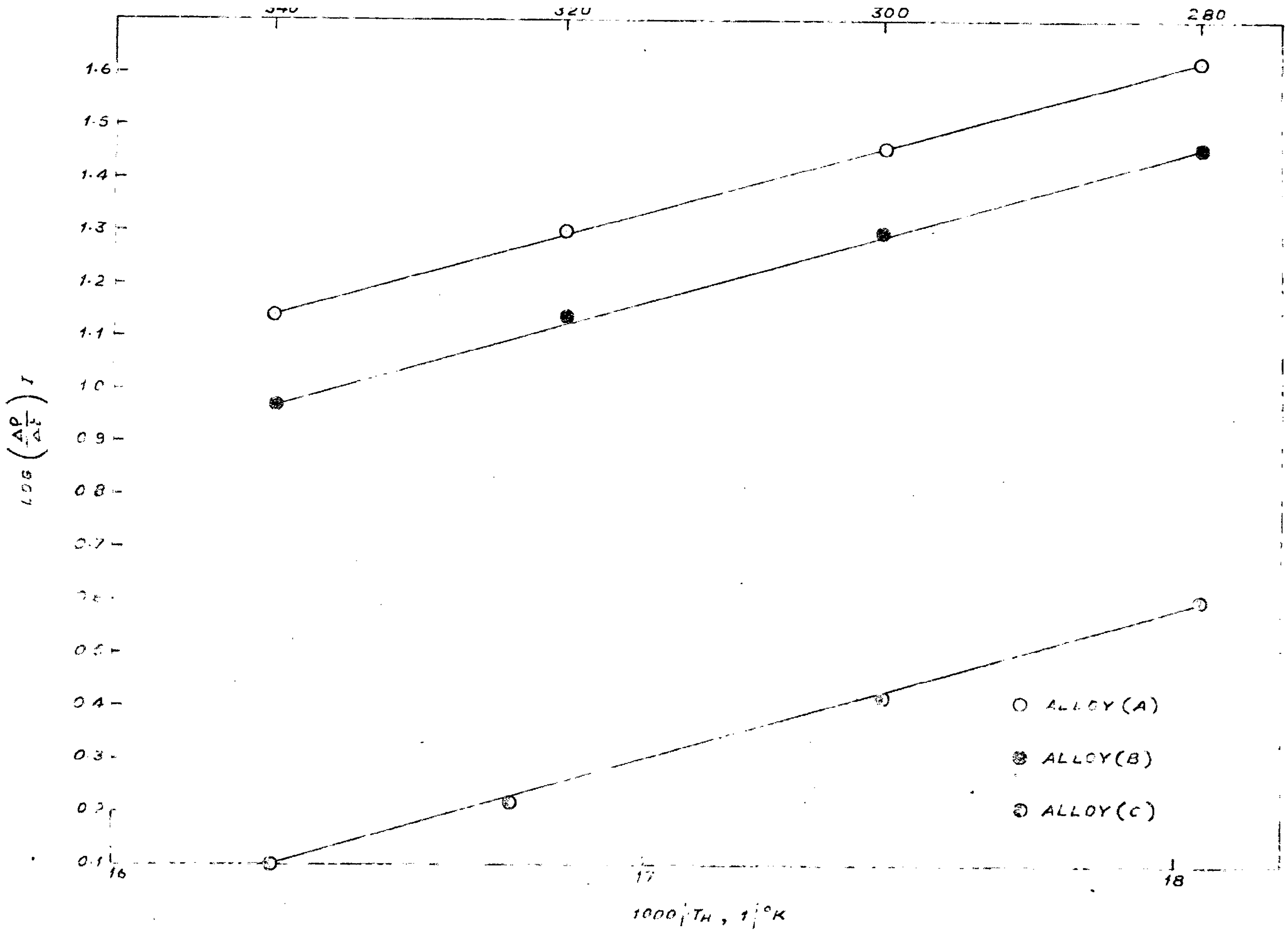

340
320
300
280
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
$\log\left(\frac{\Delta\rho}{\Delta t}\right)_I$
16
17
18
1000/TH, 1/°K
○ ALLOY (A)
● ALLOY (B)
◎ ALLOY (C)

FIG 3.22

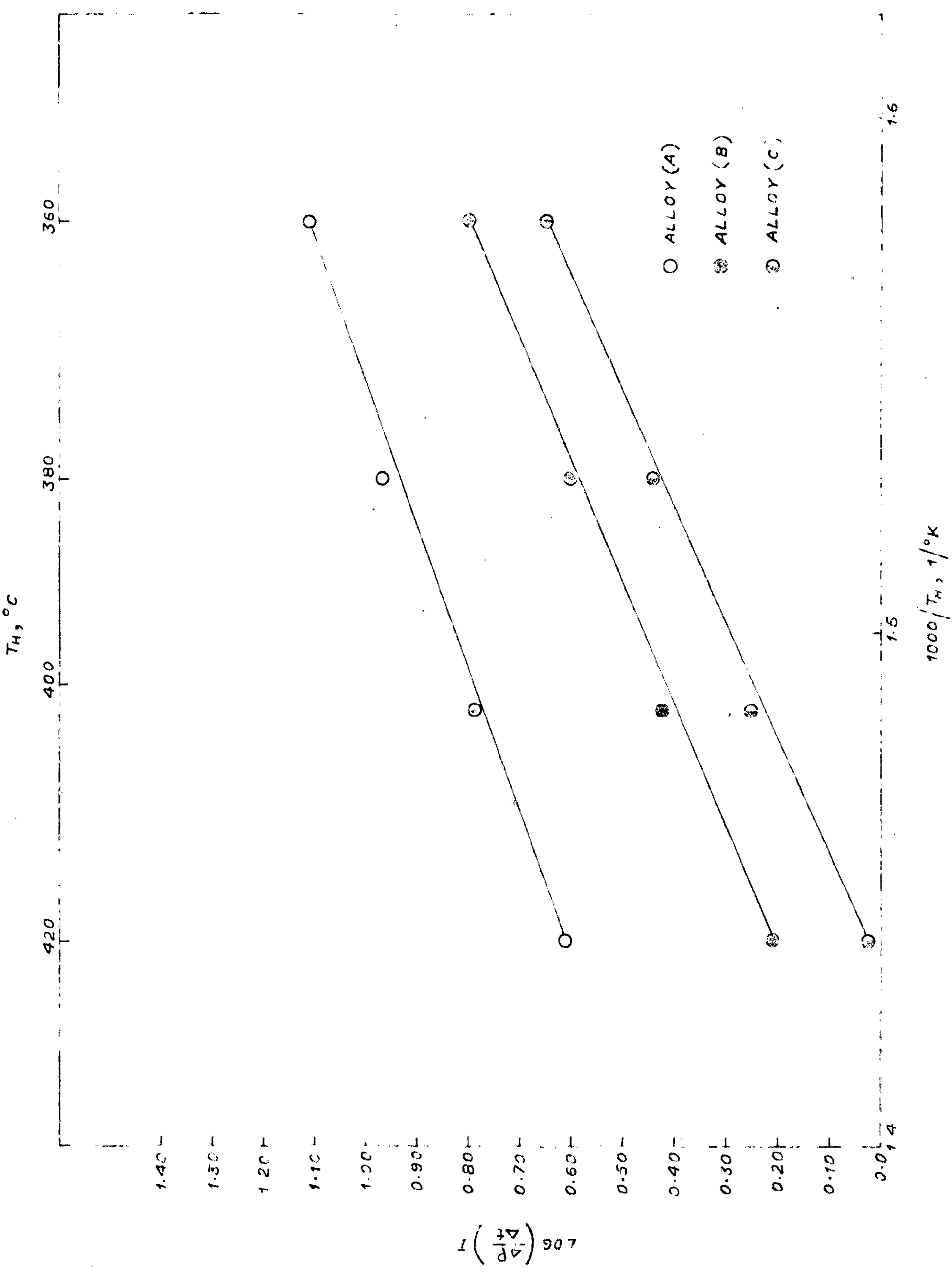
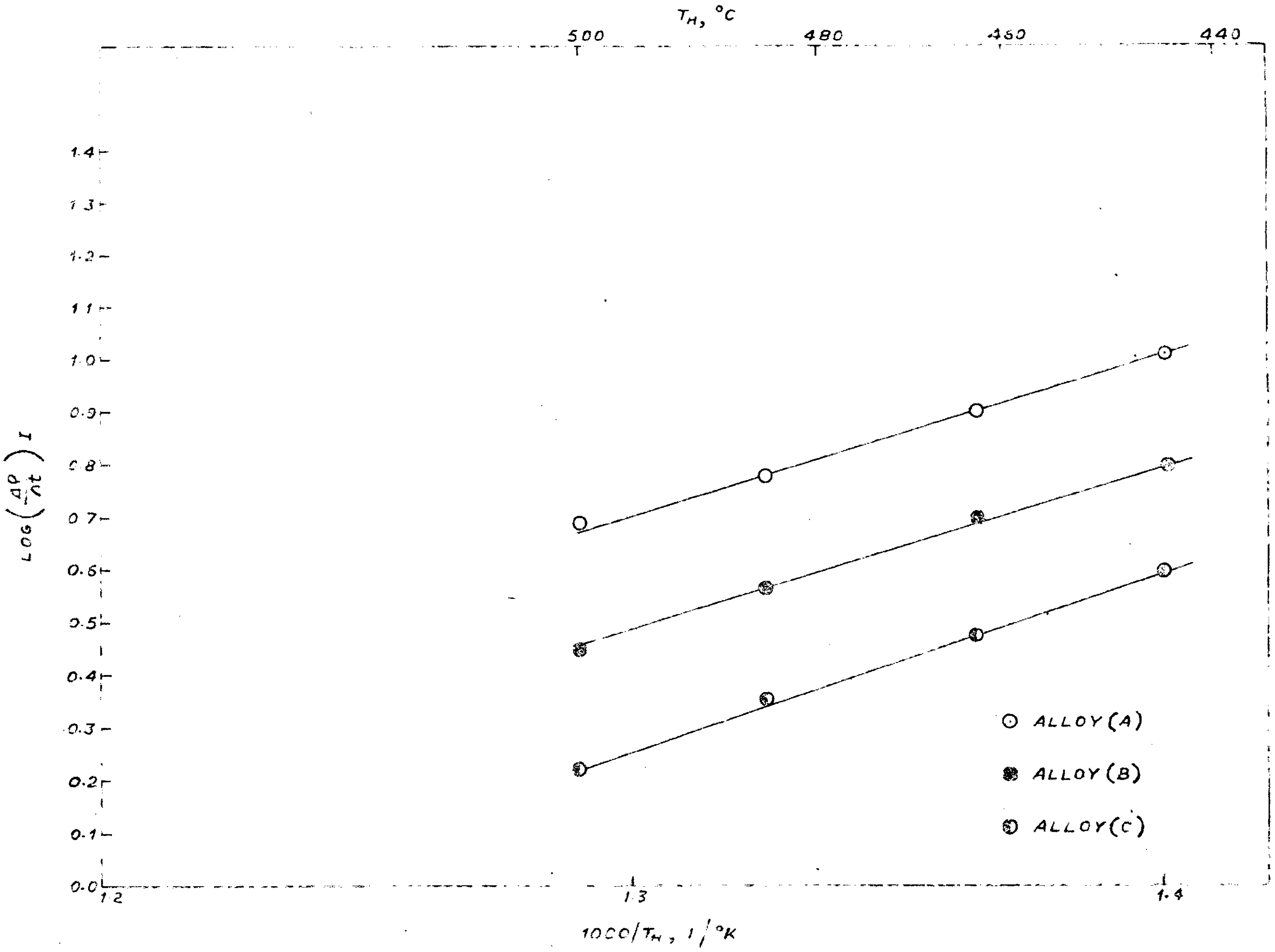

T_H, °C
360
380
400
420
1000/T_H, 1/°K
1.4
1.5
1.6
LOG (ΔP/Δt) T
0.0
0.10
0.20
0.30
0.40
0.50
0.60
0.70
0.80
0.90
1.00
1.10
1.20
1.30
1.40
○ ALLOY (A)
● ALLOY (B)
⊕ ALLOY (C)

FIG. 2


T_H, °C
500
480
460
440
LOG (ΔP/Δt) I
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
1.2
1.3
1.4
1000/T_H, 1/°K
ALLOY (A)
ALLOY (B)
ALLOY (C)

The E_M values obtained are listed in table 3.2. The table reveals that E_M values for ternary alloys lie in the range .37 to .41 eV. An increase in the E_M values for the ternary alloys predicts that migration of vacancies is showed down by Cd addition. The increased value of E_M may be attributed to pairing of Cd atoms with vacancies.

TABLE 3.1 E_F by resistivity measurement

Homogenisation Temperature	Alloy A	Alloy B	Alloy C
280°C - 340°C	.29 eV	.28 eV	.27 eV
360°C - 420°C	.28 eV	.27 eV	.27 eV
440°C - 500°C	.27 eV	.26 eV	.26 eV

TABLE 3.2 E_M by resistivity measurement

Ageing Temperature	Alloy A	Alloy B	Alloy C
0°C - 15°C	.38 eV	.39 eV	.40 eV
20°C - 35°C	.37 eV	.38 eV	.38 eV
40° C -55°C	.40 eV	.40 eV	.41 eV

3.3.3 Binding Energy :

Having known the values of E_F for the binary and ternary alloys, the binding energies between a Zn atom and a vacancy E_b V-Z_n and that between Cd atom and a vacancy, E_b^{V-Cd}, can be deduced.

Panseri and Federighi[31] have used the following equation to calculate the binding energy between a Zn atom and a vacancy :

$$E_b^{V-Zn} = E_F^{Al} - E_F^{Al-Zn}$$

Assuming $E_F^{Al} = 0.76$ eV and taking 0.60 eV as the mean value of E_F^{Al-Zn}, the value of E_b^{V-Zn} comes out to be 0.16 ~~auV~~ eV.

A similar expression to calculate E_b^{V-Cd} has been employed by Panseri & Federighi[33] and using this, the value of E_b^{V-Cd} turns out to be in the range of 0.27 to 0.30 eV.

CHAPTER - IV

CONCLUSION AND SUGGESTIONS FOR FURTHER WORK

4.1 CONCLUSION :

In light of the results discussed in the preceeding chapter, the following conclusions may be drawn:

1. There is a marked influence of Cd on the pre-precipitation stage of ageing. Ageing is delayed to a great extent by addition of Cd.

2. Role of defect structure, mainly vacancy concentration, is very important. Dependence of rate of pre-precipitation on homogenisation and ageing temperatures can be explained in terms of quenched-in vacancy concentration and their mobility respectively.

3. Resistometric study during pre-precipitation stage of quenched aluminium-zinc-cadmium alloys offers a method of estimating the

activation energies associated with formation and migration of vacancies. The values of activation energies so estimated are comparable with reported values.

4.2 SUGGESTIONS FOR FURTHER WORK :

On the basis of the experimental results already obtained it is evident that the scope of precipitation hardening of Al base ternary alloys is very extensive. However, a number of parameters are still necessary to understand the picture completely and give a clear cut base. In this regard the following types of work may be further extended.

1. Bow angle X-ray scattering may be used to study the characteristics of zones.

2. Role of defect structure i.e. dislocations, vacancies and stacking faults can well understood with the help of Electron Microscope.

3. Some more additions of Cd may be chosen and efforts be made to correlate the Cd-vacancy binding energy with the amount of Cd.

4. Other ternary additions, forming strong bonds with vacancies like In, Sn or those forming weak bonds like Ag, may be tried.

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