STUDIES IN PRECIPITATION HARDENING OF SOME ALUMINIUM BASE ALLOYS

By

T. V. RAJAN

A Thesis
submitted in fulfilment
of the requirements for the degree
of
DOCTOR OF PHILOSOPHY
in
METALLURGICAL ENGINEERING
of the
UNIVERSITY OF ROORKEE

DEPARTMENT OF METALLURGICAL ENGINEERING
UNIVERSITY OF ROORKEE
ROORKEE
October, 1969

CERTIFICATE

Certified that the dissertation entitled "Studies in precipitation hardening of some Aluminium base alloys" which is being submitted by Sri T.V.Rajan for the award of the Degree of Doctor of Philosophy in Metallurgical Engineering of University of Roorkee is a record of student's own work carried out by him under my supervision and guidance. The matter embodied in this dissertation has not been submitted for the award of any other Degree of Diploma.

This is further to certify that he has worked for a period of two years and five months from May 1967 to October 1969 for preparing dissertation for Doctor of Philosophy Degree at the University.

October 25, 1969

(M.N.SAXENA)
Professor & Head
Deptt. of Metallurgical Engg.
University of Roorkee
ROORKEE (U.P.)

ABSTRACT

The experimental investigations presented in this thesis, were undertaken to study the effect of quenched-in vacancies, lattice distortions and dislocations on the ageing characteristics of some binary and ternary Aluminium base precipitation hardening alloys. Activation energies of migration and formation of vacancies were also estimated on the basis of study of Portevin-LeChatelier phenomenon.

Effects of trapped thermal vacancies on the process of precipitation in ternary Al-Cu-Mg alloys were studied. A comparative study was made on binary Al-Cu alloy. The results indicate that in ternary alloys, rate of quenching has a definite effect on the kinetics of hardening process and the peak-hardness values. It is suggested, that in contrast to Al-Cu binary alloy, not only is the concentration of trapped thermal vacancies higher, but also it is retained for longer period during ageing of the ternary alloys due to existence of strong solute atom (Magnesium)-vacancy pairs. This, coupled with possible condensation of vacancies to form voids and collapse of clusters of vacancies to form dislocation loops (each of which is a potential site for precipitation of intermediate phase) can account for the dependence of rate of hardening on quenching rate. The observation of maximum peak-hardness corresponding to an optimum rate of quenching may be explained in terms of size of platelets of intermediate precipitate associated with the peak.

Studies were carried out on relief of thermal strains in solution treated, quenched Al-Cu and Al-Mg precipitation hardening alloys. Initial stages of ageing were followed by hardness measurement and analysis of X-ray line profile.

It was observed that during the process of initial ageing, there is softening followed by usual hardening. The phenomenon of initial softening is observable only over a definite range of ageing temperatures. Extent of softening has been found to be a function of (a) Temperature of ageing, (b) Solute concentration and (c) Quenching medium.

These results can be explained in terms of softening due to relief of thermal strains followed by the usual hardening as a result of coherency strains developed by precipitation of zones and/or intermediate phase.

Effects of cold working on the ageing characteristics of some Al-Cu and Al-Mg precipitation hardening alloys were investigated.

It was observed that cold working can result not only in acceleration but also in retardation of the process of precipitation of intermediate phase and consequent hardening. The nature of the effect appears to be critically dependent on the degree of supersaturation of the alloy at the temperature of ageing. Effect of cold work on the transformation of the intermediate phase to the equilibrium phase, on the other hand, seems to depend on mode of transformation.

The results are explained in terms of;

(i) Dislocations acting as potential sites for precipitation of intermediate phase.

(ii) Solute atoms getting trapped in the form of atmospheres around dislocations and consequent depletion of solute atoms from the solid solution.

(iii) Diffusion barriers created around platelets of intermediate precipitate due to accumulation of dislocation.

Investigations were carried out on the phenomenon of repeated yield in quenched Al-Cu and Al-Mg alloys.

By appropriate combination of initial quenched-in vacancy concentration and their mobility during subsequent strain-ageing, it was possible to initiate Type B yielding without prior plastic deformation.

Activation energies of formation and migration of vacancies were evaluated on the basis of these studies. The values of activation energies so estimated were; $E_m = 0.40 \pm 0.02$ eV and $E_f = 0.60 \pm 0.05$ eV for Al-Cu alloys. The corresponding values for Al-Mg alloys were 0.37 ± 0.03 eV and 0.44 ± 0.02 eV respectively.

On the basis of the findings reported in this thesis, there is a possibility of development of improved heat-treatment schedule for ternary Al-Cu-Mg alloys so as to get maximum peak-hardness with an optimized quenching rate. The results also show that it is possible to evolve suitable thermomechanical treatment for high temperature use of Al-Cu alloys.

ACKNOWLEDGEMENT

I wish to express my deep sense of gratitude to Dr. M.N.Saxena, Professor & Head of Department of Metallurgical Engineering, University of Roorkee for his valuable guidance and inspiration. Bur for his encouragement at every stage of work, this thesis could not have been completed.

I am also thankful to the Director and the Head of Department of Metallurgical Engineering, Indian Institute of Technology, Bombay for having given permission to work on their X-ray diffractometer. Financial assistance provided by University Grants Commission, New Delhi, for carrying out a part of the research work is also gratefully acknowledged.

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CHAPTER-I

LITERATURE SURVEY

1.1 HISTORICAL REVIEW

The phenomenon of age-hardening was discovered by Alfred Wilm (1,2) in the years 1903-11. It was observed that some Al-Cu alloys when quenched from elevated temperatures, hardened with time at room temperature. Hence the name age-hardening was given to the phenomenon. The term, precipitation hardening is also used to denote this phenomenon, because hardening takes place due to the process of precipitation from a supersaturated solid solution. +This fact was brought home by Merica etal (3) in 1921 by carrying out a detailed study of the process.

To start with, it was assumed that the phase precipitating out from the supersaturated solid solution is the equilbirium phase. Hardening was associated with the formation of submicroscopic particles of equilibrium phase. However, resistometric study of the phase changes taking place during precipitation revealed an anomalous behaviour (4,5). If ageing involved simple precipitation of equilibrium phase, then there should be steady decrease in resistivity with ageing. On the other hand it was observed that there is first an increase in resistivity followed by the expected decrease. This behaviour was explained by Gayler and Preston (6) on the basis of two stage precipitation process, the first stage being precipitation of an intermediate or non-equilibrium phase followed by the transformation of non-equilibrium phase to equilibrium phase. Gayler and Preston arrived at their conclusions on the basis of extensive study carried out on hardness, density, electrical resistance and X-ray measurements. They attributed hardening to the internal changes in the lattice of the supersaturated alloy due to precipitation of non-equilibrium phase. Rosenhain (7) and Tammann (8) also postulated theories of two stage precipitation. However, there was little agreement between these workers on the nature of the intermediate precipitate.

Marica (9), in 1932, suggested that the first step towards precipitation is segregation of solute atoms on certain sites within the solid solution. The segregated regions were referred to as 'knots'. He further suggested that a strain field is developed around the knots due to size difference between the solute and solvent atoms. As a result the process of slip is rendered difficult and this leads to hardening. In spite of reference of Marica to this pre-precipitation stage, the existance of clusters was established (10,11) at a much later data. However, the experimental work of Jenkins and Bucknall (12) lent support to Marica's suggestions.

The discovery of zones by Guinier (13) and Preston (14) was a major breakthrough in the study of the age hardening process. Their findings were based on the observations of diffraction effects produced in X-ray line pattern of single crystals. A more thorough study of zones has been made possible by application of small-angle scattering (15-17) and it is now established (18-20) that difference between clusters and zones is only one of nomenclature. The hardening mechanism associated with zones (21-23) has undergone considerable change from the one suggested by Marica. Modified mechanisms have been proposed to explain hardening that takes place in spherical zones. Spherical zones are formed when size difference between the solvent and solute atoms is only marginal. Hence they are not associated with strain fields.

Establishment of presence of non-equilibrium transition phase θ' in Al-Cu alloys (24) contributed further to the understanding of the phenomenon of precipitation hardening. With identification of non-equilibrium phases in precipitation sequence, the concept of coherency came into existence. A precipitate is said to be coherent, partially coherent or non-coherent depending on the nature of the interface between the precipitate and the matrix. An interface is said to be coherent when continuity of lattice is maintained across it. If all the interfaces are coherent, the precipitate is said to be fully coherent with respect to matrix. If some of the interfaces are coherent and others non-coherent, then the precipitate is said to be partially coherent. If all the interfaces are non-coherent then the precipitate is also non-coherent. The matrix and the precipitate have different lattice constants. Hence to maintain coherency across an interface, the two lattices will have to be matched by a process which requires lattice distortion. Hence, whenever there is coherent precipitation, coherency strains are developed and this results in hardening. Particles of non-equilibrium precipitate, to start with, are fully coherent with respect to matrix. With growth, the elastic strain energy (25,26) associated with individual particles increases till a critical size is attained and coherency is lost. Thus it is possible to explain the process of precipitation hardening including over-ageing, with the help of this theory. The credit of putting forward a theory to explain quantitatively the strengthening process due to coherency strain goes to Mott and Nabarro (27).

The sequence of structural changes in an age-hardening system can be stated as follows:

Supersaturated solid solution → Zone formation → Precipitation of non-equilibrium phase(s) → Transformation of non-equilibrium phase to equilibrium precipitate.

Actual number of steps involved varies from system to system and with the 'degree of supersaturation' in a given system. The 'degree of supersaturation', in turn, is a function of solute concentration in the alloy and temperature of ageing.

1.2 Al-Cu SYSTEM

Of the known age-hardening systems, Al-Cu is the one that was discovered first (1,2) and is probably the system in which most extensive work has been carried out so far. The experimental work tha has been carried out on Al-Cu system can broadly be divided into two catogaries, those dealing with changes in hardness as a result of ageing and the others dealing with structural changes that accompany ageing.

Although hardness is related (28-30) to both yield stress and work-hardening rate and hence is incapable of reflecting truly in quantitative measure the strength parameter, it has always been customery to measure ageing in terms of changes in hardness. Gayler (31), obtained ageing curves for Al-4% Cu alloy aged over a wide range of ageing temperatures from 0 to 450°C. Hunsicker (32) studied age-hardening behaviour of a wide variety of Al-Cu alloys with copper content varying from 1 to 4.5% and aged at room temperature and 150°C after being quenched in cold water or boiling water. However, it was Hardy (33) who made the most systematic study on the age-hardening characteristics of Al-Cu alloys with copper content varying from 2.0 to 4.5% and aged in temperature range of 30 to 240°C. Hardy pointed out that, depending on solute concentration and ageing temperature, the alloys showed different numbers of stages of hardening and he further related the hardening curves to the structures that were known to appear in this system. The activation energies associated with formation of non-equilibrium phase θ' was also evaluated with help of age-hardening curves.

The structural ageing characteristics of Al-Cu alloys has been studied by a number of workers with help of different experimental techniques. The ageing sequences being a sequence of structural transformations, are best studied with combination of techniques rather than with any particular technique.

It is generally agreed that the structural changes, that accompany precipitation-hardening, are submicroscopic in nature. By the time any second phase becomes visible under microscope, the process of ageing has already proceeded to a stage of overageing. Hence metallographic examination of specimens can hardly be expected to be useful in studying the structural changes accompanying ageing.

Extensive investigation of structural ageing characteristics of Al-Cu alloys based on X-ray studies (13,34-38), has been carried out. Most of these studies were based on either small angle scattering when it was necessary to establish the size and shape of particles (or regions capable of scattering X-rays coherently) or regular X-ray diffraction pattern when the aim was to determine the lattice parameters of the precipitating phases. The result of the X-ray studies were later confirmed by electron microscopic work (39-44). Electron microscopic work has thrown light not only on the structure but also on the size, shape and distribution of precipitating phases. These investigations have also been useful in studying the type of nucleation (homogeneous or heterogeneous) and the existence of preferential sites for precipitation of intermediate and equilibrium precipitates.

The role of resistivity measurements (10,11) has been of special significance in studying the process of clustering which is the first of the series of transformations that take place in supersaturated solid solution during ageing. The process falls under pre-precipitation stage and is accompanied with increase in resistivity. Clustering is also accompanied with evolution of heat and hence can be followed by calorimetric measurements (10,11). Growth of zones ha~~ve~~s also been studied by resistivity determinations. The resistivity maximum that is observed during the growth of zones has been explained as due to critical scattering of electrons by zones of specific diameter (45,46), coherency strains associated with zones (47) and structural dislocations formed round the zones (48). However, in the light of observations made by a number of workers (49-51), only the theory of critical scattering by Mott (45) could be taken. to be correct. Validity of Mott's theory has also been put to question recently by Wikes (52). Also the correlation between the zone diameter and resistivity is restricted to small zones (51). Hence, appropriate utility of resistivity data lies in study of pre-precipitation stage as compared with later stages.

The first step in ageing of Al-Cu alloys is formation of clusters. The initial rate of clustering as determined by resistivity measurements is too fast to be accounted for by normal rate of diffusion of copper atoms in Aluminium matrix (at room temperature) determined by extropolation of known high temperature diffusion rate (53). This inconsistency was first pointed out by Jagodzinski and Laves (54). Excess vacancy theory, postulated by Zener (55) and later developed in detail by Federighi (56) and De Sorbo, Treaftis and Turnbull (10), explains the anomalous rate of growth of clusters. It is assumed that the excess vacancies, that are trapped during the process of quenching from homogenization temperature, account for abnormally high rates of diffusion of copper atoms.

Growth of clusters leads to formation of zones. As already pointed out clusters and zones differ~~s~~ from each other only in nomenclature. The zones that appear in Al-Cu alloys are known as Guinier-Preston (1) zones and ~~is~~ are abbriviated as G.P. (1) zones. Guinier (13) and Preston (14) reported the existence of zones for the first time. Later, different models were proposed to explain the structure of G.P.zones. Notable among these models, have been the ones propesed by Gerold (37,57) and Toman (58-60). Whereas Gerold's model assumes that a single disc of copper atoms constitutes the zone, Toman's model requires gradual fall in copper concentration on either side of the center layer of the zone. It is Gerold's model which is taken to be valid. Distribution of intensity in streaks of X-ray diffraction patterns of zones, calculated on the basis of Gerold's model, is in good agreement with the observed intensity distribution. Also there are two major drawbacks in Toman's model. Use of this model results in prediction of intensity peaks in X-ray diffracted pattern, which is not experimentally observed. Secondly, Toman's model requires loss of coherency of the lattice near the centre of zones, which is an untenable proposition.

The next stage in ageing of Al-Cu alloys leads to formation of G.P. (2) zones. What was first described by Guinier (34) as θ'', was subsequently named as G.P. (2) zones by Silcock et al (36). However, the terminology θ'' is more appropriate (44) since the structure has specific lattice parameters whereas zones are regions in a matrix where the solute concentration is much higher than the average but which do not have lattice parameter different from the matrix. The only feature, that is common between the zones and θ'' phase, is maintenance of complete coherency with respect to matrix. The orientation relationship between θ'' and matrix is that $\{100\}$ planes of θ'' are parallel to $\{100\}$ planes of the matrix. The structure of θ'' is tetragonal with a = 4.04 Å and C = 7.8 Å .

The precipitate is disc shaped with a diameter of 1500 Å and maximum thickness of 100 Å .

The precipitate with partial-coherency that appears in Al-Cu system is θ'. To start with the particles of θ' maintain high degree of coherency with the matrix but start losing coherency with growth. The structure of θ' is also tetragonal (a= 4.04 Å and c = 5.8 Å) and bears the same orientation relationships with the matrix as θ''.

When over-ageing sets in, equilibrium precipitate θ ($CuAl_2$) is formed. It has a tetragonal structure with a= 6.06 Å and c = 4.87 Å .

Hence, to conclude, the ageing sequence in Al-Cu system can be represented as :

Supersaturated solid solution → G.P. (1) zones → θ'' precipitate (fully coherent) → θ' precipitate (partially coherent) → θ precipitate (non-coherent) .

The actual number of stages encountered, in a particular alloy of Al-Cu, during ageing, depends on composition of the alloy and temperature of ageing. With decrease in solute concentration and increase in ageing temperature, the earlier steps are skipped-over and fewer stages are required to arrive at equilibrium precipitate, θ .

1.3 Al-Mg SYSTEM

A number of workers (61-63) have studied the age-hardening characteristics of Al-Mg alloys. Since nucleation of non-equilibrium precipitate is a difficult process in Al-Mg alloys and precipitation takes place heterogeneously at preferential sites, especially at grain boundaries (64-67), the precipitate is coarse as a result of which the age hardening characteristics are very poor. There has also been a great deal of work in connection with determination of the structures (61,63,68-71) of the non-equilibrium and equilibrium precipitates in Al-Mg alloys. The study of structures by X-ray diffraction has been rendered difficult in this system due to closeness of atomic scattering factors of Aluminium and Magnesium. An attempt to study the pre-precipitation and zone formation stages with help of resistivity measurements has been made by Panseri and Federight (72). Relevant electron micrographs have been obtained by Saulnier and Mirand (73).

In the light of the observations made by these workers, the following conclusions can be arrived at. Although the resistivity measurements by Panseri and Federighi (72) suggest that there is clustering and zone formation there is no electron micrographic evidence to prove the existance of zones. Geisler et/al (68) have suggested the existance of zones on the basis of streaks observed on their X-ray diffraction pattern. However, Kelly and Nicholson (74) have urged that the appearance of streaks, reported by Geisler et/al (~~86~~ 68), is noticeable only at a fairly advanced stage of precipitation when the presence of non-equilibrium phase can be observed even under a microscope. Hence these streaks can be attributed to structural discontinuities within the precipitate rather than the zones. On the other hand, a recent paper by Von Torne (~~75~~ 169) has developed a theoretical basis for clustering in Al-Mg based on their electronic structures.

The non-equilibrium precipitation in Al-Mg alloys, termed as β', is responsible for hardening of the alloys. Initially, β' precipitates out at grain boundaries. During this period there is practically no change in hardness. However, when the precipitation proceeds well within the grains, hardening sets in.

Equilibrium precipitate in Al-Mg system is termed as and has the chemical formula Mg_3Al_2.

Hence, to summarise, the age-hardening sequence in Al-Mg systems may be represented as :

$$\text{Supersaturated solid solution} \rightarrow \beta' - \beta\ (Mg_3Al_2)$$

1.4 Al-Cu-Mg SYSTEM

One of the most important series of precipitation hardening alloys of commercial importance, namely the Duralumintype, is based on Al-Cu-Mg system. The credit of carrying out most systematic work on the ageing characteristics of these ternary alloys goes to Hardy (75). He investigated two series of alloys, one containing equi-atomic ratio of copper and Magnesium and the other containing excess of Copper (Cu:Mg= 7:1 by weight ratio). Hardening characteristics were studied over a wide range of temperatures from 30 to 230°C. The structural changes, that accompany the process of ageing in these alloys, were studied in detail by Silcock (76). It was observed that in alloys containing equi-atomic ratio of Copper and Magnesium, distinct type of zones appear and they are different from those appearing in binary Al-Cu alloys. These zones which contain both Copper and Magnesium atoms, are termed as G.P.B. zones to distinguish them from G.P. zones. The non-equilibrium precipitate, which appears in the subsequent stage of ageing, is termed (77) as S'. The structure of S' could not be well defined either by Silcock (76) or any one of the earlier workers. The equilibrium structure in the alloy (containing equi-atomic ratio of Copper and Magnesium) is S (Al_2CuMg). S phase is orthorhombic (78) with a=4.00 Å, b=9.23 Å and c=7.14 Å. Those alloys in which Copper to Magnesium ratio is higher than the equi-atomic, the process of ageing proceeds with simultaneous appearance of phases connected with Al-Cu and the ones mentioned i.e. G.P. (1), θ'', θ' and θ on the one hand and G.P.B., S' and S on the other hand.

Weatherly (79) is of the opinion that there is no distinct phase like S'. Difference between S' and S lies only in morphology. Whereas S' constitutes lath precipitates, S is massive in nature and is formed by prolonged ageing at higher temperatures. Both terminologies (S' as well as lath-precipitate S) are in vogue at present to denote the early stage of precipitate that is formed in the systems (80-82).

1.5 ROLE OF VACANCIES ON PRECIPITATION HARDENING

The role played by vacancies during the ageing process is very significant. The structure that is produced by quenching from the temperature of solution treatment is essentially a defective one and contains excessively large number of trapped vacancies (10,56,83). Existance of excess vacancies is precisely the cause behind observed high diffusion rates of solute atoms, determined on the basis of initial rate of clustering (55). The study made by De Sorbo et al (10) on the effect of step-quenching, reversion and cold work on initial rate of clustering also confirms the significant role played by vacancies during pre-precipitation stage. The observation made by different workers that trace additions of solute atoms, capable of forming strong pairs with vacancies, reduce the initial rate of clustering and zone formation can be explained in terms of reduced mobility of vacancies (84-87).

As a natural consequence of instability of trapped thermal vacancies at elevated temperatures, it is to be expected that vacancies cannot play any significant role on precipitation of intermediate precipitate which is a product of ageing at comparatively high temperatures. However, vacancies can alter the kinetics of precipitation of non-equilibrium phases under certain conditions, namely;

(i) When the vacancies get stabilized due to formation of strong pairs with solute atoms (88).

(ii) When the concentration of unassociated vacancies is large enough so that collapse of such group of vacancies can result in formation of secondary defects likes dislocation loops (89-91) and voids (92,93).

In the former case annihilation of vacancies is slow and spread over time. Thus the diffusion rate, during precipitation of intermediate phase, gets controlled by concentration of quenched-in vacancies. In the latter case, the secondary defects, that are formed, are relatively very stable and act as potential sites for precipitation. Hence quenched-in vacancies which form secondary defects, alter nucleation rate of the intermediate phase.

1.6 ROLE OF DISLOCATIONS ON PRECIPITATION HARDENING

The role played by dislocations on different stages of precipitation hardening can be studied by observing the effect of prior plastic deformation on ageing.

Generally speaking, there is no direct effect of dislocations on zone formation. However, there is very strong indirect effect because dislocations are effective sinks for vacancies (94,95). Hence creation of dislocations suppresses zone formation. On the contrary, the role of dislocations on the kinetics of zone formation in dilute alloys and the alloys which have been step-quenched is to accelerate the kinetics of zone formation.

Dislocations have a distinct role to play in precipitation of non-equilibrium phase due to creation of potential sites for precipitation (40,50,96). Hence the rate of nucleation is accelerated as a result of presence of dislocations. The accelerating effect is modified as a result of trapping of solute atoms around the dislocations due to formation of atmospheres and consequent reduction in mobility of the solute atoms.

1.7 PRESENT STUDY

The experimental investigations presented in this thesis, were undertaken to study the effect of (a) quenched-in vacancies, (b) Lattice distortions and (c) Dislocations on the ageing characteristics of certain binary and ternary aluminium base precipitation hardening alloys.

Quenched-in vacancies in different concentrations were introducedby varying the quenching media. The alloys that were studied consisted of a binary Al-Cu and ternary Al-Cu-Mg alloys with a constant copper content (same as that in binary) and variable magnesium content. The purpose of the study was to compare the'Quench-sensitivity' of the binary with ternary alloys, because the binary alloy contains solute atoms (Copper) that form moderately strong bonds with vacancies and the ternary alloys contain solute atoms (Magnesium) that have very high binding energy with vacancies. Quenched-in vacancies were estimated by resistivity measurements. 'Quench-sensitivity' was evaluated in terms of time to reach peak-hardness, determined from age-hardening curves.

Lattice distortions were produced in the matrix of some Al-Cu and Al-Mg precipitation hardening alloys by quenching. The lattice strains so produced were measured in terms of X-ray line width. It was found that relief of lattice strain during the initial stages of ageing at elevated temperatures led to softening. Extent of initial softening was evaluated as a function of solute concentration, temperature of ageing and severity of quench.

Dislocations were introduced by cold working prior to ageing and the effect of dislocations on the process of precipitation was evaluated in Al-Cu system. Effect of dislocations on two steps namely, precipitation of θ' from α -solid solution and transformation of θ' to θ, was studied at different degrees of supersaturation (determined by solute concentration and temperature of ageing). Precipitation was followed up with hardness measurements, resistivity measurements and integrated X-ray line intensity measurements. For the purpose of comparison, additional work was also carried out on Al-Mg alloys.

Studies on Portevin-Le Chatelier phenomenon was also carried out on Al-Cu and Al-Mg alloys. Activation energies of formation and migration of vacancies were evaluated. These activation energies play a very significant role in kinetics of precipitation since they control the concentration of quenched-in vacancies (which ~~is~~ are related to activation energy of formation of vacancies) and stability of the trapped vacancies during ageing (which is related to binding energy between vacancies and solute atoms).

CHAPTER-II

EFFECT OF RATE OF QUENCHING ON THE AGEING CHARACTERISTICS OF SOME TERNARY Al-Cu-Mg ALLOYS

2.1 INTRODUCTION

For a large number of age hardening systems, it has been established that vacancies act as potential sites for precipitation of zones and do not play any significant role in precipitation of intermediate precipitate (97). Hence, rate of quenching (from the temperature of solution treatment) which controls the concentration of trapped thermal vacancies should not have any noticeable effect on the time to reach peak hardness that is associated with the intermediate precipitate.

Silcock (36) has studied the effect of quenching medium on ageing process of Al-4% Cu alloy at 130°C and 190°C and has reported that oil or acetone quenching retards the ageing process as compared with water quenching. Silcock (76), while comparing the ageing behaviour of acetone-and water-quenched single crystals of Al-3.15% Cu-1.52% Mg aged at 190°C, has reported higher peak hardness with acetone-quench.

The present work was undertaken to make a systematic study of the effect of rate of quenching on the ageing characteristics of some ternary Al-Cu-Mg alloys with Magnesium content varying from 0.5 to 1.5 weight percent and aged at various ageing temperatures in the range 130 to 190°C. Comparative study was also made on a binary Aluminium-Copper alloy.

The purpose of these studies was to find out whether it is true that rate of quenching should neither be very fast nor very slow for attaining maximum peak-hardness for various Al-Cu-Mg alloys aged at different temperatures. In other words existence of optimized rate of quenching for attainment of maximum'peak-hardness' was investigated.

Systematic analysis of 'Quench-sensitivity' was carried out. 'Quench-sensitivity' which can be expressed as a ratio of 'time to reach peak-hardness' under two different rates of quenching, was studied as a function of Magnesium content and ageing temperature of the ternary alloys.

2.2 EXPERIMENTAL PROCEDURE

2.2.1 Preparation of Alloys

Binary Al-Cu and ternary Al-Cu-Mg alloys were prepared from Aluminium (99.9% pure), Copper (99.92% pure) and Magnesium (99.35% pure). All melting was carried out in graphite crucibles placed in electrical resistance furnaces. Master alloy of suitable composition was prepared as a first step to fecilitate addition of Copper to Aluminium. Required quantity of Magnesium wrapped in Aluminium foil was added to the melt. Loss of Magnesium in the form of oxide was substantially reduced by keeping the metal dipped in the molten binary alloy till all of it got melted. The alloys were chill-cast in mild steel moulds. Hexachloroethane was used as degassent.

The cast alloys were forged and then annealed at 350°C for three days to ensure removal of microinhomogeneity and cast structure. Annealing was followed by machining out disc shaped specimens 20mm dia. X 8mm thick. On one side of the specimens, numbers were punched for identification and the other side was polished up to 1/0 emery paper so that subsequente to heat treatment one could simply polish on 2/0 emery paper to take hardness values, thus reducing the handling of heat-treated specimens to the minimum.

One set of annealed rods ~~were~~ was rolled and drawn into wires for resistivity studies.

The ternary alloys that were cast had the nominal compositions as shown in Table 2.1.

Table 2.1 Compositions of ternary Al-Cu-Mg alloys.

Alloy No.	Weight Percent		
	Cu	Mg	Al
1	3.5	0.5	Rest
2	3.5	1.0	Rest
3	3.2	1.5	Rest

The binary alloy that was cast had the nominal composition of Al-3.5 weight % Cu.

In all these alloys, the actual composition varied from the nominal withingthe limits of 0.05%.

The composition of the ternary alloys were so chosen that alloys 1 and 2 ~~lie~~ lay in a three phase region whereas alloy 3 ~~lies~~ lay in a two phase region (98-100). Alloys 1 and 2, when slowly cooled will precipitate out θ (Al_2 Cu) and S (Al_2CuMg) from the primary solid solution. Alloy 3 on the other hand behaves as quasi-binary system precipitating out only the S (Al_2CuMg) phase. Theoretically, the quasi-binary system should have equi-atomic ratio of Copper & Magnesium which works out to be a weight ratio of 2.61:1. However, it has been observed that to supress the precipitation of θ from the ternary solid solution during normally encountered rates of cooling, it is necessary to add excess of Magnesium and it has been estimated that the required weight ratio of Copper:Magnesium should be 2.2:1 if the system is to behave as quasi-binary.

2.2.2 Heat Treatment

Initial solution treatment was carried out for at least 48 hours at 520°C for the binary Al-Cu alloys and at 505°C for the ternary Al-Cu-Mg alloys. The solution-treated specimens were quenched in (1) water at (20 ± 1)°C or (2) oil at (20 ± 1)°C. For carrying out quench ageing, the specimens after being solution-treated, were transferred directly into an oil bath maintained at the temperature of ageing. In all cases microscopic examination of as quenched specimens revealed complete absence of second phase.

The solution treated, quenched specimens were aged at 130°C, 150°C, 170°C and 190°C. Within 5 minutes of quenching, the specimens were subjected to ageing treatment. It has been shown by previous workers that the heat treatment does not result in loss of either Copper (33) or Magnesium (75).

22.3 Hardness Measurement

Hardness values were determined on Vickers Hardness tester with 5kg load. Two specimens were taken out at the end of each ageing period and 3 hardness values were determined on each specimen. Average of a set of 6 readings was taken for plotting each point on the ageing curves.

2.2.4 Resistivity Measurement

The purpose of resistivity measurements was to estimate the quenched-in vacancy concentration in the binary and ternary alloys at different rates. After giving the initial annealing and solution-treatment for prolonged periods, final solution-treatment was carried out for 2 Hrs. at appropriate temperature. The wire specimens were wound on dummy hardness-specimens and then solution-treated. This procedure was adopted to ensure that the vacancy concentration produced in the wire specimen and the hardness specimen was same under similar conditions of quenching. Resistivity measurement was also carried out on a set of wire specimens which were air-cooled after homogenization . The hardness values of air-cooled specimens and the corresponding as-quenched specimens were nearly the same. Also, microscopic examination of air-cooled specimens revealed complete absence of second phase. These two observations establish the fact that in the air-cooled specimens all the solute atoms are in solid solution and neither the zones nor the intermediate phases have precipitated during air-cooling. All resistivity measurements were carried out at 0°C with help of Bajaj Vernier potentiometer (VP-1 type).

2.3 RESULTS

2.3.1 Hardness Measurements

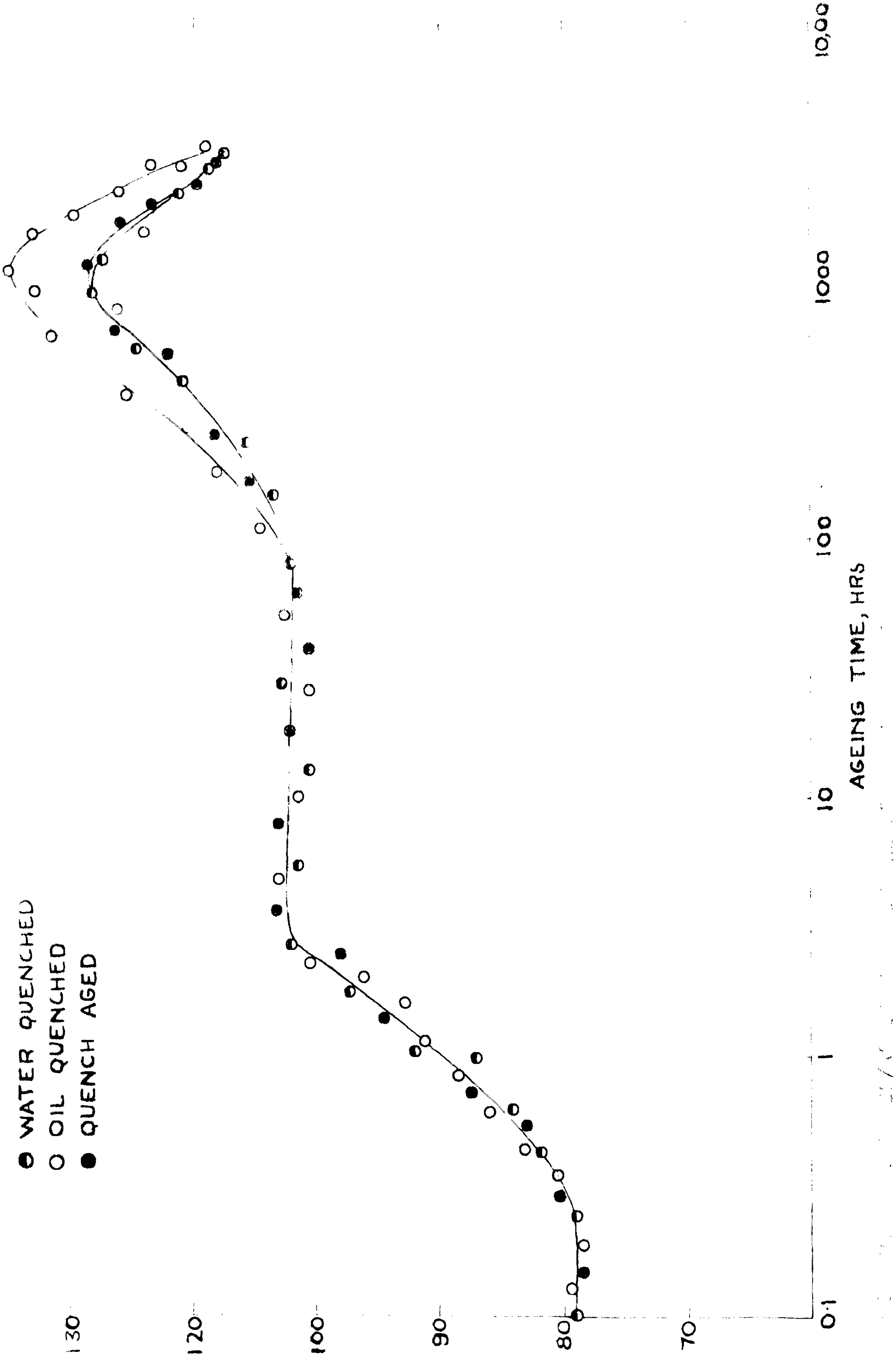
As quenched hardness values are given in Table 2.2

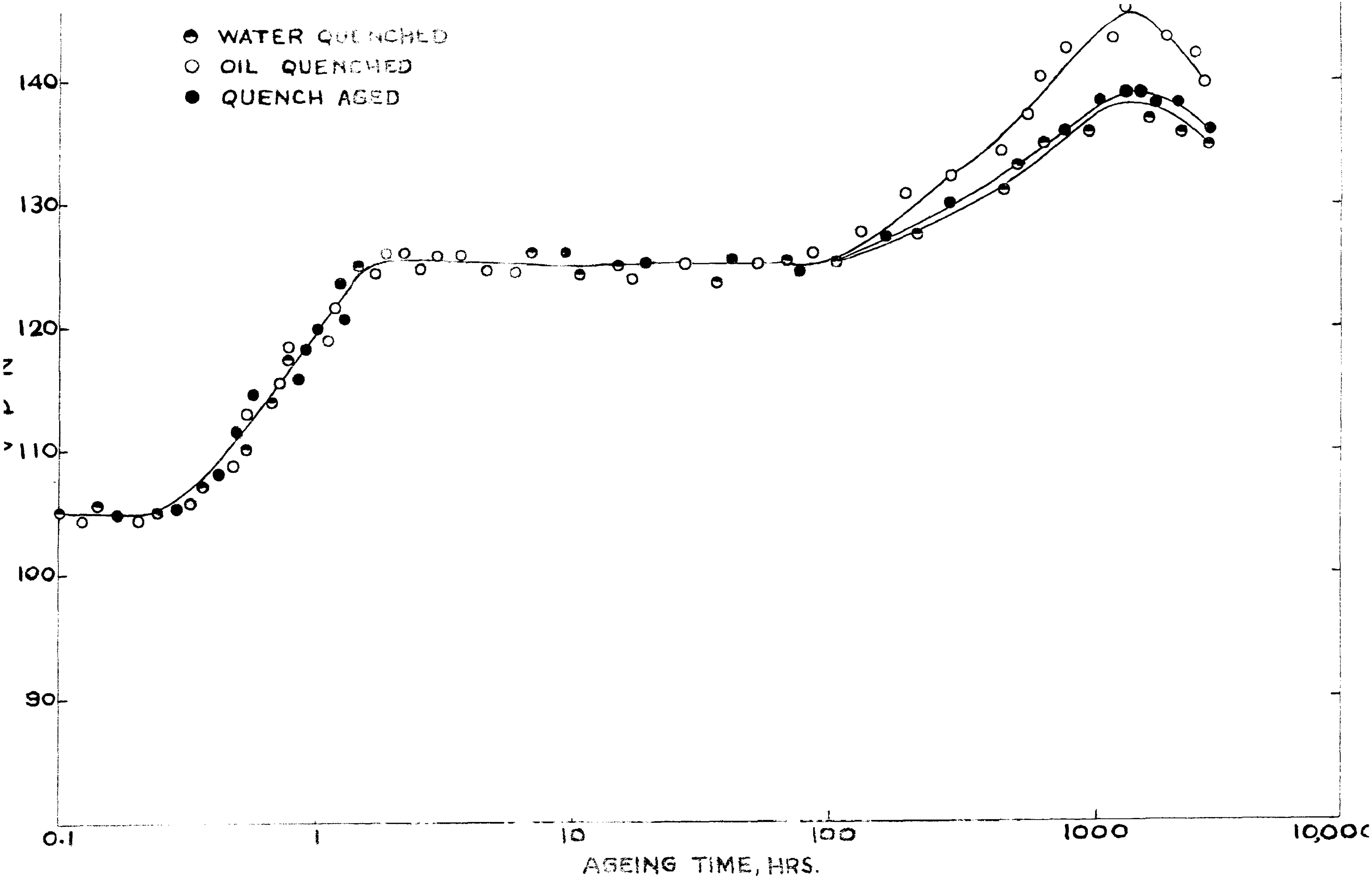
Table 2.2: Hardness values of alloys on quenching in water at 20°C after solution treatment

Alloy	Hardness (VPN)
Al-3.5% Cu(binary)	51
Alloy 1	63
Alloy 2	68
Alloy 3	72

The hardness values of specimens quenched in oil at 20°C and oil at appropriate ageing temperatures were slightly lower (by 2 to 3 VPN) than the values given in Table 2.2.

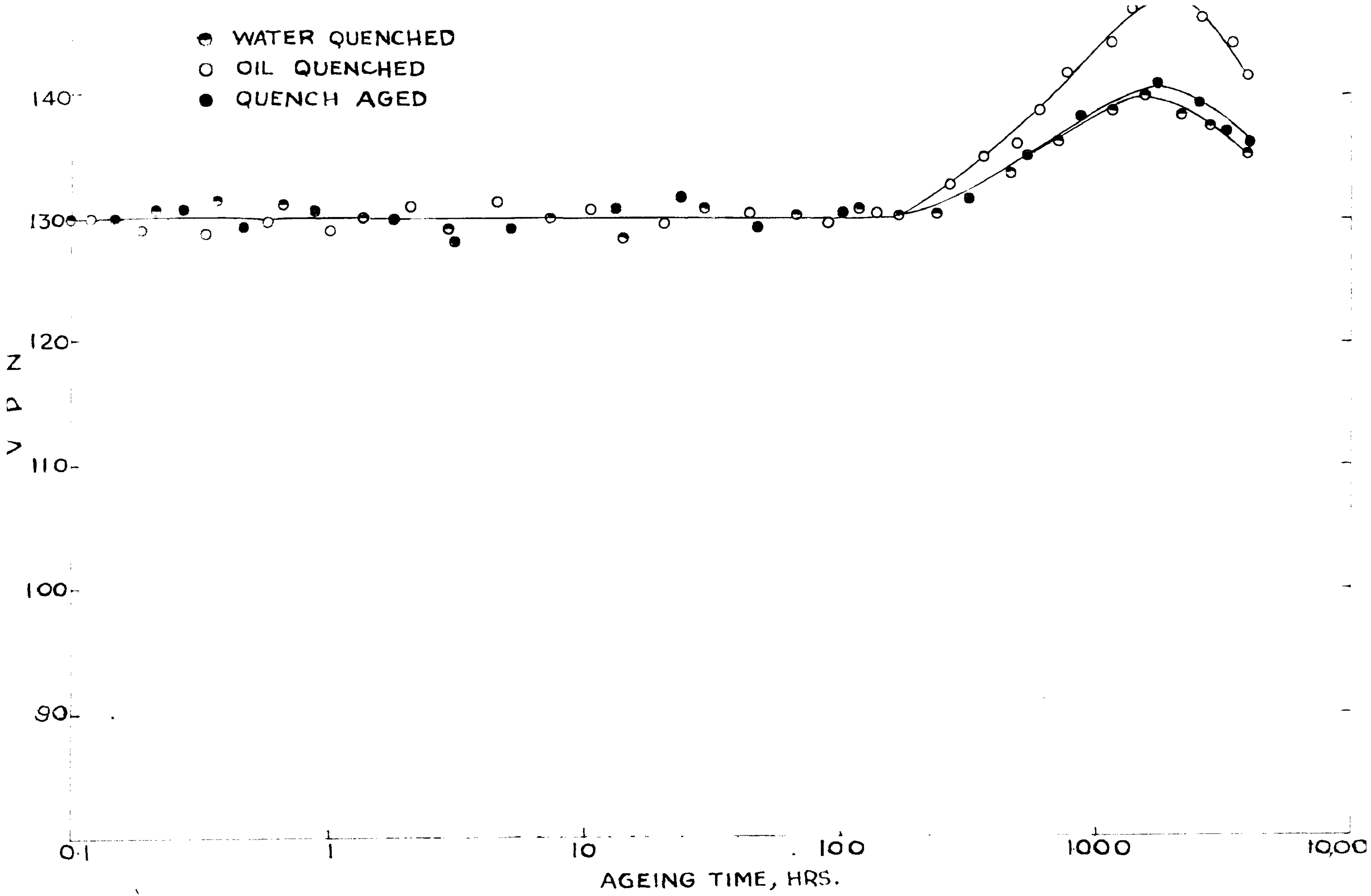
Figures 2.1 to 2.12 are the ageing curves for the ternary alloys. It was observed that alloys 1 and 2 showed three stage hardening curve at 130°C. Rest of the ageing curves were two stage ones. Stages of hardening have been determined by number


◐ WATER QUENCHED
○ OIL QUENCHED
● QUENCH AGED
130
120
100
90
80
70
0·1
1
10
100
1000
10,00
AGEING TIME, HRS

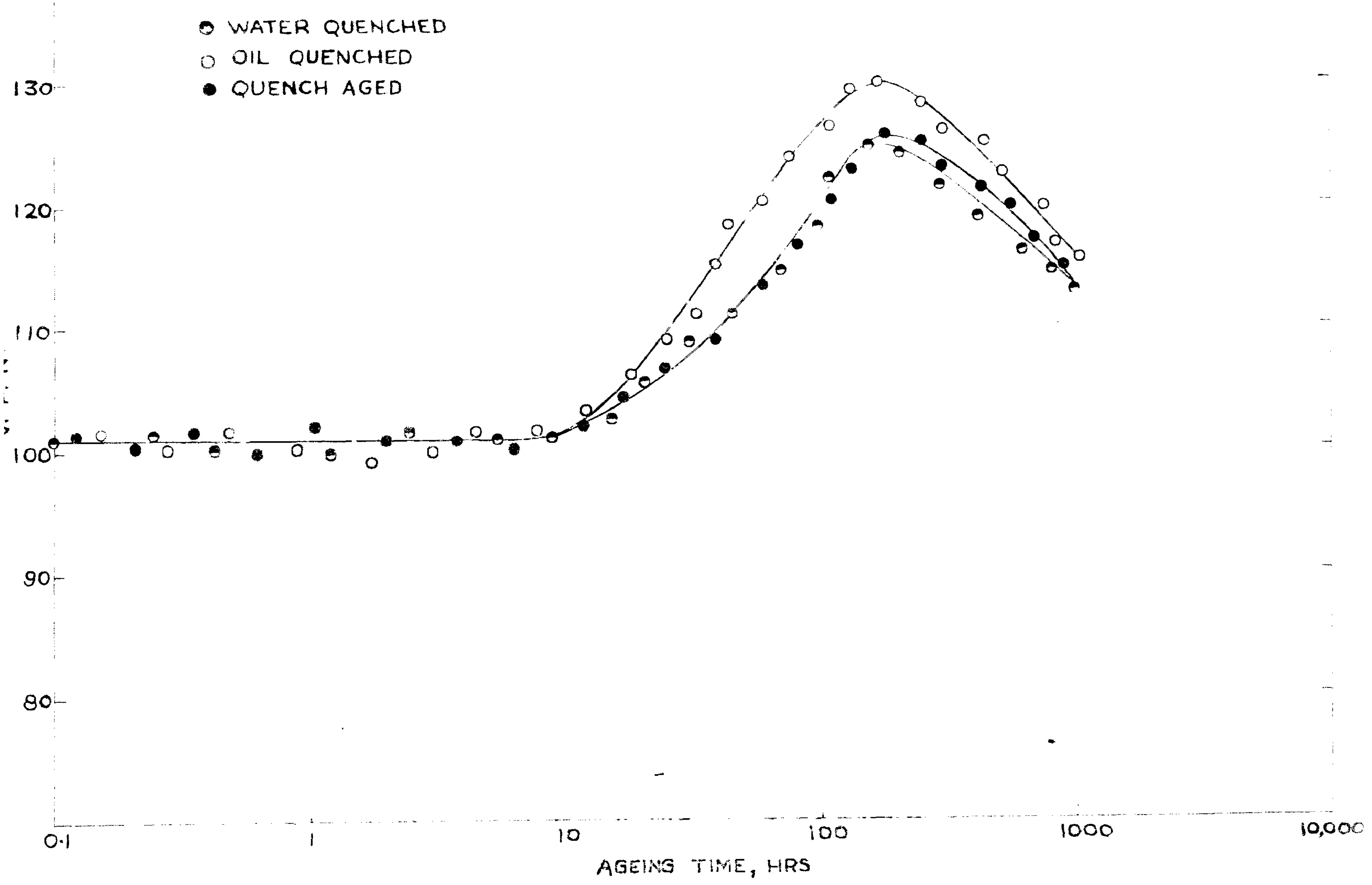


WATER QUENCHED
OIL QUENCHED
QUENCH AGED
V P N
140
130
120
110
100
90
0.1
1
10
100
1000
10,000
AGEING TIME, HRS.

[illegible]



[illegible] AT 130°C FOR ALLOY [illegible]


WATER QUENCHED
OIL QUENCHED
QUENCH AGED
130
120
110
100
90
80
0·1
1
10
100
1000
10,000
AGEING TIME, HRS

[illegible]

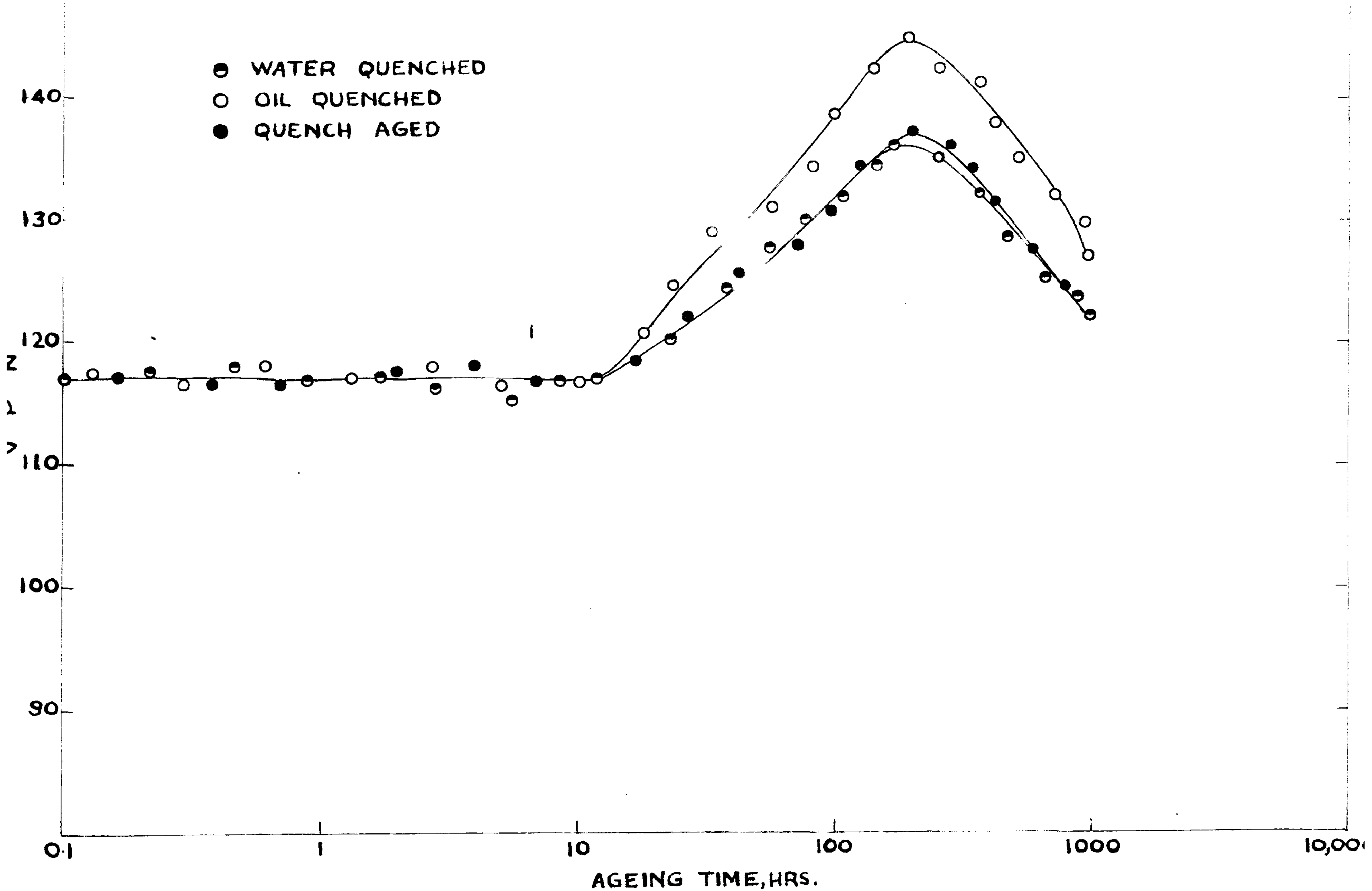


FIG. 2.5 HARDNESS/AGEING TIME CURVES AT 150°C FOR ALLOY 2.

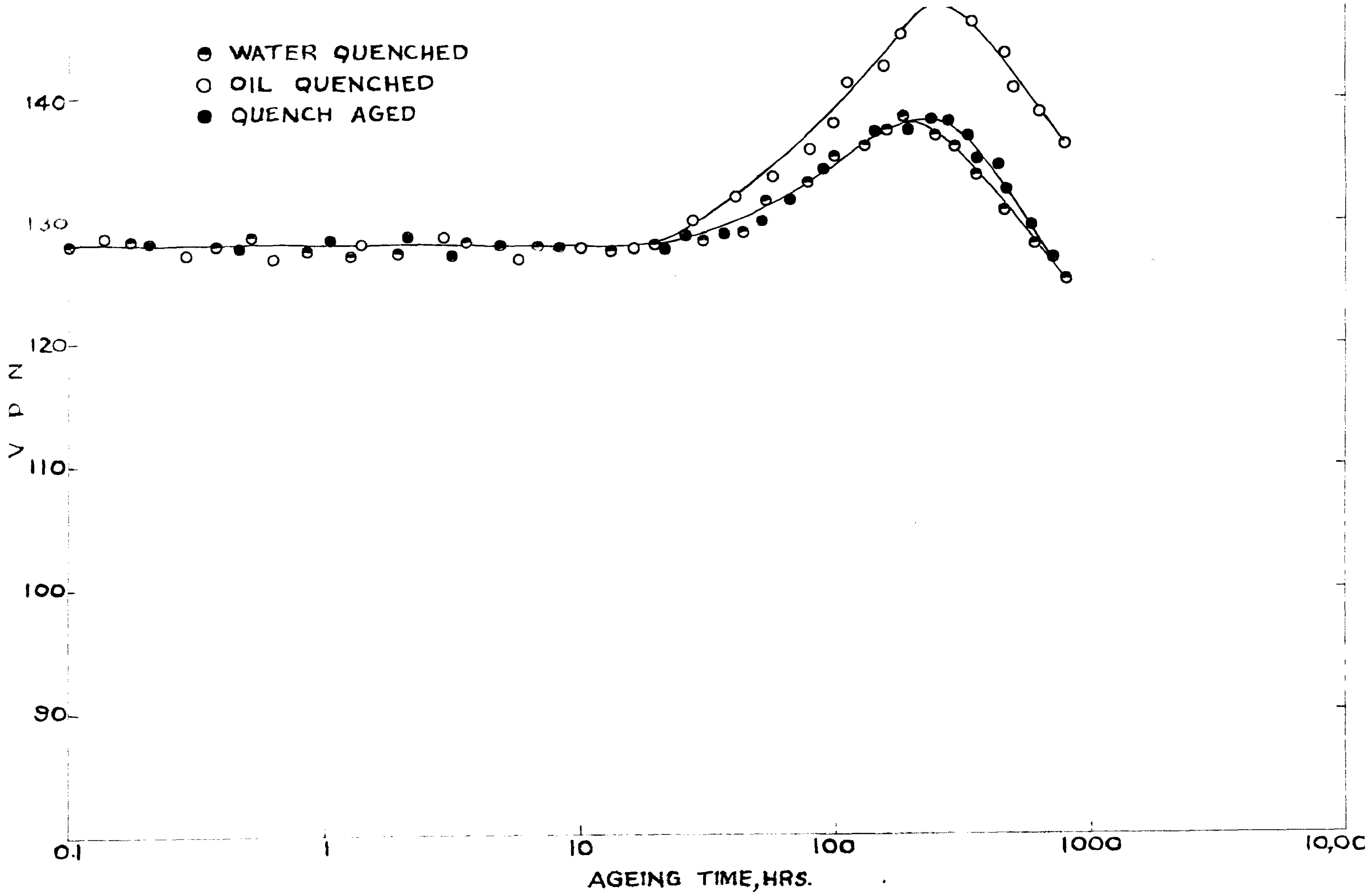


FIG. 3.6 HAR [illegible] TIME CURVES AT 150°C FOR ALLOY 3

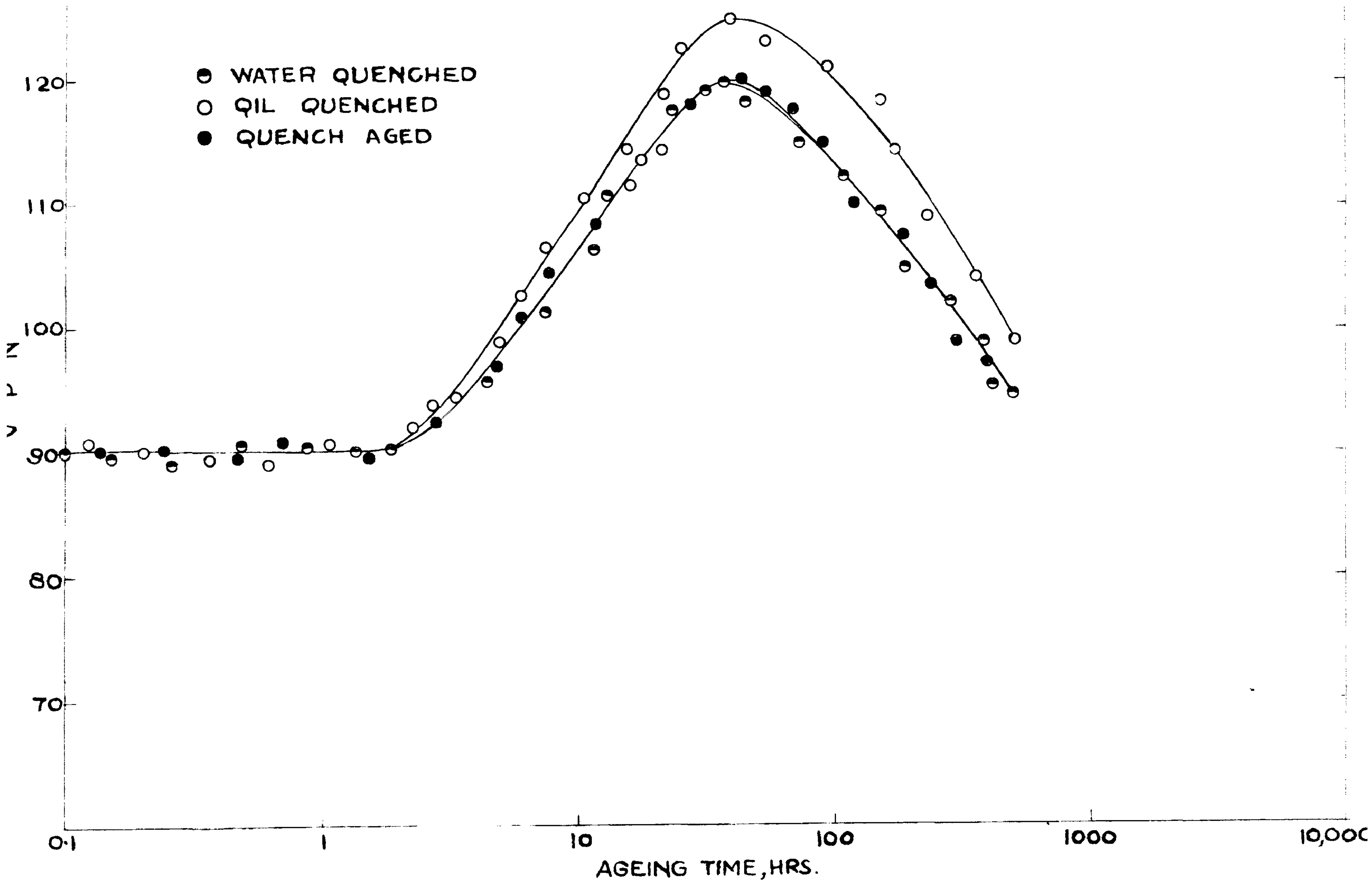
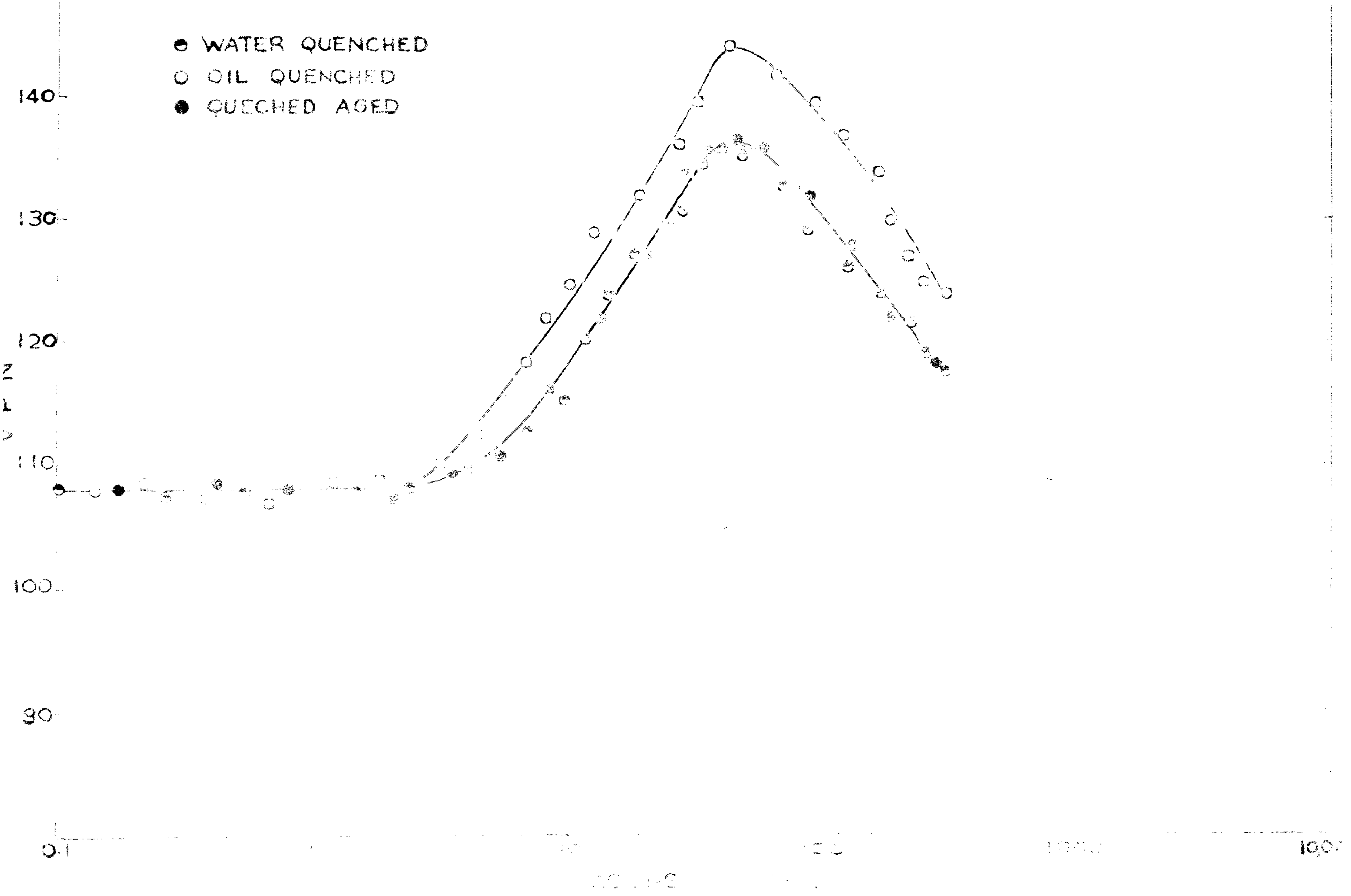
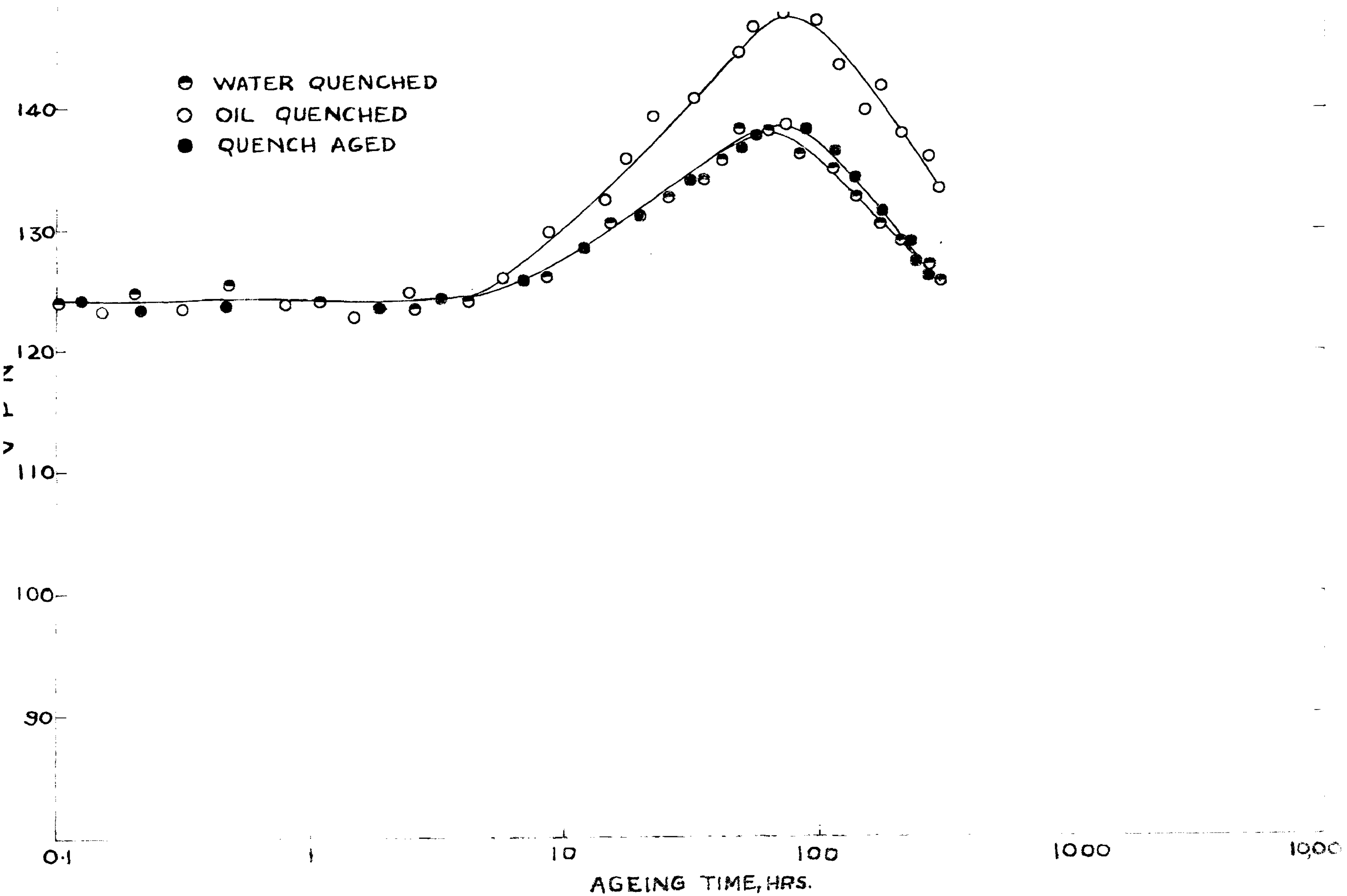
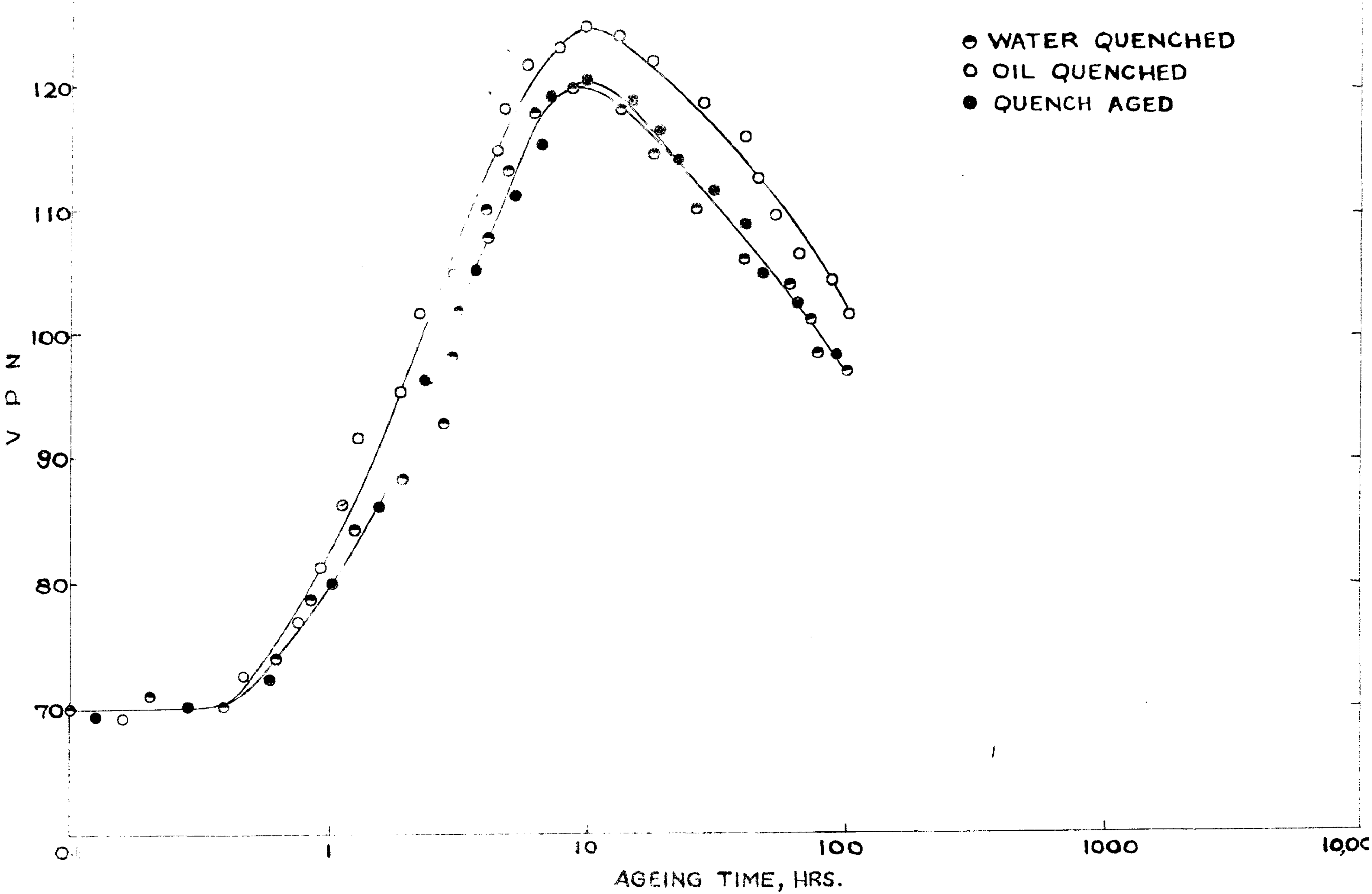


FIG. [illegible].7 HARDNESS/AGEING TIME CURVE AT 170°C FOR ALLOY 1


WATER QUENCHED
OIL QUENCHED
QUECHED AGED
140
130
120
110
100
90
VPN
0.1



[illegible] 170°C FOR ALLOY 3



G.10 HARDNESS/AGEING TIME CURVES AT 100°C FOR ALLOY 1.

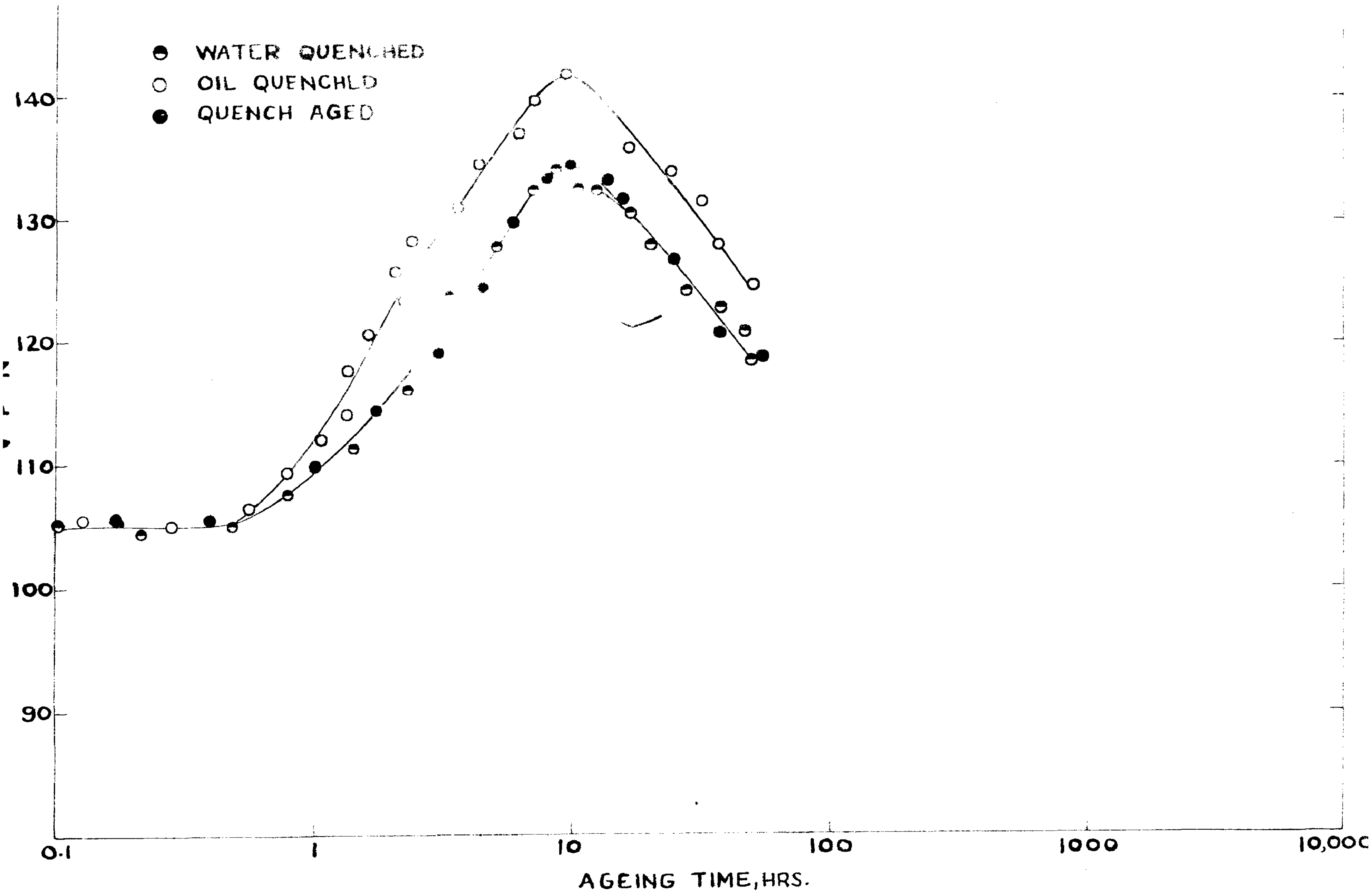


FIG.2.11 HARDNESS/AGEING TIME CURVES AT 190°C FOR ALLOY 2.

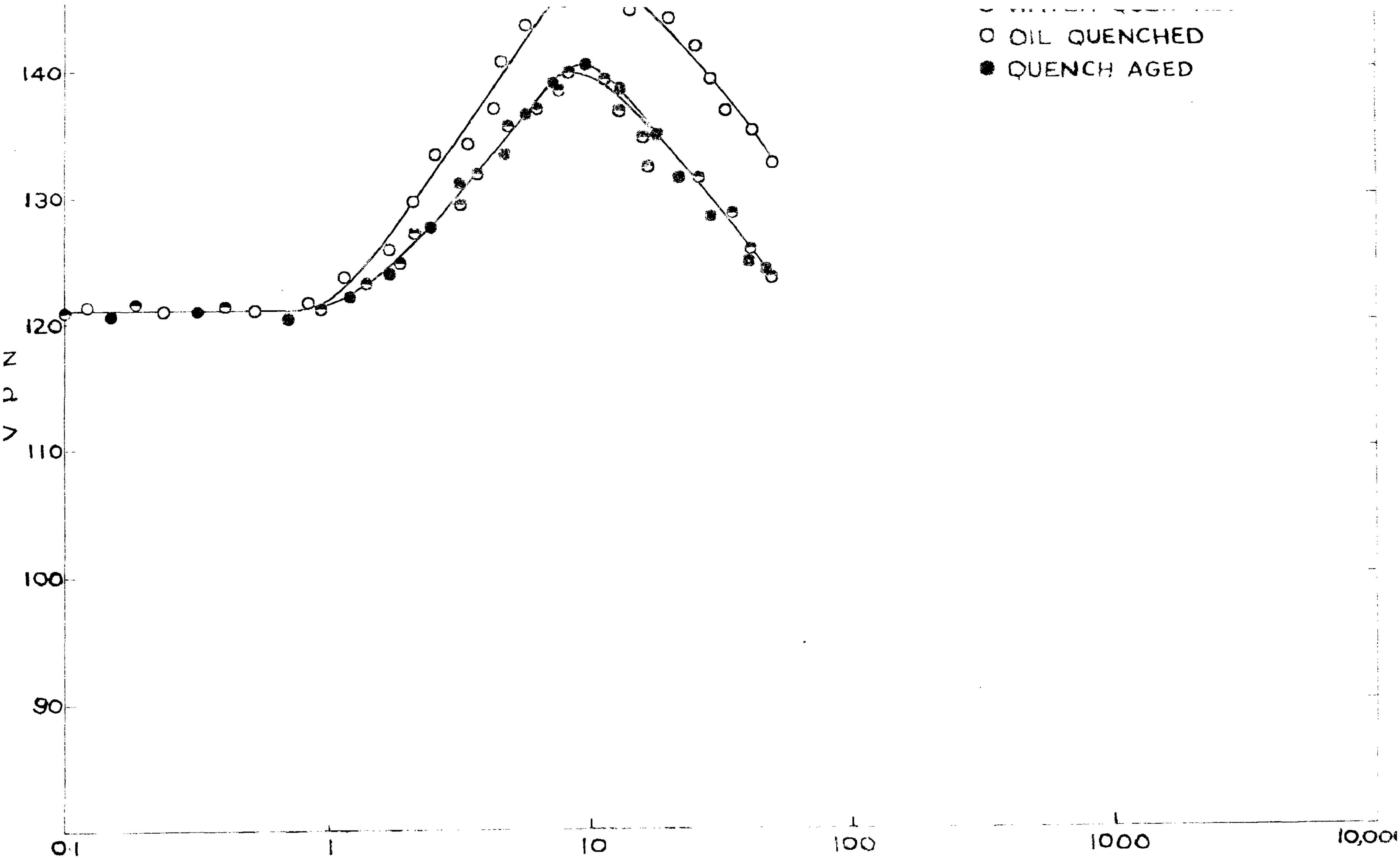
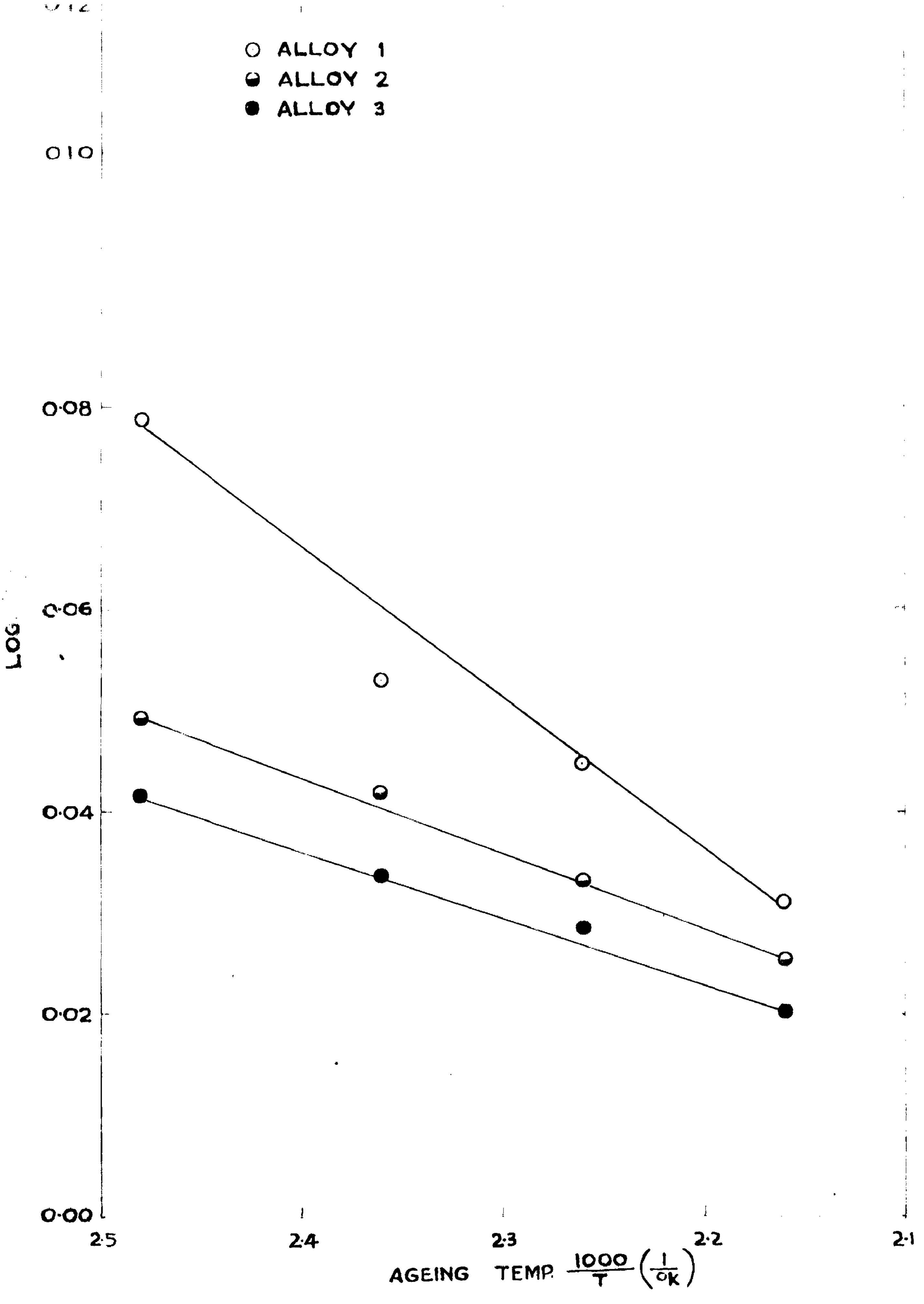


FIG. 12 HARDNESS/A[illegible] [illegible] AT 100°C [illegible]

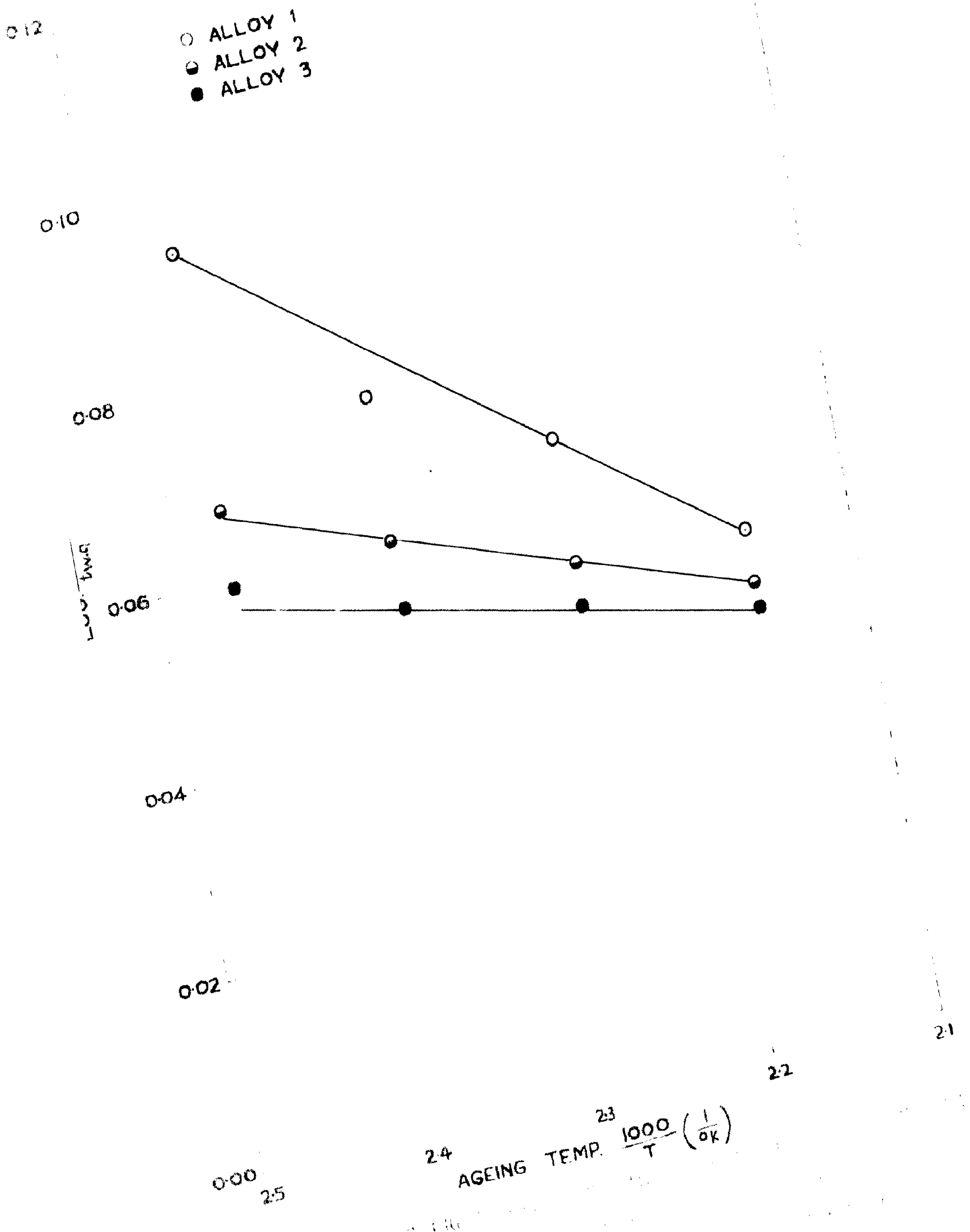
of plateaux observed. An ageing curve with a single plateau is the one that ages in two stages. Three stage ageing curve on the other hand consists of two plateaux. The first rise namely from the quenched hardness to the 'flat' hardness of the plateaux was observed to be extremely rapid, the time required being less than 3 minutes. The flat hardness might have been achieved during the process of heating to ageing temperature from room temperature. It may also be observed that 'flat' hardness value remains unaltered when rate of quenching is changed.

It may be noted from Figure 2.1 to 2.12 that, for a given alloy, at a particular ageing temperature the time taken to attain peak-hardness is minimum for water-quenching and maximum for quench-ageing and intermediate for oil-quenching. It can also be observed from these figures that the value of peak-hardness is higher in case of oil quenched specimens as compared with the water-quenched and quench-aged specimens. The latter two rates of quenching more or less result in the same value of peak-hardness.

Figures 2.13 and 2.14 have been drawn to bring out clearly the difference in the time required for reaching the peak-hardness value with different compositions and rates of quenching. It may be observed from Figures 2.13 and 2.14 that the lower the Magnesium content in a given alloy and the lower the temperature of ageing, greater is the "Quench sensitivity".



.13 [illegible] TO REACH PEAK-HARDNESS [illegible] AGEING TEMPERATURES.
[illegible] TO REACH PEAK-HARDNESS WITH OIL QUENCHING.
[illegible] TO REACH PEAK-HARDNESS [illegible] WATER QUENCHING.


○ ALLOY 1
◒ ALLOY 2
● ALLOY 3
0·12
0·10
0·08
0·06
0·04
0·02
0·00
LOG. tM.D
2·5
2·4
2·3
2·2
2·1
AGEING TEMP. 1000/T (1/°K)

In contrast to the above results, the binary Aluminium-Copper alloys showed little effect of rate of quenching on 'time to reach peak-hardness' and the peak-hardness value. There was only a marginal retardation in the process of ageing when water-quenching was replaced by oil-quenching or quench-ageing. There was no noticeable change in the peak hardness value due to change in quenching rate. Thonson (101) has reported similar observations on Aluminium-4.25 weight percent copper alloy aged at 150°C. Silcock (84) has also observed retardation in formation of θ' on acetone-quenching as compared with water quenching on ageing Al-4% Cu alloy at 190°C.

2.3.2 Resistivity Measurements

Table 2.3 summerizes the results obtained with resistivity measurements. Resistivities of quenched samples are compared with the corresponding resistivities of the air-cooled specimens. Air-cooled specimens are identical to quenched specimens in all respects except with respect to vacancy concentration. The air-cooled specimens have a vacancy concentration which is equal to or slightly higher than the equilibrium value at room temperature (84). This is because of slow rate of cooling which allows annealing out of excess vacancies during the process of cooling. The equilibrium vacancy concentration at room temperature is smaller than the quenched-in vacancies by many orders. Hence the excess resistivity of a quenched specimen over the corresponding air-cooled specimen is a measure of the quenched-in vacancies.

Different values have been reported by various workers (102-106) for the resistivity associated with vacancies. The reported values lie over a range from 1.0 x 10^{-6} ohm. cm/atomic percent to 1.8 x 10^{-6} ohm. cm/atomic percent of vacancies. In the present work, a value of 1.5 x 10^{-6} ohm. cm/atomic percent has been adopted in confirmity with Bradshaw and Pearson (107).

Table 2.3 Quenched-in vacancy concentration in binary and ternary alloys

Alloy	Type of quenching	$\Delta\rho$ ($\rho_{quenched}$- $\rho_{air-cooled}$ (micro ohm.cm)	Vacancy concentration
Al-3.5%Cu	Water-quenched	3.9 x 10^{-3}	2.6 x 10^{-5}
	Oil-quenched	3.5 x 10^{-3}	2.3 x 10^{-5}
	Quenched to 130°C	3.4 x 10^{-3}	2.3 x 10^{-5}
	Quenched to 150°C	3.5 x 10^{-3}	2.3 x 10^{-5}
	Quenched to 170°C	3.4 x 10^{-3}	2.3 x 10^{-5}
	Quenched to 190°C	3.3 x 10^{-3}	2.3 x 10^{-5}
Alloy 1	Water-quenched	3.023 x 10^{-1}	2.015 x 10^{-3}
	Oil-quenched	1.986 x 10^{-1}	1.324 x 10^{-3}
	Quenched to 130°C	8.02 x 10^{-2}	5.34 x 10^{-4}
	Quenched to 150°C	6.93 x 10^{-2}	4.62 x 10^{-4}
	Quenched to 170°C	5.83 x 10^{-2}	3.89 x 10^{-4}
	Quenched to 190°C	5.63 x 10^{-2}	3.73 x 10^{-4}

Table continued.

Alloy	Type of quenching	$\Delta\rho$ (ρquenched- ρair-cooled (micro ohm.cm)	Vacancy concentratio
Alloy 2	Water-quenched	3.257×10^{-1}	2.171×10^{-3}
	Oil-quenched	2.388×10^{-1}	1.592×10^{-3}
	Quenched to 130°C	8.32×10^{-2}	5.55×10^{-4}
	Quenched to 150°C	7.25×10^{-2}	4.83×10^{-4}
	Quenched to 170°C	6.07×10^{-2}	4.05×10^{-4}
	Quenched to 190°C	5.12×10^{-2}	3.41×10^{-4}
Alloy 3	Water-quenched	3.530×10^{-1}	2.373×10^{-3}
	Oil-quenched	2.507×10^{-1}	1.671×10^{-3}
	Quenched to 130°C	8.57×10^{-2}	5.71×10^{-4}
	Quenched to 150°C	7.36×10^{-2}	4.91×10^{-4}
	Quenched to 170°C	6.19×10^{-2}	4.13×10^{-4}
	Quenched to 190°C	4.81×10^{-2}	3.21×10^{-4}

From Table 2.3, it may be observed that;

(1) For all ternary alloys under study, the vacancy concentration produced as a result of water and oil-quenching is distinctly higher ($\sim 10^{-3}$) as compared with those produced by quenching to ageing temperature ($\sim 10^{-4}$). There is only a marginal change in vacancy concentration as a result of changing the temperature of quench-ageing.

(2) Binary alloy (Al-3.5% Cu) has quenched-in vacancy concentrations which are uniformely of the order of 10^{-5} . They are ~~It is~~ smaller than the corresponding values of the ternary alloys by one to two orders of magnitude. Also, the variations that are produced in the quenched-in vacancy concentration, due to changes in quenching rate, is very small for the binary alloy as compared with the ternary alloys.

(3) In case of the ternary alloys, the variation in quenched-in vacancy concentration, that is produced in a given alloy as a result of changes in quenching rate, is more pronounced as compared with the changes produced in vacancy concentration due to change in Magnesium content for a given rate of quenching.

2.4 DISCUSSION

2.4.1 Structural Ageing Characteristics

Silcock (76) has made an extensive study on the structures that appear at various stages of ageing of the ternary Aluminium-Copper-Magnesium alloys. In the range of ageing temperature under consideration, it has been shown that for the quasi-binary alloy, ageing proceeds with formation of (a) G.P.B. Zones, (B) Intermediate phase S and (c) Equilibrium precipitate S (Al_2CuMg). However, some workers are of the opinion that there, is no distinct phase like S' (79-82). It is further contended that S' and S differ from each other only in morphology.

On the other hand for those alloys which contain excess of copper than that required for the quasi-binary system (i.e. Copper:Magnesium greater than 2.2:1), ageing proceeds with simultaneous formation of zones and phases associated with binary Al-Cu system and quasi-binary Al-Cu-Mg system viz. G.P. (1), G.P. (2), θ' and θ and G.P.B. (2), S$'$ and S.

The essential difference in the structure of specimens quenched at various rates is with respect to the concentration of vacancies. In all the quenched specimens, there are excess number of vacancies than the one produced at the ageing temperature under equilibrium conditions. If the rate of quenching is extremely fast, then the concentration of retained thermal vacancies is the one that is produced at the temperature of solution treatment. For slower rates of quenching, the vacancy concentration will correspond to a temperature intermediate between that of solution treatment and ageing. Rate of quenching is fastest for water-quenching, intermediate for oil-quenching and slowest for quenching-ageing.

2.4.2 'Flat' Hardness

It is known that vacancies act as potential sites for formation of zones(97). Hence the rate of quenching to start with will affect the nucleation of zones. Also the diffusion rates, being influenced by vacancies, will vary with rate of quenching, and alter the rate of growth of zones. The combined effect of higher nucleation rate and higher growth rate should then be faster rate of zone formation with increasing severity of quench. In other words the initial rate of hardening should be a function of rate of quenching. Such effects have been reported by earlier workers (108). However, in the present work, the temperature of ageing was such that the initial raise in hardness was so rapid that differences in rates of hardening for various quenching rates could not be evaluated.

The fact that the 'flat' hardness is independent of rate of quenching can be explained as follows. The 'flat' hardness is due to the hardening effect of zones. Zones are those regions which are different from matrix only with respect to solute concentration and not the lattice. Thus zones are fully coherent with the matrix (109).

Since the zones are fully coherent with matrix, the elastic energy associated with individual zones increases with size (25,26). However, the total strain energy per unit volume of matrix (and hence the extent of hardening) will remain unaltered with change in the size of the zones provided the volume fraction of zones remains constant. It has been established that the volume of solute that migrates to form clusters and zones attains a constant value by the time the initial raise in hardness is completed and thereafter there is only further growth of some of the zones at the expense of others by a process of migration of clusters of solute atoms (110).

Thus the factor which decides the value of 'flat' hardness is the volume fraction of solute that gets migrated to zones- a quantity determined by metastable phase boundary (17,111-114) for the zones under consideration. Hence for a given alloy the 'flat' hardness value depends only on the ageing temperature and is independent of rate of quenching.

2.4.3 '<u>Time to Reach-Peak-Hardness</u>'

As pointed out earlier, in contrast to binary Al-Cu alloys, the rate of quenching plays a distinct role in altering the time required for attaining peak-hardness. In case of ternary Al-Cu-Mg alloys, vacancies play a definite role in precipitation of intermediate phase by accelerating the process.

The alloy that is quenched from the temperature of homogenization is essentially a defective one with respect to structure and contains excessively large number of vacancies as compared with the equilibrium number of vacancies at the temperature of ageing (10,56,83). Due to the process of homogenization at a temperature T_H, the concentration of vacancies that is produced is given by the equation (115)

$$C = \exp. (-u/k\ T_H) \text{------------------------------------} (2.1)$$

where C = vacancy concentration

u = Internal energy associated with a vacancy

k = Boltzmann constant

and T_H = Temperature of homogenization (in °k)

The above equation by Cottrell can be rewritten as suggested by Bradshaw and Pearson (107,106) as

$C = A \exp. (-E_f/k\,T_H)$ ----------------------------(2.2)

where A = Entropy factor

and E_f = Activation energy for vacancy formation

For different rates of quenching, the concentration of quenched-in vacancies is different due to the fact that the vacancies are annihilated continuously during the process of quenching. So, slower the rate of quenching, greater is the extent of annihilation during quenching. Or, for different rates of quenching there are different effective temperatures of homogenization. Hence,

$C = A \exp. (-E_f/k\,T'_H)$ ----------------------------(2.3)

where T'_H = Effective temperature of homogenization.

Equation (2.3) is the modified equation that is applicable to a set of alloys quenched at different rates. However, it has been well established that the quenched-in vacancies are not retained as single unassociated vacancies unless the concentration is very small (117). For all cases of high vacancy concentration (~~which is ture in all cases under consideration in this paper~~) there is formation of vacancy clusters. The vacancy clusters, so formed are unstable and tend to collapse into dislocation loops. The collapse of dises of aggregates of vacancies into dislocation loops ha~~ve~~s been observed in pure metals like Au (118-120)

Cu (121), Al (122-125) and Aluminium alloys (86,96,117,126-129). Several mechanisms have been proposed (89-91) to explain the collapse of discs of vacancies to form loops. Vacancy clusters are also known to form voids (92,93).

There is yet a second process by which a part of the quenched-in vacancies is consumed, namely absorption of vacancies by edge and screw dislocations. An edge dislocation absorbs vacancies by a process of climb, the detailed mechanism for which has been derived by Seitz. (94). Screw dislocations absorb vacancies and in this process, get converted to helical dislocations. Such helical dislocations have been observed in flourite crystals (13), Germanium (131) and Aluminium alloys (50,127,129,132,133) and the mechanism of the process has been developed by Cottrell(95).

In addition to two modes of consumption of quenched-in vacancies discussed above, another point to be taken into consideration is the existence of strong binding force between the vacancies and solute atoms leading to formation of solute atom-vacancy pairs. In the light of the fact that such strong interactions have been postulated and reported for Cu atom-vacancy pairs (94,110,129) and Mg atom-vacancy pairs (72,86,88,108,134) in the respective Aluminium base alloys, it is reasonable to expect that a considerable fraction of the vacancies will be in the associated form (i.e. in the form of pairs) in the alloys under consideration. Zones and clusters are also known to act as traps for vacancies (110,135-137). These trapped vacancies account for the "Slow reaction" observed during resistivity measurements made during the process of ageing (138).

Thus the trapped thermal vacancies in the as quenched alloys is essentially distributed in the following four conditions:

(i) Vacancies in unassociated form

(ii) Vacancies in the bound condition-those which have been trapped by solute atoms or zones/clusters.

(iii) Vacancies which have collapsed into prismatic dislocation loops and voids.

(iv) Vacancies which have migrated to existing dislocations.

The effect of vacancies distributed in one or more of the above conditions on precipitation of intermediate phase can be considered after the comparative vacancy concentration in the binary and ternary alloy is estimated.

The value of activation energy for formation of vacancies (E_f) in Al-Cu system can be taken to be (139) 0.76 eV. Different values of the binding energy between Magnesium atom and vacancy (E_b Mag-Vac) have been reported by various authors from 0.20 eV to 0.54 eV, the latest one being 0.36 eV. Taking the last value to be correct, E_f in Al-Cu-Mg alloy works out to 0.40 eV (0.76-0.36) on the basis of arguments put forward by Lomer (140).

As a result, as compared with binary Al-Cu alloy, the vacancy concentration in the ternary alloys will be higher by a factor of 7 (substituting the values of E_f for Al-Cu and Al-Cu-Mg in equation 2.3) under similar homogenization conditions. On the other hand the solute concentration (measured in terms of atomic concentration) increases by a factor of 1.4 only.

Hence the vacancy concentration at the homogenization temperature is increased by a much larger factor than the increase in concentration of the solute atoms. As a result the concentration of unassociated vacancies at the temperature of homogenization is higher in the ternary alloy as compared with binary alloys and this leads to higher "quench-sensitivity" of the ternary alloys as compared with the binary alloys, the relevant discussions for which follow.

The results reported by Thomas (129) that the Magnesium content required to suppress the formation of dislocation loops (which are generated by collapse of clusters of unassociated vacancies as discussed above) is higher as compared with copper in the respective binary alloys inspite of the fact that the Mg-vacancy binding is much stronger than Cu-vacancy pair (133), also supports the arguments put forward in the paragraph above.

The fact that the solute diffusion coefficient of Magnesium in Aluminium is higher thet of copper in Aluminium at a given homogenization temperature as reported by Mehl (141), Buckle (142) and Beerwald (143) also strongly supports the arguments extended above.

(i) Vacancies in the unassociated form at room temperature: The possibility of existence of such a group of vacancies is limited to binary alloy due to weak interaction between Cu-vacancy pair compared to Mg-vacancy pair. Panseri et/al (88) have observed that in Al-Mg alloys, 0.13 atomic % of Magnesium is sufficient to bind the free vacancies at room temperature. Hence for all practical purpose it can be assumed that the ternary alloy is ~~divided~~ devoid of unassociated vacancies. Even in the binary alloys, the unassociated vacancies ~~is~~ are not likely to affect the precipitation of intermediate phase since such vacancies are known to anneal out very fast and hence will get annihilated even before nucleation of θ' takes place. However, presence of unassociated vacancies and their subsequent annealing out process can lead to acceleration in formation of zones which are forerunners of intermediate phase. But taking into account the fact that 'time to reach peak-hardness' (associated with intermediate phase) is at least one to two orders higher than the time to attain platue (associated with zones), the contribution of unassociated vacancies should only be marginal towards the process of growth of θ'.

(ii) Vacancies that are bound to solute atoms or zones/clusters by pair formation: Such vacancies have considerably lower mobility and can hardly contribute to diffusion at room temperature. However, at elevated temperatures of ageing, the trapped vacancies get released and can then contribute to diffusion. The ease with which the pairs get broken depends on the value of E_b (solute atom-vacancy). The higher ~~is~~ the value of E_b, higher is the temperature and time required for release of the trapped vacancies and their subsequent annihilation. Thus it is reasonable to expect that in the ternary alloys (where Mg atom-vacancy pair exists) the trapped vacancies will require higher temperature for getting released and will be retained for a longer time at any given temperature of ageing as compared with the binary alloy (where comparatively weaker Cu atom-vacancy pair exists). Thus in the former case there is more probability for the liberated vacancies to be available for aiding the growth of intermediate phases (after nucleation has taken place) than the latter. Panseri et/al (88) have observed that the Mg atom-vacancy pairs are broken in the temperature range 80-120°C in Al-Mg alloys and the annealing out of such liberated vacancies takes place over a duration of 100 minutes.

(ii) <u>Vacancy clusters that have condensed to form dislocation loops and voids</u>: Conversion of a fraction of vacancies into dislocation loops and viods is of great significance while considering the precipitation of intermediate phases. These dislocation loops and voids are permanent defects which have little chance of annihilation during the initial stages of precipitation when nucleation of intermediate phase takes place. The loops also get stabilized due to locking by solute atmospheres (129). The imperfections (dislocation loops and viods) have been shown to be potential sites for precipitation (40,95,144-147). Thus we arrive at the conclusion that the vacancies which are present as single units (in the unassociated or associated form with solute atoms), can only marginally reduce the time to reach peak-hardness (associated with intermediate phase). But the same vacancies, when present as dislocation loops and viods, can substantially alter the nucleation rate of intermediate phase due to creation of potential sites.

These potential sites are created only if there are sufficient number of unassociated vacancies which, in turn, ~~is~~ are favoured by (i) lower solute concentration, (ii) higher homogenization temperature and (iii) higher quenching rate. However, Thomas and Whelen (132) have observed that even severe quenching of Al-4% Cu alloy does not produce dislocation loops and essentially results in the formation of helical dislocations. Hence the binary alloy under consideration can be thought to be free of dislocation loops. On the other hand the observation made by Thomas (129) that to suppress the formation of dislocation loops in Al-Mg alloy the percentage of Magnesium required is 8 atomic % suggests that the ternary alloys will contain dislocation loops the density of which for a given alloy will be determined by fraction of unassociated vacancies available during the process of quenching- a factor governed by rate of quenching.

(iv) Vacancies that have migrated to existing dislocations:

Migration of vacancies to sinks like dislocation line and screw dislocation leads to climb of dislocation and formation of helical dislocations as already discussed. The condition favourable for such a process is the one in which the unassociated vacancy concentration is not large enough to for secondary defects (i.e. dislocation loops and viods). Such a condition seems to have been satisfied in the binary alloy under consideration as revealed by the observations made by Thomas and Whelen (132). The process is favoured by (i)lower temperature of hangenization (ii) higher solute concentration and (iii) lower quenching rate. It should however be clearly understood that migration of vacancies to existing dislocations does not lead to formation of additional potential sites. The vacancies so trapped are also lost as far as the growth of either the zones or intermediate phases are concerned.

In light of the discussion given above, the conclusion arrived is that in case of binary Al-Cu 3.5% alloys, as a result of faster rate of quenching, there is only a marginal acceleration in the overall rate of precipitation due to change in the rate of nucleation and growth of G.P. zones which precedes formation of θ'. Whereas in case of the ternary Al-Cu-Mg alloys, quenching rate affects not only the nucleation and growth rate of G.P. and G.P.B. zones but also alters the nucleation and possibly the growth rate of S' and θ'. This conclusively establishes the reason behind the conspicuous "Quench-sensitivity" of the ternary alloys as compared to the binary alloys.

It has been reported by Hardy (148) that addition of In and Sn (which are known to form strong pairs with vacancies) in quantities of the order of 0.05%, to Al-Cu alloys containing 2.5 to 4.5% Cu, accelerates the process of ageing and reduces the time to reach peak hardness when aged at 110°C . This observation is in agreement with present results.

2.4.4 "Quench-Sensitivity" as a function of Magnesium content

From figs. 2.13 and 2.14 it is clear that the "Quench-sensitivity" of the ternary alloys decreases with increase in Magnesium content. Such a behaviour is to be expected since the value of E_f remains practically constant with increase in solute content (149). As a result the vacancy concentration produced at the temperature of homogenization is practically the same for all the 3 alloys. However, with increasing Magnesium content, more number of vacancies get entrapped by Magnesium atoms. This leads to steady decrease in the fraction of unassociated vacancies at temperature of homogenization. As a result, the "Quench-sensitivity" decrease since it is the presence of unassociated vacancies which ~~is~~ are responsible for creation of potential sites.

2.4.5 Quench-Sensitivity as a function of Ageing Temperature

From figs. 2.13 and 2.14 it may be observed that 'Quench-sensitivity' decreases as the temperature of ageing is increased.

This behaviour can be attributed to two reasons:

(i) With increase in ageing temperature, the Mg atom-vacancy pairs are broken and the vacancies so created get annihilated in shorter duration due to which the available vacancies for growth of the intermediate phase decreases steadily. In other words the 'Quench-sensitivity' that is dependent on associated vacancies is lost as ageing temperature is raised.

(ii) The dislocation loops that have been formed as a result of collapse of unassociated vacancies are also likely to anneal out partially as the temperature of ageing is increased. Thomas (129) has observed that under the influence of heat generated by the electron beam in an electron microscope, the dislocation loops start gliding and may ultimately be lost. Due to this effect, the quench-sensitivity of the ternary alloys is prone to diminish when ageing temperature is increased.

In addition to the potential sites that are created as a result of collapse of vacancy clusters, there are two more modes of formation of dislocations dependent on quenching rate. They are:

(i) Dislocations created as a result of plastic deformation due to quench-stresses.

(ii) Dislocations created as a result of anisotropic elastic and plastic properties of single crystals (150).

It is reasonable to expect that the contribution by the two factors is only marginal. The 'Quench-sensitivity' due to the former depends on (i) thermal conductivity and (ii) coefficient of thermal expansion and that due to the latter depends on anisotropy of single crystals. To a first approximation, these factors can be taken to be of the same magnitude in both the binary and ternary alloys and hence affecting 'Quench-sensitivity' to the same extent in both the alloys.

2.4.6 Peak Hardness

The results suggest that there is an optimum rate of quenching for attaining maximum peak hardness on ageing the ternary Al-Cu-Mg alloys.

Creation of dislocation loops as a result of collapse of discs of vacancies (that has been discussed in the previous section) has a profound effect on the kinetics of precipitation of θ' and S' which are associated with peak in the hardness curves.

The dislocation loops have a double role to play, namely;

(i) To create ~~of~~ potential sites for precipitation of intermediate phase;

(ii) To act as sinks for the vacancies that are unassociated or have been liberated from the associated condition (associated with solute atoms or zones/clusters).

The former factor affects nucleation rate and helps the process of nucleation. The latter factor alters the number of jumps that the vacancies can make before getting annihilated and hence reduces growth rate with time i.e. the effectiveness of vacancies as growth promoters gets reduced. If the rate of nucleation and that of growth are symbolized by letter N and G respectively, then the rate of precipitation can be written as

$$r = f(N) \times g(G)$$

where r is rate of precipitation of intermediate phase and f (N) and g (G) are functions of rate of nucleation and rate of growth respectively. The fact that the time to reach peak-hardness is maximum for quench ageing and minimum for water quenching with oil quenching lying at an intermediate value establishes the point that the product of the two functions listed above increases with increase in concentration of the vacancies created at the effective temperature of homogenization. This is to be expected because the vacancies that are lost for the growth factor (G) are available for nucleation factor (N)- thus there is no effective loss of vacancies during the process of quenching as far as the overall picture of precipitation of intermediate phase is concerned. (However, the above discussion does not take into account the variation in dislocation density in quenched condition due to changes in thermal strains. If these dislocations are also taken into account, the result will be enhanced 'Quench-sensitivity').

Although the product f (N) x g(G) increases in accordance with severity of quenching, the individual factors N and G behave differently because;

(a) Dislocation loops are formed only when the concentration unassociated vacancies at the temperature of homogenization is above a critical value;

(b) Only a small fraction of total available excess vacancies take part in dislocation loop formation. and

(c) A dislocation loop that is formed acts as a powerful sinks for other vacancies.

As a result, the growth factor (G) will pass through minimum with increasing rate of quenching. The fact that the growth rate passes through a minimum has been observed by Panseri and Fedlighi (50)in Al-Zn alloys with increasing homogenization temperature (which is equivalent to increase in quenching rate as far as vacancies are concerned).

When G passes through a minimum, the ratio N/G passes through a maximum. The ratio N/G has a profound effect on the size distribution of platelets of intermediate phase as explained below:

The process of precipitation of intermediate phase, is one of nucleation and growth. The process of nucleation of intermediate phase has to overcome nucleation barrier. Hence it is reasonable to expect that the nucleation of particles takes place over a period of time. Taking into consideration that fact that the nucleation of S' and θ' takes place after redissolution of G.P. zones and G.P.B. zones (which results in creation of regions of supersaturation) and since redissolution of zones is not instantaneous but spread over a period of time (starting from just before the end of plateau associated with zone and continuing to practically just before reaching the peak), it is certain that nucleation takes place over a period of time. Since nucleation of particles of S' and θ' is spread over time and then the growth of the particles takes place by diffusion, the particle size available at any instant will be spread over a range of sizes. The spectrum of the size of platelets will strongly depend on the relative values of nucleation rate and growth rate i.e. N/G ratio. When N/G passes through a maximum, the spectrum will have the narrowest range. Under such conditions, the particles that are nucleated earlier do not grow up to sufficient size before other platelets are nucleated. Due to availability of larger number of potential sites, the nucleation of the platelets from the supersaturated solid solution (created as a result of redissolution of zones) is facilitated and the time for transition (covering the period of redissolution of zones and precipitation of S' or θ') is minimized. Both these factors favour the process of narrowing down of spectrum of particle size observed at any given time of precipitation.

Peak-hardness in the ageing curve corresponds to a situation wherein softening process has come into operation due to loss of full coherency in some of the platelets of intermediate phase that have crossed the critical size up to which coherency can be maintained (151).

Viewed from strengthening effects the total volume fraction of the solute that has precipitated out, can be divided into four categaries:

(i) Solute in the form of zones.

(ii) Solute that is in transient state i.e. the solute which has gone back into matrix due to redissolution of zones but which is yet to precipitate out into intermediate phase.

(iii) Solute that is contained in the platelets of intermediate phase which are fully coherent with the matrix; and

(iv) Solute that is contained in the platelets of intermediate phase which are in various degrees of partial coherency with the matrix depending on the individual size of the platelets.

Of the various categories listed above, it is volume fraction of solute atoms in category (iii) which is the most effective strengthener. Compared with zones, the fully coherent intermediate phase is a better strengthener for the same volume fraction since the coherency strain developed by intermediate phase is far higher than the zones because crystal lattice of intermediate phase is distinctly different from that of matrix whereas the zones maintain continuity of lattice with the matrix. The solute atoms in the transition state has the least hardening effect because the volume fraction in transition state is equivalent to as-quenched alloy which is softest as compared with any other state during the process of ageing (except as compared with annealed material that is highly over-aged). Hence maximum peak-hardness will be obtained in a condition when maximum volume fraction of the solute atoms ~~are~~ is in condition (iii) and minimum under condition (iv) and (ii). This is precisely the condition that is satisfied by N/G maxima as discussed below.

When N/G is maximum the volume fraction of solute atom in the transition condition is minimum because the dissolved solute atoms readily find nucleation sites for precipitation. Maxima in N/G leads to narrow spectrum in size of platelets. Hence the transition from full coherency to partial coherency gets delayed. In other words the volume fraction of intermediate phase under condition of full coherency (which is a quantity decided by the difference between integrated value of rate of formation from zones and rate of growth beyond the critical size into partial coherency) is maximum when N/G is maximum. The observation (as evident from figs. 2.1 to 2.12) that rate of softening after peak is maximum in case of oil-quenched specimen as compared with water-quenched and quench-aged specimen is an evidence which strongly supports the suggestion that have been put forward.

Hence, to sum up, as the severity of quench is increased steadily, the ratio N/G passes through maximum. When N/G passes through maximum, peak-hardness value also passes through maximum. This clearly explains the reason behind optimization of quenching rate for obtaining maximum peak-hardness.

2.4.7 Analysis of Resistivity Data

From Table 2.3 it is evident that whereas in ternary alloys different rates of quenching result in appreciable variation in vacancy concentration, in binary alloys there is hardly any preceptable change in quenched-in vacancy concentration due to variation in rate of quenching. This explains the "Quench-sensitivity" of ternary alloys in contrast to binary alloys.

The fact that faster the rate of quenching, higher is the quenched-in vacancy concentration explains the observation that faster the rate of quenching, shorter is the time required to reach peak-hardness.

The quenched-in vacancy concentration estimated on the basis of resistivity data, can further be analysed in the light of observations made by various workers (118,119,129,132) regarding the minimum vacancy concentration that is required for producing secondary defects of permanent nature like dislocation loops. This minimum vacancy concentration that is required is a function of (a) the matrix (i.e. the metal) under consideration and 'b) the solute concentration. For example Hirsch et al (118) stimated that the initial concentration of vacancies d to produce dislocation loops in Aluminium should be order of 10^{-4} whereas Silcox and Hirsch have estimated nched-in vacancy concentration of the order of 6 x 10^{-5} ficient to cause formation of such secondary defects in Thomas (129) and Thomas and Whelan (132) have made r observation in quenched Al-Cu and Al-Mg alloys of ent compositions.

Comparing the reported values of minimum required quenched-ancies for formation of secondary defects in the binary and y alloys under consideration with those estimated in t investigation, it may be noted that:

In the binary alloy no secondary defect can be formed from the quenched-in vacancies by any one of the quenching rate under study;

In all the ternary alloys, the quenched-in vacancy concentr ion in quench-aged condition is too small to result in secondary defects;

In all the ternary alloys, the quenched-in vacancy concentration in oil-quenched specimens is just a little higher than the minimum required for formation of secondary defects;

In all the ternary alloys, the quenched-in vacancy concentration in water-quenched specimen is much higher (by a factor of about two) than the one required for formation of secondary defects.

It may be noted that the conclusions arrived at are in agreement with the postulates extended to explain the "optimization of quenching rate" for attaining maximum peak-hardness. Thus the resistivity data lends strong support to the explanation that has been extended to explain the relationship between peak-hardness value and rate of quenching.

2.5 CONCLUSIONS

The rate of quenching from the temperature of solution treatment has noticeable effect on the subsequent ageing characteristics of ternary Al-Cu-Mg alloys. This is in contrast to the ageing characteristics of binary Al-Cu alloys for which rate of quenching does not play any significant role. It has been observed that:

1) Faster the rate of quenching, shorter is the time required to reach peak-hardness;
2) For a given alloy, the lower the temperature of ageing, greater is the 'Quench-sensitivity';
3) For a given temperature of ageing, the lower the Mg content of an alloy, higher is the 'Quench-sensitivity';

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CHAPTER-III

INITIAL SOFTENING IN SOME ALUMINIUM BASE PRECIPITATION HARDENING ALLOYS

4) 'Flat' hardness associated with first stage of hardening is independent of rate of quenching;

5) There is an optimum rate of quenching, corresponding to which the peak-hardness value is maximum; Optimization of quenching rate can form the basis of improved heat-treatment schedule for these alloys.

3.1 INTRODUCTION

It has been reported by previous workers (33,63) that some extent of softening is observed before setting in of the usual hardening process when ageing is carried out on the Al-Cu and Al-Mg precipitation hardening alloys. The possible reason for the initial softening has been suggested as relief of thermal strain. No detalied experimental evidence in support of this postulate has been reported sofar.

Present work was undertaken to make a systematic study of initial softening in certain Al-Cu and Al-Mg alloys. It was proposed to study the phenomenon of initial softening as a function of solute concentration, quenching medium, and temperature of ageing. Hardness measurements were carried out to follow the process of softening and relief of thermal strain was studied by analysing X-ray line profile.

3.2 EXPERIMENTAL PROCEDURE

3.2.1 Preparation of Alloys

Binary Al-Cu and Al-Mg alloys were prepared from high purity Aluminium (99.9%), Copper (99.92%) and Magnesium (99.32%) as described in Chapter-II. All the specimens were disc shaped (20 mm dia x 8mm thick).

The nominal compositions of six binary Al-Cu alloys were from Al-2% Cu to Al-4.5% Cu at intervals of 0.5% Cu. The actual composition varied from the nominal within the limits of ± 0.05%.

The nominal compositions of binay Al-Mg alloys were Al-6% Mg, Al-8% Mg and Al-10% Mg. The actual composition varied from the nominal within the limits of ± 0.1%.

3.2.2 Heat-Treatment

Initial solution treatment was carried out for at least 48 hours at 520°C for all the Al-Cu alloys except Al-4.5% Cu which was solution treated at 530°C. Al-Mg alloys were solution treated at 450°C. The solution treated specimens were quenched in (1) water at (20 ± 1)°C or (2) brine water at 0°C. Microscopic examination of as quenched specimens revealed the complete dissolution of the second phase into the parent phase.

The solution treated, quenched specimens were aged at 110°C, 130°C, 150°C, 170°C, 190°C and 210°C for the binary Al-Cu alloys and 200°C, 250°C and 300°C for the Al-Mg alloys. Within 5 minutes of quenching, the specimens were put for ageing treatment. It has been shown by previous workers that heat treatment does not result in loss of either Copper (33) or Magnesium (75).

3.2.3 Hardness Measurements

Hardness values were determined on Vickers Hardness tester with 5 Kg load. Four specimens were taken out at the end of each ageing period and 3 hardness values were determined on each specimen. Average of a set of 12 readings was taken for determining each hardness value on ageing.

3.2.4 X-Ray Diffraction Studies

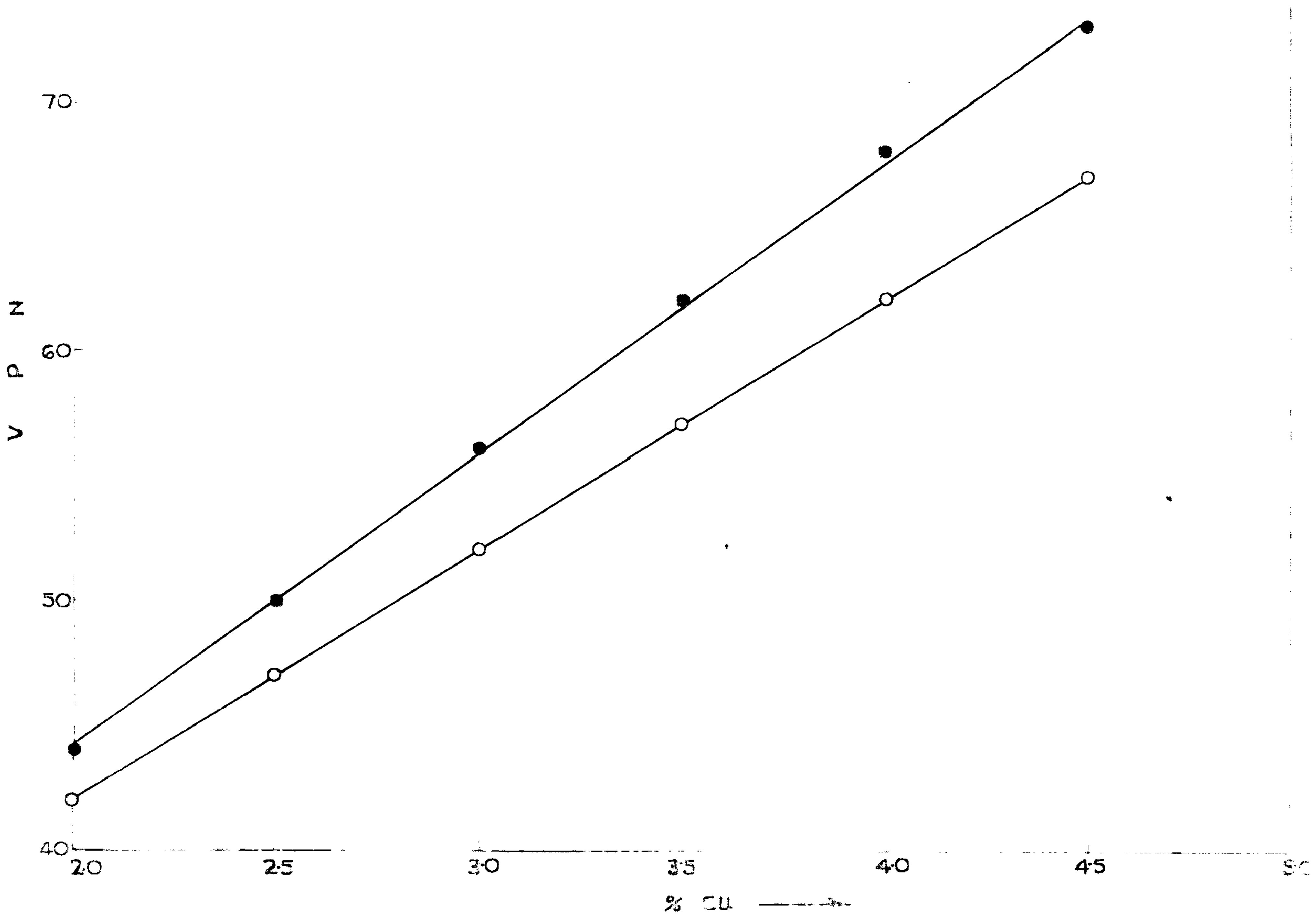
For the purpose of X-ray studies the specimens were mounted on perspex sheet after polishing them. A blank run with perspex sheet was carried out to ascertain that no peaks appear due to perspex. The target used in the X-ray tube was Iron. Manganese filter was used to cut off K_β radiation. However, as no crystal monochromotizer was used, the radiation consisted of K_α doublet.

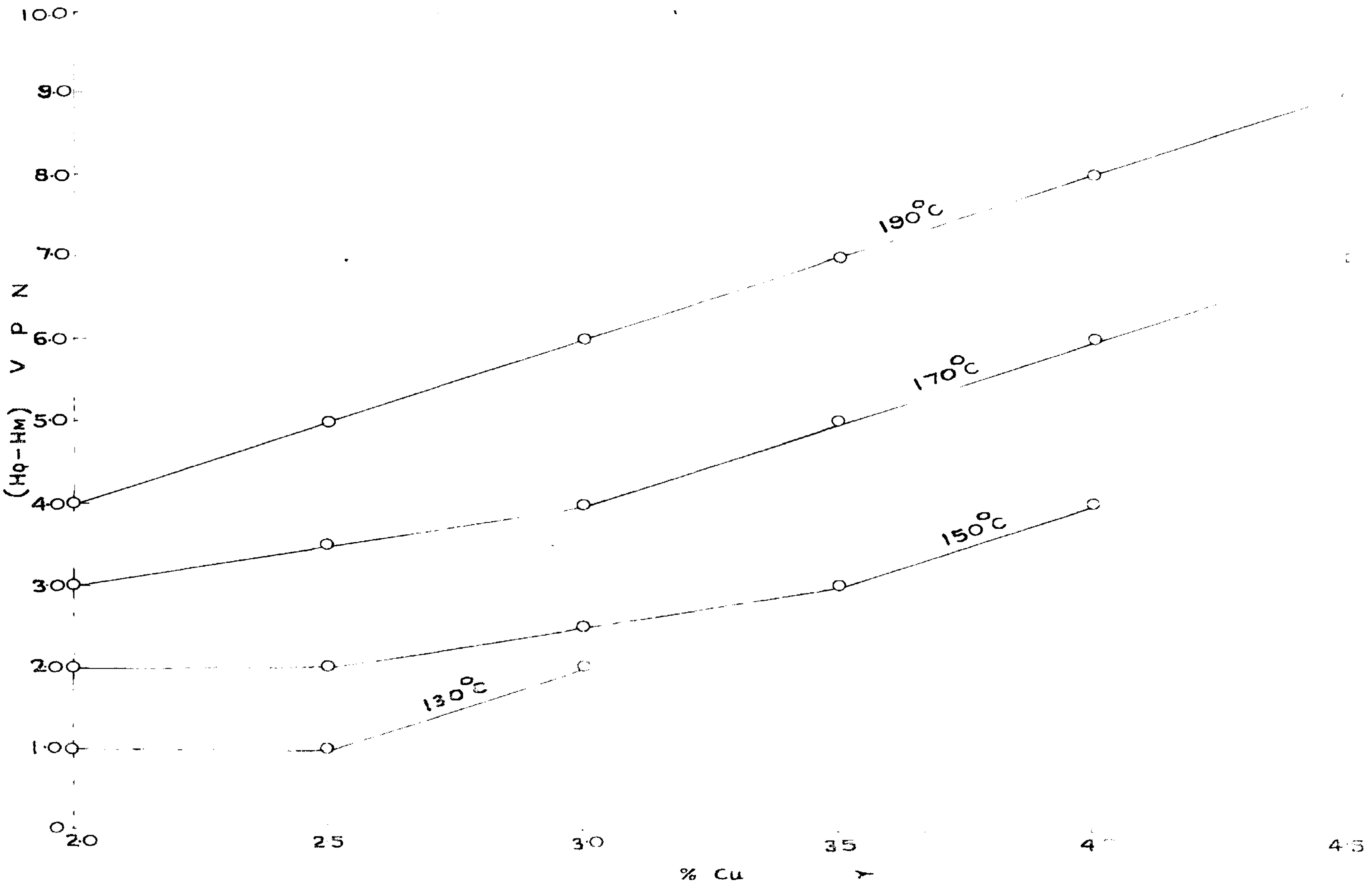
YPC-50 type X-ray diffractometer unit was used. The counter was run at the rate of ½° per minute. Bragg angle Vs intensity graph was plotted with automatic strip-chart potentiometer. The graph was run for 2° on either side of the peak position to determine the background. The half width (β) of the diffracted line was evaluated by dividing the area under the curve by the peak height above the background.

3.3 RESULTS

Figures 3.1 and 3.2 show the quenched hardness values of binary Al-Cu and Al-Mg alloys with (a) water at 20°C and (b) brine water at 0°C as quenching media.

In figures 3.3. to 3.5 are plotted the relationships between the extent of softening and solute concentration in binary Al-Cu


70
60
50
40
V P N
2·0
2·5
3·0
3·5
4·0
4·5
5·0
% Cu


10.0
9.0
8.0
7.0
6.0
5.0
4.00
3.00
2.00
1.00
0
(Hq-HM) V P N
190°C
170°C
150°C
130°C
2.0
2.5
3.0
3.5
4
4.5
% Cu

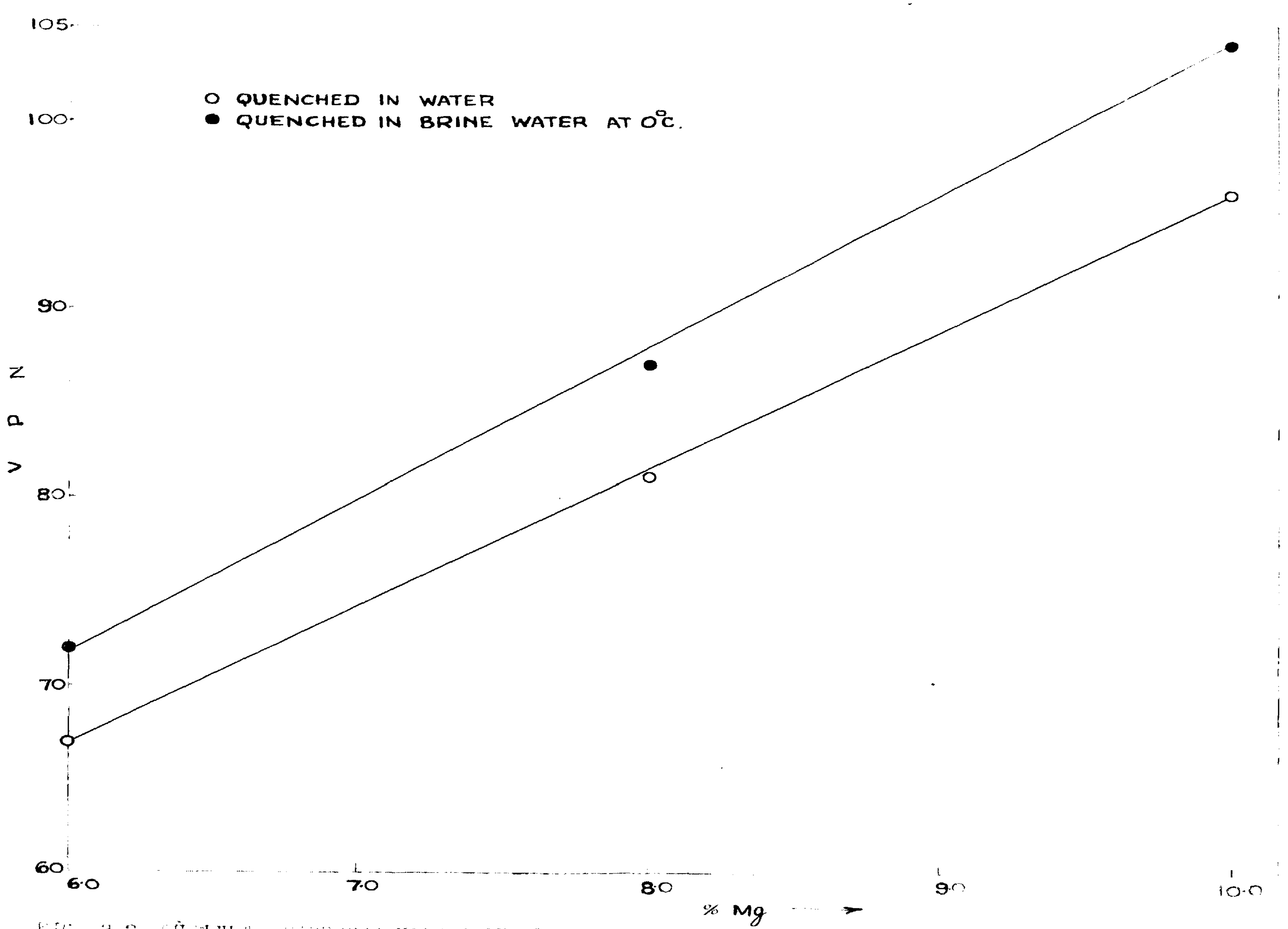
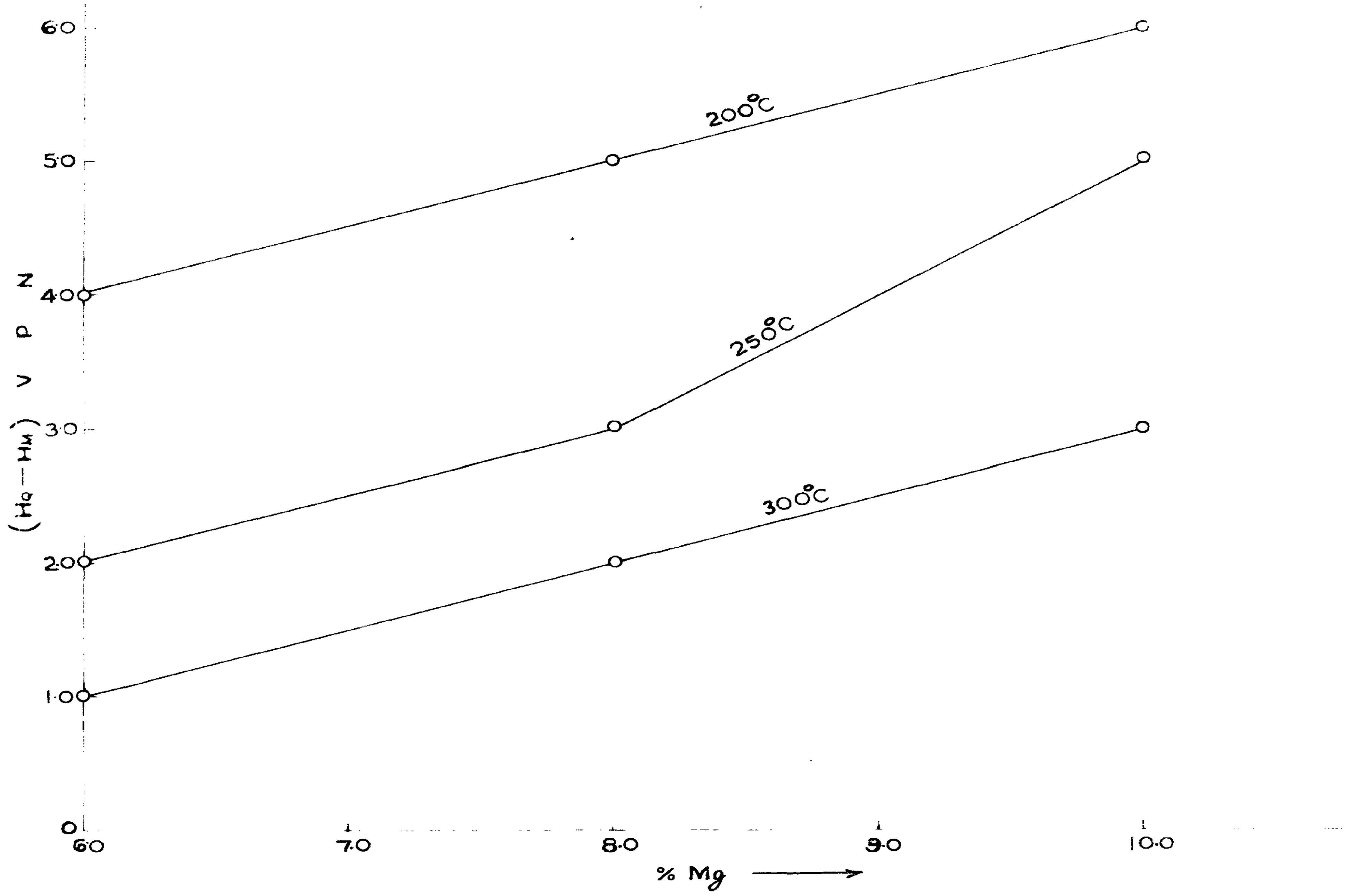
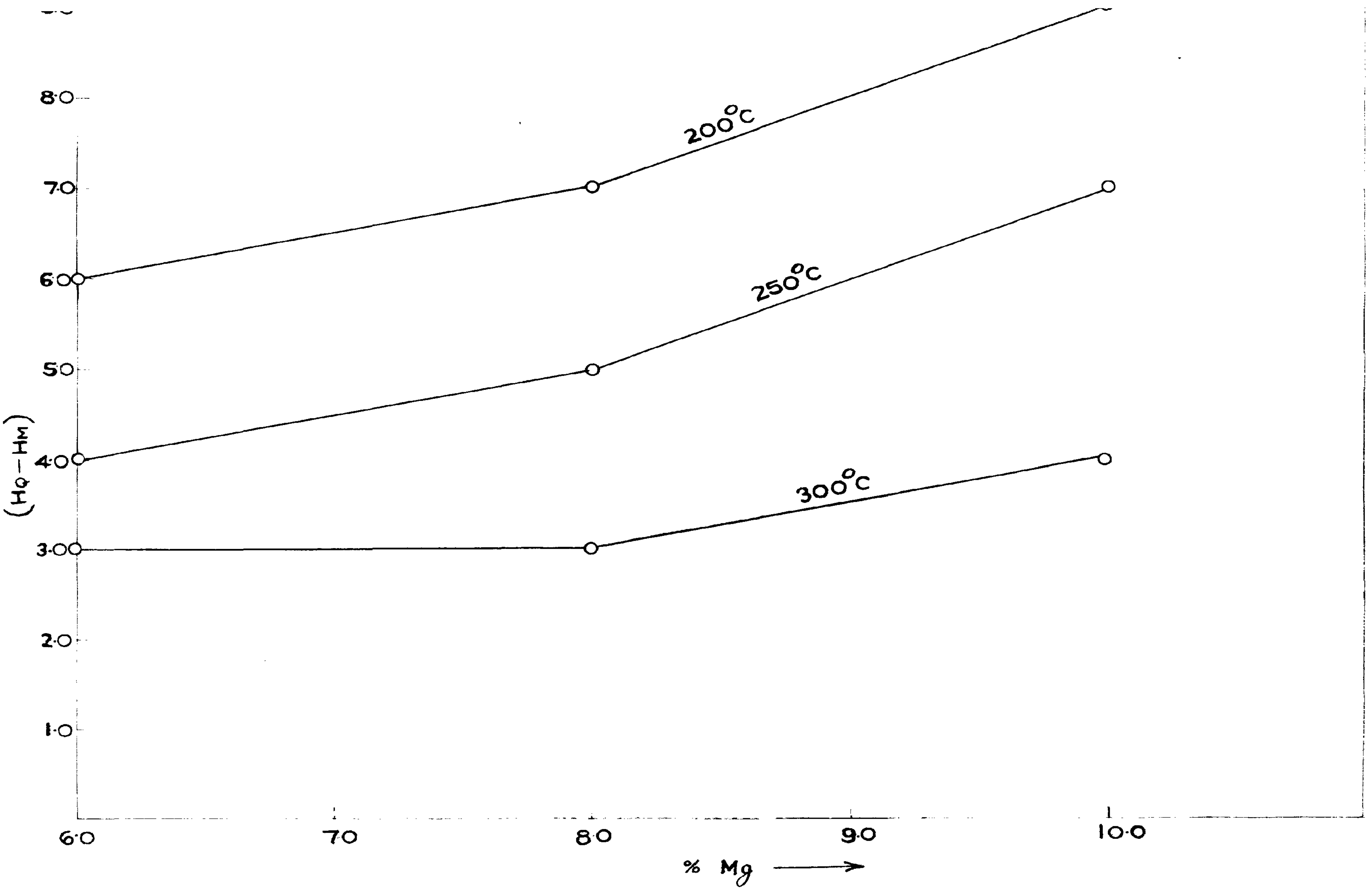


FIG. 3.2 QUENCHED HARDNESS VALUES OF Al-Mg ALLOYS.


6·0
5·0
4·0
3·0
2·0
1·0
0
(H₀ − H_M) V P N
200°C
250°C
300°C
6·0
7·0
8·0
9·0
10·0
% Mg

[illegible]



[illegible] 3.5 EXTENT OF SOFTENING [illegible] ALLOYS QUENCHED IN BRINE WATER OF 0°C AND AGED AT VARIOUS TEMPERATURES
H_Q = QUENCHED HARDNESS

[illegible]

Composition of alloy	Quenching medium	Ageing Temperature(°C)	Ageing Time	Indices of plane of reflection	β (Degrees)
Al-4% Cu	Brine water at 0°C	As-quenched	-	(111)	0.37
"	"	"	-	(200)	0.46
"	"	150	0.5 t_m*	(111)	0.31
"	"	"	t_m	"	0.32
"	"	"	2.0 t_m	"	0.40
"	"	"	0.5 t_m	(200)	0.41
"	"	"	t_m	"	0.34
"	"	"	2.0 t_m	"	0.40
"	"	170	0.5 t_m	(111)	0.34
"	"	"	t_m	"	0.30
"	"	"	2.0 t_m	"	0.35
"	"	"	0.5 t_m	(200)	0.39
"	"	"	t_m	"	0.29
"	"	"	2.0 t_m	"	0.48
"	"	190	0.5 t_m	(111)	0.32
"	"	"	t_m	"	0.24
"	"	"	2.0 t_m	"	0.35
"	"	"	0.5 t_m	(200)	0.40
"	"	"	t_m	"	0.27
"	"	"	2.0 t_m	"	0.35

Composition of alloy	Quenching medium	Ageing Temperature(°C)	Ageing Time	Indices of plane of reflection	β (Degrees)
Al-3.5% Cu	Brine Water at 0°C	As-quenched	-	(111)	0.32
"	"	"	-	(200)	0.40
"	"	150	0.5 t_m*	(111)	0.28
"	"	"	t_m	"	0.20
"	"	"	2.0 t_m	"	0.25
"	"	"	0.5 t_m	(200)	0.32
"	"	"	t_m	"	0.26
"	"	"	2.0 t_m	"	0.43
"	"	170	0.5 t_m	(111)	0.26
"	"	"	t_m	"	0.19
"	"	"	2.0 t_m	"	0.34
"	"	"	0.5 t_m	(200)	0.30
"	"	"	t_m	"	0.25
"	"	"	2.0 t_m	"	0.37
"	"	190	0.5 t_m	(111)	0.19
"	"	"	t_m	"	0.14
"	"	"	2.0 t_m	"	0.30
"	"	"	0.5 t_m	(200)	0.28
"	"	"	t_m	"	0.22
"	"	"	2.0 t_m	"	0.42

and Al-Mg alloys at various ageing temperatures. Figures 3.4 and 3.5 compare the extent of softening in Al-Mg alloys with the two types of quenching media. In case of binary Al-Cu alloys the extent of softening with water-quench was very small, expecially with lower copper contents (Cu less than 3.5%) and hence the results have not been plotted for comparison..

Table 3.1 summarises the results obtained on the X-ray diffractometer.

Table-3.1

Composition of alloy	Quenching medium	Ageing Temperature(°C)	Ageing Time	Indices of plane of reflection	β (Degrees)
Al-4.5% Cu	Brine Water at 0°C	As-quenched	-	(111)	0.41
"	"	"	-	(200)	0.52
"	"	170	0.5 t_m*	(111)	0.38
"	"	"	t_m	"	0.29
"	"	"	2.0 t_m	"	0.36
"	"	"	0.5 t_m	(200)	0.47
"	"	"	t_m	"	0.32
"	"	"	2.0 t_m	"	0.45
"	"	190	0.5 t_m	(111)	0.36
"	"	"	t_m	"	0.21
"	"	"	2.0 t_m	"	0.37
"	"	"	0.5 t_m	(200)	0.41
"	"	"	t_m	"	0.25
"	"	"	2.0 t_m	"	0.48

Composition of alloy	Quenching medium	Ageing Temperature(°C	Ageing Time	Indices of plane of reflection	β (Degrees)
Al-3% Cu	Brine water at 0°C	As-quenched	-	(111)	0.28
"	"	"	-	(200)	0.35
"	"	130	0.5 t_m*	(111)	0.28
"	"	"	t_m	"	0.20
"	"	"	2.0 t_m	"	0.23
"	"	"	0.5 t_m	(200)	0.31
"	"	"	t_m	"	0.27
"	"	"	2.0 tm	"	0.37
"	"	150	0.5 t_m	(111)	0.25
"	"	"	t_m	"	0.20
"	"	"	2.0 t_m	"	0.31
"	"	"	0.5 t_m	(200)	0.23
"	"	"	t_m	"	0.24
"	"	"	2.0 t_m	"	0.37
"	"	170	0.5 t_m	(111)	0.26
"	"	"	t_m	"	0.17
"	"	"	2.0 t_m	"	0.29
"	"	"	0.5 t_m	(200)	0.27
"	"	"	t_m	"	0.22
"	"	"	2.0 t_m	"	0.36
"	"	190	0.5 t_m	(111)	0.23
"	"	"	t_m	"	0.18
"	"	"	2.0 t_m	"	0.26

Composition of alloy	Quenching medium	Ageing Temperature(°C)	Ageing Time	Indices of plane of reflection	β (Degrees)
Al-3% Cu	Brine water at 0°C	190	0.5 t_m*	(200)	0.29
"	"	"	t_m	"	0.20
"	"	"	2.0 t_m	"	0.39
Al-2.5% Cu	"	As-quenched	-	(111)	0.24
"	"	"	-	(200)	0.30
"	"	130	0.5 t_m	(111)	0.24
"	"	"	t_m	"	0.20
"	"	"	2.0 t_m	"	0.27
"	"	"	0.5 t_m	(200)	0.28
"	"	"	t_m	"	0.24
"	"	"	2.0 t_m	"	0.32
"	"	150	0.5 t_m	(111)	0.26
"	"	"	t_m	"	0.17
"	"	"	2.0 t_m	"	0.21
"	"	"	0.5 t_m	(200)	0.27
"	"	"	t_m	"	0.24
"	"	"	2.0 t_m	"	0.31
"	"	170	0.5 t_m	(111)	0.24
"	"	"	t_m	"	0.16
"	"	"	2.0 t_m	"	0.23
"	"	"	0.5 t_m	(200)	0.25
"	"	"	t_m	"	0.20
"	"	"	2.0 t_m	"	0.29

Composition of alloy	Quenching medium	Ageing Temperature(°C)	Ageing Time	Indices of plane of reflection	β (Degrees)
Al-2.5% Cu	Brine Water at 0°C	190	0.5 t_m*	(111)	0.22
"	"	"	t_m	"	0.11
"	"	"	2.0 t_m	"	0.34
"	"	"	0.5 t_m	(200)	0.30
"	"	"	t_m	"	0.18
"	"	"	2.0 t_m	"	0.32
Al-10% Mg	"	As-quenched	-	(111)	0.48
"	"	"	-	(200)	0.59
"	"	200	0.5 t_m	(111)	0.43
"	"	"	t_m	"	0.34
"	"	"	2.0 t_m	"	0.47
"	"	"	0.5 t_m	(200)	0.59
"	"	"	t_m	"	0.51
"	"	"	2.0 t_m	"	0.51
"	"	250	0.5 t_m	(111)	0.46
"	"	"	t_m	"	0.37
"	"	"	2.0 t_m	"	0.40
"	"	"	0.5 t_m	(200)	0.54
"	"	"	t_m	"	0.44
"	"	"	2.0 t_m	"	0.56
"	"	"	t_m	"	0.39
"	"	"	2.0 t_m	"	0.50

Composition of alloy	Quenching medium	Ageing Temperature(°C)	Ageing Time	Indices of plane of reflection	β (Degrees)
Al-10% Mg	Brine water at 0°C	300	t_m*	(200)	0.46
"	"	"	2.0 t_m	"	0.53
Al-8% Mg	"	As - quenched	-	(111)	0.44
"	"	"	-	(200)	0.53
"	"	200	0.5 t_m	(111)	0.34
"	"	"	t_m	"	0.32
"	"	"	2.0 t_m	"	0.41
"	"	"	0.5 t_m	(200)	0.50
"	"	"	t_m	"	0.41
"	"	"	2.0 t_m	"	0.52
"	"	250	0.5 t_m	(111)	0.45
"	"	"	t_m	"	0.33
"	"	"	2.0 t_m	"	0.32
"	"	"	0.5 t_m	(200)	0.50
"	"	"	t_m	"	0.40
"	"	"	2.0 t_m	"	0.45
"	"	300	0.5 t_m	(111)	0.48
"	"	"	t_m	"	0.44
"	"	"	2.0 t_m	"	0.58
"	"	"	0.5 t_m	(200)	0.52
"	"	"	t_m	"	0.37
"	"	"	2.0 t_m	"	0.44

Composition of alloy	Quenching medium	Ageing Temperature(°C)	Ageing Time	Indices of plane of reflection	β (Degrees)
Al-6% Mg	Brine water at 0°C	As-quenched	-	(111)	0.39
"	"	"	-	(200)	0.45
"	"	200	0.5 t_m*	(111)	0.39
"	"	"	t_m	"	0.25
"	"	"	2.0 t_m	"	0.33
"	"	"	0.5 t_m	(200)	0.46
"	"	"	t_m	"	0.32
"	"	"	2.0 t_m	"	0.39
"	"	250	0.5 t_m	(111)	0.36
"	"	"	t_m	"	0.27
"	"	"	2.0 t_m	"	0.33
"	"	"	0.5 t_m	(200)	0.42
"	"	"	t_m	"	0.35
"	"	"	2.0 t_m	"	0.48
"	"	300	0.5 t_m	(111)	0.37
"	"	"	t_m	"	0.29
"	"	"	2.0 t_m	"	0.29
"	"	"	0.5 t_m	(200)	0.43
"	"	"	t_m	"	0.37
"	"	"	2.0 t_m	"	0.46

Composition of alloy	Quenching medium	Ageing Temperature(°C)	Ageing Time	Indices of plane of reflection	β (Degrees)
Al-6% Mg	Water at 20°C	250	0.5 t_m*	(111)	0.29
"	"	"	t_m	"	0.21
"	"	"	2.0 t_m	"	0.27
"	"	"	0.5 t_m	(200)	0.31
"	"	"	t_m	"	0.22
"	"	"	2.0 t_m	"	0.28
"	"	300	0.5 t_m	(111)	0.26
"	"	"	t_m	"	0.23
"	"	"	2.0 t_m	"	0.32
"	"	"	0.5 t_m	(200)	0.32
"	"	"	t_m	"	0.24
"	"	"	2.0 t_m	"	0.37

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* t_m - Time to reach minimum hardness.

3.4 DISCUSSION

3.4.1 Quenched Hardness

From figures 3.1 and 3.2, it is evident that quenched hardness increases with increase in solute concentration (viz. Cu or Mg as the case may be). The hardness of quenched alloy is attributable to

(a) Solid solution hardening;

(b) Hardening due to lattice distortions produced by supersaturation; and

(c) Hardening due to lattice distortions produced as a result of quenching.

In comparing the quenched hardness of alloys quenched under similar conditions, it is only supersaturation that alters the hardness value. This explains the linear increase in as quenched hardness with increase in (a) % Copper and (b) % Magnesium.

The quenched-hardness, with brine water at 0°C as the quenching medium, is higher than with water at 20°C as the quenching medium. This is true for every alloy of Al-Cu and Al-Mg and the difference in theas-quenched hardness values increases with increase in solute concentration.

The extra hardness with brine water-quench is attributable to (i) higher lattice distortion due to greater severity of quenching; and (ii) creation of dislocation loops due to possible collapse of vacancy clusters (90) created due to large number of trapped thermal vacancies.

The greater effectiveness of rate of quenching to alter the as-quenched hardness, with increase in solute concentration may be attributed to the following reason:

When the solute concentration is higher, larger number of solute atoms are available in the matrix and they are helpful in setting up lattice distortion during the process of quenching.

3.4.2 Extent of Softening

From fig. 3.3, it can be observed that the extent of softening increases with increase in ageing temperature for Al-Cu alloys. The obvious reason is that, with higher ageing temperatures, the process of relief of thermal strain is nearer to completion. It is also seen from fig. 3.3 that larger the solute concentration, greater is the degree of softening for Al-Cu alloys. With larger solute concentration, larger amount of lattice distortion is introduced while quenching (as discussed already) and relief of this distortion leads to a larger degree of softening.

It may be observed from fig. 3.4 and 3.5 that in contrast to Al-Cu alloys, degree of softening decreases with increase in ageing temperature in the case of Al-Mg alloys. It has been reported (63) that in Al-Mg alloys, there is first discontinuous precipitation of β' followed by continuous precipitation. The discontinuous precipitation starts at the grain boundaries (64-67) and then proceeds into the grains. The precipitation at the grain boundaries hardly contributes to any hardening and it is only after precipitation within the grains has taken place that increment in hardness results. At low temperature, the grain boundaries act as potential sites for precipitation of β'. However, with increasing ageing temperatures, imperfections like dislocations within the grains also assume importance as potential sites for precipitation of β'.

In other words, with increasing ageing temperatures the process of hardening is accelerated doubly fast (i) due to faster precipitation of β' and (ii) due to precipitation of β' taking place within the grains simultaneously with precipitation at grain boundaries. The process of softening also gets accelerated due to faster rate of relief of thermal strain. It is suggested that hardening process is accelerated to a greater extent than the softening process and hence the observed decrement in extent of softening with increase in ageing temperature:

From figs. 3.4 and 3.5, it is also clear that higher the solute concentration, greater is the extent of softening. The explanation is the same as for Al-Cu alloys.

It is also revealed from figs. 3.4 and 3.5 that extent of softening is higher for specimens quenched in brine water than for specimens quenched in water. Specimens quenched in brine water have undergone more severe quenching and hence the process of relief of thermal strain is faster and more appreciable. As a result the extent of softening is greater.

3.4.3 Time to reach Minimum Hardness

On comparing the time to reach minimum hardness between Al-Mg alloys specimens quenched in water (at 20°C) and brine water at 0°C it was found that the former always takes larger time than the latter for a given alloy at a given temperature of ageing. It is possible to explain the above observation in terms of faster rate of ageing process in latter case due to

(i) Presence of strains which facilitate precipitation;

(ii) Presence of large number of thermally trapped vacancies which increase effective rate of diffusion; and

(iii) Possible collapse of cluster of vacancies to form dislocation loops (40) or condensation of cluster of vacancies to form voids (93) each of which can act as potential site for precipitation of intermediate phase.

It was also observed that for Al-Cu as well as Al-Mg alloys the time to reach minimum hardness at a given temperature decreased with increase in solute concentration ~~(fig. 3.6)~~. The explanation lies in the fact that higher the solute concentration in the alloy, greater is the degree of supersaturation and higher is the resulting driving force for precipitation and consequently faster is the rate of hardening.

3.4.4 Range of Softening

From fig. 3.3, it can be been that for each Al-Cu alloy there is a range of temperature only within which the initial softening can be observed. Existence of such temperature range for softening may be explained as follows:

Below the lower limit, the slow rate of stress relief is overcompensated by zone formation. Hence no effective softening is observable. Above the upper limit, the formation of intermediate phase is so fast that the softening effect is masked. It is also possible that softening might have occurred within the first five minutes when hardness values were not recorded.

It can also be noted from fig. 3.3 that the temperature range of softening narrows down with increase in copper content. With increase in copper content there is increase in supersaturation and resulting increase in driving force for (a) zone formation and (b) precipitation of intermediate phase. Also, with increase in Copper content the zones appear at higher ageing temperature (36). The net result is raising of lower limit and lowering of upper limit i.e. narrowing down of temperature range of softening.

3.4.5 X-ray Line Width

The line broadening (152) that takes place in X-ray diffraction pattern is due to (a) particle size and (b) microstresses. If the line broadening is due to particle size alone, then the line width β_p is related to the effective particle size ϵ, the X-ray wave length λ and Bragg angle θ by the equation:

$$\beta_p = \frac{K\lambda}{\epsilon\cos\theta}$$

Where K is a constant nearly equal to unity.

For pure stress broadening the width β_s is related to the effective strain and the Bragg angle by the equation:

$$\beta_s = \eta\tan\theta$$

If both types of broadening are present then,

$$\beta = \beta_p + \beta_s \text{ , or}$$

$$\frac{\beta\cos\theta}{\lambda} = \frac{1}{\epsilon} + \frac{\eta\sin\theta}{\lambda}$$

In a distorted lattice, the effective particle size ϵ may be interpreted as a measure of the volume of region in the lattice which diffracts coherently.

Extending the analysis of Wheeler and Jawson (153), it may be concluded that the line broadening observed in the initial stages of hardening in Al-Cu and Al-Mg is due to balanced internal stresses rather than small particle size.

That is, $\beta = \beta_s = \eta\tan\theta$

If the microstress in the same material under two different conditions ~~are~~ is to be compared, it is sufficient to compare the β values of the lines due to same set of planes.

As Jones (154) has pointed out, ~~that~~ the observed line widths can be influenced by a number of factors other than particle size and microstress in the specimens. Even a fully annealed specimen, which is relieved of all microstresses and which has "infinite particle size" (i.e., particle size greater than 10 microns), will produce X-ray diffracted lines of finite width. Hence a correction is to be made to observed line width before proceeding to estimate particle size or microstress.

The correction to be applied is:

$$\beta^2 = B^2 - b^2$$ (Assuming Gaussion distribution for the profile of the lines).

where β is pure diffraction broadening,

B is the observed width with given specimen, b is the observed width when the specimen is in standard condition i.e. in the fully annealed condition.

Yet another correction is to be applied for non-homogeneity of the radiation used for X-ray diffraction work. The K_α radiation used consists of a doublet which causes broadening of the lines since in general the two components are not resolved. Necessary correction has been carried out on the basis of the method suggested by Jones (154).

The values of β so obtained and shown in Table-I are in accordance with hardness values. Initially the value of β is large and there is sharpening when the hardness value attains a minimum, followed by broadening on further ageing. The plausible explanation is that the initial width is due to distorted lattice produced as a result of quenching. Subsequent broadening can be attributed to coherency strains developed between the matrix and zones or precipitating phases.

3.5 CONCLUSIONS

The study of initial ageing indicates that:

1. There is initial softening followed by usual hardening;
2. Only within a definite range of temperature of ageing, initial softening can be observed; With increase in solute concentration the range narrows down;
3. The extent of softening increases with (a) severity of quench and (b) solute concentration;
4. For Al-Cu alloys, the extent of softening increases with increase in ageing temperature in contrast to Al-Mg alloys where the reverse is found to be true;
5. X-ray line profile analysis reveals an initial sharpening followed by the broadening of the lines.

CHAPTER-IV

EFFECT OF COLD WORKING ON THE AGEING CHARACTERISTICS OF SOME Al-Cu AND Al-Mg ALLOYS

4.1 INTRODUCTION

While a number of workers (147,155-160) have observed that plastic deformation prior to ageing accelerates the process of precipitation in Al-Cu alloys, there are also reports (161-163) that plastic deformation retards the process of ageing especially when deformation is due to creep loading. However, it is not certain whether the effect of plastic deformation on precipitation is dependent on type of deformation, i.e. cold working prior to ageing or creep. Also, since the process of precipitation in Al-Cu alloys aged at elevated temperatures involves two steps, viz:

(i) Precipitation of θ' from the supersaturated solid solution and

(ii) Transformation of θ' to θ (the effect of deformation on each one of these two steps is to be ascertained individually).

The work reported in this chapter was undertaken to investigate the effect of prior plastic deformation over a range of ageing temperatures and compositions on each of the two steps involved in precipitation of the θ phase. The transformations were studied with help of hardness, resistivity and integrated X-ray line intensity measurements. For comparison purposes, additional work was also carried out on Al-Mg alloys.

4.2 EXPERIMENTAL PROCEDURE

4.2.1 Preparation of Alloys

Binary Al-Cu and Al-Mg alloys were prepared from high purity Aluminium (99.9% pure), copper (99.92% pure) and Magnesium (99.35% pure) as already described.

The cast alloys were forged, and then annealed at 350°C for three days to ensure removal of microinhomogeneity and cast structure. Disc shaped specimens (20 mm dia x 8 mm thick) were machined out from annealed rods for hardness and integrated X-ray line intensity measurements. A set of annealed rods ~~were~~ was rolled and drawn into wires for resistivity studies. The compositions of the binary Al-Cu and Al-Mg alloys are given in Table 4.1.

Table-4.1

Composition of binary Aluminium alloys

Alloy No.	weight percent		
	Cu	Mg	Al
1	1.62	-	Rest
2	1.71	-	Rest
3	1.82	-	Rest
4	1.95	-	Rest
5	2.5*	-	Rest
6	3.0*	-	Rest
7	3.5*	-	Rest
8	-	5.0*	Rest
9.	-	6.0*	Rest
10	-	7.0*	Rest

* These figures denote the nominal compositions. Actual composition varied from the nominal within the limits of ± 0.05%.

4.2.2 Heat-Treatment

Initial solution treatment was carried out for at least 48 hours at 520°C for the binary Al-Cu and at 450°C for the binary Al-Mg alloys. The solution treated specimens were quenched in water at (20 ± 1)°C. Microscopic examination of as-quenched specimens revealed complete dissolution of second phase into the parent phase.

Plastic deformation of the disc shaped specimens was carried out by compression. The solution treated, quenched specimens were compressed 15% with help of universal testing machine. It was observed that the extent of acceleration or retardation that is produced in the process of ageing due to prior plastic deformation, gets a saturation value between 10 and 15% compression. Percentage of compression higher than 15% did not seem to have additional accelerating or retarding effect on the ageing process. Similar results have also been reported by previous workers (159). Also, there is ample evidence (155,156, 163-166) which shows that heavy deformation leads to direct precipitation of θ instead of θ' followed by transformation of θ' to θ. Since the aim of present investigation was to study the effect of cold working on precipitation of θ' from α-solid solution and θ' to θ transformation, prior plastic deformation was restricted to 15%. Appropriate deformation was given to wire specimens by redrawing the solution treated, as-quenched wires to smaller sizes without any intermediate anneal. The specimens in the deformed and underformed conditions were aged at different temperatures and followed by hardness, resistivity and integrated X-ray line intensity measurements.

4.2.3 Hardness Measurements

Hardness values were determined on Vickers Hardness tester with 5 Kg load. Two specimens were taken out at the end of each ageing period and minimum of 3 hardness values were determined on each specimen. Average of sets of a minimum of six readings was taken for plotting each point on the ageing curves.

4.2.4 Resistivity Measurements

Changes in resistivity produced as a result of ageing were determined on wire specimens with a potentiometer. All resistivity measurements were carried out at 0°C.

4.2.5 X-ray Line-intensity Measurements

The aim of these measurements was to determine the progress of θ' to θ transformation. The transformation was followed by measuring the integrated intensity of the (110) reflection of CuAl$_2$ in a YPC-50 diffractometer. Minimum of four readings was ~~were~~ taken on each sample. Only one diffracted line from θ' could be observed as reported by earlier workers (162,167). This is possibly due to Widmanstatten precipitation. Consequently, the integrated line intensity measurements on the diffracted line of θ' is unreliable(168). The only purpose served by scanning the reflection from θ' was to ascertain that θ formed by transformation of θ' to θ and not directly from the α-solid solution.

4.3 RESULTS

4.3.1. Hardness Measurements

Age-hardening curves were plotted for the alloys aged at various temperatures after (a) quenching from the temperature of solution treatment and (b) quenching followed by compression. From these curves "time to reach peak-hardness" was determined in each case.

In the range of ageing temperature employed, most of the binary Al-Cu alloys aged by direct precipitation of θ' instead of zones followed by θ' in accordance with the known metastable phase boundaries of zones for this system (36,111). Hence, "time to reach peak-hardness" can be used as a measure of rate of precipitation of θ' since the hardness peak is associated with θ'. In those cases where formation of zones precedes precipitation of θ', more than one stage of hardening is observable and the last stage of hardening (due to precipitation of θ') is followed by overageing. Thus, the peak associated with θ' is distinctly separable from others. So the effect of cold working on the kinetics of formation of θ' can be evaluated in terms of "time to reach peak-hardness".

Hardening takes place in Al-Mg alloys (63) essentially due to precipitation of β'. Though, with origin in electronic structure, a theoretical basis for clustering in Al-Mg alloys has been developed recently (196), there is no clear evidence for formation of clusters (72,129), and zones (70) in this system. Accordingly, the peak-hardness can be associated with β' and any shift in "time to reach peak-hardness" can be attributed to change in the kinetics of precipitation of β'.

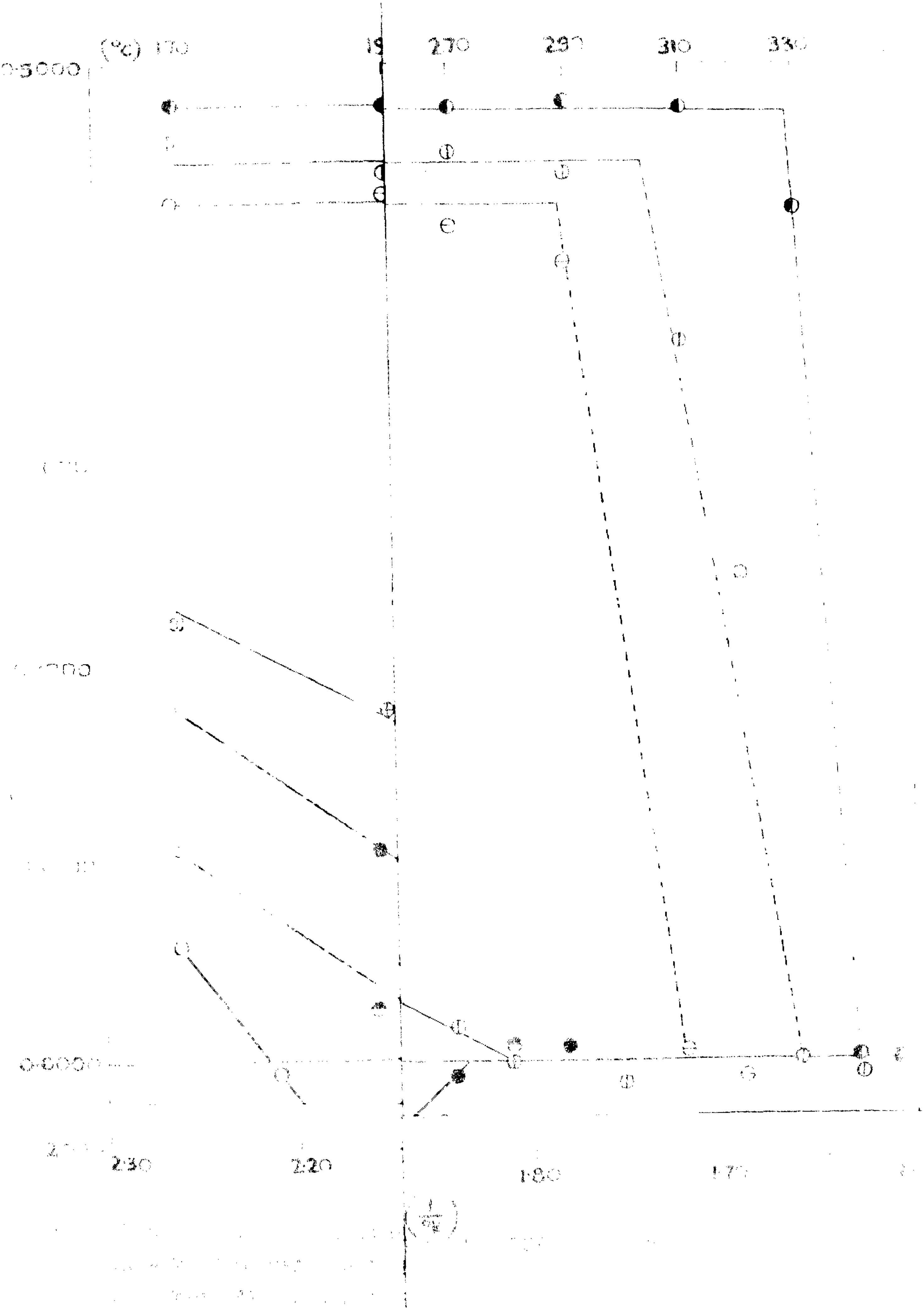
Figures 4.1 and 4.2 show the relationship of log $\frac{t_o}{t_c}$ Vs $\frac{1000}{T}$ for the Al-Cu and Al-Mg alloys respectively,

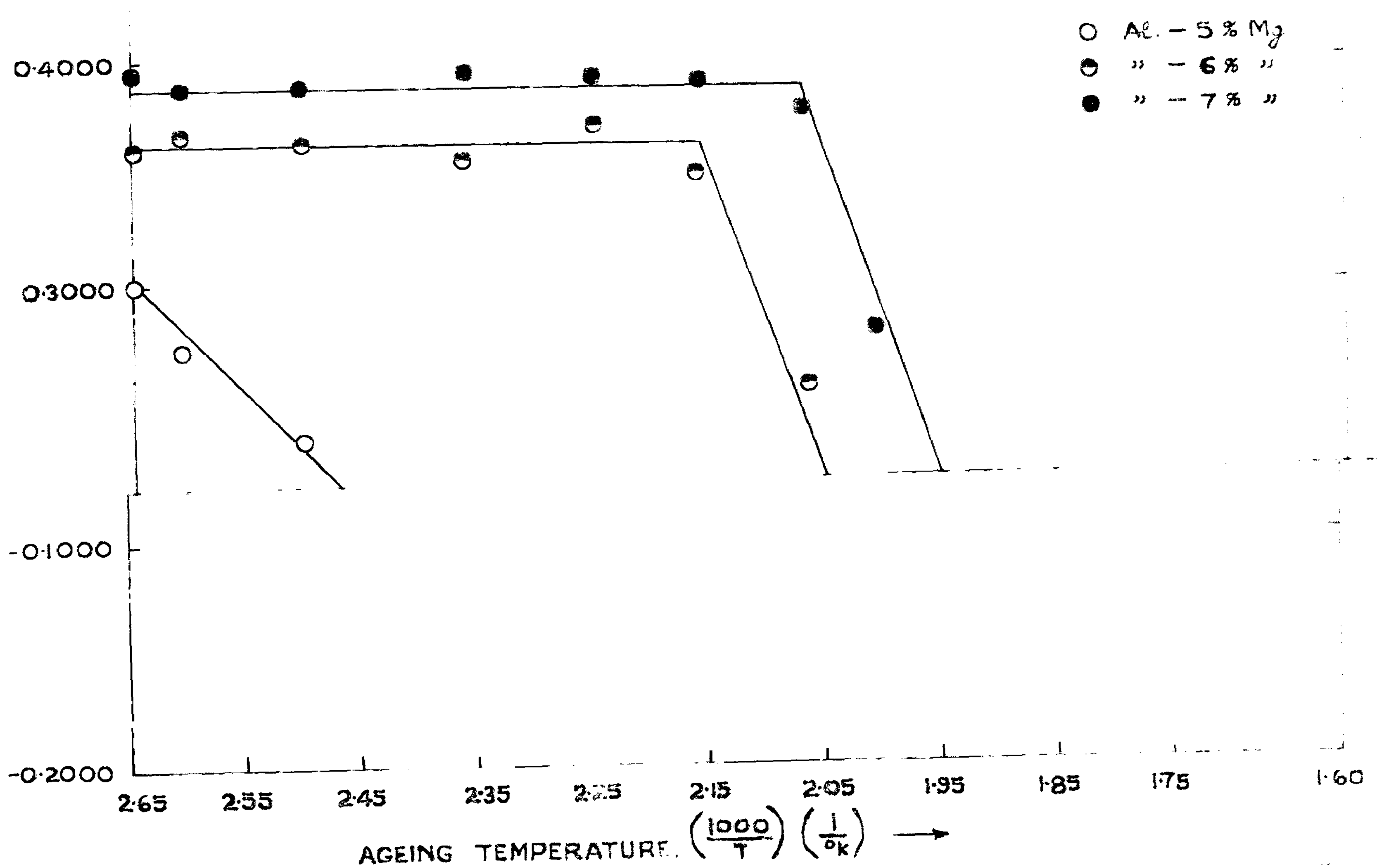
where t_o = 'time to reach peak-hardness' for uncompressed specimens ,
t_c = 'time to reach peak-hardness' for compressed specimens
and T = ageing temperature in °K.

In case of Al-Cu alloys, it became increasingly difficult to determine accurately the values of 't_o' and 't_c' with increasing ageing temperatures due to lack of well defined ageing curves and peaks. Hence, at elevated ageing temperatures, the values of 't_o' and 't_c' were confirmed with resistivity measurements.

4.3.2 Resistivity Measurements

Resistivity measurements had to be confined to Al-Cu alloys since it was not possible to redraw the wires of Al-Mg alloys in

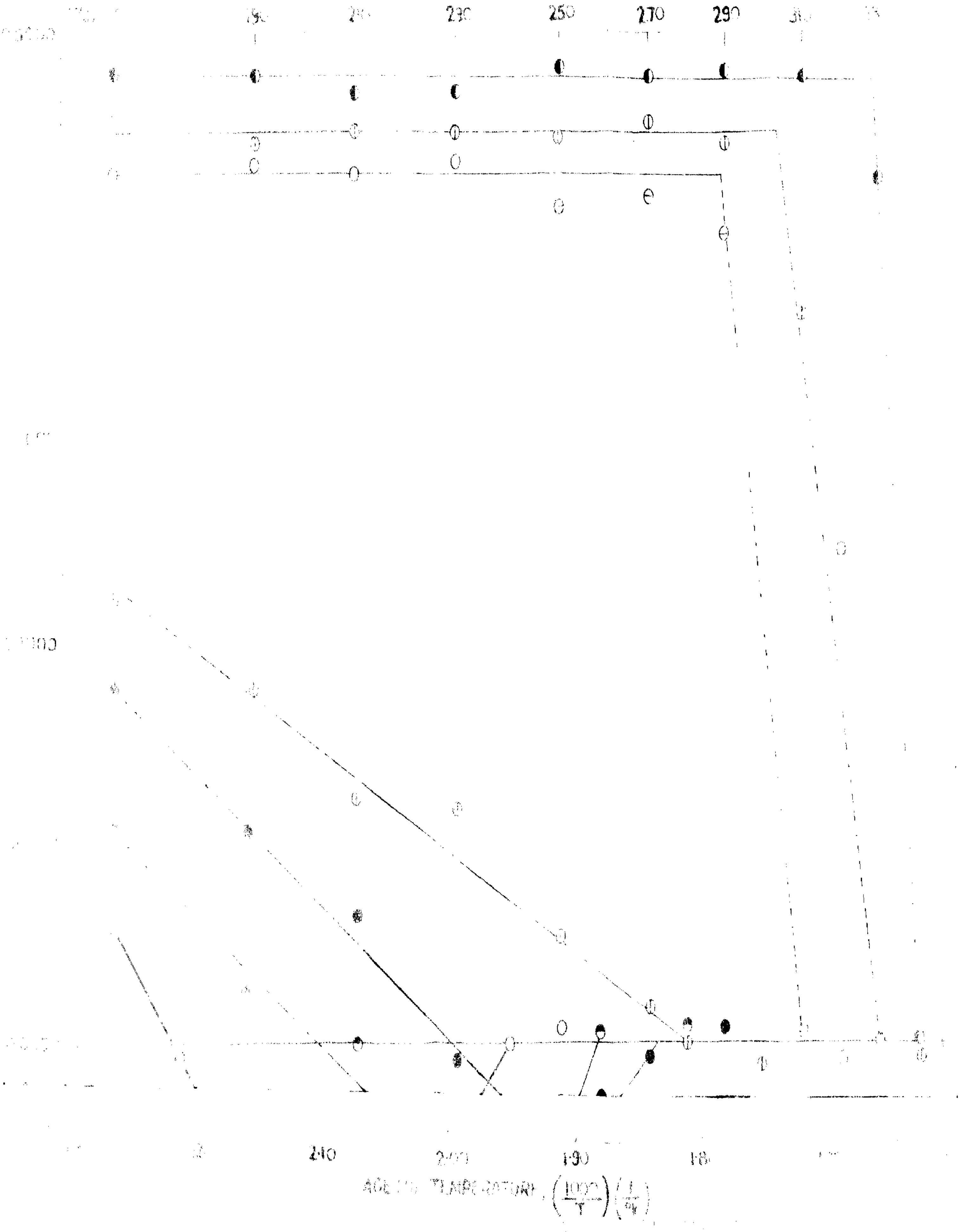

(°C) 170
19
270
290
310
330
0·5000
0·0000
2·30
2·20
1·80
1·70

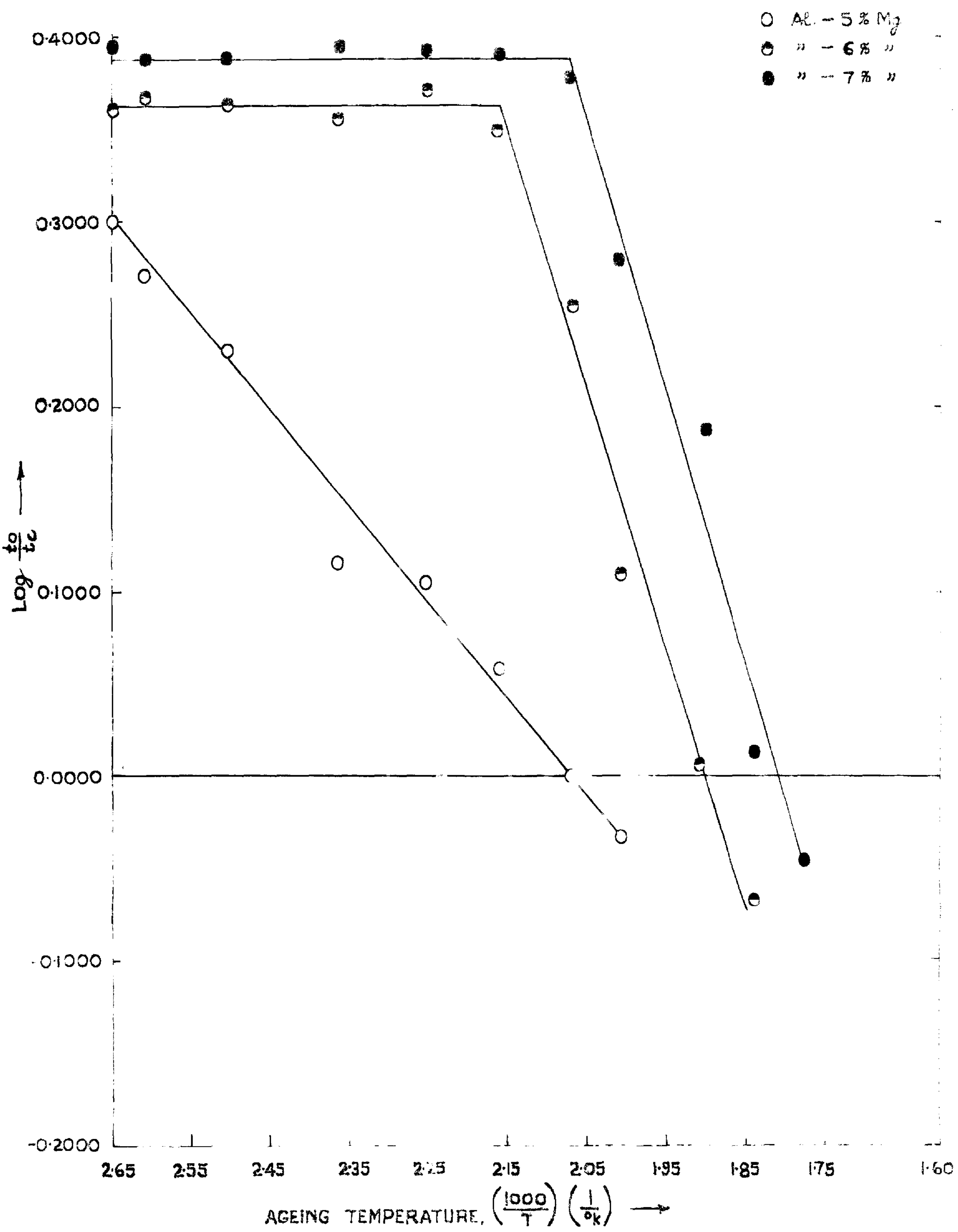


EFFECT OF COLD WORKING [illegible] VARIOUS [illegible]

t_0 = TIME TO [illegible] COLD WORKING

t_c = TIME TO [illegible] PEAK [illegible] WORKING


250
270
290
2·10
2·00
1·90
1·8
AGEING TEMPERATURE, $\left(\frac{1000}{T}\right)\left(\frac{1}{°K}\right)$



EFFECT OF COLD WORKING ON THE TIME TO REACH PEAK HARDNESS AT VARIOUS [illegible]

t_0 = TIME TO REACH PEAK HARDNESS WITHOUT COLD WORKING

t_c = TIME TO REACH PEAK HARDNESS AFTER COLD WORKING the as-quenched condition for studying the effect of cold working. Resistivity was plotted as a function of ageing time. These resistivity curves were analysed for determining (i) Order of reaction and (ii) Activation energy associated with each of the reaction as revealed by resistivity changes (170). The results reveal three distinct reactions for cold worked alloys viz:

(i) A zero order reaction with an activation energy of 1.04 eV-designated as reaction 'A';

(ii) A second order reaction with an activation energy of 0.48 eV-designated as reaction 'B'; and

(iii) A zero order reaction with an activation energy of 1.50 eV-designated as reaction 'C'.

The reactions appear as distinctly separated or overlapping on each other depending on temperature of ageing. This is in contrast to ageing behaviour of as-quenched wire specimens which show only reaction 'A'. The results are summarised in table 4.2.

Table-4.2

Processes observed during ageing of cold worked Al-Cu alloys (on the basis of resistivity measurements)

Alloy	Range of ageing temperature (°C)	Sequence of processes
Al-1.54% Cu	180-205	Process 'B' Process 'A'
Al-1.54% Cu	215-240	Process 'B' Process 'C' Process 'A'
Al-1.72% Cu	200-230	Process 'B' Process 'A'
Al-1.71% Cu	240-260	Process 'B' Process 'C' Process 'A'
Al-2.5% Cu	170-270	Process 'A' Process 'B'
Al-3% Cu	170-290	Process 'A' Process 'B'
Al-3.5% Cu	170-310	Process 'A' Process 'B'

4.3.3 X-ray Integrated Line Intensity Measurements

These measurements had to be confined to study of θ' to θ transformation. Reproducible results could not be obtained with Al-Mg alloys due to difficulties in scanning the reflections from β (Mg_2Al_3). Transformation of θ' to θ followed the usual sigmoidal curve. Data regarding time required for transformation computed from these curves is reported in Table 4.3.

Table-4.3

Effect of prior plastic deformation on θ' to θ transformation

Alloy	Ageing temperature (°C)	t_o / t_c
Al-1.54% Cu	190	0.55
	210	0.21
	230	0.92
Al-1.71% Cu	190	0.63
	210	0.34
	230	0.95
	250	1.07
Al-1.82% Cu	190	0.67
	220	0.49
	240	1.12
	260	1.04

Table continued.

Alloy	Ageing temperature(°C)	t_o/t_c
Al-1.95% Cu	190	0.76
	210	0.52
	230	0.44
	250	0.97
	270	1.10
Al-2.5% Cu	190	3.11
	230	3.56
	270	3.37
	310	1.23
Al-3.0% Cu	190	4.54
	230	4.62
	270	5.17
	320	0.95
Al-3.5% Cu	190	8.28
	240	9.81
	290	7.67
	340	1.20

t_o = Time required for transformation of θ' to θ in as-quenched Al-Cu alloys.

t_c = Time required for transformation of θ' to θ in quenched, worked Al-Cu alloys.

4.4 DISCUSSION

As already pointed out, effect of cold working on precipitation has to be studied in two steps; namely, the effect on precipitation of intermediate phase and the effect on transformation of the intermediate phase to equilibrium phase.

4.4.1 Effect of prior cold working on Precipitation of θ' from α-Solid Solution

It has been observed by a number of worker (40,95,145-147) that, in general, dislocations act as potential sites for precipitation of a second phase from parent matrix: ~~and~~ The particular case of precipitation of θ' from α-solid solution preferentially on dislocations has been reported by Roberge et al (171). Since dislocations are created a as result of plastic deformation, increased number of nucleation sites are provided and the process of precipitation of θ' from α-solid solution should get accelerated as a result of prior plastic deformation.

Existence of strong interaction between dislocations and solute atoms is an established fact. This force of interaction has its origin in elastic (172) and electrical interaction (173) and has formed the basis of explanation for formation of atmospheres around dislocations and consequent appearance of yield point phenomenon. Although this concept was initially developed by Cottrell for interstitial atoms, it was later extended to substitutional atoms (174) and in turn explains the appearance of serrations on deformation i.e. the Portevin-LeChatelier phenomenon. The fact that serrations have been observed in Al-Cu (175) and Al-Mg (176) alloys, proves that there is strong interaction between these solute atoms and dislocations.

As a result of these interactions, the solute atoms get entrapped and their mobility decreases. So, the rate of precipitation is retarded. Dijkstra (177) has observed such decrement in the rate of precipitation of Nitrogen from α-iron as a result of cold working. Similar observations have been made by Wilson (178) with respect to precipitation of carbides during the process of tempering of quenched plain-carbon steel.

As a consequence of formation of atmospheres around dislocations, there is depletion of solute atoms in rest of the solid solution. Since the driving force for precipitation is due to supersaturation, any depletion of the solute atoms is prone to have a retarding effect on precipitation of θ'.

It may be argued that in light of experimental evidence presented by previous workers (179,180) there is strong evidence for dislocation climb in Al-Cu and Al-Mg alloys at about 150°C and hence there is little likelihood of effect of cold working being observed in the range of ageing temperatures under study. However, it should be noted that: (1) Even if recovery is to take place by a process of climb of dislocations, the process is not instanteneous; So the cold working will be effective in the initial stages of precipitation. If the time for recovery and that required for precipitation of θ' is of the same order of magnitude, then the effect of cold work is present thoroughout the process of precipitation; (2) As far as the accelerating effect of cold working is concerned the effect will be conspicuous even if the dislocation climb takes place just after nucleation of θ' is completed; (3) Climb of dislocation does not necessarily result is redissolution of solute atmosphere back into matrix. The electron micrographic evidence by Gane and Parkins (32) shows that the atmospheres that are formed around dislocations are stable to much higher temperatures even after dislocation climb is completed.

In summary, therefore, the effect of prior cold working on precipitation of θ' is:

(a) Acceleration due to potential sites created by dislocations;
(b) Retardation due to trapping of solute atoms around the dislocations; and
(c) Retardation due to depletion of solute atoms from solid solution.

It is the accelerating effect that normally predominates and the overall effect is acceleration of the process of precipitation of θ' due to cold working. The Retarding effect can be of significance only when substantial fraction of solute atoms available for precipitation get entrapped at dislocations and consequently there is an appreciable extent of depletion of solute concentration. This, in turn, is possible only when degree of supersaturation is small. Degree of supersaturation is a function of composition of alloy and temperature of ageing; lower the solute concentration and higher the ageing temperature, smaller is the degree of supersaturation. The fact that retarding effect, if present, is observeable only at higher ageing temperatures for a given alloy (fig. 4.1 and 4.2) is in confirmity with these disucssions.

This brings in the concept of "critical degree of supersaturation". If, for a given alloy, at the given temperature of ageing, the degree of supersaturation is higher than the critical value, then the result is acceleration of the process of precipitation of θ'. For 'degree of supersaturation' lower than the critical value, the effect of cold work is to retard the precipitation of θ'.

It is also seen that the alloys, with relatively higher solute concentrations, fail to show the retarding effect. The obvious reason for this behaviour is that recrystallization sets in these alloys at a temperature which is lower than that required for changeover from accelerating to retarding effect. Once recrystallization sets in, the effect of cold working is lost. Further support to these postulates is obtained by analysis of resistivity data.

4.4.2 Analysis of Resistivity Data

As already pointed out, the analysis of resistivity data shows three distinct processes which may be identified in light of known data in this system.

Process A: It may be noted that:

(a) This is the only process that accompanies ageing in alloys which have not been cold worked and is common to both the cold worked and uncold worked alloys;

(b) The activation energy associated with the process is in close agreement with the activation energy for precipitation of θ' reported by Hardy (33); ~~h~~ence it may be concluded that this process denotes precipitation of θ'.

Process B: Process B is associated with an activation energy which is in good agreement with the reported value (10,11) of activation energy for migration of vacancy/solute atom (Em) in the system under study. On the basis of reported values of activation energies associated with the process of recovery on annealing of a number of cold worked metals, Mott (181) has concluded that the activation energy associated with recovery is the one requied for motion of solute atoms. Recent resistivity studies made by Rosch et/al (170) on the recovery of cold worked Platinum also confirms the same. Hence it is reasonalbe to identify Process 'B' as the one involving climb of dislocations. Additional support to this conclusion is provided by noting that both the process under consideration and recovery process observed by Rosch et/al (170) represent second order reaction. However, these workers have reported that the initial stage of recovery in cold worked Platinum does not fall into a second order reaction. Analysis of Process B, on the other hand, failed to show any deviation from second order even in the early stage. This is to be expected since the initial stage of recovery, determined on the basis of resistivity measurements, is attributable (182,183) to annihilation of excess vacancies created during cold working. In the present study, there is little likelihood of this early stage being observed because the vacancies that are created as a result of cold working (which as a matter of fact should be negligible compared to the thermally trapped vacancies) should have got annihilated even during the process of heating the alloys to the ageing temperature.

Process C : The activation energy associated with this process is in close agreement with the reported value (184) of activation energy for diffusion of copper ~~of~~ in Aluminium. So, the process should be one involving diffusion of copper atoms in Aluminium lattice. Taking into account the fact that whenever process C occurs, it is always preceded by process B (denoting dislocation climb) and followed by process A (associated with precipitation of θ'), and in light of the arguments advanced with regard to stability of solute atmospheres even after the occurrence of dislocation climb, this process can be associated with redissolution of solute atmospheres back into solvent matrix after climb of dislocation has taken place.

In the light of what has been discussed so far, the sequence of processes that take place during ageing of cold worked alloy at different temperatures may be identified as follows:

1. Range of temperature over which the plot of log t_o/t_c Vs $\frac{1000}{T}$ has zero slope: Effect of prior plastic deformation on precipitation of θ' is fully retained. The accelerating effect is appreciably predominant and nucleation and growth of major part of θ' is completed before the process of climb of dislocations comes into operation.

2. Range of temperature over which the plot of log t_o/t_c has a positive slope: This part is itself capable of being subdivided into two parts:

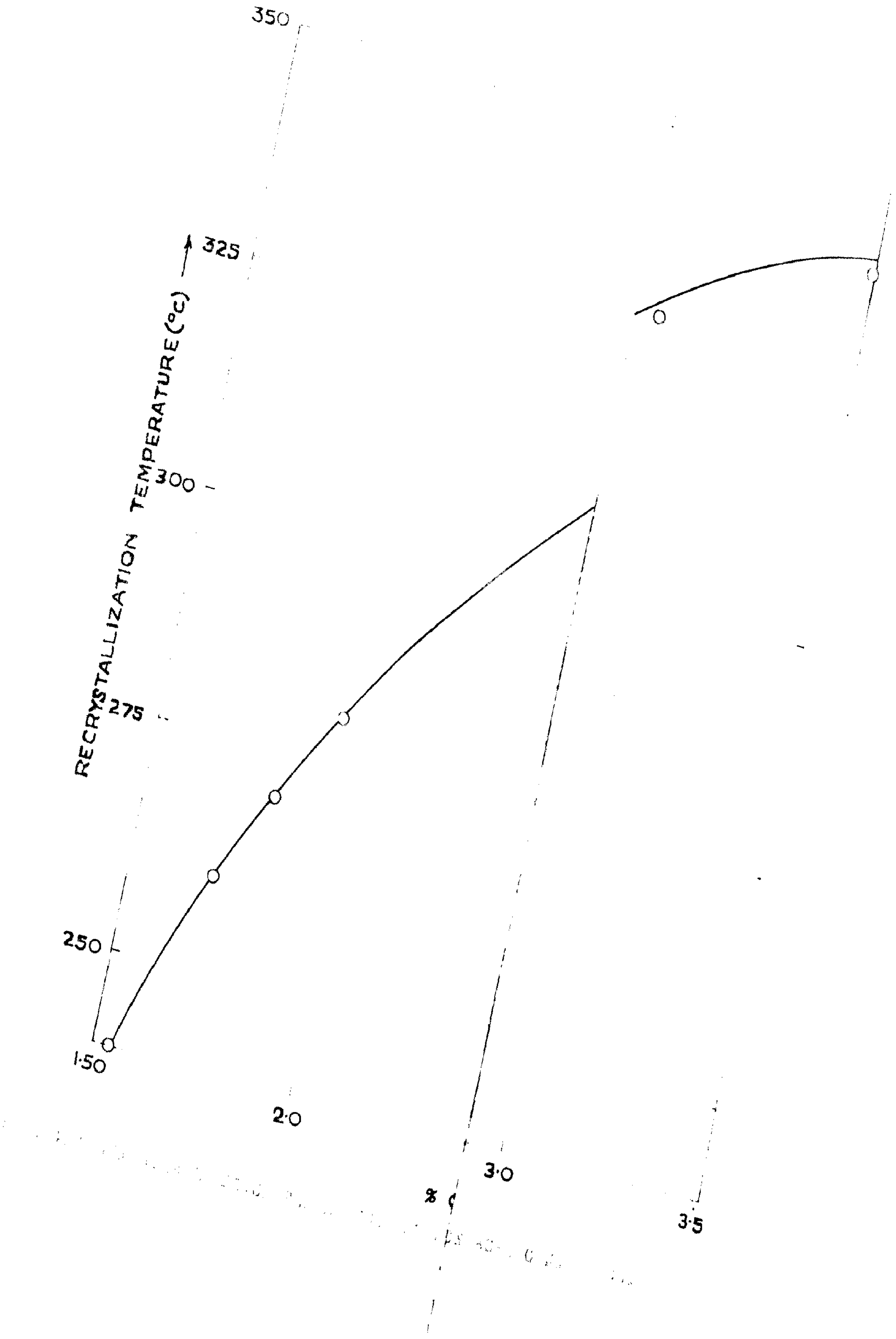
   (a) Log t_o/t_c is greater than zero: This part denotes a situation where both the accelerating and retarding factors are operative. With increase in temperature the process B (dislocation climb) starts overlapping larger part of process A (precipitation of θ'). However, process B is always preceded by nucleation of θ'. Hence the accelerating effect is present over the complete range. With increasing temperature, the degree of supersaturation decreases steadily thereby increasing the predominance of retarding effect.

(b) <u>Log t_o/t_c is less than zero:</u> The overall effect in this temperature range is retardation. The process of dislocation climb starts taking place even before θ' nucleates. Hence importance of accelerating effect is gradually lost. However, the retarding effect, associated with depletion of solute atoms in the parent matrix, assumes greater significance due to decreasing supersaturation.

It may be observed from fig. 4.1 that in this region, there is a reversal in the slope of the plot of log t_o/t_c versus $\frac{1000}{T}$, and the plot tapers off towards zero. This precisely is the region wherein process C (redissolution of solute atmosphere into the matrix) is observable. Hence, the sequence of processes that possibly takes place in this temperature range is climb of dislocations (resulting in loss of accelerating effect), redissolution of solute atmospheres that had formed earlier around dislocations (resulting in loss retarding effect) and then precipitation of θ' without either accelerating or retarding effect.

4.4.3 Recrystallization

It may be observed from fig. 4.1 that for every alloy, there is a particular minimum ageing temperature above which the


350
325
300
275
250
RECRYSTALLIZATION TEMPERATURE (°C)
1·50
2·0
3·0
3·5
% C

effect of cold working on the kinetics of precipitation of θ' is absent. This, coupled with the fact that, above these ageing temperatures, the initial hardness and resistivity of cold worked material drops down to the same level as that of material which has not been cold worked, establishes the identity of these temperatures as recrystallization temperatures for the respective alloys. Recrystallization temperature determined on this basis (from fig.4.1) is plotted as a function of solute concentration in fig. 4.3. These recrystallization temperatures are in good agreement with reported values.

The results obtained in the Al-Mg alloys where hardening effect is due to precipitation of β', can also be discussed on the same lines as for the Al-Cu system.

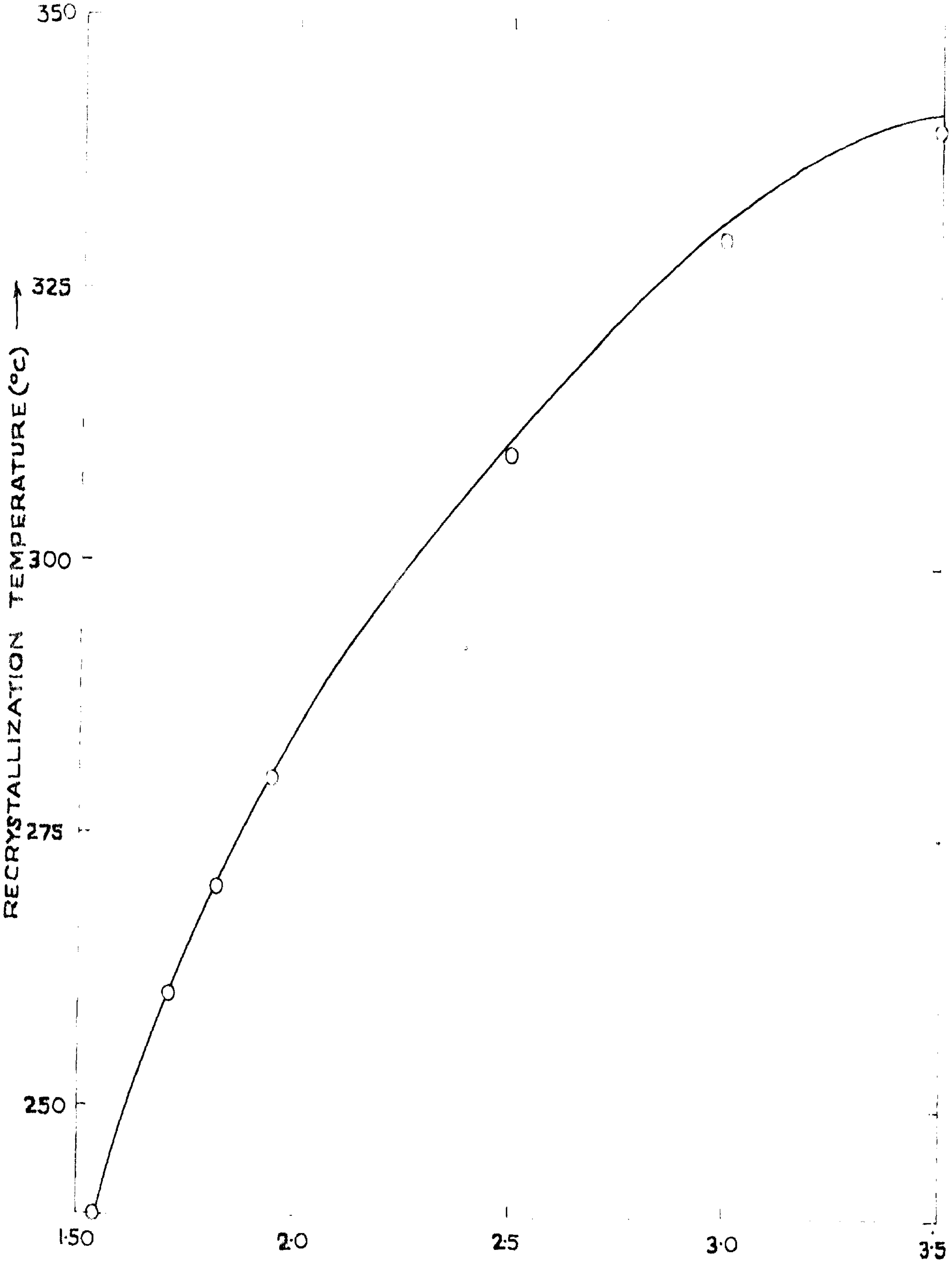
4.4.4 Effect of Prior Plastic Deformation on θ' to θ Transformation

From the observations made by a number of workers, there seems to be two distinct modes of transformation of θ' to θ. They are;

(i) Direct transformation by an allotropic modification(36,162); an

(ii) Dissolution of θ' platelets into the matrix and reprecipitation of θ (163,185,186).

Effect of prior plastic deformation on these two modes of transformation should be evaluated separately and the conditions under which one or the other transformation mode that operates


350
325
300
275
250
RECRYSTALLIZATION TEMPERATURE (°c) →
1·50
2·0
2·5
3·0
3·5
% COPPER →

[illegible] ALLOY [illegible]

effect of cold working on the kinetics of precipitation of θ' is absent. This, coupled with the fact that, above these ageing temperatures, the initial hardness and resistivity of cold worked material drops down to the same level as that of material which has not been cold worked, establishes the identity of these temperatures as recrystallization temperatures for the respective alloys. Recrystallization temperature determined on this basis (from fig.4.1) is plotted as a function of solute concentration in fig. 4.3. These recrystallization temperatures are in good agreement with reported values.

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(ii) Dissolution of θ' platelets into the matrix and reprecipitation of θ (163,185,186).

Effect of prior plastic deformation on these two modes of transformation should be evaluated separately and the conditions under which one or the other transformation mode that operates preferentially during ageing of an alloy is to be studied.

(i) Direct transformation by an allotropic modification:
In the first stage of growth of θ', all the interfaces between the matrix and θ' platelets are coherent, thereby rendering the platelets fully coherent with respect to matrix. However, with growth, the elastic strain energy associated with individual particles increases (25,26). As a result, at a particular stage of growth of θ', partial coherency sets in. Loss of coherency of the interfaces is accompanied by appearance of dislocation tangles around the platelets. These dislocation tangles known as Van der Merwe network (187-190) have been observed in many systems (191-193) including Al-Cu. Laird and Aaronson (144), have gone into theoretical details of appearance of such dislocation network.

The role of dislocation network as diffusion barriers for movement of solute atoms has been discussed by Garstone and Nileshwar (161), and is supported by observed suppression of θ' to θ transformation by creep loading. Thus, creation of diffusion barrier is inherent in the very process of growth of θ'. The effect of prior plastic deformation is to shift the appearance of diffusion barrier to an earlier stage of growth of θ' platelet. The stage at which dislocation network comes into existence is decided by (1) the mismatch between the parent matrix and the precipitate and

i) the state of lattice strain present in the matrix. nce plastic deformation leads to increase in lattice strain, e diffusion barriers should appear at an earlier stage of owth of θ' platelets in a cold worked material. As a sult, prior plastic deformation should lead to retardation θ' to θ transformation by allotropic modification.

ansformation of θ' to θ by a process of redissolution of θ' d precipitation of θ : The type of transformation require ucleation of θ as the first step. Since dislocations can rovide potential sites for nucleation of θ, the effect of lastic deformation should be to enhance the rate of transformation. ~~fact that~~ ucleation of θ has been observed to take place preferentiall t α/θ' boundary (160,185,186) and prior plastic deformatio elps to creat dislocation tangles at such boundaries (as lready discussed), it is evident that cold work should have n accelerating effect on θ' to θ transformation.

In light of these discussions, it is clear that the verall effect of prior plastic deformation on θ' to θ ransformation depends on mode of transformation. Since t is probable that both the modes may be operative imultaneously, it is the relative quantity of θ' that is ransformed by one or the other mode, that will decide the esultant effect. Of the two modes of transformation, the driving force for the latter (namely the one involving dissolution of θ' and reprecipitation of θ from α-solid solution) is provided by the solute atoms present in solid solution and this decides the kinetics of the transformation(160). Hence, the driving force for this mode of transformation is "degree of supersaturation" which, as already pointed out, is a function of composition and temperature of ageing. Hence for alloy with high degree of supersaturation, the overall of effect of cold working on θ' to θ transformation should be acceleration due to predominance of latter mode of transformation. On the other hand, for alloys with low degree of supersaturation the overall effect should be that of retardation due to predominance of former mode of transformation. This postulate is confirmed by the results reported in Table 4.3.

4.5 CONCLUSIONS

1. As a result of cold work, the process of precipitation of θ' from α-solid solution can be either accelerated or retarded.

2. Effect of cold working on the process of precipitation of θ' is critically dependent on the 'degree of the supersaturation' of the alloy at the given temperature of ageing.

3. On the other hand, effect of cold working on θ' to θ transformation seems to depend on mode of transformation and independent of its effect on precipitation of θ'.

n the basis of hardness curves, the conclusions arrived t for precipitation of θ' and transformation of θ' to θ n Al-Cu alloys can be extended to precipitation of nd transformation of β' to β in Al-Mg alloys.

he possibility of suppression of precipitation of θ' rom α-solid solution can form the basis of development f a suitable thermomechanical treatment for high emperature use of these alloys.

CHAPTER-V

STUDIES ON PORTEVIN-LeCHATELIER PHENOMENON ON SOME Al-Cu AND Al-Mg BINARY ALLOYS

5.1 INTRODUCTION

The first systematic study of appearance of serrated stress-strain curve in case of steel was made by Portevin and LeChatelier (195) in 1923. Hence the phenomenon is named as 'Portevin-LeChatelier effect'. The phenomenon of repeated yield is also termed as Type B yield. Type B yield is to be distinguished clearly from the usual sharp yield, termed as Type A yield, that occurs at the end of elastic deformation. Occurrence of repeated yield has been reported in a large number of systems like Soft iron (196), Al-Cu (175), Al-Mg (197,198), Al-Zn (199) and Duralumin alloys (176,200-202), α-Brass (203), Sn-bronze (204,205) and Uranium (206).

With extension of theory of yield to include both the interstitial (172,207) and substitutional (174) solid solutions, the phenomenon of serrated yielding in every system can be explained in terms of simultaneious yielding and strain-ageing. The important condition to be satisfied is that formation of atmosphere around the dislocation is so fast that when a dislocation gets released from an atmosphere and travels ahead, it is surrounded by next atmosphere resulting in repeated yields. Thus, for repeated yield to take place the solute atoms should have very high diffusion rate. The rate of diffusion of substitutional solute atoms can be enhanced substantially by increasing vacancy concentration. In majority of the cases that have been cited, the high level of vacancy concentration is achieved by plastic deformation. This, in turn, necessitates occurrence of some amount of plastic deformation before the appearance of repeated yield. The investigation presented in this paper which concerns with Al-Cu and Al-Mg alloys is based on the thermal vacancies trapped by a process of quenching from elevated temperature. The aim of these experiments was to evaluate activation energies of formation and migration of vacancies for the two systems under consideration.

5.2 EXPERIMENTAL PROCEDURE

5.2.1 Preparation of Alloys and Heat-Treatment

Binary Al-Cu and Al-Mg alloys of composition given in Tables 5.1 and 5.2 were cast as cylindrical rods and then forged and annealed. Tensile specimens with gauge length of 150 mm were machined out from these rods. The tensile specimens were given initial solution treatment of 48 hrs. at 520°C for Al-Cu alloys and 450°C for Al-Mg alloys. Further homogenization at appropriate temperature was carried out by step-quenching.

Table-5.1 Compositions of binary Al-Cu alloys

Alloy No.	Alloy 1	Alloy 2	Alloy 3	Alloy 4	Alloy 5	Alloy 6
Copper (atomic %)	0.45	0.65	0.88	1.02	1.42	1.67

Table 5.2 Compositions of binary Al-Mg alloys

Alloy No.	Alloy 1	Alloy 2	Alloy 3	Alloy 4	Alloy 5	Alloy 6
Magnesium (Atomic %)	0.107	0.156	0.194	0.243	0.327	0.361

5.2.2 Tensile Testing

A constant strain-rate apparatus similar to the one described by Krupnik and Ford (208) was constructed to give a constant strain rate of $\dot{\epsilon} = 1.4\text{x}10^{-4}$ Sec.$^{-1}$. Load on the tensile specimen was evaluated in terms of strain measurements made on a mild steel rod connected in series with the specimen. Appropriate arrangements were made for circulating water around the specimen so as to carry out the experiment at different temperatures.

Two types of experiments were conducted. One of them consi~~der~~sted in keeping the temperature of homogenization (T_H) constant and increasing the temperature of tensile testing (which is also the temperature of strain-ageing, T_a) in steps of 3°C till serrations appeared without any prior plastic deformation. Thus, the minimum temperature of strain-ageing, that is required for producing serrations in the as-quenched alloy for a given homogenization temperature, was determined. The other set of experiments consisted of keeping the temperature of strain-ageing (tensile testing) constant and increasing the temperature of homogenization (in steps of 10°C for Al-Cu alloys and 5°C for Al-Mg alloys) till serrations appeared in as-quenched alloys. Thus the minimum temperature of homogenization that is required for producing serration in the as-quenched alloy for a given strain-ageing temperature was determined.

5.3 RESULTS

Figs. 5.1 to 5.4 summarizes the results obtained on the binary Al-Cu and Al-Mg alloys.

5.4. DISCUSSION

5.4.1 Estimation of Activation Energies

The diffusion coefficient that is required to initiate Type B yielding in a given alloy is given by the expression (174,204);

$$D = \frac{K_1 \dot{\epsilon}}{p} \qquad (5.1)$$

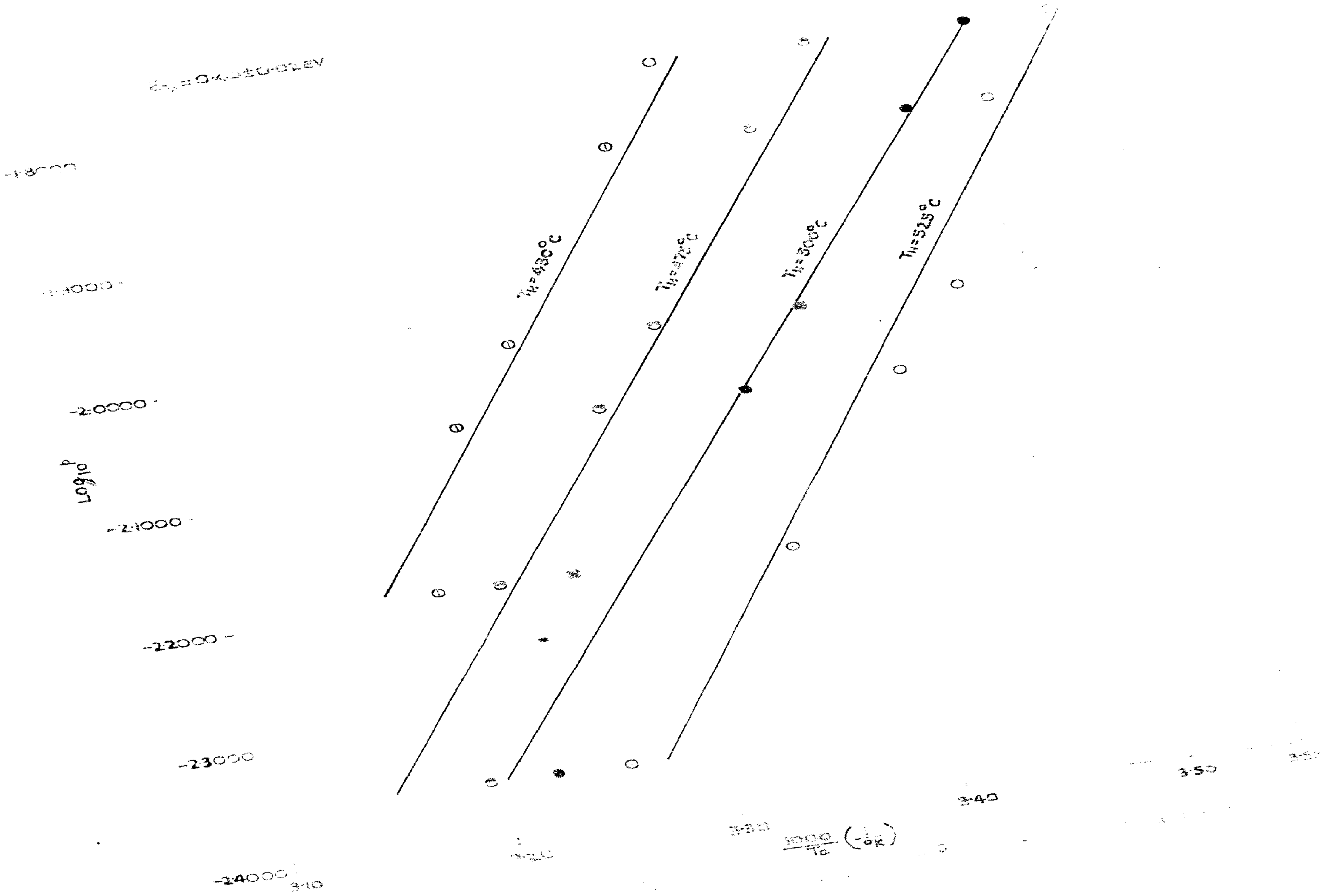
where D = Diffusion coefficient,

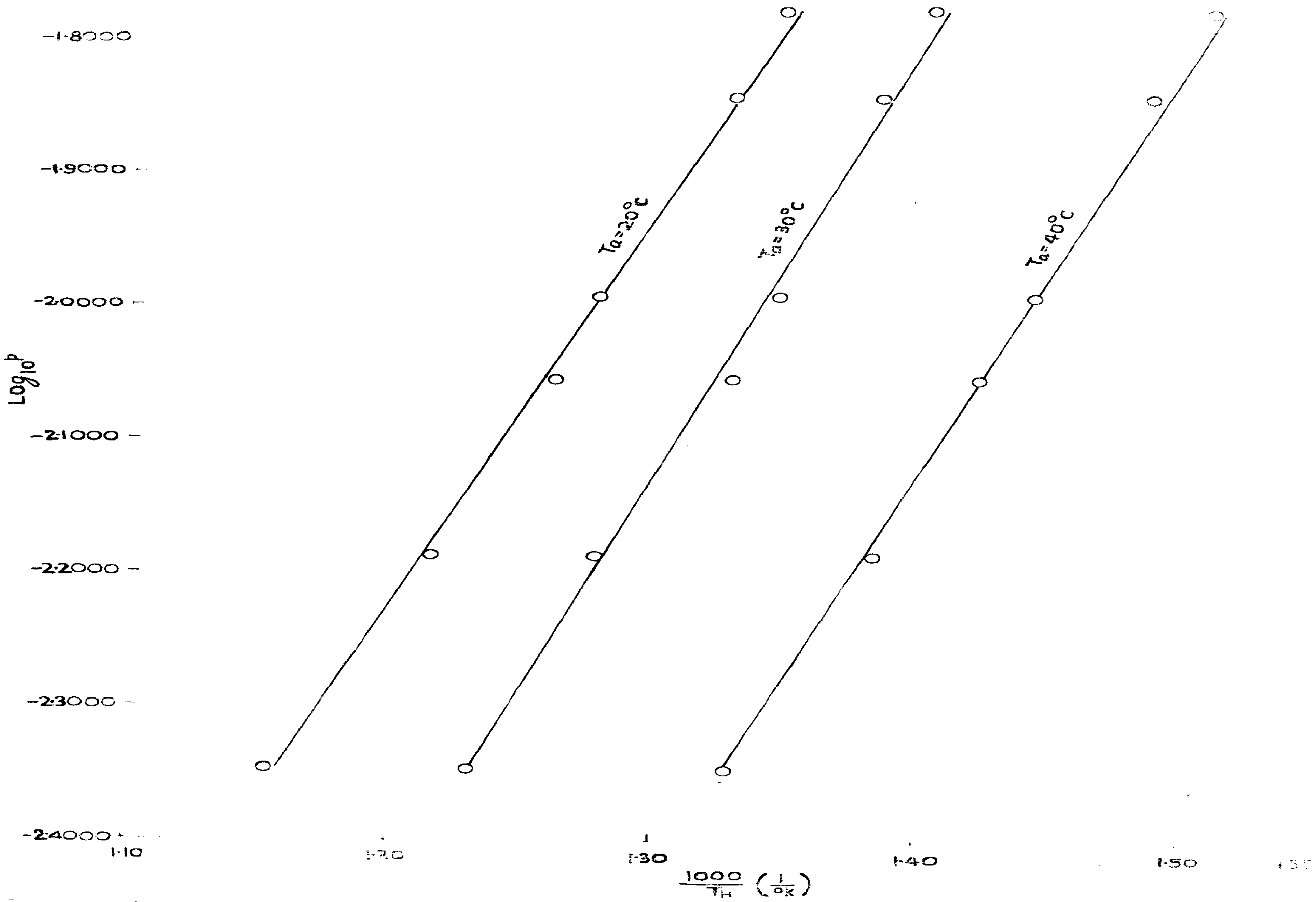
$\dot{\epsilon}$ = Strain rate,

p = Solute concentration in the alloy (expressed in atomic fraction),

and K_1 = Constant.

K_1 takes into account the interaction between the solute atoms and dislocations. The interaction has elastic (192) and electrical (173) origin. Higher the force of interaction, smaller is the value of K_1.


$E_A = 0\cdot4 \pm 0\cdot02$ eV
-1·8000
-1·9000
-2·0000
$\log_{10} p$
-2·1000
-2·2000
-2·3000
-2·4000
$T_H = 430°C$
$T_H = 475°C$
$T_H = 500°C$
$T_H = 525°C$
3·10
3·20
3·30
$\frac{1000}{T_D}\ (°K^{-1})$
3·40
3·50


-1·8000
-1·9000
-2·0000
-2·1000
-2·2000
-2·3000
-2·4000
$Log_{10}P$
1·10
1·20
1·30
1·40
1·50
$\frac{1000}{T_H}\left(\frac{1}{°K}\right)$
$T_a=20°C$
$T_a=30°C$
$T_a=40°C$

[illegible]

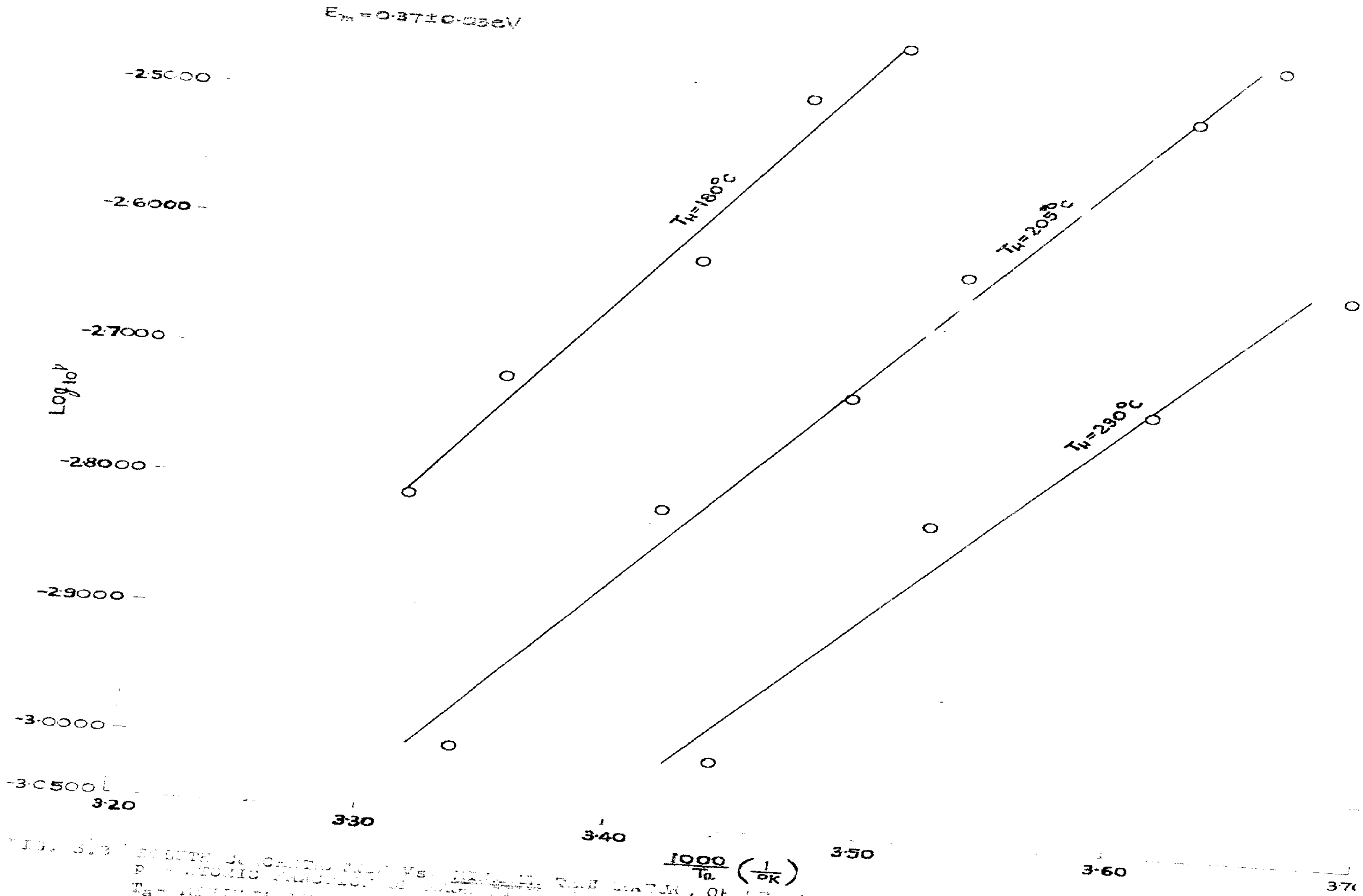


FIG. 5.[illegible] [illegible] Vs [illegible] OF [illegible] FOR Al-[illegible] [illegible]S.
P = [illegible]
Ta = [illegible]
TH = [illegible]

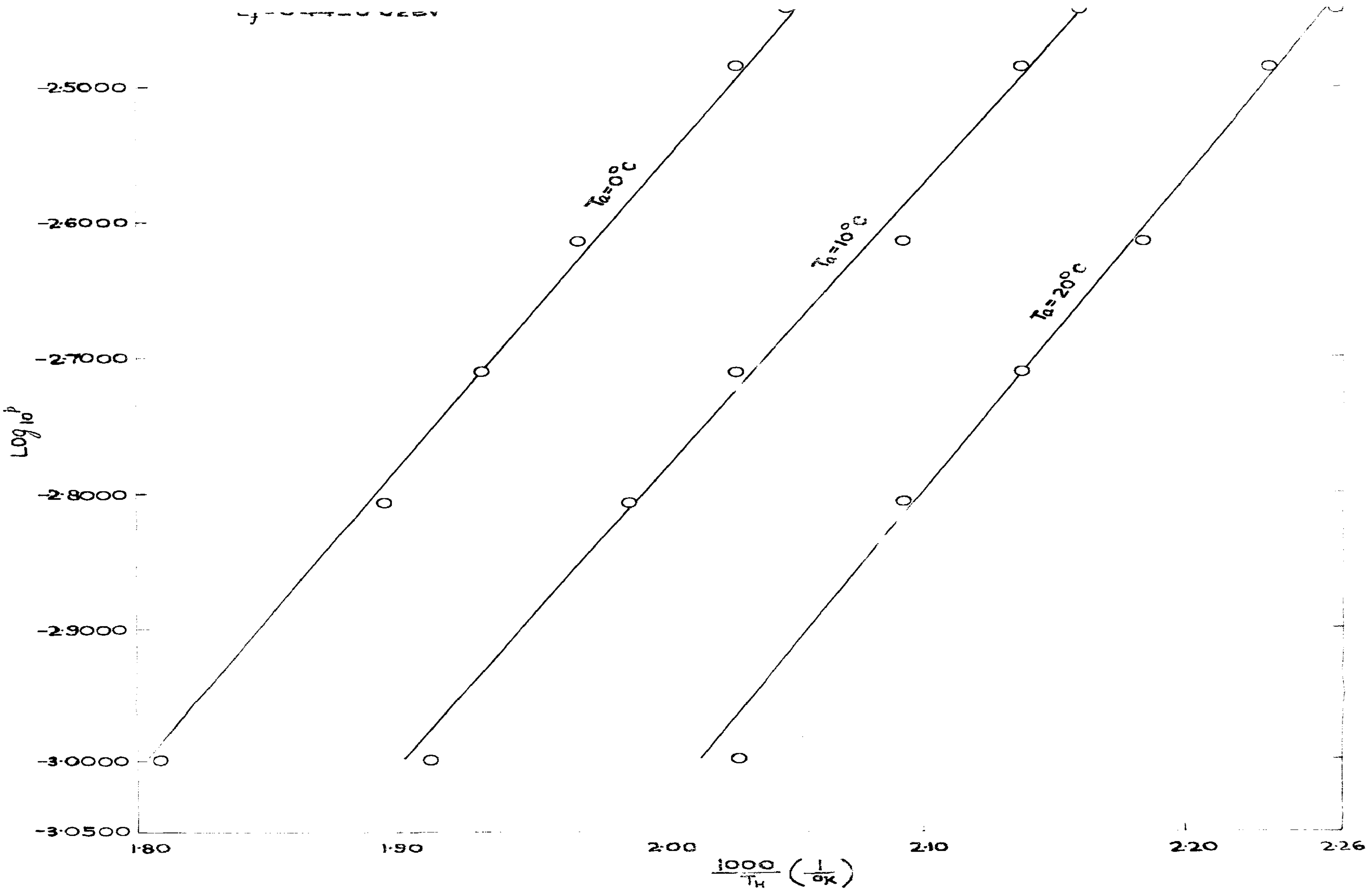


FIG. 5.2 SOLUTE CONCENTRATION [illegible] MONOCRYST[illegible]
p = ATOMIC FRACTION [illegible]
T_H = MAXIMUM TEMP[illegible]
T_a = TEMPERATURE [illegible]

If diffusion coefficient is vacancy controlled (which is true for the alloys under consideration since the solute atoms are substitutional in nature), then diffusion coefficient D of the solute atoms can be expressed as a function of vacancy concentration C_v by the relation:

$$D = a^2 \gamma Z C_v \text{ exp. } (-E_m/k\,T_a) \text{ ----------------------(5.2)}$$

where a = Interatomic spacing,

γ = Frequency of atomic vibration,

Z = Co-ordination number of the lattice,

E_m = Activation energy for migration of vacancies/solute atoms,

k = Boltzmann's constant,

and T_a = Temperature in °K.

Vacancy concentration C_v that is produced by quenching from homogenization temperature T_H is given by the relation :

$$C_v = A \text{ exp. } (-E_f/k\,T_H) \text{ ----------------------------(5.3)}$$

where A = Entropy factor,

and E_f = Activation energy for formation of vacancy.

Substituting equation (5.3) in equation (5.2);

$$D = Aa^2 \gamma Z \text{ exp. } (-E_f/k\,T_H) \text{ exp. } (-E_m/k\,T_a) \text{------(5.4)},$$

Hence serrations will occur when

$$Aa^2 \gamma Z \text{ exp. } (-E_f/k\,T_H) \text{ exp. } (-E_m/k\,T_a) = K_1 \frac{\dot{\epsilon}}{p} \text{ -----(5.5)}$$

where T_H and T_a refer to a set of minimum homogenization and strain-ageing temperatures required for producing serrations without any prior plastic deformation.

If the strain rate is constant, equation (5.5) reduces to;

$$p = K_2 \exp.\,(E_f/k\,T_H)\,\exp.\,(E_m/k\,T_a) \text{ -----------(5.6)}$$

where K_2= Constant.

E_m and E_f can be evaluated by plotting log p Vs. $1/T_a$ (with T_H = constant) and log p Vs. $1/T_H$ (with T_a = constant) respectively. Figs. 5.1 to 5.4 are such plots from which the activation energies have been evaluated.

In the analysis carried out, it is assumed that E_m and E_f are constant over the range of compositions and temperatures investigated. This assumption seems to be quite valid in light of the recent observations made by Berry and Orehotsky (14[illegible]). The variations, if any, in the activation energies are negligible compared with the inaccuracies inherent in the measurement.

Table 5.3 summarizes the activation energies of migration of vacancies/solute atoms estimated on the basis of present study and the values already reported.

Table-5.3 Activation energies of migration (E_m) of vacancies/solute atoms in binary Al-Cu and Al-Mg alloys.

System	Activation energy	Reference
Al-Cu	$E_m = 0.51$ eV	(10)
Al-Cu	$E_m = 0.51 \pm 0.05$ eV	(11)
Al-Cu	$E_m = 0.40 \pm 0.02$ eV	Present study
Al-Mg	$E_m = 0.35$ eV	(209,210,211)
Al-Mg	$E_m = 0.37 \pm 0.03$ eV	Present study

The value of activation energy of formation of vacancy (E_f) has been estimated as 0.60 ± 0.05 eV and 0.44 ± 0.02 eV in the Al-Cu and Al-Mg system respectively. The binding energy between the respective solute atom and vacancy can be evaluated on the lines suggested by Lomer (14). Value of $E_f = 0.76$ eV in pure Aluminium (212,213) is assumed for these calculations. The binding energies so evaluated are compared with reported values in Table 5.4.

Table 5.4 Binding energy between solute atoms and vacancies.

System	Bond	E_b	Reference
Al-Cu-Mg	Vac.-Mg	0.45 eV	(108)
Al-Mg	Vac.-Mg	0.20 eV	(214)
Al-Zn-Mg	Vac.-Mg	0.54 eV	(72)
Al-Zn-Mg	Vac.-Mg	0.36 eV	(134)
Al-Mg	Vac.-Mg	0.32 ± 0.02eV	Present study
Al-Cu	Vac.-Cu	0.10 eV*	(143)
Al-Cu	Vac.-Cu	0.12 eV*	(141)
Al-Cu	Vac.-Cu	0.10 eV*	(142)
Al-Cu	Vac.-Cu	0.16 ± 0.05eV	Present study

* These values are based on solute diffusion coefficients at 500°C.

5.4.2 Effect of Grain Size on Yielding

It has been reported by a number of workers that there is considerable effect of grain size on Type A and Type B yielding. Theoretical considerations and experimental observations (214-218) show that grain size is a critical factor which decides:

(a) The possibility of appearance of Type A yield and

(b) The activation energy associated with Type B yield.

McReynold (175) has observed that increase in grain size results in decrease of the plastic strain required for initiating serrations in Aluminium base alloys. Munz and Macherauch (219) and Vohringer and Macherauch (220) have also reported that the activation energy associated with appearance of serrations decreases with increasing grain size in α-Brass. In a recent paper Charnock (221) has explained the apparent grain size of dependence of the activation energy in terms of dependence of dislocation density, produced by plastic deformation, on the grain size (222). Charnock has further arrived at the conclusion that activation energy derived from experiment in which the critical strains involved are smaller than 0.1, are the most reliable. Since, no plastic deformation precedes appearance of serrations in the present experiments, the activation energies estimated in the present investigations are independent of grain size.

5.5. CONCLUSION

It is possible to initiate Type B yielding in Al-Cu and Al-Mg alloys without prior plastic deformation. The level of vacancy concentration, that is required for this process, can be produced by trapping thermal vacancies. Necessary degree of mobility of vacancies can be achieved by controlling the temperature of strain-ageing. From such sets of minimum homogenization and strain-ageing temperatures, activation energies of formation and migration of vacancies can be estimated.

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LIST OF PAPERS PUBLISHED/COMMUNICATED

(1) 'EFFECT OF COLD WORKING ON PRECIPITATION HARDENING' - Published in Mid-Year Number of Eastern Metals Review, 1968.

(2) 'EFFECT OF TRACE-ELEMENTS ON PRECIPITATION HARDENING' - Published in University of Roorkee Research Journal, Volume X, 1968.

(3) 'EFFECT OF RATE OF QUENCHING ON THE AGEING CHARACTERISTICS OF SOME TERNARY Al-Cu-Mg ALLOYS' - accepted for publication in Indian Journal of Technology.

(4) 'INITIAL SOFTENING IN SOME ALUMINIUM BASE PRECIPITATION HARDENING ALLOYS' - Presented at International Symposium on Non-Ferrous metallurgy held at N.M.L., Jamshedpur in Dec. 1968. Published in proceedings of Symposium (In Press).

(5) 'EFFECT OF COLD WORKING ON THE AGEING CHARACTERISTICS OF SOME Al-Cu and Al-Mg ALLOYS' - Communicated to Transactions of Indian Instit of Metals.

(6) 'STUDIES ON PORTEVIN-LeCHATELIER PHENOMENON ON SOME Al-Cu AND Al-Mg BINARY ALLOYS' - Communicated to Acta Metallurgica.