GRAIN GROWTH IN METALS

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ABSTRACT

The process of grain growth of four face-centred-cubic metals - lead, silver, copper and nickel has been investigated. The specimens used were in the form of small rectangular bars, at least 10 grains in thickness. The specimen had to be cross-rolled in order to reduce the grain size. The grains after cross-rolling appeared to be very irregular in shape but recrystallization from scattered nuclei produced an assemblege of grains of characteristic polygonal shape. With lead, the recrystallization takes place satisfactorily at atmospheric temperature but with other metals in question maintenance at a higher temperature is needed. After complete recrystallization, the specimens were raised successively to certain higher temperatures, at each of which the measurements of grain diameter were made, the surface of the specimen being etched before each grain count.

It has been established by Andrade & Aboav (1966) that maintenance at a fixed temperature leads ultimately to a stable average grain diameter D_e characteristic of the temperature, if the initial value of the diameter D_i, has been less than D_e. The relation between D_e and temperature T is

$$D_e^{\frac{1}{2}} = C(T-T_o)$$

where C and T_o are constants, characteristic of the metal.

This relation holds good for the metals of cubic structure namely lead, silver, copper and nickel. In the present work, we established the validity of the law of grain growth for the f.c.c. metals. In the case of lead, the increase of grain size with time falls into 3 stages as for the c.p.h. metals. (Andrade & Aboav 1966).

, as shown in the present work,

In stage I, for which the initial grain diameter D_i is very small compared to the equilibrium grain diameter, the grains grow very rapidly. In the extreme case at higher temperature, very near to the melting point of the metal, an approximating three-fold increase of grain size in 1 second was established.

In the normal stage, namely stage III, when D_i reaches a value of about 0.65 D_e, the grains increasing in diameter according to the law $D = D_e\,(1 + pe^{-qt})^{-1}$ where $q = ae^{-\epsilon/kT}$, giving an activation energy ϵ, which is 2.92 times the latent heat of fusion. Andrade and Aboav (1966) gave a value of 2.25 for the c.p.h. metals. Particular attention has been devoted to the grain growth in the normal stage, since in this case the observed grain growth, in accordance to the above law, is slow, permitting precise measurements. There is an intermediate stage to which not much attention has been devoted since it appears to be of relatively little significance. The difficulty with silver, copper and nickel was the inability to obtain sufficiently small grain size to permit grain count in stage I, so with these metals, most of the grain size measurements were made in stage III. It was found that the annealing atmosphere strongly influences the rate of growth as well as the stable grain size at the end of growth.

The statistical distribution of grain size was determined for all the four metals in question. The plots of grain size distribution for these metals are identical, in spite of the fact that each metal was maintained at different temperature to attain equilibrium grain size.

1. INTRODUCTION

The work of Andrade & Aboav (1966) on grain growth in metals of c.p.h. structure suggested systematic investigation to find if these laws of grain growth apply to metals of f.c.c. structure.

Tadanac lead, the purest lead available was the first of the cubic metals to be investigated.

It was found that, as established for c.p.h. metals, to each maintained temperature corresponded an equilibrium grain size and further that the variation of this equilibrium grain size with temperature obeyed the law established for c.p.h. metals. The distribution of grain size in an equilibrium state was found to be similar to, although not identical with, that valid for c.p.h. metals. These results apply to metals silver, copper and nickel as well as to lead, on which the main investigations were carried out.

2. GRAIN GROWTH

(A) Review

The work on the structure of metal started as early as 1829, when the French physicist Felix Savart published his remarkable paper. In spite of the inadequacy of research methods then available, it was an excellent piece of work. His studies were mainly connected with acoustic anisotropy in specimens cut from cast ingots of various metals. He concluded that cast ingots of such metals as lead, tin, zinc and copper were made up of crystal grains of different orientations. Savart found that heating an ingot to high temperature even near the melting point did not change the acoustic anisotropy. Plastic deformation of the ingot at room temperature however did bring about a great change and so did also annealing, if it was preceded by plastic deformation. This appears to be the first recorded evidence for a change in grain structure on annealing of a cold-worked metal.

In 1858, A.F. Nogues reported that platinum wire exposed to prolonged heating at high temperatures, below its melting point showed some crystals of very large size. John Percy in his monograph on "Metallurgy of iron and steel 1864" referred to the observation that bar iron and cold-rolled zinc sheet acquired a crystalline structure on long exposure to a temperature which though high was yet far below the melting point of the metals.

Kalischer (1881) appears to be the first to state explicitly the view that cold-worked metal sheet lacked marked crystalline structure, until it was annealed.

A paper by P. Curie published in 1885 dealt with the thermodynamic stability under the effect of surface tension of interfaces between crystals and saturated liquid solution. Curie recognized that the configuration of maximum stability corresponds to the single crystal state and that in the presence of a mixture of larger and smaller crystals in contact with the liquid, the large crystals, having greater stability, will tend to grow at the expense of smaller ones.

H.C. Sorby (1887) was able to resolve optically the outlines of the cold-worked grains in cold-hammered iron bar. He recognized that when distorted, the grain must be in a "state of unstable equilibrium" and that this instability is the reason why recrystallization "so easily takes place whenever the circumstances are such as to permit the particles to rearrange themselves in a state of stable equilibrium" i.e. the temperature is sufficiently high.

G. Charpy in 1893, described the cold-rolled structure of polycrystalline brass as 'amorphous' probably because his metallographic techniques were not sufficiently good to allow him to discern the cold-worked grains. In 1898, Stead demonstrated that in addition to temperature, the duration of anneal is also of great importance to the formation of coarse grains in ferrite.

Although the work of Sorby and of Stead already showed the presence of crystalline grains even in heavily cold-worked metals, it was not until the publication of a lecture by Ewing and Rosenhain in 1900 that the idea of metal becoming amorphous on cold-working was decisively shown to be wrong. Having excellent metallographic techniques, they were able to observe slip-bands and etch pits and demonstrated that the structure of metals is crystalline even under conditions which might be supposed to destroy crystalline structure.

Stead believed that grain growth takes place by gradual orientation change in the entire volume of certain grains until their orientation is exactly the same as that of a neighbouring grain at which point the intervening boundaries suddenly disappear in coalescence. On the contrary, Ewing and Rosenhain recognized that grain growth takes place by boundary migration.

In discussing boundary migration they claimed that "the action is one of solution and diffusion of the pure metal constituting the crystals into the fusible and mobile eutectic forming the intercrystalline cement. This diffusion results in the grwoth of one crystal at the expense of the other crystal, owing to the differences in solubility of the crystal faces on opposite sides of the eutectic film and it seems probable that this phenomenon of directed diffusion is really a form of electrolysis".

Humfrey (1902) was able to detect recrystallization taking place at room temperature over a period of time after his single crystal lead specimens had been strained by bending or tension. He also observed that the rate of recrystallization increased with increasing temperature.

In 1914, Rosenhain presented a revised version of his "eutectic film theory" and called it "amorphous cement theory". In this modified theory, the ideas of electrolysis and breaking up of intergranular layers were abandoned and there remained under the name of recrystallization a reasonable and clear formulation of what is now called normal grain growth. Rosenhain refers to the "universal tendency of the constituents of crystalline aggregate to increase in size and to decrease in number." Accordingly some of these crystals grow at the expense of their neighbours.

Grard (1908), Bengough and Hudson (1910), considered recrystallization as a result of the instability of the cold-worked state. They observed that after the completion of recrystallization the new grains rapidly grow at each others expense. They also found that at a given annealing temperature, after a certain time rapid grain growth slows down and the size of the crystal approaches a value characteristic of the temperature - ultimate grain size.

H. Altarthum (1922) recognized that both the stored energy of cold-work and the interface energy of the grain boundaries may serve as driving energy for grain boundary migration, and that accordingly, two different boundary migration processes may take place on annealing;recrystallization (cold-work recrystallization) and grain growth, (surface tension recrystallization).

Chappel in 1914 once again revived Stead's suggestion of "coalescence of adjacent grains by means of a gradual orientation change in the entire volume of certain grains during annealing". Robin in the same year observed the migration of boundaries directly by means of a microscope on the polished surface of a variety of metals. The boundaries became visible as dark lines on the polished face when the specimen was heated, presumably due to the offset resulting from differences in the vapour pressure of disordered layers.

The work of Carpenter and Elam (1920) proved conclusively "that growth always took place by boundary migration and not by coalescence". They found that at higher deformations, annealing produced a decrease of grain size and for strains above a certain value, annealing may actually produce a grain size smaller than that before the deformation preceding anneal. This they attributed to the growth of new grains from recrystallization centres.

Carpenter and Elam also studied the formation of very large grains in rolled commercial aluminium after prolong annealing at high temperatures, where primary recrystallization resulted in a small grain size and was completed long before the large grains started to grow.

Jeffries (1916) work represents the most significant contribution to the understanding of grain growth. He suggested that the condition of the formation of very large grains growing at the expense of a fine-grained strain-free matrix is the inhibition of normal grain growth in the matrix itself by finely dispersed particles of foreign metals.

The work of H.W. McQuaid (1935), Feitknecht (1926), Mathewson and Phillips (1927) and Masing (1921) clearly demonstrated that inhibition of growth and coarsening occurred only in materials of commercial purity. Masing also showed, that in addition to annealing temperature, duration of anneal is also of great importance.

In recent years, works of Burgess (1941), Burke (1949), Burke and Turnbull (1952), C.S. Smith (1948), Beck (1954), Andrade and Aboav (1966), have greatly improved our understanding of recrystallization and grain growth in metals.

(B) Theory of Grain Growth

(i) Introduction

When a metal is cold-worked a certain amount of energy is stored in it. There are several basically different methods by which release of stored energy is accomplished. Two of the most important ones are:

(a) Anisothermal anneal method.

The cold-worked metal is heated continuously from a lower to a higher temperature and the energy release is determined as a function of temperature.

(b) Isothermal annealing.

Here the release of stored energy is measured while the specimen is maintained at a constant temperature.

The free energy of a deformed metal is greater than that of an annealed metal by an amount approximately equal to the stored strain energy. The effect of plastic deformation is to increase the entropy of a metal but it is small compared to the increase in internal energy - the retained strain energy. Neglecting the term (-TS) in the free energy equation, the free energy increase may be directly equated to the stored energy

$F = E - TS$ becomes

$$F = E$$

where F = free energy associated with cold-work.

E = internal energy (or stored strain energy).

S = entropy increase due to cold-work.

T = Absolute temperature.

Since the free energy of cold-worked metal is greater than that of annealed metals, they may soften spontaneously.

Annealing a cold-worked metal results in three different processes occurring in the metal.

Recovery

Recrystallization

Grain growth

(ii) Recovery

In the recovery stage of annealing the physical and mechanical properties that suffered changes as a result of cold-working tend to recover their original values. While a complete explanation of the recovery process has not been achieved, much has been learnt about it in the past decade.

The rate of recovery in crystals deformed by simple glide can be expressed in terms of a simple activation or Arrhenius type law, of the form

$$\frac{1}{t} = Ae^{-Q/RT}$$

where t = time required to recover a given fraction of the total yield-point recovery.

Q = activation energy.

R = universal gas constant.

T = absolute temperature.

A = a constant.

Another recovery process called polygonization is normally associated with crystals that have been plastically bent. Polygonization involves dislocation climb, consequently higher temperatures are required for rapid polygonization. At low temperature recovery process is considered as a matter of reducing the number of point defects to the equilibrium value. The most important point defect is a vacancy which may have a finite mobility even at relatively low temperature.

(iii) Recrystallization

Recovery and recrystallization are two basically different phenomenon. In an isothermal anneal, the rate of recovery always decreases with time i.e. it starts rapidly and proceeds at a slower and slower rate as the driving force for the reaction is expended.

Recrystallization occurs by nucleation and growth process. It begins very slowly during an isothermal anneal and builds up to a maximum reaction rate. After which it finishes slowly.

The recrystallization temperature varies from metal to metal and depends on the amount of deformation. The higher the deformation, the lower will be the temperature at which the metal will recrystallize.

The rate of recrystallization can also be described by Arrhenius type equation

$$\text{rate} \quad \frac{1}{t} = Ae^{-Q_r/RT}$$

Q_r = activation energy for recrystallization.

R = gas constant (2 cal/mole °K).

T = absolute temperature.

A = a constant.

$\frac{1}{t}$ = rate at which 50% of the structure is recrystallized.

The rate of recrystallization depends on two important factors.

(a) Nucleation rate (N) - number of nuclei that form per second in a c.c. of unrecrystallized matrix.

(b) Nucleus growth rate (G) - rate of change of diameter of a recrystallized grain.

These factors depend in turn on

(i) Grain size before deformation.
(ii) Amount of deformation.
(iii) Annealing temperature.
(iv) Purity of the metal.
(v) Annealing atmosphere.

In practice G, is measured by annealing a number of identical specimens for different lengths of time at a chosen isothermal temperature. The diameter of the largest grain in each specimen is measured after specimens are cooled to room temperature and prepared metallographically. The variation of this diameter with isothermal annealing time gives the rate of growth G.

The rate of nucleation can be determined from the same specimen by counting the number of grains per unit area on the surface. These surface density measurements can then be used to give the number of recrystallized grains per unit volume. The early work of Humfrey (1902) showed clearly that many new grains may form when a strained single crystal is allowed to recrystallize. Similarly in heavily deformed polycrystalline metals recrystallization results in many new grains. New crystals are nucleated at points of high lattice strain energy such as slip line intersections, deformation twin intersections and in areas close to grain boundaries. Humfrey's work also showed that the number of nuclei which start to grow on recrystallization increased with the degree of deformation.

The driving force for recrystallization in fact comes from the stored energy of cold-work. It was Van Liempt (1931) who first suggested that some kind of thermally activated mechanism must operate to transform on annealing some of the most highly strained regions of the grains into strain-free ones. With the development of the nucleation during recrystallization after plastic deformation, Von Goler and Sachs (1932) investigated the possibility of describing the kinetics of recrystallization process i.e. the increase of the recrystallized volume fraction with annealing time at a constant temperature in terms of rates of nucleation and growth.

It is a well-known fact that extremely pure metals have very rapid rates of recrystallization.

It has been observed that the change in the recrystallization temperature caused by the presence of foreign atoms depends markedly upon the nature of solute atoms. The fact that very small number of solute atoms have such a pronounced effect on recrystallization rates is believed to indicate that solute atoms interact with grain boundaries. The proposed interaction is similar to that between dislocation and solute atoms. When a foreign atom migrates to a grain boundary both its elastic field as well as that of the boundary are lowered. In recrystallization grain boundary motion occurs as the nuclei form and grow. The presence of foreign atoms in atmospheres associated with grain boundaries strongly retard the motion and therefore the rate of recrystallization.

(iv) Grain Growth

Theories of grain growth

A number of theories dealing with grain growth in metals which have been put forward in the past are summarized here.

(1) Ewing and Rosenhain's Eutectic layer hypothesis

According to this hypothesis, the metallic impurities which are present in a metal play an important part in the mechanism of grain growth. When a metal solidifies from a fluid state, the metallic impurities separate into a fusible and mobile eutectic forming the intercrystalline cement, an example being the pearlite layer in slowly cooled mild steel. The changes of crystalline structure are due to the action of eutectic film between crystals, dissolving metal from the surfaces of some crystal grains and depositing it on the surfaces of others. This solution and deposition results in the growth of one crystal at the expense of other crystals owing to the difference in solubility of the crystal faces due to differences of orientation of the crystals on either side of the intercrystalline cement.

When a metal is severely strained, these films of eutectic will also be strained and in many places broken, thus allowing the actual crystals to come into contact with one another. Ewing and Rosenhain (1901) supposed that there was a difference of electric potential between the faces of crystal grains which are brought into contact by severe strain. Assuming that a film of eutectic alloy, when fluid or in the pasty condition that precedes fusion, can act as an electrolyte, any two crystals thus in contact may be regarded as a very low resistance circuit and growth of the positively charged crystal at the expense of negatively charged one would result. Such growth would be enhanced at higher temperature and its rate at a given temperature would vary in different specimens according to the nature and quantity of the impurities present.

A consequence of this hypothesis is that an intercrystalline boundary containing no eutectic would be an impassable barrier to crystalline growth, but if the eutectic could in any way be supplied, growth across the boundary might take place. In an absolutely pure specimen, there would be no eutectic at the intercrystalline junctions, but minute traces of impurities would have a local effect sufficient to set up the action.

The view that in the purest metals, there is sufficient impurity to surround the crystal completely, has been proved wrong (Carpenter & Elam - 1920). Moreover this theory fails to explain why growth occurs in a worked and annealed metal when impurities are no longer in the crystal boundaries but are distributed throughout the crystal grains themselves.

(2) Amorphous film theory

Rosenhain & Humfrey (1913) substituted a layer of amorphous metal for the eutectic cement of Rosenhain's earlier theory. Rise of temperature would cause an increased vibration in the crystal as well as in the amorphous cement layer, a consequence of which might be that the free atoms would join several others and together they might form a new crystal unit.

(3) Jeffries (1918) proposed that when the temperature is such that grain growth occurs, an atom forming part of an amorphous structure will be forced into regular arrangement owing to its greater vibrational energy. The equilibrium between amorphous and crystalline phases is now disturbed and the heat of recrystallization of the amorphous atom causes the other amorphous atom to vibrate still more and this tends to "amorphise" an atom from the smaller and hence weaker crystal.

The author has shown that the cohesion of the amorphous phase of a metal is the same as that of the crystalline phase at the lowest recrystallization temperature, but decrease in cohesion is faster in the amorphous phase than in crystalline phase with the rise in temperature. This is indicative of the fact that both the amorphous and crystalline phases must reach a condition of considerable mobility before grain growth occurs provided cohesion of the crystalline phase is greater than that of the amorphous phase.

Neither of these theories account for the absence of growth in cast metals since there is presumably an amorphous (intercrystalline) cement layer between such grains or there is some fundamental difference between the boundaries of castings and those of worked and annealed metals.

(4) Chappell (1914) suggested two possible explanations of the role of plastic deformation, in promoting the union of ferrite grains.

(a) If the identity of orientation is the only condition necessary for union of adjacent crystals as the Tammann hypothesis assumes, then the plastic deformation may be considered to increase the potential energy of crystals, thus enabling them to bring the rotation of their axes parallel to each other with greater ease and rapidity on the rise of temperature.

(b) The union of ferrite crystals may be considered analogous to the welding together of two pieces of iron in which work is necessary to break up any separating layer of oxide or flux and thus establish molecular contact between metallic surfaces.

Such a view would be compatible with Ewing and Rosenhain's conception of a layer of inter-crystalline cement, the local vanishing of which might be regarded as being a function of plastic deformation. This will allow the actual crystals to come into contact and at a sufficiently high temperature weld together directly and not by a process of gradual transference. The idea of crystal growth taking place by a sudden complete coalescence between two crystals had to be discarded and it is now generally held that grain growth takes place gradually by boundary migration.

Z. Jeffries (1918) classified the grain growth in metals into two classes; (a) Normal grain growth

(b) Abnormal or exaggerated grain growth.

Normal grain growth occurs when a metal is composed of grains or grain fragments smaller than what would be under given conditions, the equilibrium size, provided the usual grain growth laws were obeyed. Jeffries suggested that any metal consisting wholly or largely of grains of a single metal will result in a single grain, if annealed for a sufficiently long time at a temperature slightly below the melting point of the metal.

In abnormal grain growth, some grains grow faster than the others, due perhaps to strain gradient or temperature gradient. This differential range of growth is most pronounced within a certain temperature range called "germinative temperature range". Certain grain growth laws have been formulated by different workers which are summarized here.

(i) The attacking power of a grain increases with its size and grain size contrast favours grain growth.

(ii) The velocity of grain growth increases as the temperature increases. There is no grain growth below the recrystallization temperature of the metal.

(iii) A grain which has been deformed below its recrystallization temperature, no longer acts as a unit as regards grain growth, but acts as if it had been disintegrated into fragments smaller than the initial grain size and these become still smaller as the degree of deformation increases, as the temperature of deformation decreases, and as the grain size prior to deformation decreases.

(iv) Any process of deforming metals below their recrystallization temperature produces different degrees of strain in different parts of the metal, owing to directional properties of grains. These differential strains, called strain gradient, may cause abnormal or exaggerated grain growth.

(v) For exaggerated grain growth, a temperature gradient is favourable, provided of course that the average temperature be high enough.

(vi) The higher the germinative temperature, the quicker will large grains develop and the grains will usually be larger.

(vii) If the grains or grain fragments, at the germinative temperature are much smaller than the equilibrium grain size at that temperature, the formation of coarse grained structure will be facilitated.

(viii) The rate of heating a metal through the germination temperature range will determine to a large extent the resulting grain size. If the temperature is raised quickly above that of germination, a fine grained structure will be produced.

(ix) The recrystallization time diminishes as the annealing temperature increases.

(x) Impurities in the metal increase the recrystallization temperature and reduce the growth rate as well as the grain size.

Burke (1948) established that the driving force of grain growth in annealed metals was essentially the surface energy (surface tension) of the grain boundaries which impelled the boundaries to migrate towards their respective centres of curvatures. Smith (1948) considered grain shapes and other relevant metallurgical applications of topology and Beck (1954) reviewed some of the more recent experimental work on grain growth. Cole, Feltham and Gillham in 1954 found for isothermal growth, a relation between the most probable instantaneous and the initial diameter, namely

$$(D^2) - (D_o{}^2) = K_o t \exp(-{}^H/kT)$$

where D_o, D are the initial grain diameter and the most probable instantaneous grain diameter respectively; t the time, T absolute temperature and H the activation energy for grain boundary self-diffusion. K_o is a constant proportional to lattice spacing and specific surface energy at grain boundaries. The magnitude of K_o for annealed metals should be about 0.1 cm^2/sec.

It is now generally believed that grain growth takes place by boundary migration and not by a sudden complete coalescence between two crystals. The driving forces leading to grain boundary migration in crystalline materials are determined not only by physical constants, characteristics of the substance in bulk, but also by the shapes and dimensions of the individual grains. Parameters characterising the dimensions and shapes of the distribution of grains in an aggregate must therefore appear as variables in the time laws of grain growth.

Feltham (1957) carried out extensive studies on the rate determining mechanism of grain growth and found for isothermal growth a relation between the initial and instantaneous grain diameter D_o, D and the time t for isothermal growth, namely

$$(D^2) - (D_o)^2 = ({}^{\lambda Va\,\sigma}/{}_h)\; t \exp(-{}^H/kT)$$

where λ = a numerical constant of order unity

V = volume per atom

a = lattice spacing

σ = specific grain boundary energy h = Planck's constant

H = activation energy for grain boundary self-diffusion.

Cahn (1950) undertook to explain the initiation period of nucleus growth on the following lines. After cold-working, when the dislocations have come to rest, further movement will essentially be controlled by a thermal activation process effecting either the surmounting of potential barriers of dislocations crossing each other or marked diffusion.

Climb of single dislocation or dislocation networks is governed by diffusion in the 'good' material around the dislocation.

When a specimen is maintained at a higher temperature, the dislocations are caused to move by some thermal activation process. The dislocation clouds then tend to contract so that the dislocation-free areas grow. The process would continue until the whole area was covered with sharply separated sub-grains, if recrystallization did not intervene.

It is well-known that a crystal grain is able to grow, when by its growth, the free-energy content of the system is lowered. The total free energy change of a grain is made up of the loss in volume free energy and the gain in surface free energy.

For a spherical grain, the free energy is

$$F = F_s \, 4\Pi r^2 - \Delta F_v \, \frac{4\Pi}{3} \, r^3$$

$$r_c = \frac{2F_s}{\Delta F_v}$$

where F_s = surface free energy/unit area.

ΔF_v = difference in volume free energy

r_c = critical radius

F_s is determined by the density of the network of dislocations forming the boundary.

ΔF_V is correspondingly determined by the volume density of dislocation networks adjoining the nucleus. Thus the critical radius, r_c, is not a constant but varies from point to point.

For a very small grain, the free energy will increase with radius and then, from a critical radius r_c, it will drop, which means that for $r > r_c$ the grains will grow spontaneously. As Mott (1948) pointed out, the velocity of grain growth cannot be understood in terms of the movement of single atoms but requires the assumption that larger clusters or different layers of atoms are in movement at the same time. The growth is very discontinuous. The large grains are sometimes formed in a very short time and afterwards undergo no considerable change. In other cases, they stop growing for a certain period and afterwards increase again.

W. Feitknecht (1926) assumed that in a recrystallized metal, various grains have a different amount of internal energy, the grains with the least amount of energy being thermodynamically the most stable. Accordingly all the grains in the metal will tend to reach this state. One way in which this can be done is by grains, with least energy, absorbing those with greater energy. This process will be impeded by certain resistances e.g. insoluble impurities.

The grain growth will take place, when difference of energies are great enough to overcome the resistances. The resistances are much reduced at high temperature.

The difference of energies specific to the grains may be due to,

(a) Surface energy

(b) Internal energy

(a) Surface energy:

Two factors mainly determine the surface energy - grain shape and size.

It was shown by Vogel (1923) that in certain cases, especially in lead cast on a glass plate, the shape may be the cause of a boundary migration, and that ragged boundaries tend to straighten, convex parts being absorbed by the concavities of the adjoining crystals, but this can cause only small changes.

Jeffries (1918) sees the chief cause of grain growth in the grain size contrast. This view was proved wrong by Tammann, Meissner and Pawlow (1920).

(b) Internal energy:

The internal energy may be due to difference of composition and to remaining internal strain. Differences of composition are non existent in the case of pure metals so the grain growth will be due to the remaining internal strain in the metal due to deformation. The differences of the remaining strains in different crystal grains are greater the more severely worked the samples have been. In very thin sheet of free metal, the crystals can form with greater freedom, because they are near the surface, which imposes no constraints. As the sheet becomes thicker the number of grains which are surrounded by at least one or two layers of other grains becomes greater and consequently the grains become smaller approaching an equilibrium size which pertains to a thick sheet.

The activation and growth of a nucleus requires a particular level of energy, which is the sum of strain energy and thermal energy.

The amount of deformation given to the material should exceed a certain minimum for recrystallization to occur under usual annealing conditions. For a particular input of thermal energy, in terms of annealing temperature and time, abnormally large grains will form upon recrystallization in a metal which has received a particular amount of deformation,called the critical strain. The larger the thermal energy supplied the smaller the strain energy required to obtain the same result.

It is possible for crystals to grow as a result of strain energy induced in the lattice by cold-work. Strain-induced boundary migration ceases after complete recrystallization. There are no new crystals formed during strain-induced boundary migration. As the movement occurs, the boundary leaves behind a crystalline region where the strain energy is lower than it is in the region still to be traversed. In contrast to boundary migration induced by surface tension, this form of boundary movement occurs in such a manner that the boundary usually moves away from its centre of curvature. One of the interesting aspects of strain-induced boundary migration is that the movement of the boundary of the grain, instead of lowering the surface energy, may actually increase it in consequence of the increase in area.

Beck et al (1947) have shown that if one assumes the rate of grain growth to be proportional to the total extent of grain boundary present in a specimen, then the rate of growth should be inversely proportional to the average grain diameter.

A similar relationship can be derived if it be assumed that the rate of grain growth is inversely proportional to the radius of curvature of the grain face in question. Harker & Parker (1945) contend that grain growth should continue as long as the grain face is curved.

Effect of sheet thickness on the rate of grain growth

Beck et al (1947) first demonstrated that under conditions of continuous grain growth the maximum grain diameter approximates to the thickness of the sheet within certain limits.

Burke (1948) reported that growth is more rapid in thick sheets than in thin ones, although for low temperature and short annealing times, when the grain size was small, compared to the dimensions of the sheet, there was little difference. In the thinnest specimen the equilibrium grain size approximated to the thickness of the specimen but with increasing specimen thickness, it increased less rapidly than the specimen thickness. Beck (1954) estimated from experimental data that when, with metal sheets, the grain size becomes larger than 1/10th the thickness, the growth rate decreases because of the free-surface effect. In extreme cases, this free-surface effect can completely stop grain growth. The grain boundary near any free surface of a metal specimen tends to lie perpendicular to the specimen surface, which has the effect of reducing the net curvature of the boundaries next to the surface. This means that the curvature becomes cylindrical rather than spherical, and in general, cylindrical surfaces move at a slower rate than spherical ones with the same radius of curvature. In all our experiments specimen thickness was always more than ten times the equilibrium grain size, so the sheet thickness or the free-surface effect did not affect our results.

Effect of impurity atoms and impurities in the form of inclusions

Any factor which interferes with grain boundary migration can retard grain growth although grain faces and interfacial angles have not attained equilibrium configuration. It has been recognised that foreign atoms in a lattice can interact with grain boundary migration. (Carpenter & Elam 1920, Burke 1948, C.S. Smith 1948)

If the size of a foreign atom and that of the atoms of the parent crystal are different, then there will be an elastic stress field introduced into the lattice by the presence of each foreign atom. The strain energy of the grain boundary as well as that of the lattice surrounding a foreign atom can be reduced by the migration of foreign atoms to the neighbourhood of grain boundaries. It retards their normal surface tension induced motion. In order for the boundary to move, it must carry its atmosphere along with it.

Solute atoms not in solid solution are also capable of interacting with grain boundaries. It has been known for a number of years that impurities in the form of second-phase inclusions or particles can inhibit grain growth in metals. When they are present, the boundary must pull itself through the inclusions that lie in its path. An increase in temperature lowers the retarding effect of the solute atoms.

At higher temperature, the inclusions can go into solution or coalesce more rapidly so that their effectiveness in inhibiting growth will be reduced. If the inclusions are made to coalesce by a prior anneal, the rate of growth will not be subject to the rate of coalescence and higher rate of growth will be observed even though the final equilibrium grain size may be the same.

It was shown by Zener (1948) that inclusions will inhibit the migration of grain boundaries and when the inhibiting force is equal to the growth force due to boundary curvature, growth will cease.

Zener's relationship $\frac{r}{R} = \frac{3}{4} \xi$

where r = radius of inclusions

R = is the radius of curvature of average grain and

ξ = the volume fraction of inclusions.

gives a first approximation of the effect of inclusions on grain growth based on the assumptions that growth force is inversely proportional to the radius of curvature of grain boundary. Zener also assumed the particles to be spherical in shape and uniformly distributed within the metal, neither of which assumptions applies exactly.

Effect of preferred orientation

Preferred orientation also affects the rate of grain growth, the term "preferred orientation" signifying a nearly identical orientation in almost all the crystals of a given specimen of metal. It has been generally observed that rates of grain growth are reduced considerably in such cases. To reduce the specimen thickness and obtain smaller grain size, all the specimens were cross-rolled to avoid conditions of preferred oreintation.

Effect of the annealing atmosphere

It was observed that the annealing atmosphere affected the grain growth in certain metals. Some metals are readily oxidized at high temperature which oxidation retards the grain boundary migration. The effects of the annealing atmosphere were investigated for silver and nickel.

Identical specimens of silver were annealed at atmospheric pressure in air and dehydrated-oxygen-free nitrogen. There was a marked difference in the rate of grain growth and the equilibrium grain size, under two different annealing conditions. In figure 11-A $\ln(N/N_e - 1)$ has been plotted against time for the specimens JMS(6) and JMS(7), annealed in air at 740°C and 660°C respectively. In the same figure the lines A, B correspond to temperatures 740°C and 660°C respectively, for annealing in nitrogen instead of in air. There is a significant increase in the rate of grain growth when the specimens are annealed in nitrogen as shown by figure 11-A, and the equilibrium grain size is much larger. The variation of N $(= \frac{1}{D})$ with time has been shown in Tables (6)a and (6)b.

Another specimen of silver JMS(3) was annealed for a time sufficiently long, for the grains to have reached the equilibrium grain size, at different temperatures ranging from 450°C to 900°C. The variation of equilibrium grain diameter D_e was plotted against temperature as shown in figure 3-A. This is in agreement with the relation.

$$D_e^{\frac{1}{2}} = C(T - T_o)$$

established by Andrade and Aboav (1966) for c.p.h. metals. Table (7) shows the variation of N_e $(= \frac{1}{D_e})$ with temperature, a plot of which is shown in figure (3)B.

Similar investigations with nickel verified the effect of the annealing atmosphere in retarding the grain growth.

One of the nickel specimens NR(1) was annealed at atmospheric pressure in air at 740°C and the grain behaviour compared with that of a similar specimen annealed at the same temperature but at a pressure of 10^{-3} torr. The stable grain size at the end of the growth was found to be smaller in the former case. Further the rate of grain growth was considerably less than for the specimen annealed at low pressure, as shown in figure (13)A.

3. EXPERIMENTAL METHODS

(a) Preparation of Specimens

(i) Tadanac Lead

The specimens of metal to be examined were cut from a large lead plate 1.3 cms thick. Some of these specimens had to be cross-rolled to obtain smaller grain size for grain measurement at lower temperature. The surface area for grain counting was normally 4.0 x 1.8 cm^2, after each anneal the metal was etched for grain count. To reveal the grain boundaries the specimens were first etched with full-strength Russel's reagent. Then they were sprayed with the Worner and Worner reagent, which gave a fine polish to the counting surface.

For smaller grain size, specimens were cold cross-rolled. Some of the specimens were cooled down to liquid nitrogen temperature (-196°C) before each pass through the rollers. The reduction in thickness during each pass through the rollers was about 1% of the specimen thickness. To avoid contamination, especially by minute amounts of foreign metals, the rollers must be cleaned before use. The reduction in thickness of the specimen at each pass through the rollers should be small, between 1% to 2% of the specimen thickness. Great reductions at passage is liable to lead to preferred orientation and bending of the specimen.

The specimen should be given least mechanical treatment possible, for instance, cutting, drilling etc., as the strain produced by such mechanical operations give rise to growth of abnormally large grains. These abnormally large grains disturb the region of normal grain structure when the specimen is annealed at higher temperature. Every possible care was taken to avoid any such mechanical disturbances and where possible the specimen (especially lead) was cooled below 0 °C before cutting or drilling.

Measurements should not be made in the neighbourhood of places where the metal has been strained by cutting and drilling or other similar mechanical treatment.

(ii) Silver

A silver sheet 6 mm in thickness and 10 cm x 6 cm surface area was specially prepared for our experiments by Messrs Johnson Matthey by extrusion at high temperature ($\sim$800°C) of metal that had been melted in vacuo and deoxidised with carbon.

Spectrographic analysis carried out by Johnson Matthey showed the following impurities:

Elements	ppm	Elements	ppm
Au	3	Mn	5
Bi	1	Na	5
Ca	1	Pb	2
Cd	20	Si	20
Cu	50	Sn	5
Fe	50	Zn	10
Mg	5		

giving a purity of 99.98 per cent.

The sheet of metal was given a preliminary rolling at room temperature which reduced it to a thickness of 3.5 mm. Specimens cut from this sheet were then reduced by light cross-rolling in jeweller's rollers to a thickness of 3.25 mm and finally compressed in a hydraulic press to flatten the surfaces. Specimens for grain counting were prepared from this cross-rolled silver sheet having a surface area (6 cm x 1.0 cm) for grain counting.

The specimen was ground on successively finer grades of emery paper (240-600 grit) then polished on selvyt cloth with Silvo metal polish and finally, to reveal the grain boundaries, it was etched with potassium dichromate solution.

The composition of the etchant, potassium dichromate was as follows:-

Saturated solution of potassium dichromate in water	=	100 cc
Saturated solution of sodium chloride	=	2 cc
H_2SO_4 (conc)	=	10 cc

The solution was normally diluted (1:15) in distilled water.

(iii) <u>Copper</u>

The metal was supplied by the Enfield Rolling Mills, in the form of oxygen free high conductivity (O.F.H.C.) copper disc.

The specimens used for grain counting were rectangular blocks of surface 3.5 x 1.0 cm^2 and of thickness 2.5 mm, machined from a large copper disc 20 cms in diameter.

For grain counting, the specimens were first ground on 600 grit emery paper, then polished with Bluebell metal polish, followed by etching with alcoholic ferric chloride made up as follows:

Ferric chloride crystals (hydrated)	=	5 gms
Hydrochloric acid (conc)	=	2 cc
Ethyl Alcohol	=	95 cc

The polished specimen was etched by immersing it into the solution for about 1.5 minutes then washed in running cold water and warm air dried.

(iv) Nickel

International Nickel Co. Ltd. supplied the high purity nickel, specifically prepared for our experiments. The outline of the process by which the bar was produced, is as follows;

(a) After degassing at 600°C, the 'green' compact was sintered at 1200°C in hydrogen atmosphere.

(b) The compact was then forged at 1100°C.

(c) The forged bar was cross-rolled, reduction at any stage not being less than 50% of the thickness of the bar.

(d) The cold-rolled metal was finally annealed at 700 - 750°C.

The metal sheet received was 1 cm thick, which was again 50% cold cross-rolled and specimens 4 cms long and 1 cm wide were cut from this plate.

The specimens were ground on successively finer grades of emery paper (240, 320, 400, 600 grit respectively) to remove the thick work layer. Afterwards one of the surfaces of each specimen was polished with gamma-alumina powder on rotating wheel covered with selvyt cloth, until a fine mirror-finish surface was obtained. The specimen was then immersed in Marble's reagent, with polished surface facing upwards, for about 1.5 minutes. Finally it was washed in running cold water and dried.

All the cross-rolled specimens before anneal showed elongated grains with distorted and diffused boundaries. The specimens were then isothermally annealed at 400°C at a pressure of 10^{-3} torr for recrystallization. The specimen had to be annealed for about 400 hours to recrystallize completely.

After all the specimens had completely recrystallized each one was raised to a pre-determined temperature maintained for suitable periods to study the grain growth at that temperature. All the specimens were annealed isothermally at a pressure of 10^{-3} torr and the chosen temperatures were 670, 740, 790, 840°C.

After each anneal the counting surface of the specimen was ground successively on 400, 600 grit emery paper, then polished with fine-grade gamma-alumina powder followed by etching with Marble's reagent, to show the new grain boundaries.

The composition of Marble's reagent is as follows:-

cupric sulphate	8 gms
hydrochloric acid (conc)	40 ml.
distilled water	40 ml.

(b) Heat Treatment

(i) Tadanac Lead

For each grain measurement, the specimen had to be maintained at a fixed temperature for a duration which was increased with increase of the ratio $R = D_i/D_e$ where

D_i = initial grain diameter

D_e = final grain diameter

The specimens were annealed at different temperatures, using a series of liquids (acetone, ethyl alcohol, water, paraldehyde, bromobenzene, ethanolamine) boiling at a range of temperature from 59°C to 170°C.

For prolonged anneal the specimen was placed in an inclined glass tube sealed into a flask so as to be completely surrounded by boiling liquid. For short time anneal, the specimen was placed straight into the boiling liquid, so as to minimise the delay in attaining the required temperature, which was measured with a substandard mercury thermometer giving a maximum error of ± 1.0°C.

The specimen was arranged to be in contact with the bulb of the thermometer.

Grain growth was studied at 7 different temperatures, the lowest being 59°C and the highest 170°C. At each temperature, counts were made after time intervals selected so as to show appropriate increase in grain size.

For each temperature, a new specimen was used which was cleaned and chemically etched to remove the thick worked layer. After each subsequent anneal, the chosen surface of the specimen was etched for grain count.

(ii) Silver

For anneal at different temperatures the specimen was put in a silica glass tube which was placed in an electric furnace as shown in figure 1. Oxygen-free dehydrated nitrogen was passed through the silica tube so that the specimen was always contained in an atmosphere of nitrogen while being annealed. To effect this, commercially pure nitrogen containing less than 5 ppm of oxygen was passed through a flask containing phosphorous pentaoxide to absorb water vapours and then over red-hot copper filings maintained at about 800°C to absorb the residual oxygen, after which it passed over the specimen.

The temperature of the furnace was controlled by a "transitrol" type "ether" temperature controller.

A platinum platino-rhodium thermocouple giving the temperature to within ± 1°C was used to measure temperature of the specimen.

Grain growth for silver has been studied at four different temperatures 800°C, 855°C, 900°C and 940°C. After each anneal, the specimen had to be ground on successively finer grades of emery paper, polished on selvyt cloth with Silvo metal polish and etched with potassium dichromate solution to reveal the new grain structure.

(iii) Copper

To anneal the specimen, similar arrangement was used as in the case of silver.

Four different temperatures 676°C, 730°C, 780°C and 807°C were chosen to study the grain growth. As in the case of Lead and Silver, time intervals for annealing the specimen were selected so as to show appropriate increase in grain size and to reveal the new grain boundaries, the specimens had to be ground on 600 grit emery paper, polished with Bluebell metal polish and etched with alcoholic ferric chloride.

(iv) Nickel

It was decided to anneal nickel specimens in vacuo because of its rapid oxidation if heated at higher temperature in air. The specimen was enclosed in a silica glass tube, which was connected to the vacuum equipment as shown in fig. (20). After inserting the specimen the tube was evacuated to a pressure of 10^{-3} torr. The pressure in the glass tube was kept down at 10^{-3} torr by continuously running the diffusion and oil pumps, while the specimen was being annealed and during the cooling period. This procedure was repeated each time the specimen was annealed.

The grain growth measurements were made at four different temperatures 670, 740, 790 and 840°C. To investigate the effect of the annealing atmosphere on grain growth, an identical specimen was annealed at 740°C at atmospheric pressure in air. The grain size at the end of growth at atmospheric pressure was found to be appreciably smaller than for the specimen which was annealed at a pressure of 10^{-3} torr, at the temperature in question.

(c) Determination of Grain Size

The grain count was made by means of an inverted Nachet microscope, the specimen being placed with the face to be examined downwards. Grain sizes were determined by the total number of grains traversed by a line of given length passing through the centre of a known field of view, fraction of a grain greater than $\frac{1}{2}$ falling on the line being counted and those less than $\frac{1}{2}$ being ignored (Andrade & Aboav 1964, 1966).

With the help of the mechanical stage of the Nachet microscope, the specimen was traversed to different positions for grain count. About 200 observations were recorded in both transverse and longitudinal directions, a count of some thousands of grains of the specimen being made for a single determination of grain size. Different magnifications were used for different average grain sizes. From the observations, an average grain diameter was computed by the method described by Andrade and Aboav (loc-cit).

The result was an average number of grains pertaining to the field of view. It was divided by the field of view to give the average number of grains 'N' intersected by a line of unit length or the average grain diameter $D = 1/N$

For the most accurate work, an average from about 2000 grains was taken for a single determination.

The method of counting has the advantage of being reasonably rapid and of covering large areas of the specimen so that due allowance is made of local fluctuations in grain size. The surface of the specimen for grain counting had to be ground, polished and etched after each anneal because unless a thickness approaching the grain radius is removed, the surface after anneal is not fully representative. The grain boundaries in the surface layer tend during anneal to place themselves normal to the surface, as demonstrated by Smith (1948).

The final thickness of the specimen was always more than 10 times the average grain diameter at the end of growth except in the case of lead, at high temperature, when it was more than 5 times the equilibrium grain diameter.

For small values of $R = {}^{D_i}/D_e$ rapid grain growth takes place, the rate depending on the temperature at which the specimen was maintained.

The areas of the specimen chosen for grain counting were well away from the edges of the specimen to avoid possible edge effects.

Before giving any heat treatment, silver, copper and nickel specimens were ground on successively finer grades of emery paper and polished. After the heat treatment, these specimens were ground and polished again followed by chemical etching to reveal the new grain structure. For lead, chemical etching only is sufficient.

The grain structure observed was fairly normal after complete recrystallization for lead and copper as can be seen from the photographs Fig. (A) but in case of silver and nickel there were certain number of excessively large grains, and in silver they were elongated along the length of the specimen even after recrystallization. Recrystallization is particularly important in the study of grain growth as the precise laws of grain growth formulated by Andrade and Aboav (1966) are valid for metals that have completely recrystallized after deformation, that is metals having stable grain size. Without this recrystallization, the grain size at a given temperature depends upon the extent of working on the metal.

In the case of lead, recrystallization took place satisfactorily at room temperature but other metals e.g. silver and nickel had to be annealed at higher temperature for a number of hours before they recrystallized completely. In spite of annealing at high temperature for fairly long time, a number of grains in silver were elongated along the length of the specimen, although the specimens have been cross-rolled.

Copper as supplied by Enfield Rolling Mills, did not need any cross-rolling, as the grains were fairly small. The average initial grain diameter before any heat treatment was $D_i = 0.052$ mm except in one case when it was 0.064 mm.

At the highest temperature of anneal i.e. 807°C, the average equilibrium grain diameter $D_e = 0.097$ mm was only about 1/20th of the specimen thickness, so that the grain growth was not affected by the thickness of the specimen.

4. STABLE GRAIN SIZE AND TEMPERATURE

It was found that with prolonged anneal at a fixed temperature above atmospheric, the average grain diameter finally reaches a constant value D_e. This was confirmed at four different temperatures for copper, nickel and silver and seven different temperatures for lead.

The variation of D_e with T in °K, is in accordance with the relation

$$D_e^{\frac{1}{2}} = C(T - T_o) \qquad (1)$$

This relation was first established by Andrade and Aboav (1966) for close-packed-hexagonal (c.p.h.) metals. In equation (1) C, T_o are constants, T represents the annealing temperature.

The constant T_o has been called the inceptive temperature (Andrade and Aboav 1964, 1966).

In figures (2) to (5) are shown the results for different metals. In all cases there was a good linear relationship in accord with equation (1), the values of constants C and T_o being shown in table (1).

TABLE (1)

	Pb	Ag	Cu	Ni
10^4 C ($mm^{\frac{1}{2}}$ deg $C)^{-1}$	68.50	6.07	4.30	5.67
T_o (°K)	239.6	422.3	359.5	404.4

In figures 6, 7, 8, 9 the variation of grain size expressed as number of grains per mm $N(=^1/D)$ is plotted against time of anneal for various temperatures for the four metals.

It is clear from the figures that the rate of grain growth decreases with increase in annealing time until after a certain time it reaches an equilibrium size. Also the rate of grain growth increases with increase in annealing temperature, so that at higher temperature the grains reach equilibrium size in shorter time, than at low temperature.

Calculation of constants C and T_o

The line in figures (2, 3, 4, 5) is given by an equation of the type $D_e^{\frac{1}{2}} = \bar{M} + \bar{N}\theta$

where θ is the temperature in °C.

From figure (2) for Tadanac lead

At 60°C : $D_e^{\frac{1}{2}} = 0.640$

At 160°C : $D_e^{\frac{1}{2}} = 1.325$

$\therefore\ 0.640 = \bar{M} + 60\bar{N}$ (a)

$1.325 = \bar{M} + 160\bar{N}$ (b)

Equations (a) and (b) give

$\bar{N} = 0.00685 = 68.5 \times 10^{-4}$ (mm$^{\frac{1}{2}}$ deg C^{-1})

$\bar{M} = 0.229$

In equation $D_e^{\frac{1}{2}} = C(T - T_o)$

$C = \bar{N} = 68.5 \times 10^{-4}$ (mm$^{\frac{1}{2}}$ deg C^{-1})

$T_o = 239.6$ oK

$\therefore\ D_e^{\frac{1}{2}} = 68.5 \times 10^{-4}\ (T - 239.6)$

The values of C and To for Ni, Cu and Ag were similarly calculated.

Calculation of constants C and To for Nickel

From fig. (5) for Nickel

$D_e^{\frac{1}{2}} = 0.09$ mm at 290°C

$D_e^{\frac{1}{2}} = 0.26$ mm at 590°C

Using the equation $De^{\frac{1}{2}} = \bar{M} + \bar{N}\theta$

where θ is the temperature in °C;

$\bar{N}$ is the slope and M is a constant

$\bar{N} = 5.67 \times 10^{-4}$ (mm$^{\frac{1}{2}}$ deg C^{-1})

$\bar{M} = -\ 0.07$

In the equation $De^{\frac{1}{2}} - C(T - To)$

$C = \bar{N} = 5.67 \times 10^{-4}$ (mm$^{\frac{1}{2}}$ deg C^{-1})

and $T_o = 404.4$ oK

$\therefore\ D_e^{\frac{1}{2}} = 5.67 \times 10^{-4}\ (T - 404.4)$

5. LAW OF INCREASE OF GRAIN DIAMETER WITH TIME

Andrade and Aboav (1966) have shown that in the case of close-packed-hexagonal metals, grain growth takes place in three stages. Each stage is characterized by the ratio of initial grain diameter D_i, to the final stable grain diameter D_e, which has been called the relative initial diameter R (= D_i/D_e). In stage I, the value of R is less than 0.4 and the grainsgrow rapidly.

In stage III, $R \geqslant 0.65$, i.e. D_i must not be less than 0.65 D_e. Grain growth in this final stage is comparatively slow and growth to the equilibrium grain size takes hours according to the temperature of anneal, as against minutes for stage I.

The grain growth in this stage as shown by Andrade and Aboav (1966), for close-packed-hexagonal metals is given by:

$$N = N_e\,(1 + pe^{-qt}) \qquad (2)$$

where N = number of grain per mm

N_e = number of grain per mm at equilibrium

p, q are constants and t is the time for which the specimen has been annealed.

Between stage I and III, there is a range of relative average diameter for which neither system holds good and for which the growth is said to belong to stage II.

The laws of grain growth established for c.p.h. metals by Andrade & Aboav (1966) were found to be valid for metals of face-centred cubic structures.

In the case of Tadanac lead, the three stages of grain growth determined by the relative initial diameter R, were established but most attention was devoted to the stage III, i.e. normal stage of grain growth.

For silver, copper and nickel, the law $N = N_e\,(1+pe^{-qt})$ was confirmed and the relative initial diameter R was found to be ≥ 0.65 in most cases. The number of lead specimens was 7, temperatures ranging from 59°C to 170°C. For silver, copper and nickel, 4 specimens each were used at temperatures ranging from 800°C to 940°C; 676°C to 807°C; and 670 to 840°C respectively.

The comparatively small range of temperatures for silver, copper and nickel was due to the difficulty of getting small enough grain size to permit grain growth studies at lower temperatures. From equation (2)

$$N = N_e\,(1 + pe^{-qt})$$

$$({}^{N}/{N_e} - 1) = pe^{-qt}$$

$$\ln({}^{N}/{N_e} - 1) = \ln p - qt \qquad (3)$$

Equation (3) gives a straight line with a slope (-q) and constant temperature term $\ln p$. In figures 10, 11, 12, 13; $\ln({}^{N}/{Ne} - 1)$ has been plotted against time (t) for different metals at different temperatures.

An extreme case of very rapid grain growth was provided by heating a rectangular strip of lead 1 mm in thickness with a surface area of 0.35 x 6.0 cm^2 in vacuo by the passage of high electric current, a method used by Andrade and Aboav (1966).

This lead strip was etched before the passage of current and the average number of grains per mm was found to be 4. The current just necessary to melt a strip of the given dimension having been found to be 70 amperes for about 2 seconds, the same current was passed for just over a second which means that a temperature near the melting point of lead was maintained for about a second. The strip was then etched to determine the new grain size.

Photomicrographs of the specimen before and after the momentary heating are shownn in fig (B). The average grain size has increased about three fold. Assuming the temperature reached during the momentary heating to be 300°C, the value of D_e calculated from the formula $D_e^{\frac{1}{2}} = C(T - T_o)$ was found to be 5.176 mm. This gave the value of $R = 0.048$.

In table 2, actual grain growth has been compared with the equation (2) i.e. $N = N_e\ (1 + pe^{-qt})$ for each metal. The agreement between the observed and calculated values is remarkable.

It is clear from table 2 that the law does not hold for the first few values simply because the relative initial diameter $R < 0.65$.

In the normal stage of grain growth, Andrade and Aboav (1966) have established a relation between q and ϵ, the activation energy of grain growth.

$$q = ae^{-\epsilon/KT} \qquad (4)$$

where K = Boltzmann constant

a = a constant

Substituting $\epsilon/K = Q$ in equation (4)

$$q = ae^{-Q/T} \qquad (5)$$

$$\ln q = \ln a - Q/T \qquad (6)$$

Equation (6) represents a straight line with a constant $\ln a$ and slope (-Q). It was found that the relation (4) $Q = ae^{-\epsilon/KT}$ was accurately observed and this is shown in figures (14,15, 16, 17) where $\ln q$ has been plotted against $1/T$ for each metal.

The agreement between the observed and calculated values of q is excellent, as shown in table (3). From the equation $\epsilon/K = Q$, the activation energy of grain growth was determined for all the four metals. In table (4) are given, activation energy (ϵ) latent heat of fusion F, and the ratios ϵ/F_m and F_m/T_m for the four metals. T_m is the melting point of the metal in °K.

Calculation of activation energy of Tadanac Lead

From figure (14)

$$Q = \frac{1.120 - T.975}{(3.0 - 2.3)10^{-3}} = \frac{1.145}{0.7} \times 10^{3}$$

$$= 1636$$

$$\epsilon = QxK \quad = 1636 \times \frac{1.380 \times 10^{-16} \times 6.023 \times 10^{23}}{4.1855 \times 10^{7}} \text{ cal/mole}$$

$$= 1636 \times 1.986$$

$$= 3.249 \text{ kcal/mole}$$

F_m = latent heat of fusion = 1.147 kcal/mole (for Lead)

$$\epsilon/F_m = \frac{3.249}{1.147} = 2.833$$

$$\epsilon/F_m = 2.833$$

Similarly:

For Ag; $\frac{\epsilon}{F_m} = \frac{7.894}{2.70} = 2.924$

For Cu; $\frac{\epsilon}{F_m} = \frac{8.905}{3.14} = 2.836$

For Ni; $\frac{\epsilon}{F_m} = \frac{13.020}{4.21} = 3.093$

6. STATISTICAL DISTRIBUTION OF GRAIN SIZE:

The statistical distribution of grain size as expressed by the diameter, in the annealed metal was determined for lead, silver, copper and nickel. In all cases the specimen had been annealed at a pre-determined temperature for a time sufficiently long for equilibrium grain size to be reached. The temperature of anneal was 59°C, 855°C, 807°C and 840°C for lead, silver, copper and nickel respectively.

The experimental determination of the distribution of grain sizes, although it has been previously undertaken in a few cases e.g. C.S. Smith (1948), Feltham (1957), Papadakis (1964), Andrade & Aboav (1966), is generally very laborious. Measurements are made on a plane surface of the specimen which is prepared by grinding, polishing and chemical etching. As already mentioned, to investigate the grain size distribution, the specimen was first annealed at a pre-determined temperature and the grain area measurements were made when the equilibrium grain size has been attained. Photomicrographs of the surface were taken which were later enlarged to a magnification of about 500. In general, 11 equal ranges of diameter were chosen, the number of grains falling in each range being counted. The total number of grains in all the ranges was about 1,000, the ratio of the largest measured diameter to the smallest being about 15 to 1.

The grain size was expressed by the diameter of the grain cross-section visible at the surface. The methods used to measure grain diameters were as follows.

(i) Planimeter method:-

The grain areas were measured by a planimeter. From the area an arbitrary radius and hence diameter was derived by assuming that the boundary was circular, putting area = πr^2.

(ii) Intercept method:-

The grain shapes vary to a great extent, the number of corners or number of sides increasing with the size of the grain. Measurement was made of the intercepts by the grain boundary on a line of random direction and on another line normal to it, the point of interaction of the lines being central, and an average of the two intercepts taken as representative. Though the method is simpler and quicker than the first one, the great variation and irregularities in grain shapes may make it less precise.

Most of the measurements were made by the planimeter method, a number of these being also made by the intercept method. Slight variations in results were noted but these were not systematic. The diameter determined by either of the above method was called x, to avoid confusion with the average diameter D, measured by the grain boundary intercepts on a line of unit length, hitherto in question.

Grain size distribution curves were prepared showing the number of grains Z, having a diameter x, within a given range Δx, as a function of $x^{\frac{1}{2}}$ for the four metals, lead, silver, copper and nickel.

All the results were well represented by the equation of the form

$$Y = Ae^{-\alpha^2 (X - h)^2} \qquad (7)$$

where A, α, h are constants.

Putting $Y = Z/Z_m$ and $X = (x/x_m)^{\frac{1}{2}}$

and taking constants A and h as unity, the equation (7) takes the form (Andrade & Aboav, 1966)

$$Z/Z_m = \exp\left[-\alpha^2\left\{(x/x_m)^{\frac{1}{2}} - 1\right\}^2\right] \qquad (8)$$

where x_m is the value of x, for which Z has the maximum value Z_m. The constant α was found to have a value approximately equal to π. The experimental results are shown in figure (18) where (Z/Z_m) is plotted against $(x/x_m)^{\frac{1}{2}}$ for the four metals. The curve represents a Gaussian distribution according to equation (8). The curve is symmetrical about the line $(x/x_m)^{\frac{1}{2}} = 1$ and there is a maximum value of Z at $x = x_m$. This means that Z has a finite value at negative value of x, which do not exist. However this finite value at $x = o$ is $Z = Z_m e^{-\pi^2}$ or $5 \times 10^{-5}\ Z_m$, which is too small to be detected in the present investigation. The plots of grain size distribution for all the four metals agree well, in spite of the fact that each metal was raised to a different temperature to attain equilibrium grain size.

It is clear from the curve that there is considerable amount of scatter of experimental results when $(x/x_m)^{\frac{1}{2}} > 1.4$, markedly for lead and silver, and to some extent for copper. The number of grains having $(x/x_m)^{\frac{1}{2}} > 1.4$ is only about 10% of the total number of grains in the case of nickel, but for silver, copper and lead, it varies from 11% to 17% of the total number of grains. That for grains larger than the normal size the percentage at a given diameter, $(x/x_m)^{\frac{1}{2}} \simeq 1.4$, is slightly greater than that given by the formula is possibly due to identical orientation of certain neighbouring grain axes, which is favourable for rapid grain growth. The large grains observed were certainly not due to exaggerated grain growth as their number is quite small and their size is not abnormally large.

In studying the variation of grain growth with temperature, an average diameter $D = \frac{1}{N}$ was expressed by counting the average number of grains N, intercepted by a straight line of unit length, with lines taken at random position and with random orientations, whereas for the statistical distribution of grain size, measurement of the area of each grain was made on a photomicrograph with a planimeter. Andrade and Aboav (1966) found that experimentally $D = 1.09\ x_m$.

The total number of grains in terms of Z_m can be easily calculated by integrating Z dx (Andrade & Aboav, loc-cit)

$$N = \int_0^\infty Zdx = 2Z_m x_m \int_{-1} e^{-\Pi^2 u^2} (u + 1)\ du$$

if $(x/x_m)^{\frac{1}{2}} - 1 = u$

The value of $e^{-\Pi^2 u^2}$ at $u = -1$ is 5×10^{-5} as compared with 1 at $u = o$; so that the error introduced by taking the lower limit as $-\infty$ is negligible.

$$\int_{-\infty}^{\infty} e^{-\Pi^2 u^2} (u + 1)\ du = 2 \int_0^\infty e^{-\Pi^2 u^2}\ du = \Pi^{-\frac{1}{2}}$$

whence $N = 2Z_m x_m \quad \Pi^{-\frac{1}{2}} = 1.128\ Z_m x_m$

The sum of all the diameters is

$$Z_m \int_0^\infty e^{-\Pi^{-2} \left\{(x/x_m)^{\frac{1}{2}} - 1\right\}^2} xdx$$

$$= 2Z_m x_m 2 \int_{-\infty}^{\infty} e^{-\Pi^2 u^2} (u + 1)^3\ du$$

$$= 1.300\ Z_m x_m^2 :$$

Whence the mean diameter of the grains as sectioned by a random plane is

$$\frac{1.300\ Z_m x_m^2}{1.128\ Z_m x_m} = 1.152\ x_m$$

7. DISCUSSION

The following facts have been experimentally established for the f.c.c. metals.

The relation $D_e^{\frac{1}{2}} = C(T - T_0)$, originally put forward by Andrade and Aboav (1966) for hexagonal metals, has been confirmed for the four metals lead, silver, nickel and copper of the face-centred cubic structure.

Supposing the average initial diameter D_i as measured on the plane section, to be less than the average diameter at equilibrium D_e, D increases to the stable value D_e, at a constant temperature, provided the specimen is annealed for a sufficiently long time. With rise in temperature, there is a corresponding increment in grain size. The relation established by Andrade and Aboav for equilibrium grain size holds good where D_i is not less than 0.65 D_e. Under such conditions, the variation of grain size can be expressed by an exponential relation of the form $N = N_e\ (1 + pe^{-qt})$. In this equation $q = ae^{-\epsilon/kT}$ where ϵ is activation energy of grain growth. These relations, originally established for c.p.h. metals, have been shown by the present work to be equally applicable to f.c.c. metals.

The activation energy has been found to be approximately proportional to the latent heat of fusion with a constant of proportionality 2.92 as compared to 2.26 for c.p.h. metals. The validity of the laws of grain growth originally put forward by Andrade & Aboav for c.p.h. metals, has been established over a wide range of temperatures for each metal in question.

To obtain the value of the inceptive temperature T_0

extrapolation from a sufficiently large range of measurement was necessary and the law $D_e^{\frac{1}{2}} = C(T - T_o)$ was found to be well obeyed over the whole range.

The statistical distribution of grain diameter is given by the Gaussian distribution equation

$$Z/Z_m = \exp\left[-\alpha^2\left\{(x/x_m)^{\frac{1}{2}} - 1\right\}^2\right]$$

Grain size distribution was studied in the stable state only, whereas Andrade & Aboav (loc cit) found the distribution of grain diameter to be Gaussian both during growth and in the stable state.

The present work and that of Andrade & Aboav (loc cit) have established certain facts which are not yet completely understood and to explain these in detail requires elaborate equipment and an extensive knowledge of boundary conditions between grains of random orientations. Consider the equation $D_e^{\frac{1}{2}} = C(T - T_o)$ according to which, at a given temperature, diameter D should increase if maintained at a high temperature till it attains a stable diameter D_e, provided that $D_i > 0.65D_e$. The phenomenon of grain growth has been widely studied in the past but the answers to a number of crucial questions are still lacking. What leads to the cessation of grain growth? A number of causes have been suggested which may help to stop the growth. Smith (1964) pointed out that inclusions will prevent grain boundary migration entirely, if the volume fraction of inclusions is greater than the ratio of their radius to that of the grain boundary. These inclusions may be non-metallic, either produced immediately on solidification or resulting from precipitation taking place after solidification, and may be responsible for grain shape irregularities. The impurities segregated to the boundary will tend to diminish growth. A precipitate sometimes forms at a grain boundary which grows and checks grain growth.

Andrade & Aboav (loc cit) did not find any difference in the behaviour of cadmium containing 70/M of lead and cadmium containing less than 1/M, whereas addition of 40/M of copper to cadmium had a significant effect if the temperature exceeded 100°C. This they attribute to the fact that soluble impurities do not have a marked influence on the rate of growth. Beck et al (1949) reported a rapid increase of grain diameter in aluminium-manganese alloys when the solubility limit, which increases with the rise of temperature, was exceeded.

There is a considerable amount of indirect evidence that the interfacial energy of the grain boundary is responsible for grain growth but the precise nature of this driving force is not completely known. Assuming that the grain growth was due to the interfacial energy of the grain boundary, Harker and Parker (1945) have shown that grain boundary migration should occur only when the grain faces are curved or when they meet at non-equilibrium angles. Harker and Parker (loc cit) argued that when the grain face is curved with a centre of curvature within a grain A the atoms in the surface of grain B are in contact with a larger proportion of atoms belonging to grain B than of atoms belonging to grain A. At the interface the atoms will sometimes be attached to grain A and sometimes to grain B, due to thermal vibrations, but because of the curvature, the atoms are more tightly bonded to the surface of grain B than that of grain A, and there will be a net migration from A to B. Using a similar argument, they showed that if three grain faces meet along an edge at an angle other than 120° the grain included in the most acute angle will be consumed, and the grain boundary will migrate into that grain. The rate of migration will increase with increasing temperature and increasing displacement from the equilibrium configuration.

In all the specimens we found that, at equilibrium, a large percentage of grain boundaries was still curved but the curvature was never great, and the interfacial angles varied to a great extent as well.

Smith (1948) defines the net curvature of a face as the sum of the two curvatures about axes normal to each other. If the algebraic sum of these two curvatures is zero, the face will be equivalent to a plane face as far as its tendency to migrate is concerned. Smith further points out that the surface tension of all boundaries, being dependent on the relative orientation of grains, may not be equal and hence the equilibrium interfacial angle may be different from 120°.

We have been able to show that, in the case of silver and nickel, the atmosphere in which specimens are annealed strongly influences the growth. Annealing silver and nickel specimens in air resulted in a significant reduction of grain diameter and growth rate when compared with similar treatment in pure nitrogen or in vacuum (10^{-3} torr). This is most probably due to the formation of metallic oxides which accumulate at grain boundaries and retard grain boundary migration.

It has been suggested (R.E. Reed-Hill, 1966) that preferred orientation can affect the measured rate of grain growth. With this in mind, reduction to the final thickness of specimens used in experiments was effected by cross-rolling. The final thickness of the specimens was always more than 10 times the equilibrium grain diameter which renders the growth unaffected by specimen thickness. Andrade and Aboav pointed out that the rotation of plane boundaries at a given temperature which accompanies the growth of large grains, leads to the termination of grain growth.

The probability of a transfer of atom from one grain to another is governed by a number of factors, such as the stepped nature and dimension of the boundaries determined by the difference of boundary energy, due to relative orientation, a factor which varies with the temperature.

Feltham (1957) showed that the average number of grain sides increase systematically to a determined limit with the size of the grain. This was later confirmed by Andrade & Aboav. The average number of sides or number of corners for grains of critical diameter x_c, which is a determining factor in the growth process, comes out to be 5.7. Grains with the average number of sides smaller than 5.7 decrease in size, reducing the number of sides down to five, four or three before complete take over by a large grain. On the other hand, grains with the average number of sides greater than 5.7 will grow at the expense of smaller grains, till they attain characteristic stable grain size. For the large grains, some of the boundaries are slightly curved. The grains of smaller diameter which are stable at a given temperature, have three, four or occasionally five sides which may have a slight, but not marked curvature.

It has been suggested that small distortions of the lattice in the vicinity of corners is responsible for the curvature of the boundary. The equation $D_e^{\frac{1}{2}} = C(T - T_o)$ implies that at temperature close to T_o, the stable grain size will be extremely small i.e. of atomic dimensions. As the growth process is irreversible, it will not be possible to reduce the grain size appreciably by decreasing the temperature to T_o. It was in fact suggested by Andrade & Aboav that if metallic vapours could be condensed at a very low temperature, thereby producing the metal in a non-crystalline (vitreous) state, it would remain so with rise of temperature until T_o was reached and at temperatures slightly in excess of T_o, would crystallize to very small grains only. Hilsch (1960), Hilsch and Minnigerode (1961) have shown that metals can exist in a stable non-crystalline state at low temperature. They produced thin films about 500 Å in thickness of various metals by "quenching condensation" from the vapour state onto a very cold substrate. These thin films did not show properties normal for metals reduced in the solid state to temperatures approaching to that of liquid helium. X-ray and electron diffraction tests have shown that with many metals, including zinc and thallium for which the $T - T_o$ law has been established by Andrade & Aboav, the film is not amorphous in structure but consists of crystalline fragments of linear dimensions about 100 to 200 A.

It is worthwhile to draw attention to the fact that for certain metals the values of the Debye temperature and inceptive temperature are in fairly good agreement. Lindemann's values of Debye temperature for copper and nickel are 333 and 40I °K respectively as given in Solid State Physics, I6, (I964) which agree with our values of 359.5 and 404 °K for these metals but the values for lead and silver show wide differences with the Lindemann's values.

8. TABLES AND FIGURES.

Table (2) (a)

T. L. Specimen (35)

Grain growth of tadanac lead at 59°C compared with the formula $N = N_e (1 + Pe^{-qt})$

$N_e = 2.51 \ (mm^{-1})$

$q = 1.960 \ (hr^{-1})$

time t (mins)	N_{obs} (mm^{-1})	N_{cal} (mm^{-1})	$N_{obs} - N_{cal}$
0	4.088	4.094	-0.006
10	3.663	3.860	-0.197
30	3.495	3.481	0.014
60	3.100	3.110	- .010
100	2.830	2.829	0.001
140	2.679	2.681	-0.002
200	2.578	2.573	0.005
4100	2.520	2.510	0.010

contd.

Table (2)a

T. L. Specimen (33)

Grain growth of tadanac lead at 79.5°C compared with the formula $N = N_e\ (1 + Pe^{-qt})$

N_e = 1.707 mm^{-1}

q = 1.270 (hr^{-1})

time t (mins)	N_{obs} (mm^{-1})	N_{cal} (mm^{-1})	N_{obs} - N_{cal}
0	3.825	3.711	0.114
10	3.376	3.347	0.031
20	3.038	3.023	0.015
40	2.563	2.563	0
60	2.266	2.270	-0.004
80	2.066	2.081	-0.015
100	1.952	1.949	0.003
120	1.876	1.866	0.010
160	1.766	1.775	-0.009
240	1.720	1.720	0
1380	1.705	1.707	-0.002

contd.

Table (2)a

T. L. Specimen (30)

Grain growth of tadanac lead at 100°C compared with the formula $N = N_e\ (1 + Pe^{-qt})$

N_e = 1.196 (mm^{-1})

q = 1.630 (hr^{-1})

time t (mins)	N_{obs} (mm^{-1})	N_{cal} (mm^{-1})	$N_{obs} - N_{cal}$
0	2.120	2.118	0.002
10	1.912	1.915	-0.003
20	1.737	1.733	0.004
30	1.595	1.598	-0.003
50	1.440	1.438	0.002
100	1.257	1.257	0
1200	1.197	1.196	0.001

contd.

Table (2)a

T. L. Specimen (37)

Grain growth of tadanac lead at 118°C compared with the formula $N = N_e (1 + Pe^{-qt})$

$N_e = 0.905 \ (mm^{-1})$

$q = 2.04 \ (hr^{-1})$

time t (mins)	N_{obs} (mm^{-1})	N_{cal} (mm^{-1})	$N_{obs} - N_{cal}$
0	3.983	1.895	2.088
5	2.560	1.724	0.836
10	1.885	1.603	0.282
20	1.407	1.406	0.001
30	1.274	1.266	0.008
40	1.160	1.159	0.001
55	1.005	1.056	-0.001
70	0.993	0.996	-0.003
130	0.917	0.917	0
400	0.905	0.905	0

contd.

Table (2)a

T.L. Specimen (31)

Grain growth of tadanac lead at 124°C compared with the formula $N = N_e\ (1 + Pe^{-qt})$

$N_e = 0.852\ \text{mm}^{-1}$

$q = 2.13\ (\text{hr}^{-1})$

time t (mins)	N_{obs} (mm^{-1})	N_{cal} (mm^{-1})	N_{obs} -- N_{cal}
0	2.127	1.803	0.324
5	1.833	1.662	0.171
15	1.440	1.423	0.017
25	1.235	1.246	-0.011
35	1.131	1.131	0
45	1.042	1.044	-0.002
60	0.966	0.966	0
90	0.893	0.891	0.002
120	0.867	0.866	0.001
200	0.852	0.852	0

contd.

Table (2)a

T.L. Specimen (32)

Grain growth of tadanac lead at 157°C compared with the formula $N = N_e\ (1 + Pe^{-qt})$

N_e = 0.59 mm^{-1}

q = 2.90 (hr^{-1})

time t (mins)	N_{obs} (mm^{-1})	N_{cal} (mm^{-1})	N_{obs} - N_{cal}
0	2.088	1.516	0.572
10	1.174	1.162	0.012
20	0.948	0.945	0.003
30	0.801	0.807	-0.006
40	0.712	0.723	-0.011
60	0.642	0.640	0.002
720	0.60	0.590	0.010

contd.

Table (2)a

T.L. Specimen (34)

Grain growth of tadanac lead at 170°C compared with the formula $N = N_e\,(1 + Pe^{-qt})$

N_e = 0.525 (mm^{-1})

q = 3.29 (hr^{-1})

time t (mins)	N_{obs} (mm^{-1})	N_{cal} (mm^{-1})	$N_{obs} - N_{cal}$
0	1.585	1.491	0.094
13	1.020	1.010	0.010
25	0.765	0.773	-0.008
35	0.662	0.668	-0.006
45	0.609	0.607	0.002
65	0.553	0.553	0
245	0.528	0.525	0.003

Table (2) (b)

Grain growth of silver specimen J.M.S. (O) at 940°C compared with the formula $N = N_e\ (1 + Pe^{-qt})$

Temperature = 940°C

N_e = 4.34 per mm

q = 0.103 (hr^{-1})

time t (hrs)	N_{obs} (mm^{-1})	N_{cal} (mm^{-1})	$N_{obs} - N_{cal}$
0	9.23	7.25	1.98
1	7.53	6.97	0.56
3	6.54	6.48	0.06
7	5.73	5.74	-0.01
13	5.05	5.10	-0.05
19	4.72	4.75	-0.03
26	4.54	4.54	0
31	4.47	4.46	0.01
51	4.35	4.35	0
163	4.32		

contd.

Table (2)b

Grain growth of silver specimen J.M.S. (15) at 900°C compared with the formula $N = N_e \, (1 + Pe^{-qt})$

$N_e \;=\; 4.77 \text{ mm}^{-1}$

$q \;=\; 0.092 \; (\text{hr}^{-1})$

time t (hrs)	N_{obs} (mm^{-1})	N_{cal} (mm^{-1})	$N_{obs} - N_{cal}$
0	19.06	18.27	0.79
2	16.69	16.03	0.66
7	15.34	11.89	3.45
17	9.61	7.64	1.97
22	6.60	6.62	-0.02
27	5.96	5.93	0.03
32	5.50	5.50	0
37	5.21	5.22	-0.01
45	5.00	4.99	0.01
67	4.77		
131	4.73		

contd.

Table (2)b

Grain growth of silver specimen J.M.S. (19) at 835°C compared with the formula $N = N_e \ (1 + Pe^{-qt})$

$N_e \ = \ 5.44 \ (mm^{-1})$

$q \ = \ 0.080 \ (hr^{-1})$

time t (hrs)	N_{obs} (mm^{-1})	N_{cal} (mm^{-1})	N_{obs} - N_{cal}
0	22.85	41.83	-18.98
18	13.80	13.87	-0.07
40	6.95	6.93	0.02
55	5.96	5.89	0.07
80	5.50	5.50	0
105	5.44		
345	5.43		

contd.

Table (2)b

Grain growth of silver specimen J.M.S. (16) at 800°C compared with the formula $N = N_e (1 + Pe^{-qt})$

$N_e = 6.42\ (mm^{-1})$

$q = 0.067\ (hr^{-1})$

time t (hrs)	N_{obs} (mm^{-1})	N_{cal} (mm^{-1})	$N_{obs} - N_{cal}$
0	8.44	8.43	0.01
20	6.92	6.94	-0.02
42	6.54	6.54	0
107	6.43	6.42	0.01
387	6.41	6.42	-0.01

Table (2) (c)

Grain growth of copper (O.F.H.C.) compared with the formula $N = N_e\ (1 + Pe^{-qt})$

Temp. = 676°C

N_e = 15.45 (mm^{-1})

q = 2.14 (hr^{-1})

time t (mins)	N_{obs} (mm^{-1})	N_{cal} (mm^{-1})	N_{obs} - N_{cal}
0	19.30	19.22	0.08
10	18.08	18.06	0.02
20	17.26	17.27	-0.01
42	16.34	16.30	0.04
65	15.81	15.82	-0.01
95	15.48	15.57	-0.09
220	15.47		
4120	15.51		

contd.

Table (2)c

Grain growth of copper (O.F.H.C.) compared with the formula $N = N_e\ (1 + Pe^{-qt})$

Temp. = 730°C

N_e = 13.35 (mm^{-1})

q = 2.75 (hr^{-1})

time t (mins)	N_{obs} (mm^{-1})	N_{cal} (mm^{-1})	N_{obs} - N_{cal}
0	19.51	19.34	0.17
5	17.93	18.12	-0.19
15	16.42	16.39	0.03
25	15.22	15.29	-0.07
40	14.30	14.31	-0.01
75	13.60	13.54	0.06
4275	13.25		

contd.

Table (2)c

Grain growth of copper (O.F.H.C.) compared with the formula $N = N_e (1 + Pe^{-qt})$

Temp. = 780°C

N_e = 11.25 (mm^{-1})

q = 3.38 (hr^{-1})

time t (mins)	N_{obs} (mm^{-1})	N_{cal} (mm^{-1})	$N_{obs} - N_{cal}$
0	19.49	16.90	2.59
5	15.69	15.56	0.13
15	13.65	13.71	-0.06
30	12.30	12.30	0
40	11.84	11.85	-0.01
55	11.51	11.51	0
85	11.25	11.30	-0.05
145	11.28		
3145	11.23		

contd.

Table (2)c

Grain growth of copper (CC-5) compared with the formula $N = N_e\ (1 + Pe^{-qt})$

Temp. = 807°C

N_e = 10.34 (mm^{-1})

q = 3.83 (hr^{-1})

time t (mins)	N_{cal} (mm^{-1})	N_{obs} (mm^{-1})	N_{obs} - N_{cal}
0	15.56	15.56	0
5	14.15	13.91	-0.24
10	13.10	13.12	0.02
20	11.81	11.93	0.12
30	11.12	11.11	-0.01
45	10.64	10.64	0
65	10.42	10.42	0
3965	10.31		

Table (2) (d)

Specimen = NR (8) Nickel

Temperature = 840^{o}C

N_e = 6.20 (mm^{-1})

q = 3.79 (hr^{-1})

time t (mins)	N (mm^{-1})	N/N_e	$\ln(N/N_e - 1)$	$R=D_i/D_e$
0	11.59	1.869	$\bar{1}.86$	0.54
10	8.55	1.379	$\bar{1}.03$	0.72
25	7.27	1.173	$\bar{2}.25$	0.86
40	6.68	1.077	$\bar{3}.44$	
60	6.35	1.024	$\bar{4}.27$	
80	6.23	1.005	$\bar{6}.70$	
1520	6.21	1.002	$\bar{7}.79$	

contd.

Table (2)d

Specimen = NR (10) Nickel

Temperature = 790°C

N_e = 7.07 (mm^{-1})

q = 2.90 (hr^{-1})

time t (mins)	N (mm^{-1})	N/N_e	$\ln(N/N_e - 1)$	$R=D_i/D_e$
0	13.30	1.881	$\bar{1}.87$	0.53
20	8.29	1.173	$\bar{2}.25$	0.85
40	7.51	1.062	$\bar{3}.22$	0.94
60	7.25	1.025	$\bar{4}.31$	
80	7.13	1.009	$\bar{5}.29$	
160	7.11	1.006	$\bar{6}.88$	
4060	7.10	1.004	$\bar{6}.48$	

contd.

Table (2)d

Specimen = NR (9) Nickel

Temperature = 740°C

N_e = 8.30 (mm^{-1})

q = 2.15 (hr^{-1})

time t (mins)	N (mm^{-1})	N/N_e	$\ln(N/N_e - 1)$	$R=D_i/D_e$
0	12.41	1.495	$\bar{1}.30$	0.67
20	10.00	1.205	$\bar{2}.42$	0.83
40	9.29	1.119	$\bar{3}.87$	0.89
60	8.83	1.064	$\bar{3}.25$	
80	8.53	1.028	$\bar{4}.42$	
120	8.27			
5880	8.29			

contd.

Table (2)d

Specimen = NR (5) Nickel

Temperature = 670°C

N_e = 11.00 (mm^{-1})

q = 1.32 (hr^{-1})

time t (mins)	N (mm^{-1})	N/N_e	$ln(N/N_e - 1)$	$R=D_i/D_e$
0	20.81	1.892	$\bar{1}.89$	0.53
20	17.50	1.591	$\bar{1}.47$	0.63
60	15.94	1.449	$\bar{1}.20$	0.69
140	11.45	1.041	$\bar{4}.81$	
200	11.17	1.015	$\bar{5}.80$	
320	11.09	1.008	$\bar{5}.17$	
3320	11.01	1.001	$\bar{7}.09$	

contd.

Table (2)d

Specimen = NR(1) Nickel (Annealed in air at atmospheric pressure)

Temperature = 740°C

N_e = 9.50 (mm^{-1})

q = 1.97 (hr^{-1})

time t (mins)	N (mm^{-1})	N/N_e	$\ln(N/N_e - 1)$	$R = D_i/D_e$
0	16.50	1.737	$\bar{1}.70$	0.58
40	11.45	1.205	$\bar{2}.42$	0.83
80	11.00	1.053	$\bar{3}.06$	0.95
130	9.60	1.011	$\bar{5}.49$	
300	9.54	1.004	$\bar{6}.48$	
1320	9.54	1.004	$\bar{6}.48$	

Table (3) (a)

Relation between q and T for Tadanac lead:

$$\ln q = \ln a - Q/T$$

$$\ln q = 4.883 - \frac{1636}{T}$$

q in hr^{-1}

T in ^{o}K

Q = 1636

$T\ ^{o}K$	$q_{obs}\ (hr^{-1})$	$q_{cal}\ (hr^{-1})$	$q_{obs} - q_{cal}$
332.0	0.96	0.956 (0.96)	0
352.5	1.27	1.265 (1.27)	0
373.0	1.63	1.644 (1.64)	-0.01
391.0	2.04	2.011 (2.01)	0.03
397.0	2.13	2.143 (2.14)	-0.01
430.0	2.90	2.940 (2.94)	- .04
443.0	3.29	3.284 (3.28)	0.01

Table (3)b

Relation between q and T for silver

$$\ln q = \ln a - Q/_{T} \quad (q \text{ in hr}^{-1})$$

$$\ln q = 1.002 - Q/_{T} \quad (T \text{ in }^{o}K)$$

Q = 3975

t ^{o}C	T ^{o}K	q_{obs} (hr^{-1})	q_{cal} (hr^{-1})	q_{obs} - q_{cal}
800	1073	0.067	0.067	0
855	1128	0.080	0.080^{3}	-0.0003
900	1173	0.092	0.091^{9}	0.0001
940	1213	0.103	0.102^{8}	0.0002

Table (3) (c)

Relation between q and T for copper

$$\ln q = \ln a - Q/T \quad (q \text{ in } hr^{-1})$$

$$= 5.485 - \frac{4484}{T} \quad (T \text{ in } {}^{o}K)$$

$Q = 4484$

T ^{o}C	T ^{o}K	q_{obs}	q_{cal}	q_{obs} - q_{cal}
676	949	2.14	2.14	0
730	1003	2.75	2.76	-0.01
780	1053	3.38	3.41	-0.03
807	1080	3.83	3.80	0.03

Table (3)d

Relation between q and T for Nickel

$$\ln q = \ln a - Q/T$$

$$= 7.23 - 6556/T$$

where q is in (hr^{-1})

T is in ^{o}K

Q = 6556

t ^{o}C	T ^{o}K	q_{obs} (hr^{-1})	q_{cal} (hr^{-1})	q_{obs} - q_{cal}
670	943	1.32	1.32	0
740	1013	2.15	2.14	0.01
790	1063	2.90	2.89	0.01
840	1113	3.79	3.82	-0.03

Table (4)

Activation energy of grain growth and latent heat of fusion, F_M (K cal/mole)

Metal	Activation Energy ϵ	Latent Heat of Fusion F_M	ϵ/F_M	F_M/T_M
Lead	3.249	1.147	2.833	1.912
Silver	7.894	2.70	2.924	2.188
Copper	8.910	3.14	2.836	2.316
Nickel	13.020	4.21	3.093	2.439

ϵ = Activation energy (Kcal/mole)

F_M = Latent heat of fusion (Kcal/mole)

T_M = Melting Point of the metal (^{o}K)

Table (5) (a) LEAD

Specimen Number	Temp. t ^oC	T ^oK	N_e (mm^{-1})	D_e (mm)	$D_e^{\frac{1}{2}}$ ($mm^{\frac{1}{2}}$)	1/T ($^oK^{-1}$)	q (hr^{-1})	ln q
35	59	332	2.510	0.398	0.631	x10^{-3} 3.012	0.960	$\bar{1}.959$
33	79.5	352.5	1.707	0.585	0.765	2.837	1.270	0.239
30	100	373	1.196	0.836	0.914	2.681	1.630	0.489
37	118	391	0.905	1.111	1.054	2.558	2.040	0.713
31	124	397	0.852	1.174	1.084	2.519	2.130	0.756
32	157	430	0.590	1.695	1.302	2.326	2.900	1.065
34	170	443	0.525	1.905	1.381	2.257	3.290	1.191

contd.

Table (5) (b) SILVER

Specimen Number	Temp. t °C	T °K	N_e (mm^{-1})	D_e (mm)	$D_e^{\frac{1}{2}}$ ($mm^{\frac{1}{2}}$)	1/T (°K^{-1})	q (hr^{-1})	ln q
						x10^{-4}		
JMS(16)	800	1073	6.42	0.156	0.395	9.320	0.067	$\bar{3}.297$
JMS(19)	855	1128	5.44	0.184	0.429	8.865	0.080	$\bar{3}.474$
JMS(15)	900	1173	4.77	0.210	0.458	8.525	0.092	$\bar{3}.614$
JMS(0)	940	1213	4.34	0.230	0.480	8.244	0.103	$\bar{3}.727$
*JMS(7)	660	933	12.60	0.0794	0.282	10.718	0.0113	$\bar{5}.516$
*JMS(6)	740	1013	10.99	0.0910	0.302	9.872	0.0160	$\bar{5}.865$

* JMS(7) and JMS(6) have been annealed in air whereas all other specimen have been annealed in nitrogen atmosphere.

contd.

Table (5) (c) COPPER

Speci-men No.	N_e (mm^{-1})	D_e mm	$D_e^{\frac{1}{2}}$ $mm^{\frac{1}{2}}$	t (°C)	T (°K)	1/T	q_{obs} (hr^{-1})	ln q_{obs}
						$\times 10^{-4}$		
CC(4)	15.45	0.0647	0.254	676	949	10.54	2.14	0.761
CC(2)	13.35	0.0749	0.274	730	1003	9.97	2.75	1.012
CC(3)	11.25	0.0889	0.298	780	1053	9.50	3.38	1.218
CC(5)	10.34	0.0967	0.311	807	1080	9.26	3.83	1.343

contd.

Table (5) (d) NICKEL

Specimen No.	Temp. t (^{o}C)	T (^{o}K)	N_e (mm^{-1})	D_e (mm)	$D_e^{\frac{1}{2}}$	1/T ($^{o}K^{-1}$)	q (hr^{-1})	ln q (hr^{-1})
NR(5)	670	943	11.00	0.0909	0.302	$\times10^{-4}$ 10.60	1.32	0.28
NR(9)	740	1013	8.30	0.1205	0.347	9.87	2.15	0.77
NR(10)	790	1063	7.07	0.1414	0.376	9.41	2.90	1.07
NR(8)	840	1113	6.20	0.1613	0.402	8.98	3.79	1.33
*NR(1)	740	1013	9.50	0.1053	0.325	9.87	1.97	0.68

* The specimen NR(1) was annealed in air at atmospheric pressure, whereas all the other specimens have been annealed at 10^{-3} torr.

Table (6) (a)

Specimen = JMS(7) silver (Annealed in air at atmospheric pressure)

Temperature = 660°C

N_e = 12.60 (mm^{-1})

q = 0.0113 (hr^{-1})

time t (hrs)	N (mm^{-1})	N/N_e	ln ($N/N_e - 1$)	R = N_e/N_i
0	23.25	1.845	$\bar{1}.83$	0.54
7	19.63	1.558	$\bar{1}.42$	0.64
24	17.42	1.383	$\bar{1}.04$	0.72
46	16.25	1.290	$\bar{2}.76$	0.78
90	14.88	1.181	$\bar{2}.29$	
140	13.73	1.090	$\bar{3}.59$	
210	13.21	1.048	$\bar{4}.96$	
300	12.78	1.014	$\bar{5}.73$	
392	12.68	1.006	$\bar{6}.88$	

contd.

Table (6) (b)

Specimen = JMS(6) Silver (annealed in air at atmospheric pressure)

Temperature = 740°C

N_e = 10.99 (mm^{-1})

q = 0.0160 (hr^{-1})

time t (hrs)	N (mm^{-1})	N/N_e	ln ($N/N_e - 1$)	$R = N_e/N_i$
0	24.98	2.273	0.24	0.44
7	18.87	1.717	$\bar{1}.67$	0.58
24	16.81	1.530	$\bar{1}.37$	0.65
46	14.64	1.332	$\bar{2}.90$	0.75
90	12.76	1.161	$\bar{2}.17$	0.86
140	11.82	1.076	$\bar{3}.42$	
190	11.40	1.037	$\bar{4}.70$	
280	11.08	1.008	$\bar{5}.17$	

Table (7)

Specimen = JMS (3) Silver (annealed in air)

at atmospheric pressure.

Temperature t °C	N_e (mm^{-1})	D_e (mm)	$D_e^{\frac{1}{2}}$
450	22.24	0.0449	0.212
600	14.90	0.0670	0.259
660	12.60	0.0794	0.282
700	11.30	0.0830	0.297
740	10.99	0.0910	0.302
800	9.70	0.1030	0.321
900	7.66	0.1305	0.361

Table (8)a

Statistical distribution of grain size in lead, according to the formula $Z/Z_m = \exp\left[-\alpha^2\left\{(x/x_m)^{\frac{1}{2}} - 1\right\}^2\right]$

$X_m = 1.2$

$Z_m = 328$

Range of diameter (cms)	No. of grains in each range (Z)	Average diameter $\bar{x}$	$(\bar{x}/x_m)^{\frac{1}{2}}$	$(\bar{x}/x_m)$	Z/Z_m
0 - 0.50	22	0.25	0.208	0.46	0.067
0.51 - 1.00	222	0.75	0.625	0.79	0.68
1.01 - 1.50	328	1.25	1.04	1.02	1.00
1.51 - 2.00	186	1.75	1.46	1.21	0.57
2.01 - 2.50	90	2.25	1.88	1.37	0.27
2.51 - 3.00	63	2.75	2.29	1.51	0.19
3.01 - 3.50	30	3.25	2.71	1.65	0.09
3.51 - 4.00	12	3.75	3.13	1.77	0.037
4.01 - 4.50	4	4.25	3.54	1.88	0.012
4.51 - 5.00	4	4.75	3.96	1.99	0.012
5.01 - 5.50	-				

Table (8)b .

Statistical distribution of grain size in silver according to the formula $Z/Z_m = \exp\left[-\alpha^2 \{(\bar{x}/x_m)^{\frac{1}{2}} - 1\}^2\right]$

$x_m = 1.3$

$Z_m = 272$

Range of diameter (cms)	No.of grains in each range (Z)	Average diameter $\bar{x}$	$\bar{x}/x_m$	$(x/x_m)^{\frac{1}{2}}$	Z/Z_m
0 - 0.50	10	0.25	0.19	0.44	0.04
0.51 - 1.00	140	0.75	0.58	0.76	0.52
1.01 - 1.50	269	1.25	0.96	0.98	0.99
1.51 - 2.00	224	1.75	1.35	1.16	0.82
2.01 - 2.50	116	2.25	1.73	1.32	0.43
2.51 - 3.00	73	2.75	2.12	1.46	0.27
3.01 - 3.50	46	3.25	2.50	1.58	0.17
3.51 - 4.00	28	3.75	2.89	1.70	0.10
4.01 - 4.50	10	4.25	3.27	1.81	0.04
4.51 - 5.00	4	4.75	3.65	1.91	0.01^5
5.01 - 5.50	4	5.25	4.04	2.01	0.01^5
5.51 - 6.00	2	5.75	4.42	2.10	0.007
6.01 - 6.50	1	6.25	4.81	2.19	0.004

Table (8)c

Statistical distribution of grain size in copper according to the formula $Z/Z_m = \exp\left[-\alpha^2 \{(x/x_m)^{\frac{1}{2}} - 1\}^2\right]$

$x_m = 1.3$

$Z_m = 320$

Range of diameter (cms)	No.of grains in each range (Z)	Average diameter $\bar{x}$	$\bar{x}/x_m$	$(\bar{x}/x_m)^{\frac{1}{2}}$	Z/Z_m
0 - 0.50	13	0.25	0.19	0.44	0.04
0.51 - 1.00	136	0.75	0.58	0.76	0.43
1.01 - 1.50	320	1.25	0.96	0.98	1.00
1.51 - 2.00	234	1.75	1.35	1.16	0.73
2.01 - 2.50	130	2.25	1.73	1.32	0.41
2.51 - 3.00	65	2.75	2.12	1.46	0.20
3.01 - 3.51	37	3.25	2.50	1.58	0.12
3.51 - 4.00	17	3.75	2.89	1.70	0.05
4.01 - 4.50	4	4.25	3.27	1.81	0.01
4.51 - 5.00	3	4.75	3.65	1.91	0.009
5.01 - 5.50	2	5.25	4.04	2.01	0.006

Table (8)d

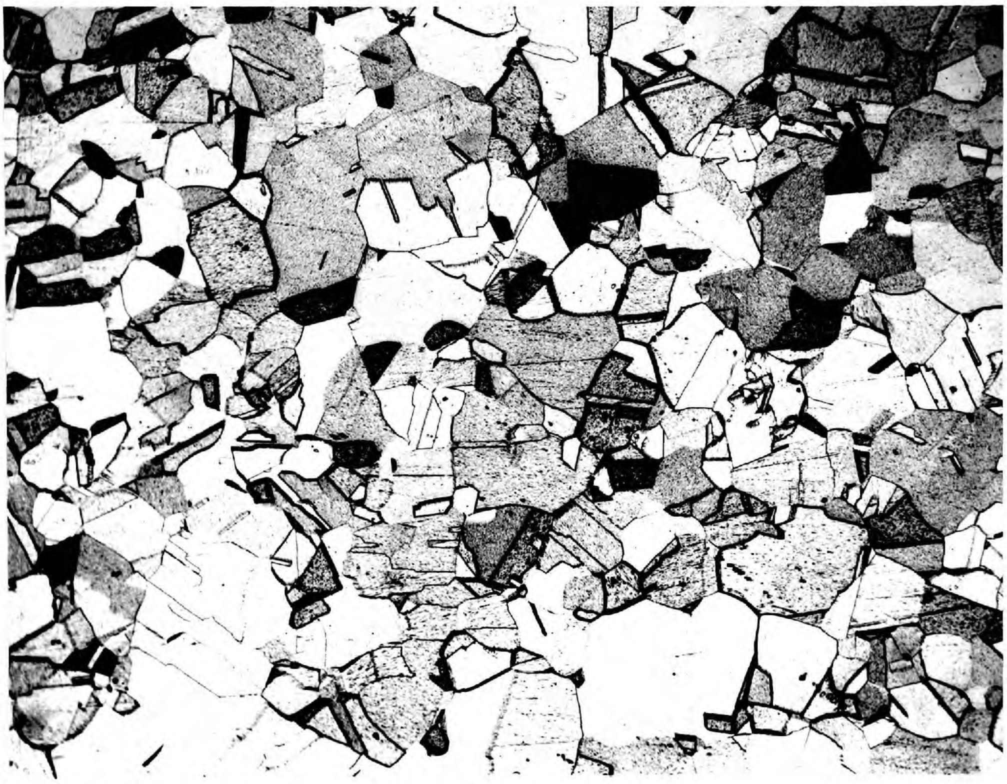
Statistical distribution of grain size in nickel according to the formula $Z/Z_m = \exp\left[-\alpha^2 \{(x/x_m)^{\frac{1}{2}} - 1\}^2\right]$

$x_m = 1.3$

$Z_m = 376$

Range of diameters (cms)	No.of grains in each range (Z)	Average diameter $(\bar{x})$	$\bar{x}/x_m$	$(\bar{x}/x_m)^{\frac{1}{2}}$	Z/Z_m
0 - 0.50	10	0.25	0.19	0.4	0.02^{7}
0.51 - 1.00	134	0.75	0.58	0.76	0.36
1.01 - 1.50	372	1.25	0.96	0.98	0.99
1.51 - 2.00	260	1.75	1.35	1.16	0.69
2.01 - 2.50	132	2.25	1.73	1.32	0.35
2.51 - 3.00	54	2.75	2.12	1.46	0.14
3.01 - 3.50	20	3.25	2.50	1.58	0.05^{3}
3.51 - 4.00	12	3.75	2.89	1.70	0.03^{2}
4.01 - 4.50	4	4.25	3.27	1.81	1.01^{1}
4.51 - 5.00	2	4.75	3.65	1.91	0.005

(i) LEAD Mag x 22.8



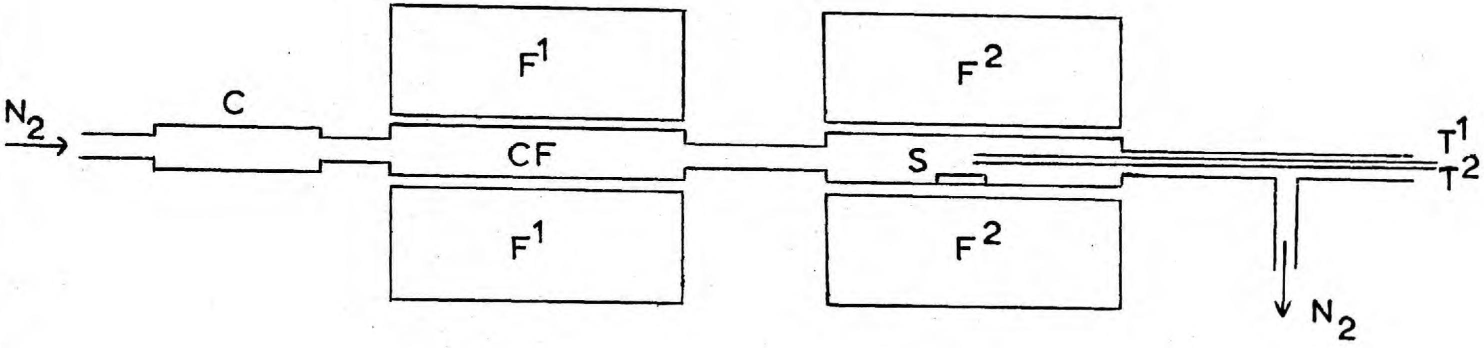
(ii) COPPER Mag x 101

FIG A

(i) BEFORE HEATING MAG X 22.8

(ii) AFTER HEATING MAG X 22.8

FIG B



N_2	Nitrogen
C	P_2O_5 container
F^1, F^2	Furnaces
CF	Copper fillings
T^1, T^2	Thermocouples
S	Specimen

FIG 1

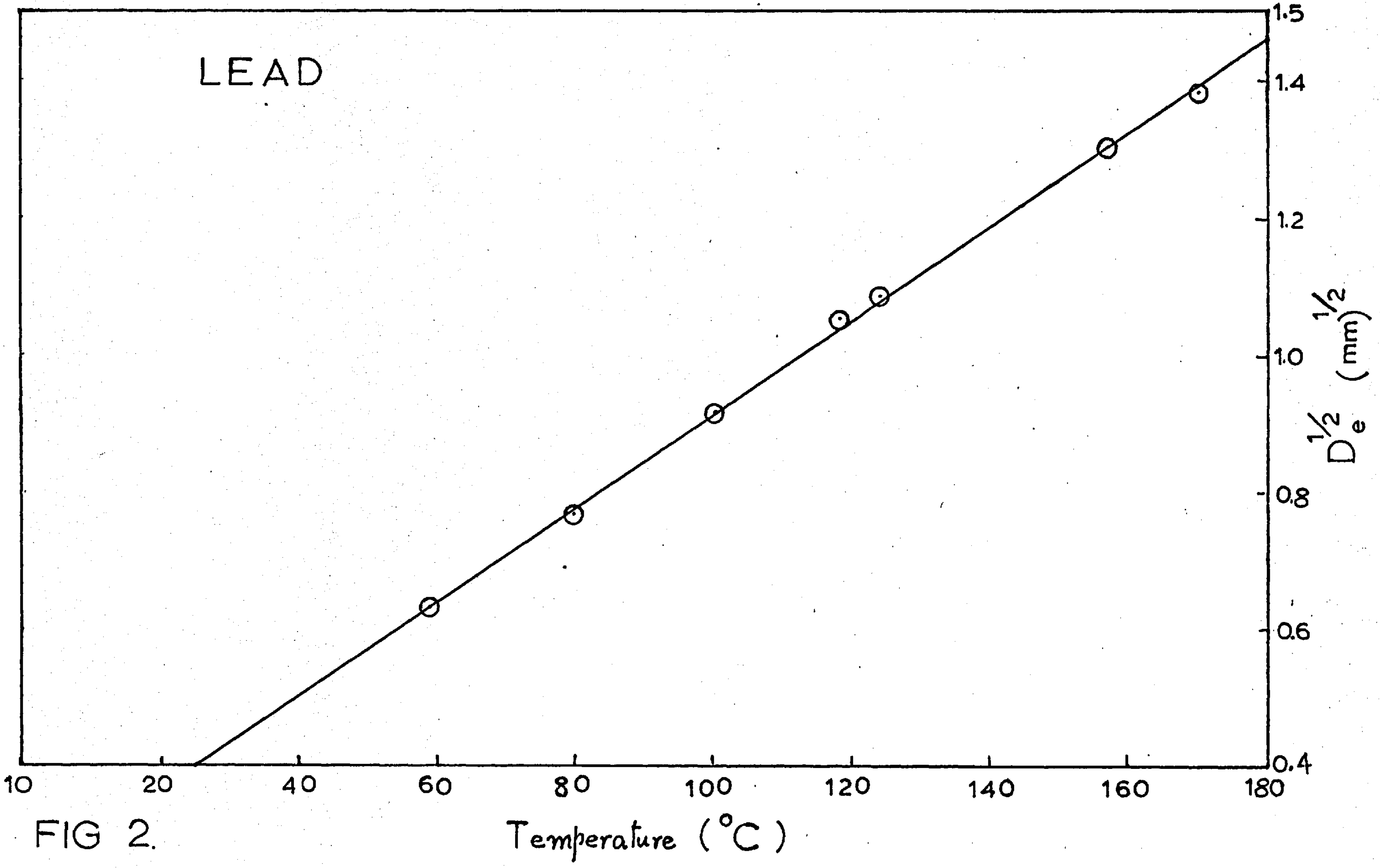

LEAD
10
20
40
60
80
100
120
140
160
180
Temperature (°C)
0.4
0.6
0.8
1.0
1.2
1.4
1.5
$D_e^{1/2}$ (mm)$^{1/2}$

FIG 2.

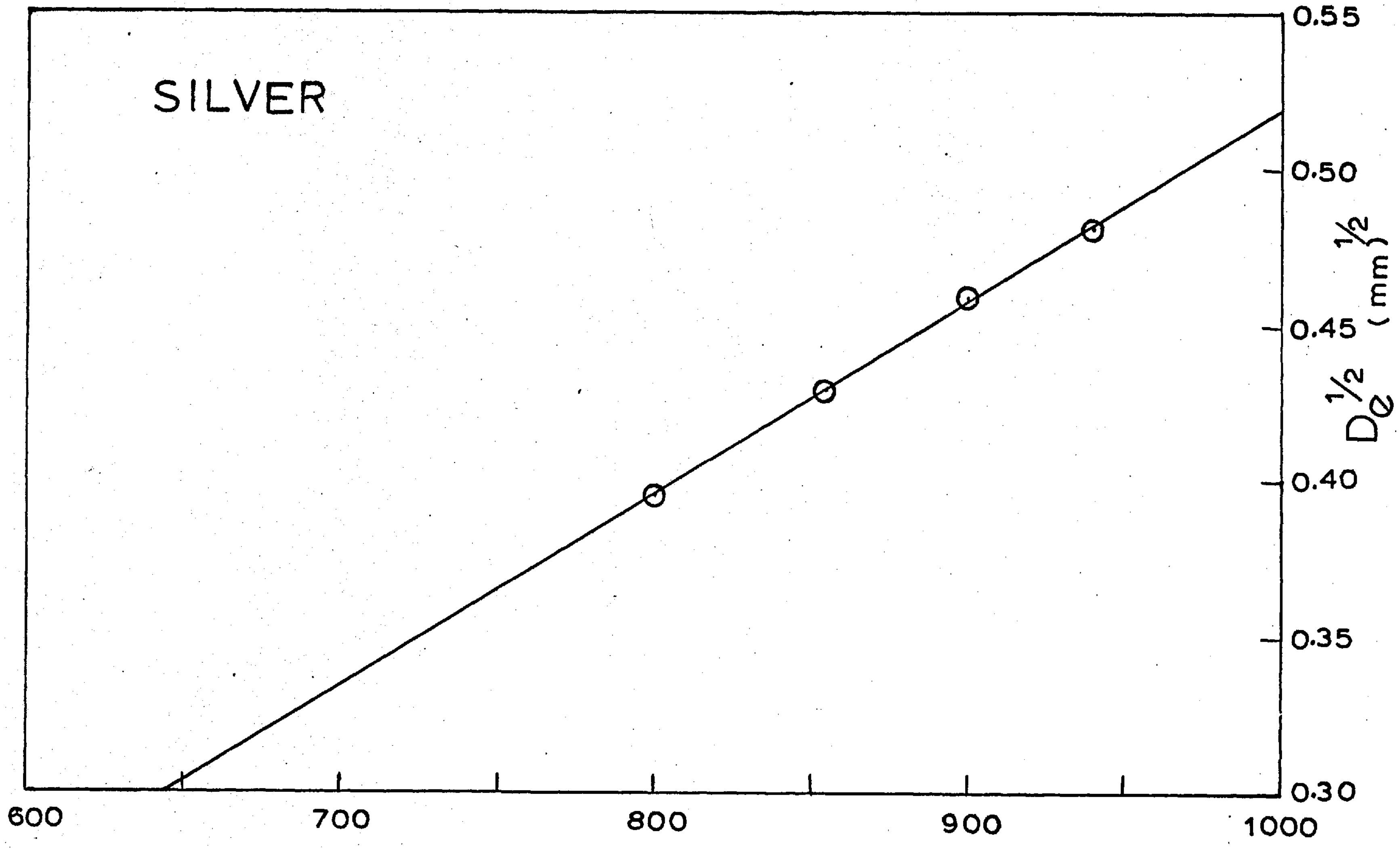

SILVER
0.55
0.50
0.45
0.40
0.35
0.30
$D_e^{1/2}$ $(mm)^{1/2}$
600
700
800
900
1000
TEMPERATURE (°C)

FIG 3

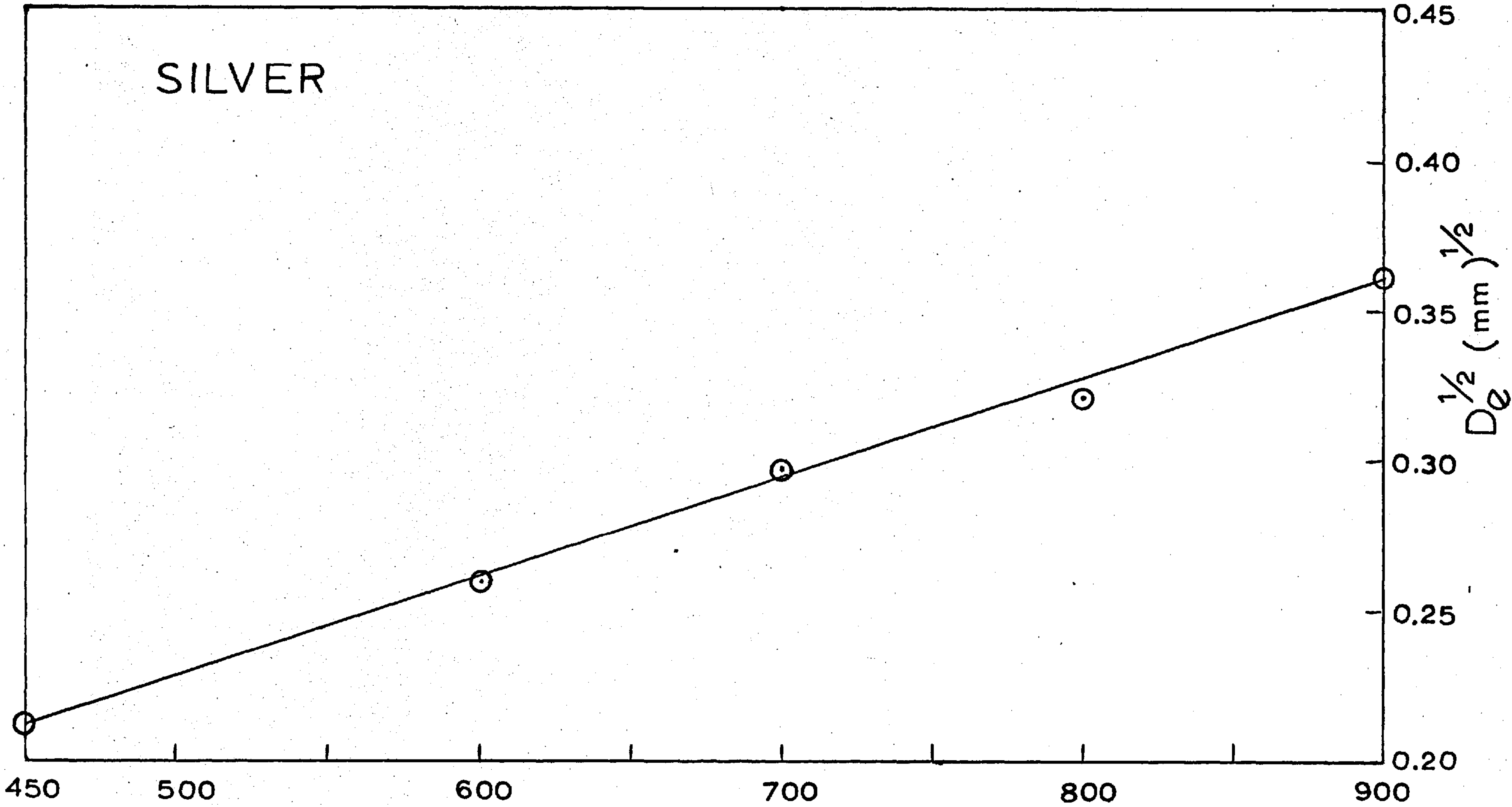

SILVER
0.45
0.40
0.35
0.30
0.25
0.20
$D_e^{1/2}$ (mm)$^{1/2}$
450
500
600
700
800
900
TEMPERATURE (°C)

FIG 3 a

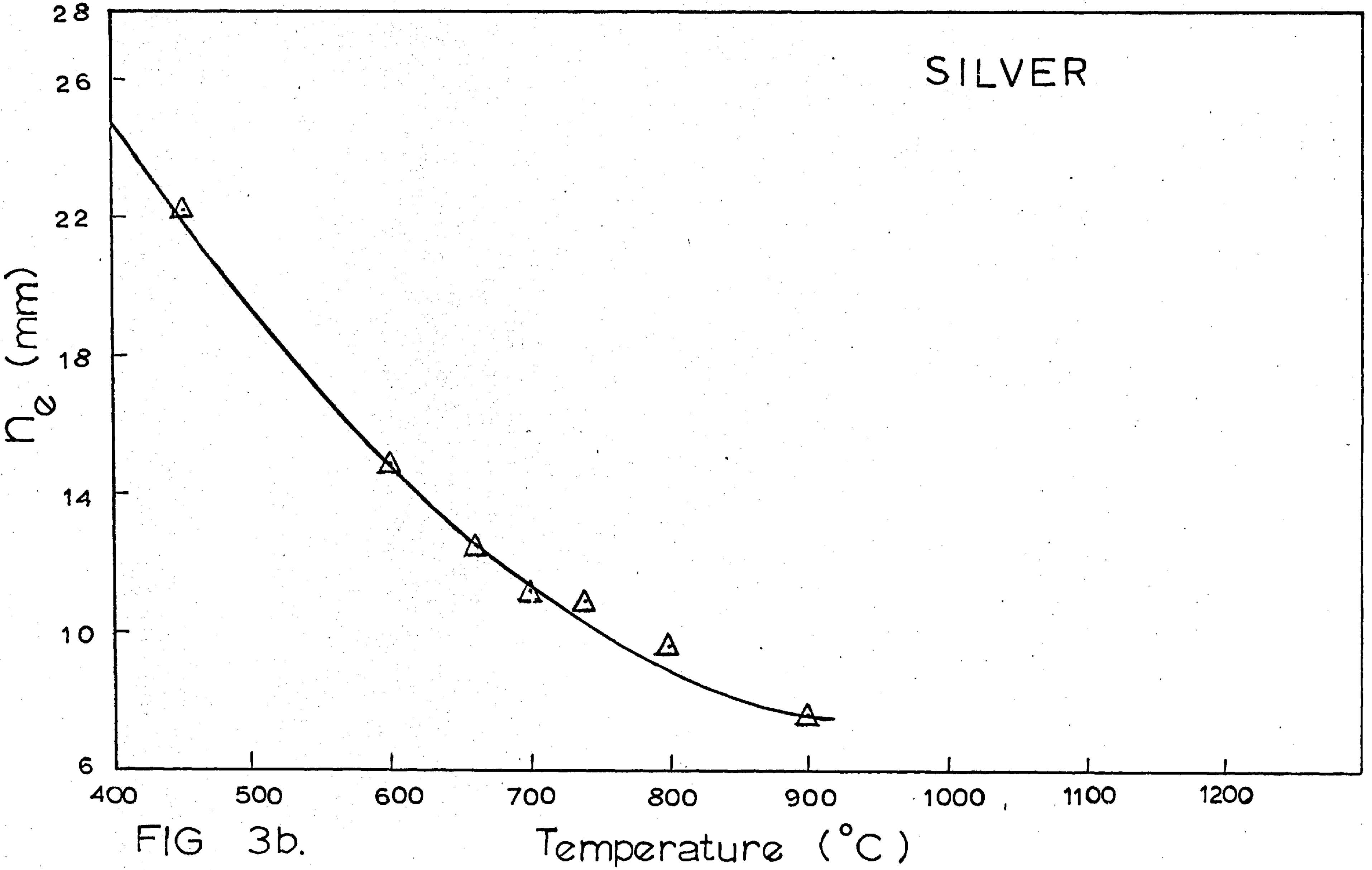

SILVER
28
26
22
18
14
10
6
n_e (mm^{-1})
400
500
600
700
800
900
1000
1100
1200
Temperature (°C)

FIG 3b.

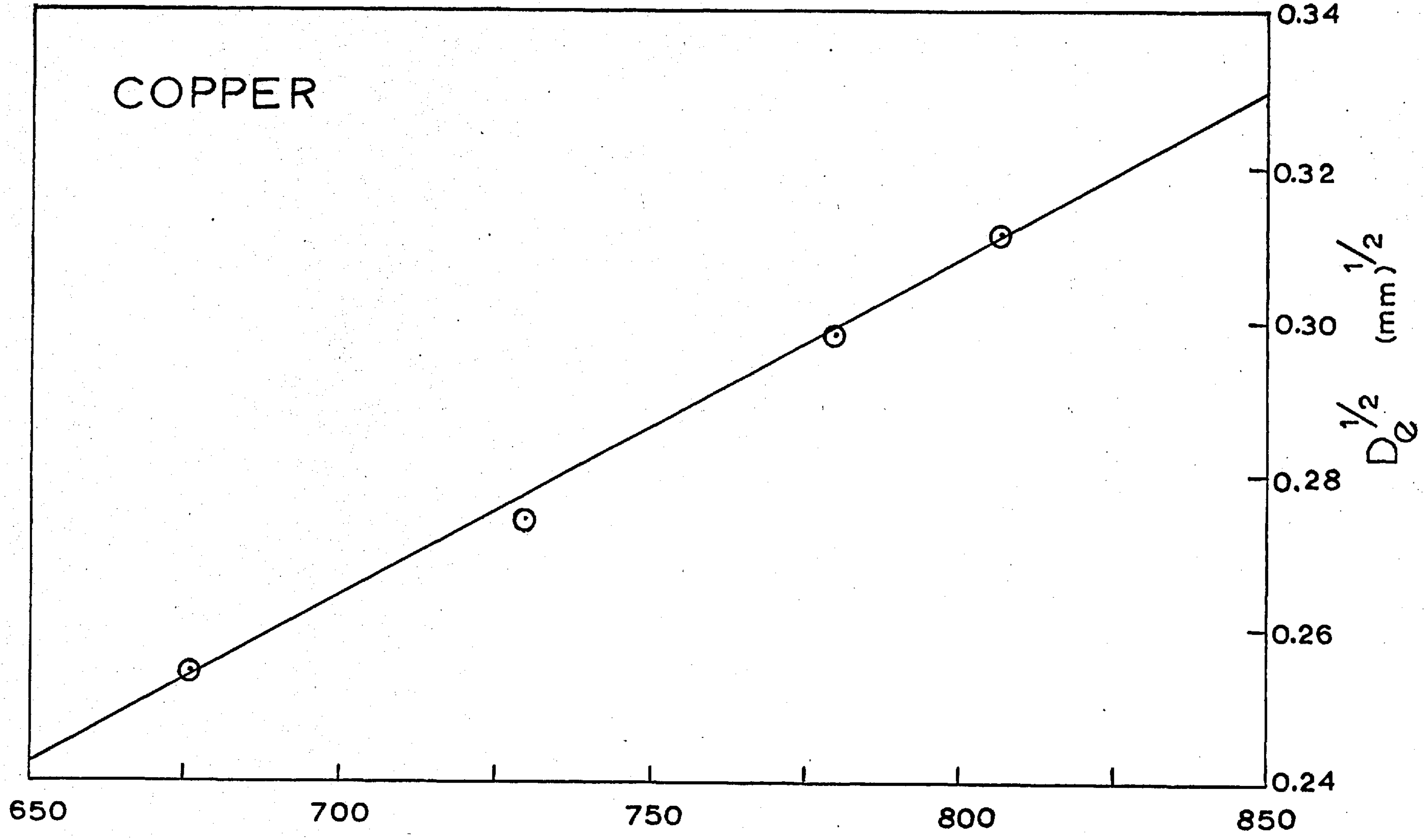

COPPER
0.34
0.32
0.30
0.28
0.26
0.24
$D_e^{1/2}\ (\mathrm{mm})^{1/2}$
650
700
750
800
850
TEMPERATURE (°C)

FIG 4

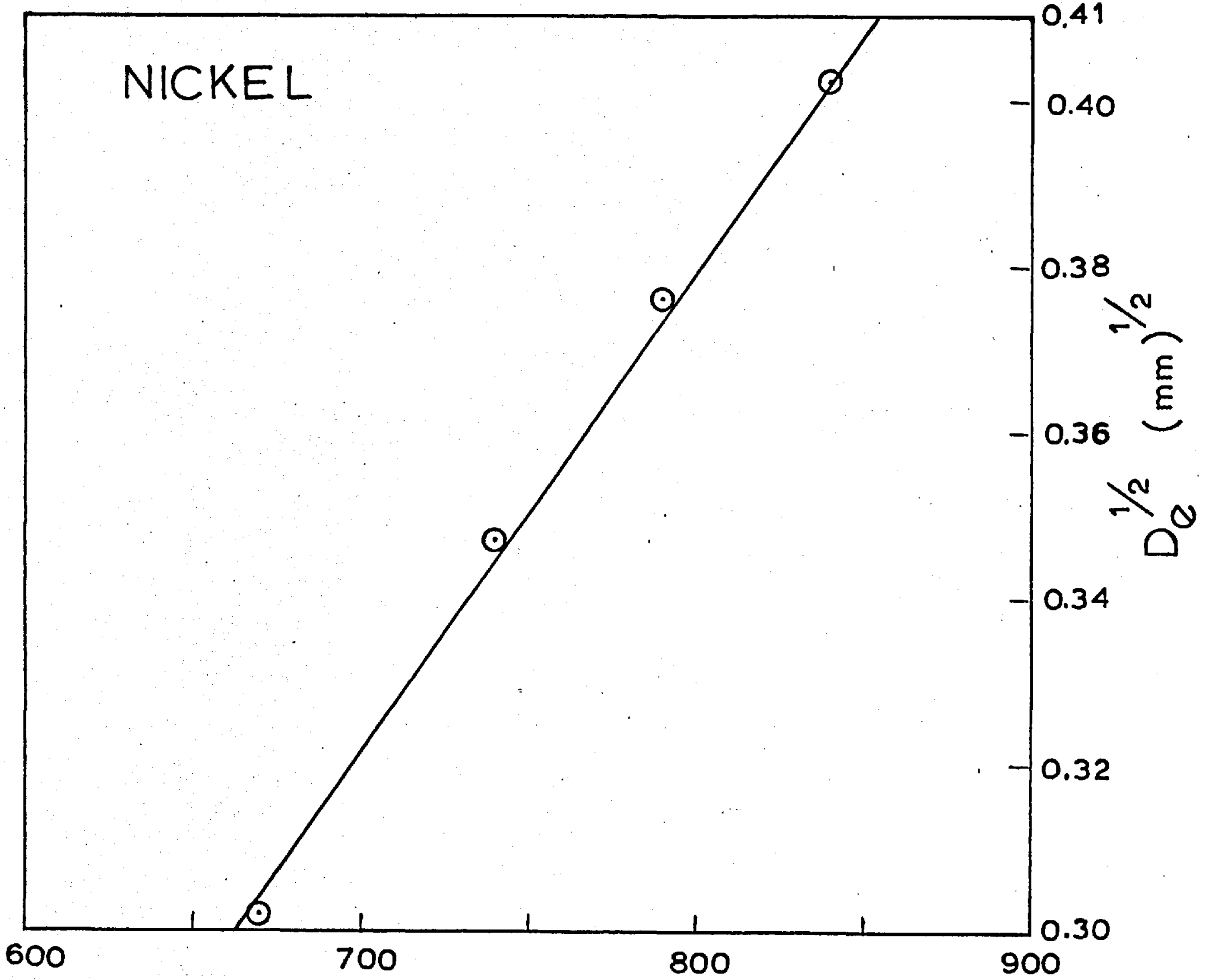

NICKEL
0.41
0.40
0.38
0.36
0.34
0.32
0.30
$D_e^{1/2}$ $(\mathrm{mm})^{1/2}$
600
700
800
900
TEMPERATURE (°C)

FIG 5

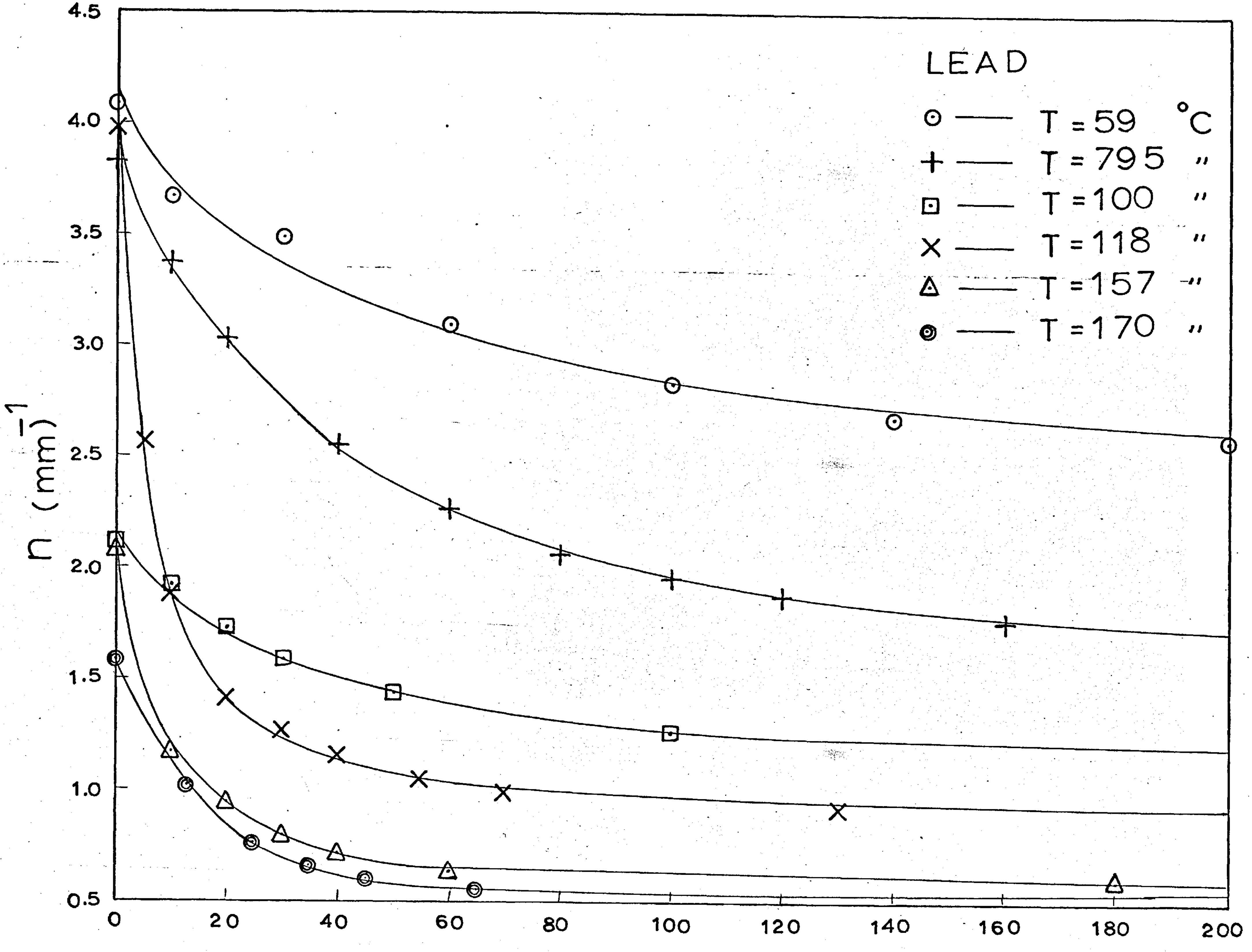

LEAD
⊙ —— T = 59 °C
+ —— T = 795 "
⊡ —— T = 100 "
× —— T = 118 "
△ —— T = 157 "
◎ —— T = 170 "
n (mm⁻¹)
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
20
40
60
80
100
120
140
160
180
200
Time (min)

FIG 6

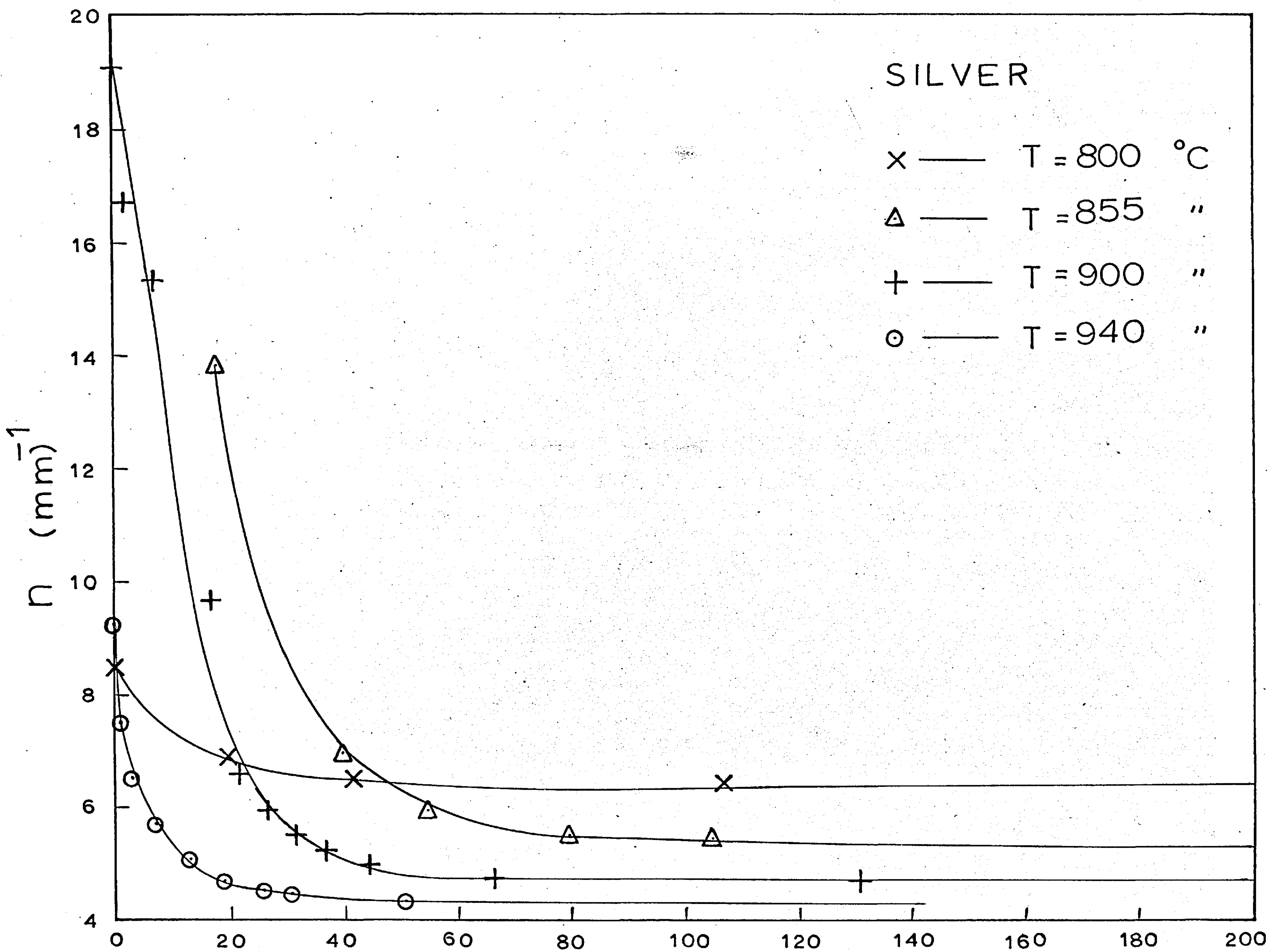

SILVER
× —— T = 800 °C
△ —— T = 855 "
+ —— T = 900 "
⊙ —— T = 940 "
n (mm^{-1})
20
18
16
14
12
10
8
6
4
0
20
40
60
80
100
120
140
160
180
200
Time (hr)

FIG 7

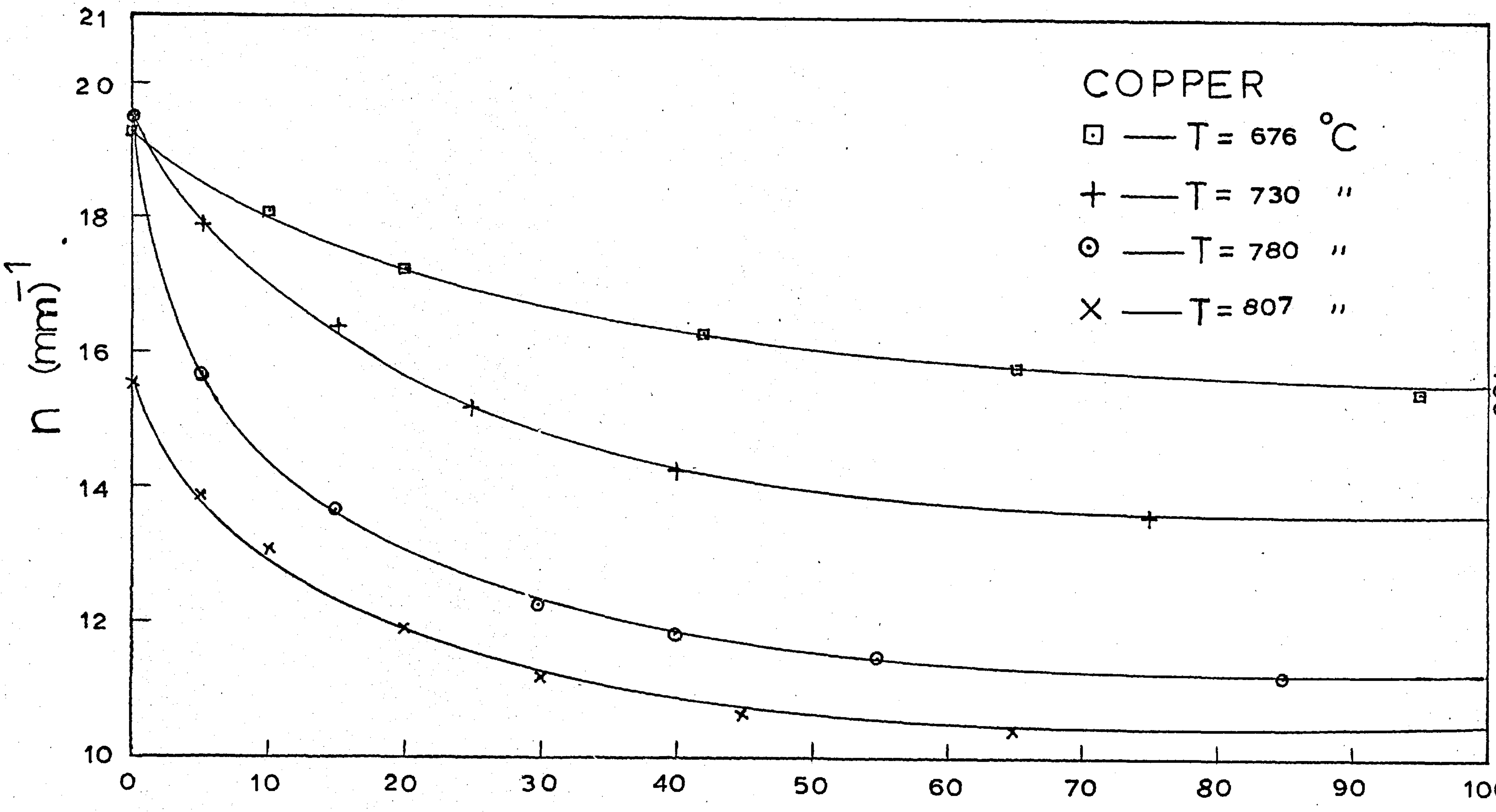

COPPER
⊡ —— T = 676 °C
+ —— T = 730 "
⊙ —— T = 780 "
× —— T = 807 "
n (mm^{-1})
21
20
18
16
14
12
10
0
10
20
30
40
50
60
70
80
90
100
Time (min)

FIG 8

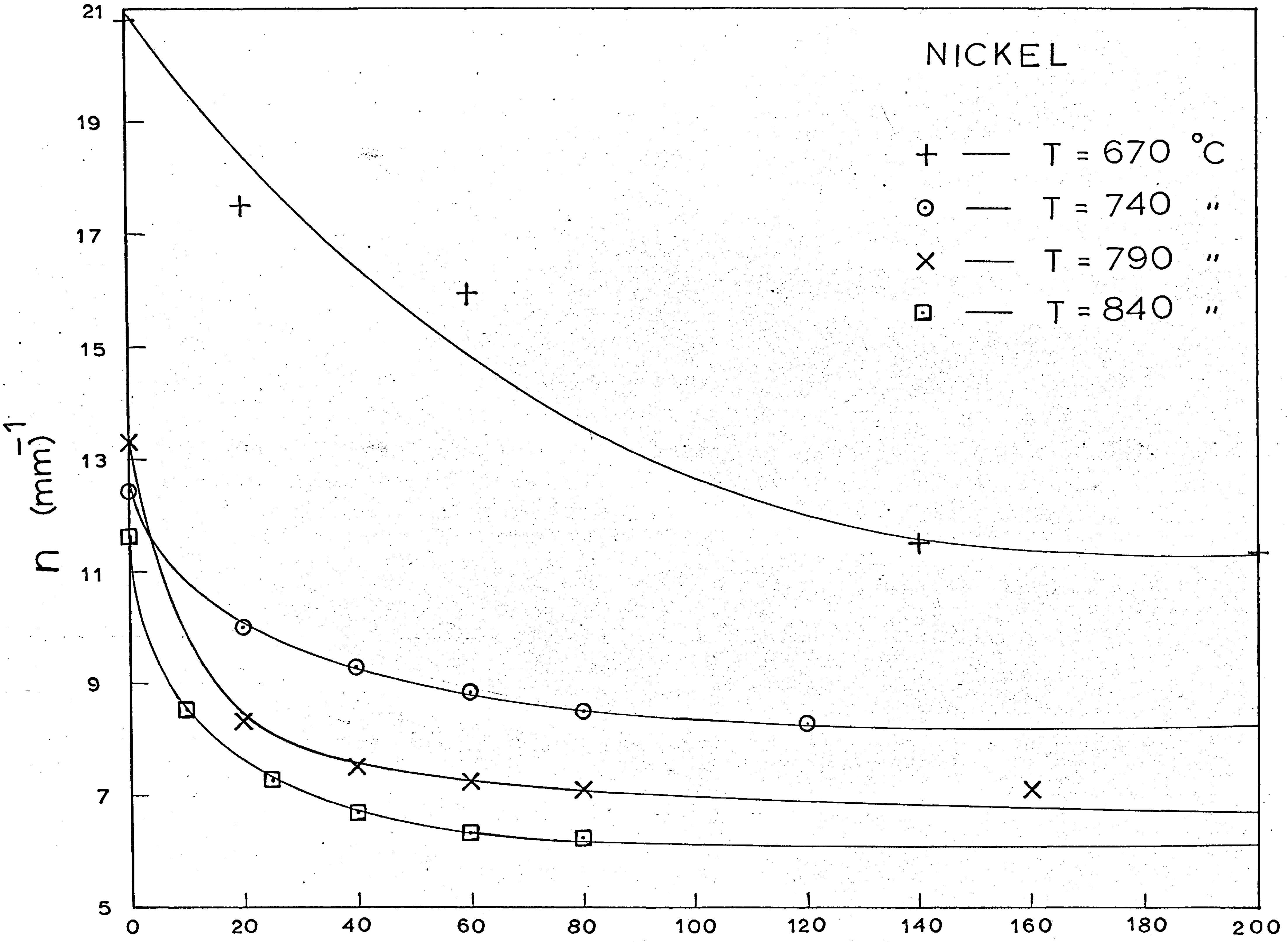

NICKEL
+ — T = 670 °C
⊙ — T = 740 "
× — T = 790 "
⊡ — T = 840 "
n (mm^{-1})
21
19
17
15
13
11
9
7
5
0
20
40
60
80
100
120
140
160
180
200
Time (min)

FIG 9

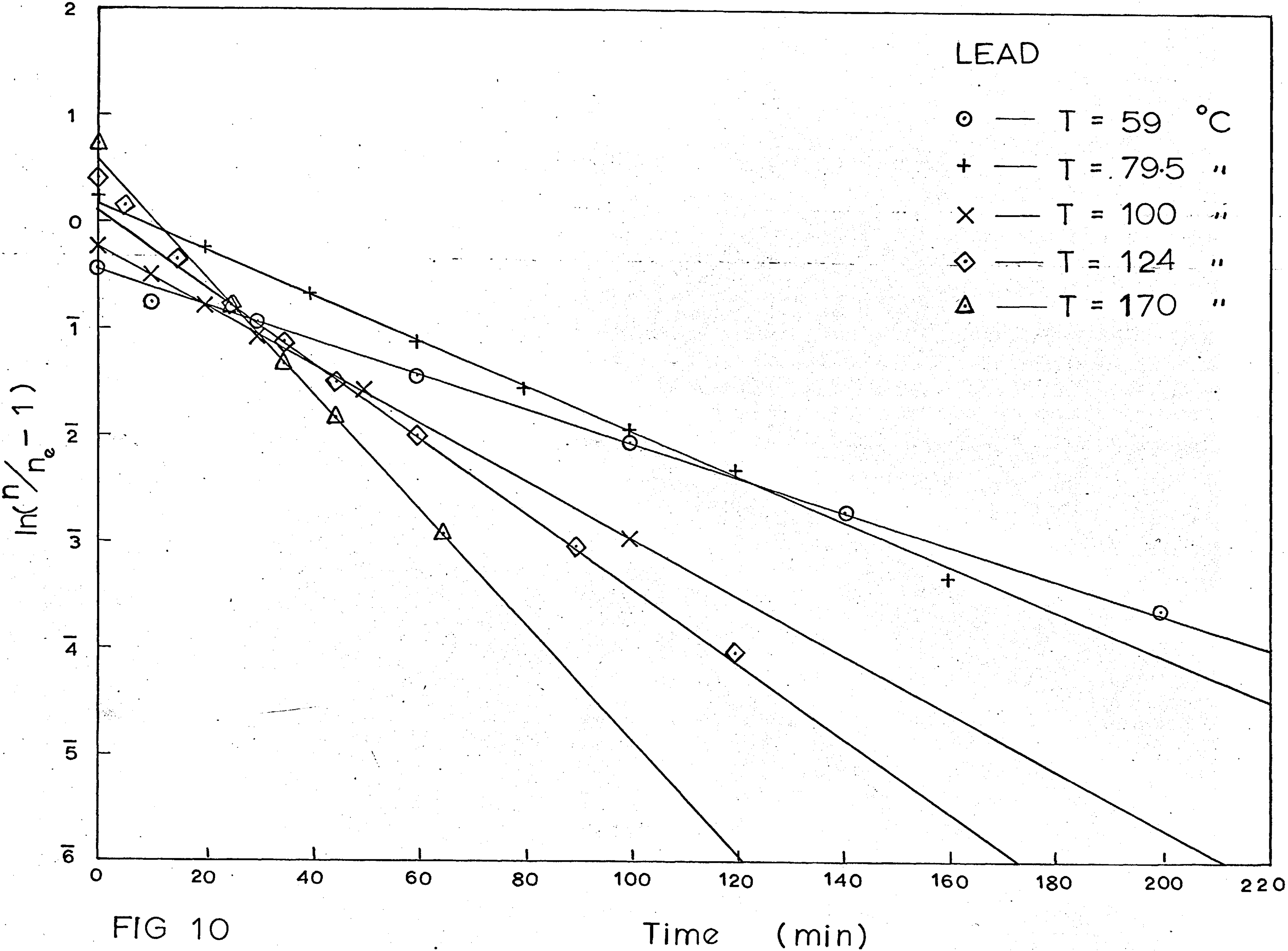

LEAD
⊙ — T = 59 °C
+ — T = 79.5 "
× — T = 100 "
◇ — T = 124 "
△ — T = 170 "
$\ln(n/n_e - 1)$
2
1
0
$\bar{1}$
$\bar{2}$
$\bar{3}$
$\bar{4}$
$\bar{5}$
$\bar{6}$
0
20
40
60
80
100
120
140
160
180
200
220
Time (min)

FIG 10

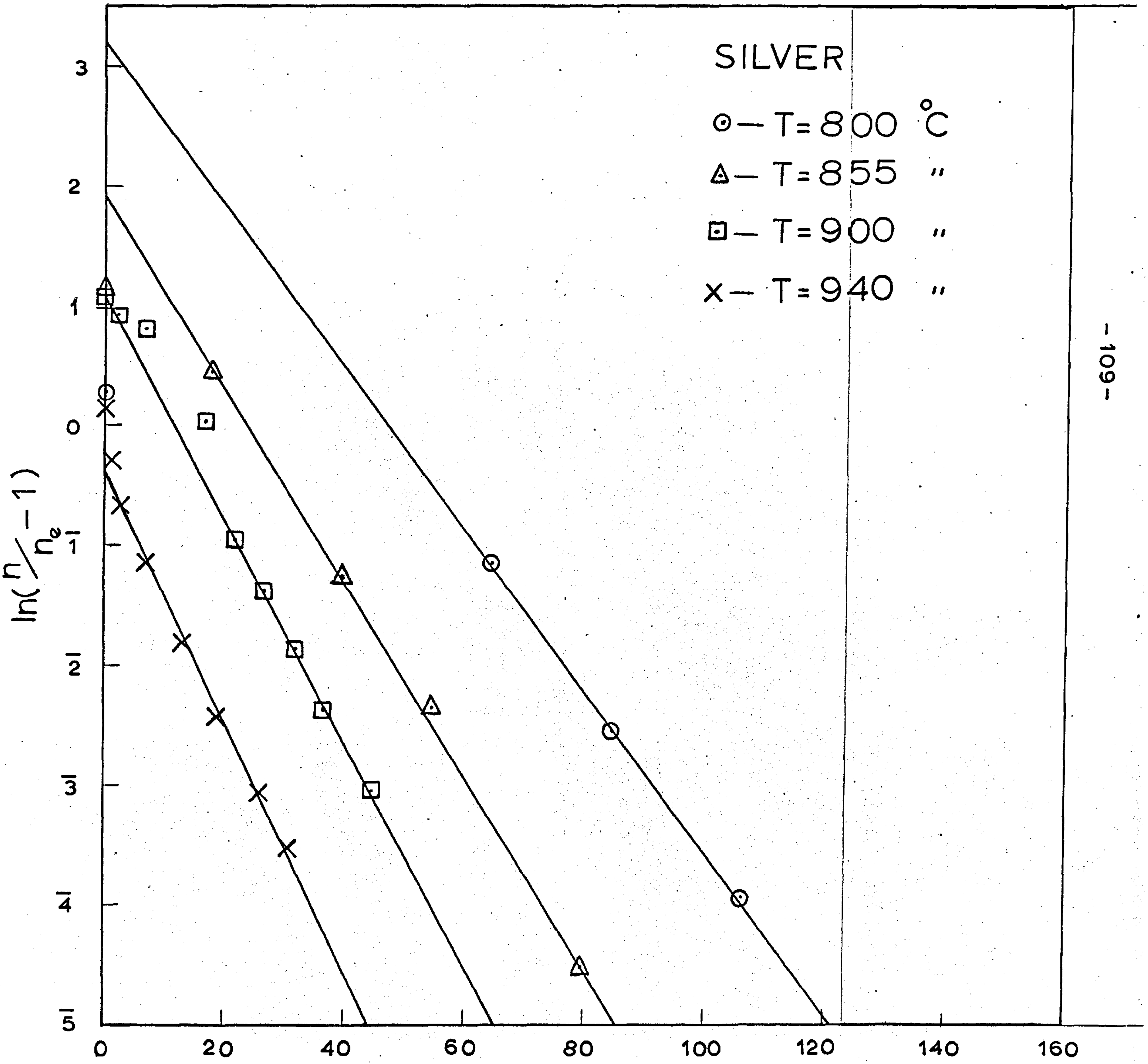


FIG 11

Time (hr)

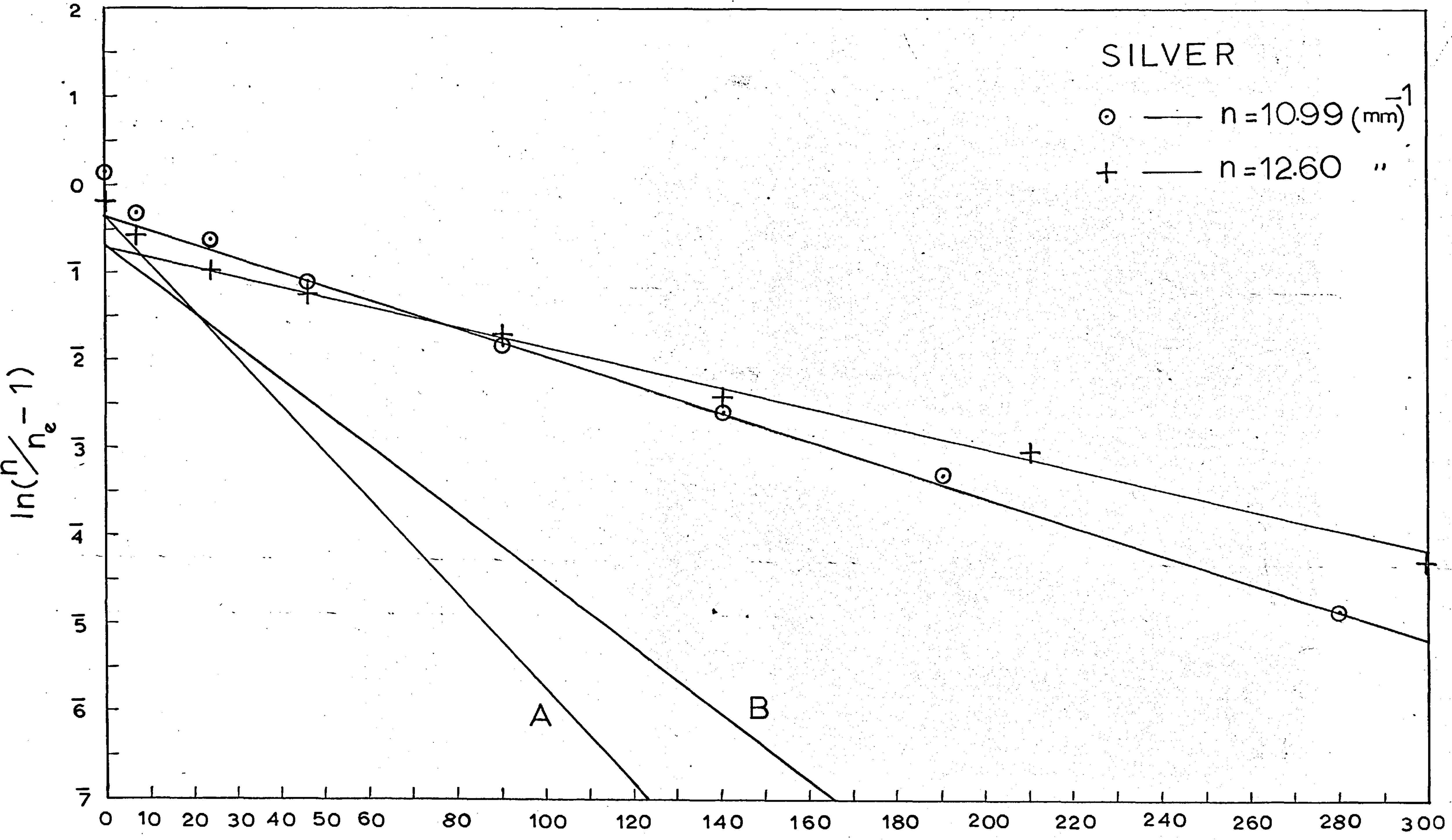


FIG 11 a

Time (hr)

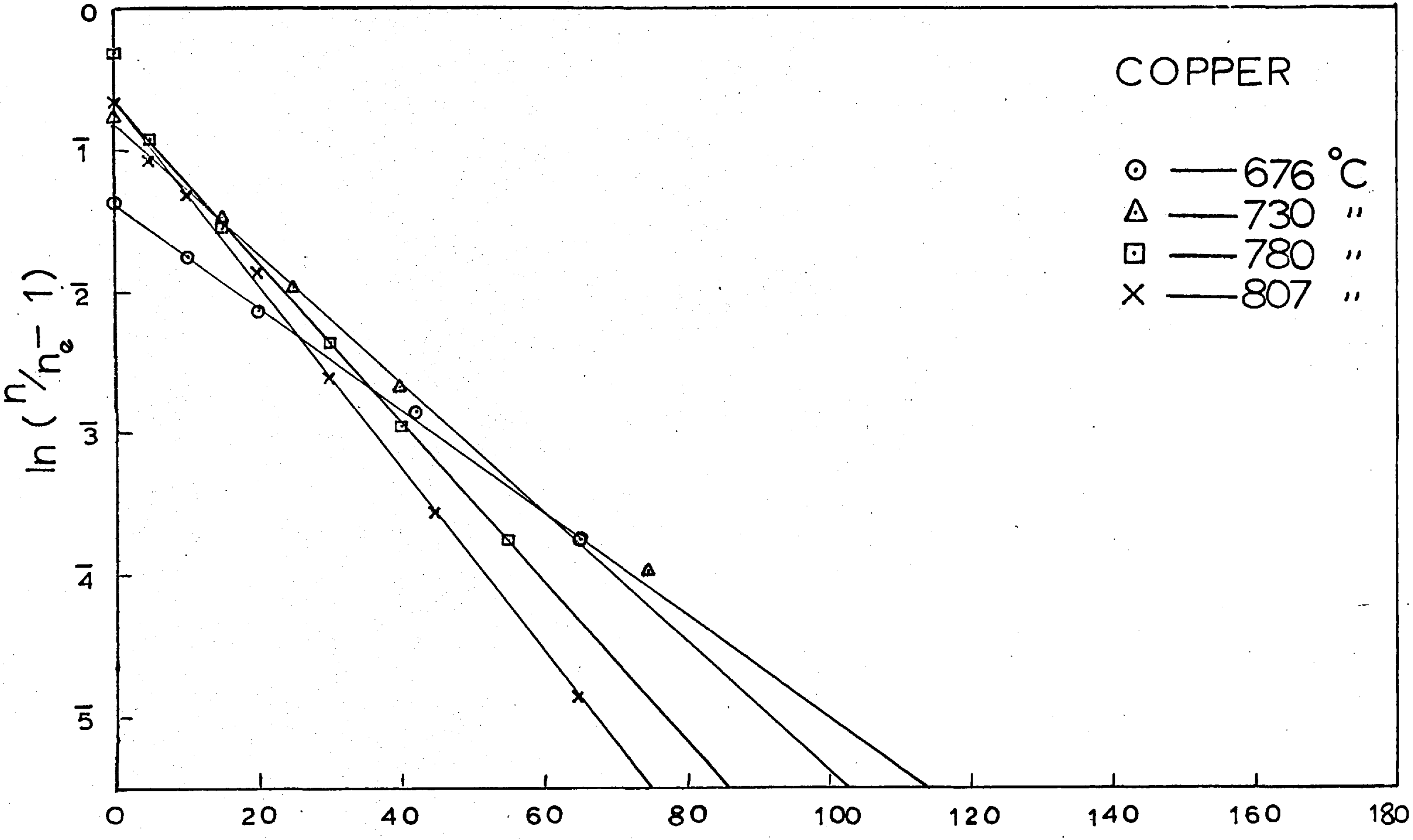

COPPER
⊙ —— 676 °C
△ —— 730 "
⊡ —— 780 "
× —— 807 "
$\ln(n/n_e - 1)$
0
$\bar{1}$
$\bar{2}$
$\bar{3}$
$\bar{4}$
$\bar{5}$
0
20
40
60
80
100
120
140
160
180
Time (min)

FIG 12.

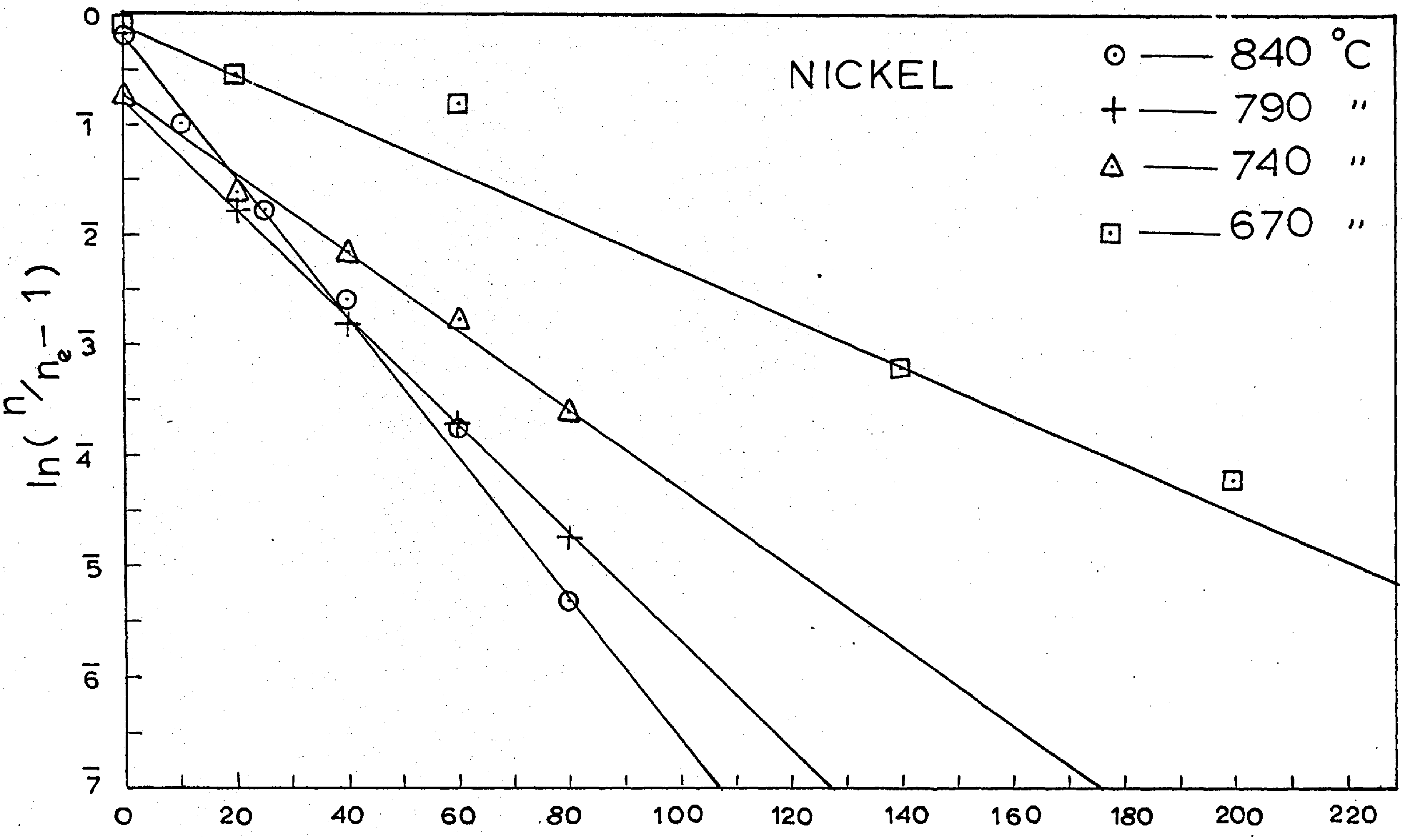

NICKEL
⊙ —— 840 °C
+ —— 790 "
△ —— 740 "
⊡ —— 670 "
$\ln(^n/_{n_e} - 1)$
0
$\bar{1}$
$\bar{2}$
$\bar{3}$
$\bar{4}$
$\bar{5}$
$\bar{6}$
$\bar{7}$
0
20
40
60
80
100
120
140
160
180
200
220
Time (min)

FIG 13

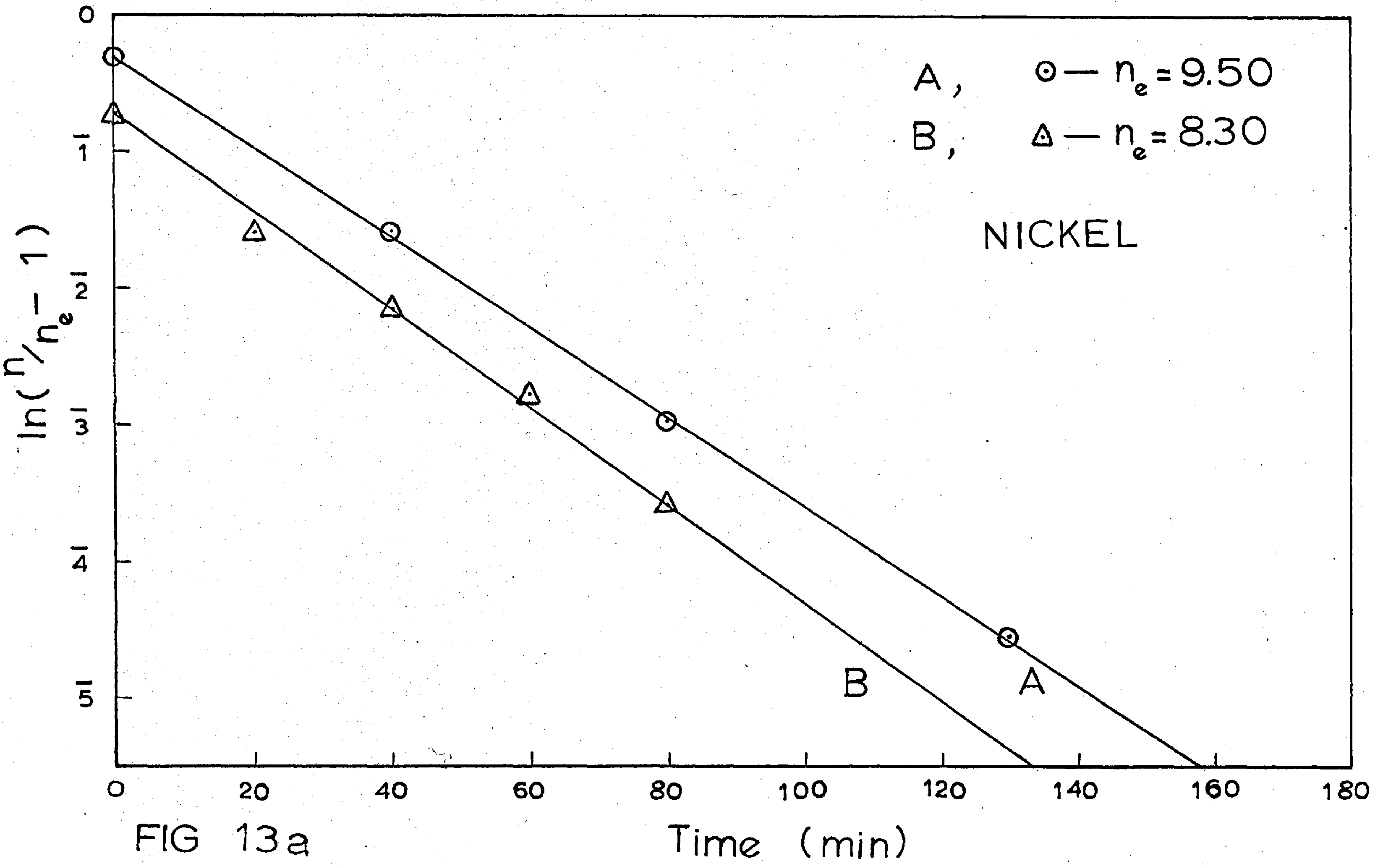

A, ⊙ — $n_e = 9.50$
B, △ — $n_e = 8.30$
NICKEL
B
A
$\ln(n/n_e - 1)$
0
$\bar{1}$
$\bar{2}$
$\bar{3}$
$\bar{4}$
$\bar{5}$
0
20
40
60
80
100
120
140
160
180
Time (min)

FIG 13a

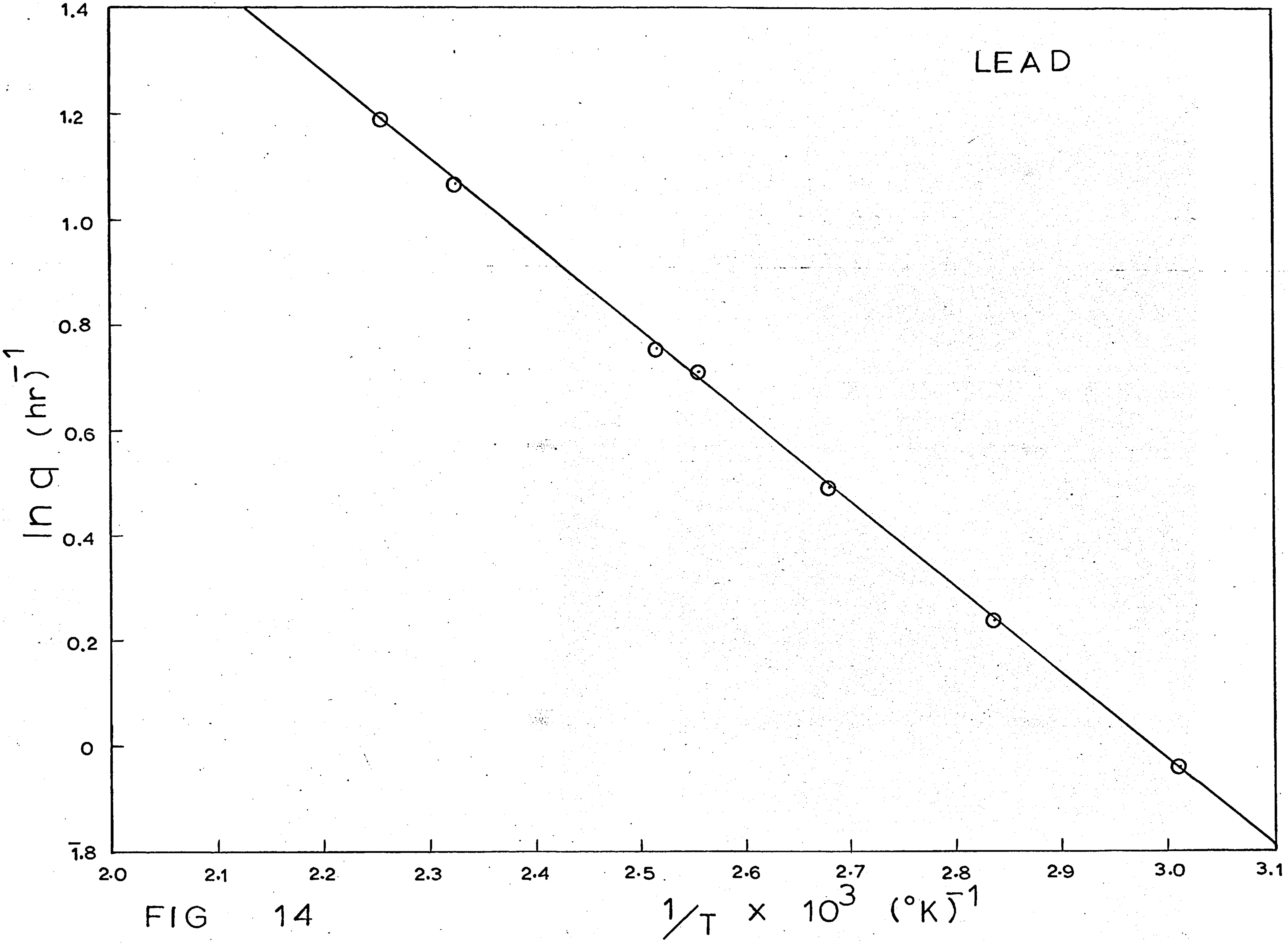

LEAD
ln q (hr)$^{-1}$
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
$\bar{1}$.8
2.0
2.1
2.2
2.3
2.4
2.5
2.6
2.7
2.8
2.9
3.0
3.1
1/T × 10^3 (°K)$^{-1}$

FIG 14

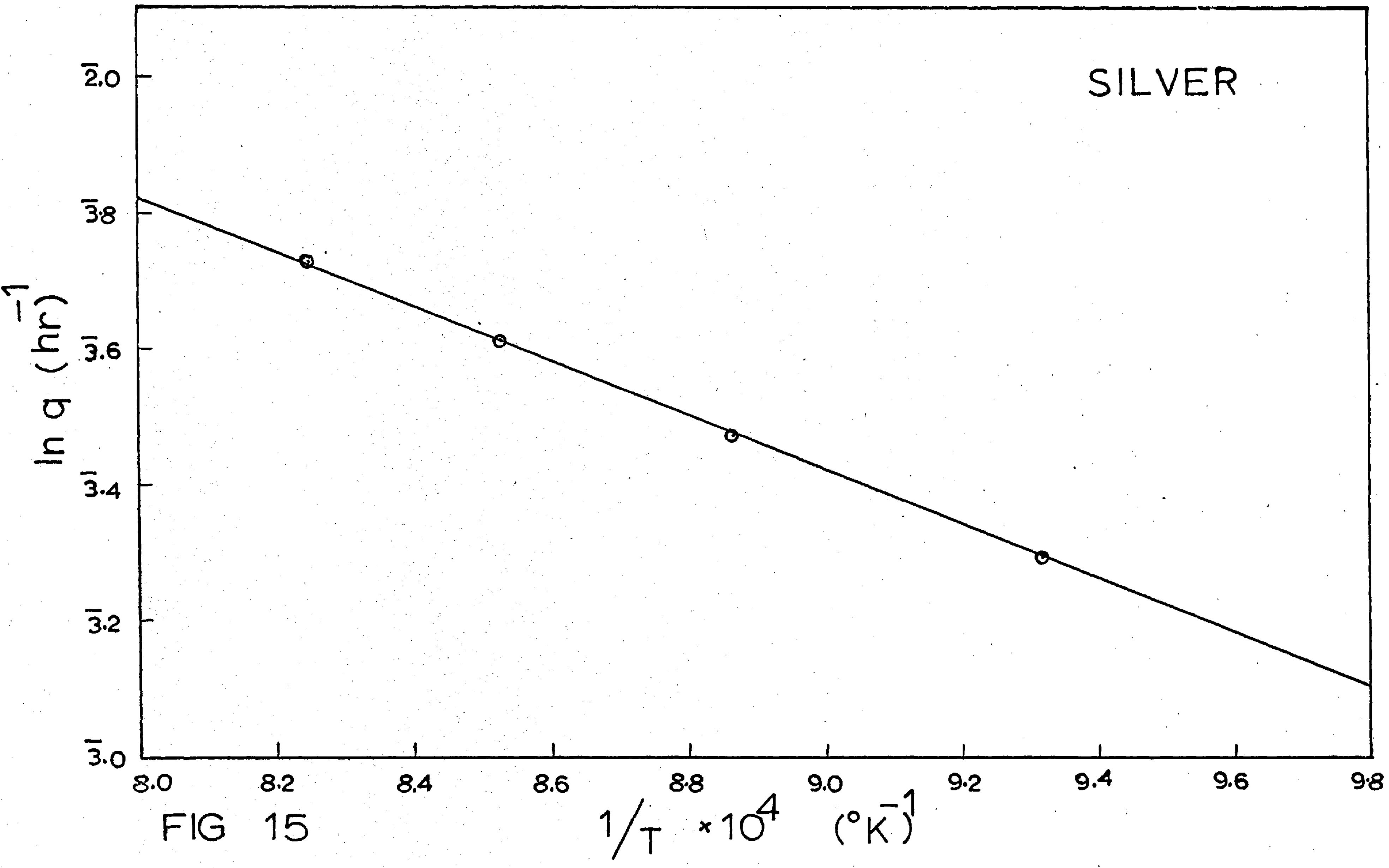

SILVER
ln q (hr^{-1})
$\bar{2}$.0
$\bar{3}$.8
$\bar{3}$.6
$\bar{3}$.4
$\bar{3}$.2
$\bar{3}$.0
8.0
8.2
8.4
8.6
8.8
9.0
9.2
9.4
9.6
9.8
$1/T \times 10^4$ (°K^{-1})

FIG 15

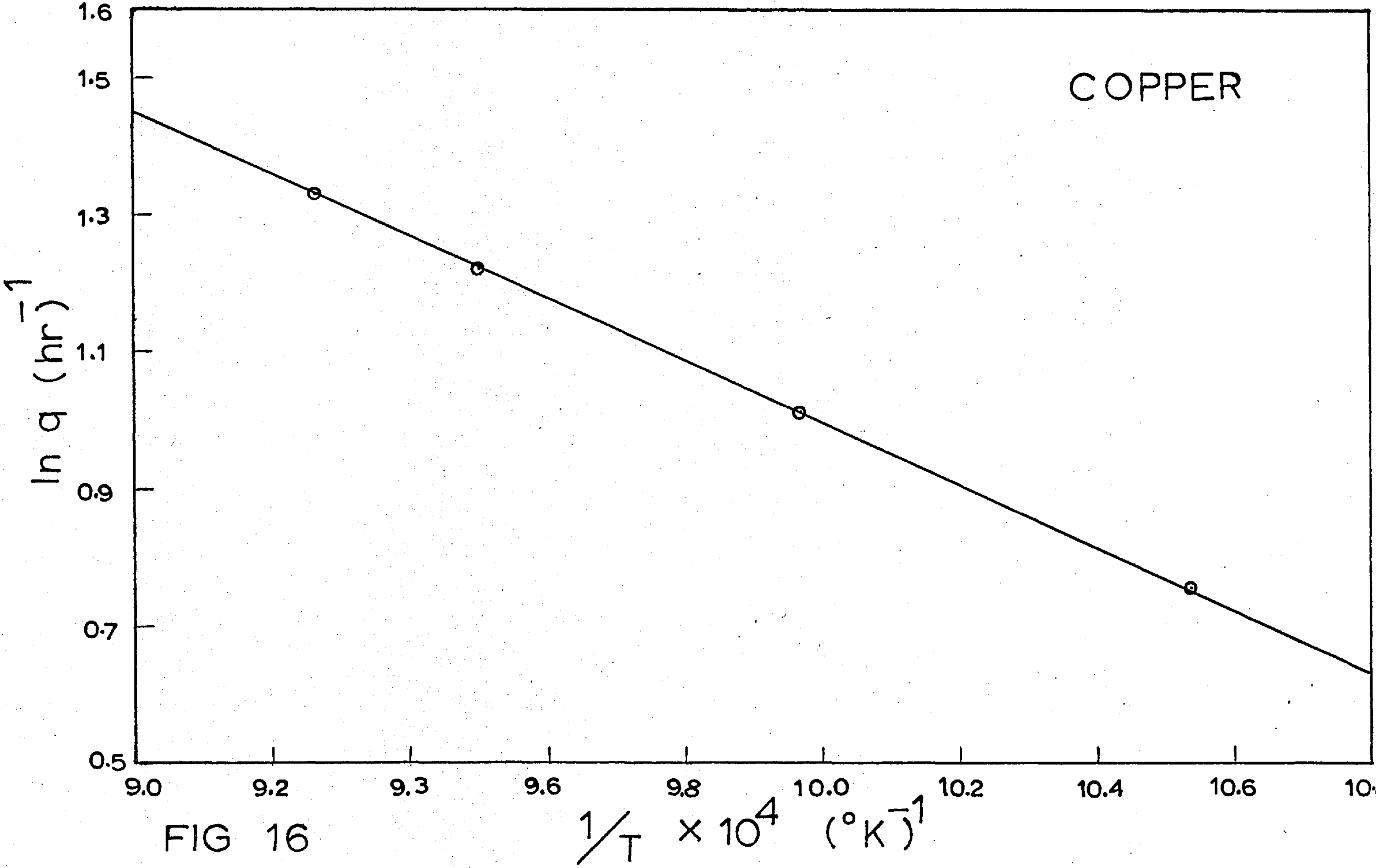

COPPER
ln q (hr^{-1})
1.6
1·5
1·3
1.1
0.9
0·7
0·5
9.0
9.2
9.3
9.6
9.8
10.0
10.2
10.4
10.6
10·8
$^1/_T \times 10^4$ (°K)$^{-1}$

FIG 16

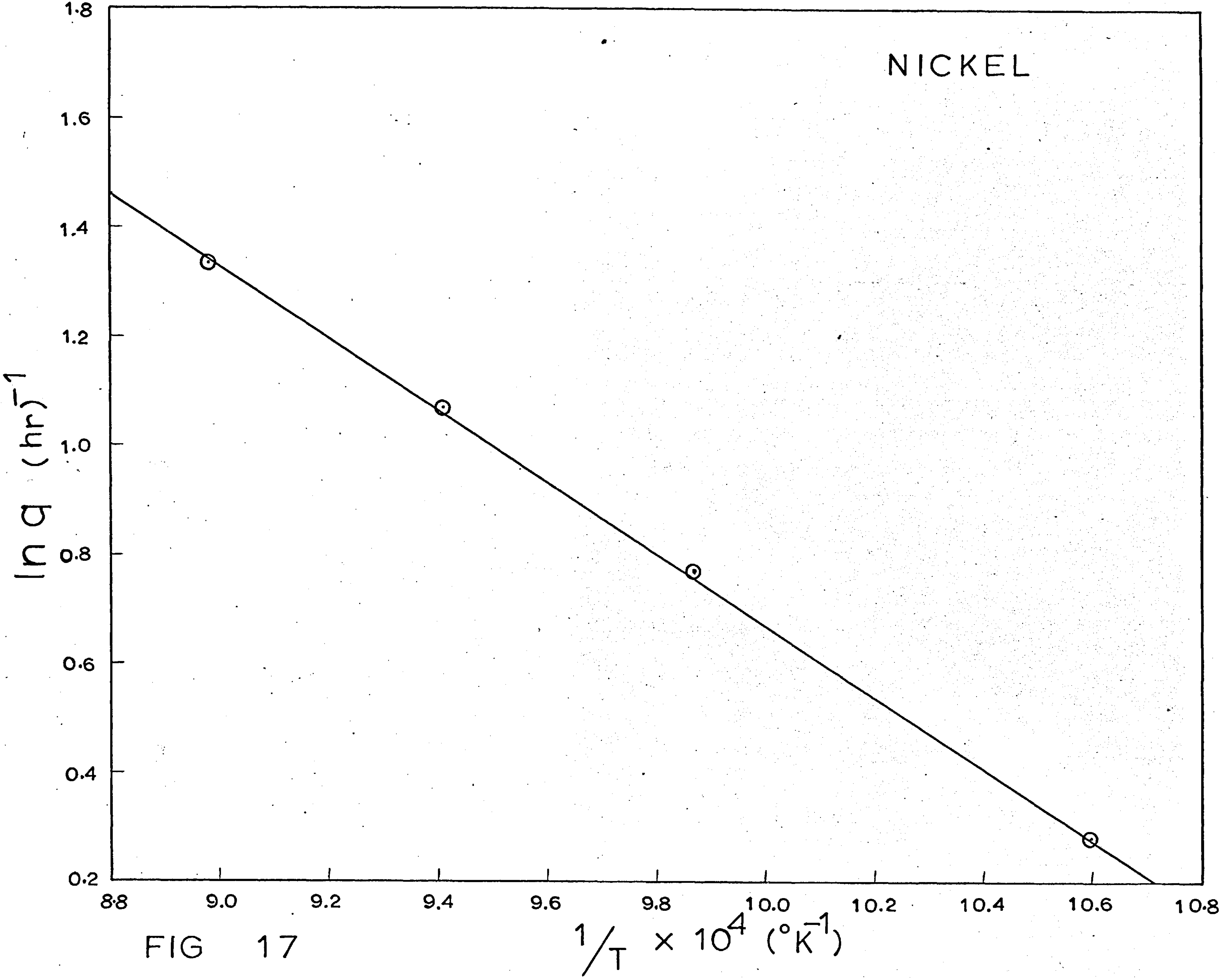

NICKEL
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
ln q (hr)$^{-1}$
8.8
9.0
9.2
9.4
9.6
9.8
10.0
10.2
10.4
10.6
10.8
$1/T \times 10^4$ (°K^{-1})

FIG 17

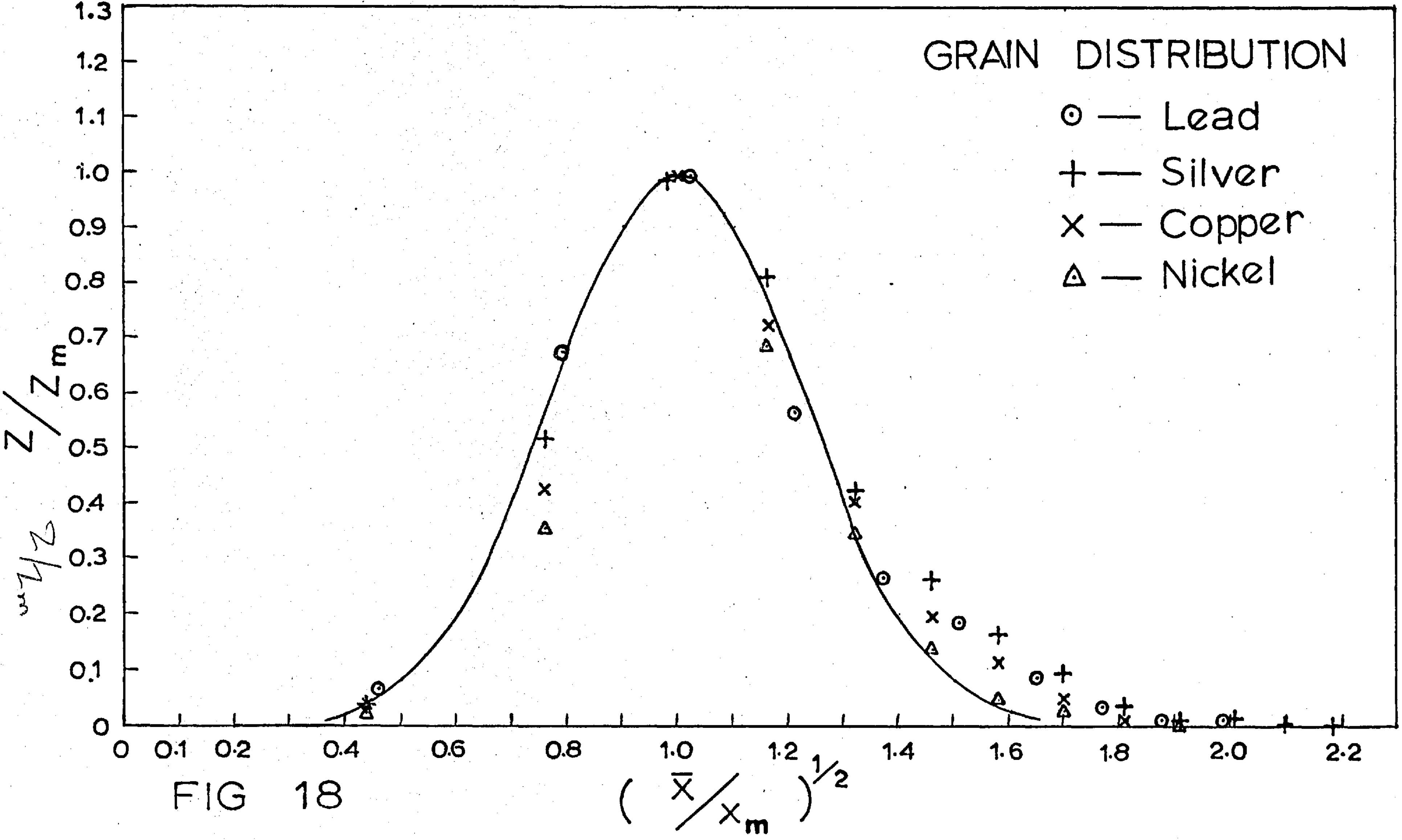

GRAIN DISTRIBUTION
⊙ — Lead
+ — Silver
× — Copper
△ — Nickel
Z/Z_m
Z/Z_m
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.1
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
$(\bar{X}/X_m)^{1/2}$

FIG 18

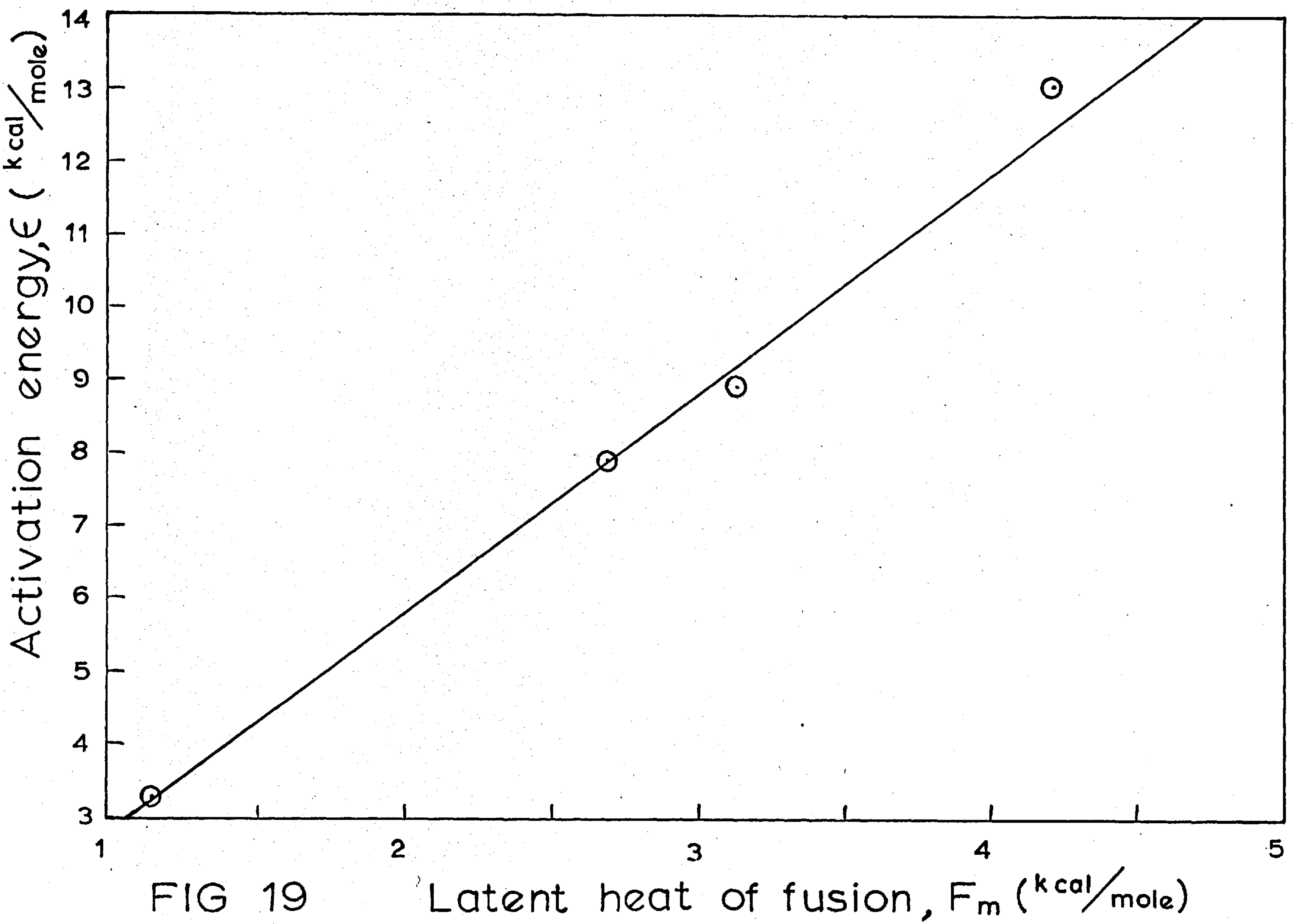
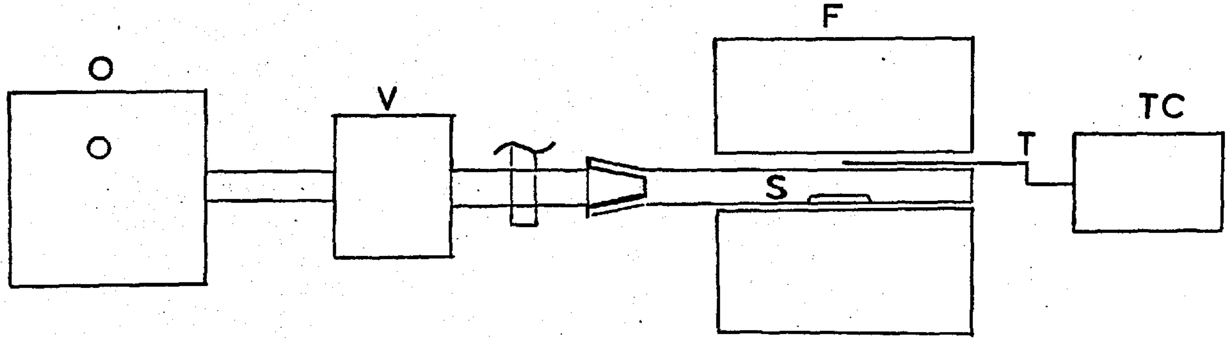

Activation energy, ε (kcal/mole)
14
13
12
11
10
9
8
7
6
5
4
3
1
2
3
4
5
Latent heat of fusion, F_m (kcal/mole)

FIG 19



O	Oil vacuum pump
V	Vapour diffusion pump
F	Furnace
S	Specimen
T	Thermocouple
TC	Temperature controller

FIG 20

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