Effect of Pressure on Precipitation in an Al-4·3% Cu Alloy

By T. Evans and E. Williams

J. J. Thomson Physical Laboratory, Whiteknights Park, Reading, Berkshire

ABSTRACT

The effect of hydrostatic pressures up to 12 kbar on the rates of formation of θ'' and θ' precipitates in an Al-4·3% Cu alloy has been studied. Pressure strongly inhibits the rates of formation of these precipitates. The θ'' precipitates were formed at 170°c and the θ' at 220°c. The activation volume for the θ'' formation was $12·4 \pm 0·4$ cm³ mole⁻¹ and that for θ' formation was $12·3 \pm 0·6$ cm³ mole⁻¹, i.e. effectively the same. Measurements of rates of formation of θ'' and θ' at various temperatures at atmospheric pressure also give the same activation energy of 27·45 kcal mole⁻¹ (1·19 ev) for the formation of the two types of precipitate.

§ 1. INTRODUCTION

COMPARED with the amount of work done by varying the ageing temperature in the examination of the formation of the various types of precipitate in the Al–Cu alloys, very little has been done using pressure as the main variable. Goliber, McKee, Kasper, Tillyard, Cahn and Phillips (1959), using a solid as the pressure transmitting medium, measured the effect of a pressure of 30 kbar on the formation of the θ precipitate at 400°c. The rate of precipitation was 40 times less than when a specimen was aged at the same temperature at atmospheric pressure, and they obtained an activation volume of 6·8 cm³ mole⁻¹. Both Goliber *et al.* and Hilliard and Cahn (1961) calculate that a pressure of 30 kbar would increase the solubility of copper in aluminium at a temperature of 400°c by only 9% compared with the solubility at atmospheric pressure and thus would have a negligible effect on the precipitation rate. The conclusion was therefore reached that the reduction in precipitation rate by pressure was due to the decrease in the diffusion rate of copper in aluminium. Work by Phillips (1961) on a Cu–Be alloy supports this conclusion. He found that the precipitation rate in this alloy was decreased by pressure although calculation had shown that pressure should markedly reduce the solubility of Be in Cu. In another investigation Harvey, Kaufman, Kulin, Leyenaar and Udin (1960) used alloys of nominal composition Al-4% Cu, 0·5% Mn, 0·5% Mg and Al-4·5% Cu, 0·6% Mn, 1·5% Mg. Specimens were aged at 100°c at atmospheric pressure and at 20 kbar. The ageing process was followed by hardness and resistivity measurements. Unfortunately, the scatter in the results was large and the only definite conclusion was that the ageing rate was reduced by pressure.

In the work reported in this paper the effect of hydrostatic pressures up to 12 kbar was determined on the rate of formation of θ'' precipitates at an

ageing temperature of 170°C and also on the formation of θ' precipitates at 220°C.   It was essential to use purely hydrostatic pressures, as the presence of shear stresses produced plastic deformation in the specimens and the results were not then reproducible.   The activation energy and the activation volume were derived for the formation of both types of precipitate. Both the activation volume and the activation energy were found to be the same in both cases.

§ 2. Experimental

The specimens of the Al–Cu alloy had dimensions of about 0·4 cm × 0·125 cm × 0·006 cm and a copper content of 4·32% by weight. The impurities present in parts per million were : Fe 10, Mg 10, Ca 8, Ag 7, Pb 6, Na 5, Si 5, Mn < 1.   The grain size was about 0·1 cm diameter, which meant that a specimen only contained a few grains.   The specimens were homogenized at 540°C for 2 hr in a restricted air-flow vertical furnace. They were then quenched into water which contained a few drops of teepol at 0°C.   Only specimens which sank immediately were used in the experiments.   The time of fall from the furnace to the quenching bath was about 0·2 sec.   After quenching, the specimens were aged in air at 20°C and atmospheric pressure for 24 hr.   This treatment allowed the fast reaction (De Sorbo, Treaftis and Turnbull 1958) to be completed and brought the specimens into a reproducible standard starting condition in the slow reaction region for ageing treatments at higher temperatures.   For the formation of θ'' and θ' precipitates at atmospheric pressure the specimens were aged in an oven at 170°C and 220°C respectively.   These ageing treatments at 170° and 220° were also done under pressure and the high pressure cell will now be described.

The high pressure apparatus used was of the tetrahedral type.   It was originally designed by Hall (1958) and lately modified by Lloyd, Hutton and Johnson (1959) and by King (1965).   Briefly, the apparatus consists of four anvils, each of which presses onto a face of a pyrophyllite tetrahedral cell which contains the specimen.   The cell, with a side length of 1·125 in., is shown in fig. 1 as it was used for the bismuth pressure calibration which will be mentioned later.   The cell is similar to one described by Curtin, Decker and Vanfleet (1965).   A hollow stainless-steel tube of diameter 0·19 in. was incorporated into the pyrophyllite tetrahedron and an electrical connection made from one end of the tube to a face of the cell by a copper tab.   The other end of the tube emerged at another face of the tetrahedron. An electrical current could be passed through the tube via the anvils which touched the two faces, and the cell could thus be heated.   The tube was filled with a silicone fluid with a viscosity of 20 cstoke at 25°C and sealed at both ends by teflon plugs.   This silicone fluid was found to remain liquid at all experimental conditions provided the pressure and temperature were increased progressively to the operating conditions.   A chromel–alumel thermocouple which was led out between the anvils measured the temperature of the silicone fluid, and the data of Hanneman and Strong (1965, 1966)

were used to apply a correction for the effects of pressure on the thermo-couple output.   The pressure calibration of the cell was done by measuring the change in electrical resistance of a manganin wire as the pressure was changed.   A length of about 30 cm insulated manganin wire of diameter 0·0112 cm was non-inductively wound into the form of an unsupported coil and placed in the silicone fluid of the cell.   Electrical contact was made to the measuring apparatus via two copper tabs which made contact with the two remaining anvils.   It was found necessary to season the manganin wire to temperature and pressure by progressively raising the temperature and pressure together to about 25 kbar and 200°c and maintaining these conditions for about 2 hr.   The resistance was very sensitive to plastic deformation and the seasoning was necessary to take account of shear stresses which were imposed on the parts of the wire emerging from the cell.

Fig. 1

UPPER SECTION OF SAMPLE HOLDER

THERMOCOUPLE

COPPER WIRE

COPPER HEATING TAB

COPPER WIRE

COPPER HEATING TAB

TEFLON PLUG

STAINLESS STEEL TUBE

INSULATED COPPER WIRE

BISMUTH SAMPLE

SILICONE FLUID

LOWER SECTION OF SAMPLE HOLDER

INSULATED COPPER WIRE

TEFLON PLUG

0·25 IN
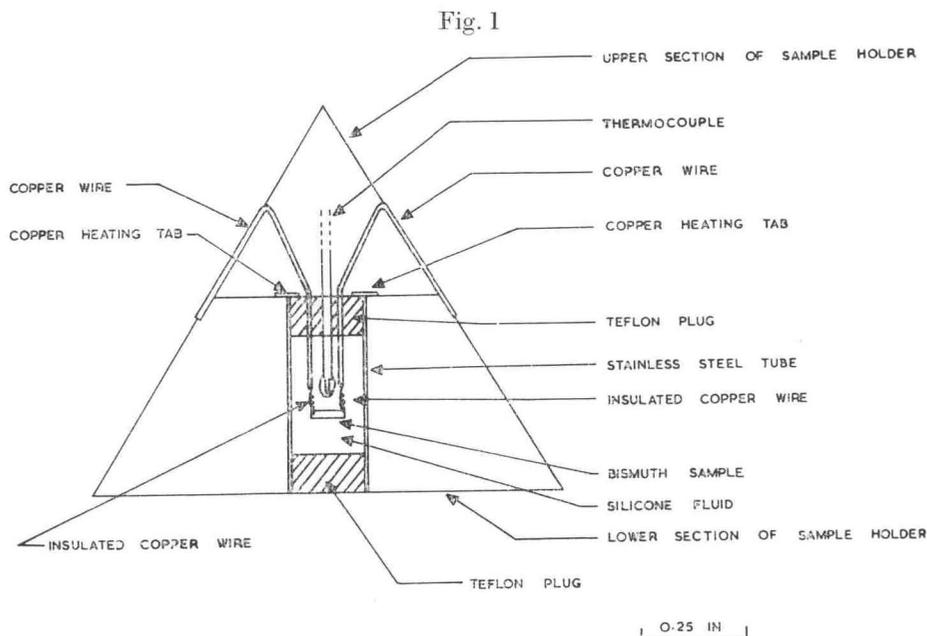
The tetrahedral pressure cell when used for the bismuth calibration.

After this procedure the change in resistance of the manganin gauge was measured as the external load was decreased at a fixed cell temperature of 170°c.   During all these treatments the liquid in the cell did not solidify. The bismuth I–II and II–III transitions were next determined by resistivity measurements of a bismuth wire at 170°c with a similar cell to give fixed points at 18·2 kbar and 22·8 kbar respectively (Butuzov 1957).   Thus, by combining the two methods a calibration curve of applied load against the pressure in the cell could be made with the silicone fluid at 170°c.   It was not possible to carry out pressure measurements during the ageing of the aluminium alloy under pressure, so all the cells were made as similar as

possible and it was assumed that the pressure–load calibration curve was applicable in all the experiments.

A standard amount of incomplete precipitation of θ'' at an ageing temperature of 170°C and atmospheric pressure was decided upon and the times required to produce the same amount of precipitation at various pressures were experimentally determined with the ageing temperature maintained at 170°C in the pressure cell by a sensitive temperature control unit. The same procedure was followed for the formation of θ' precipitates at 220°C. The amount of precipitation produced in a particular experiment was determined by transmission electron microscopy after the specimens had been suitably thinned (Nicholson, Thomas and Nutting 1958—using chromium trioxide instead of their recommended chromium oxide in the polishing solution). The standard amount of precipitation for θ'' and θ' was also produced at atmospheric pressure by varying the ageing temperatures to determine the activation energies for the two processes.

§ 3. RESULTS

3.1. *Formation of θ'' Precipitates*

It was first necessary to obtain a standard amount of precipitation at atmospheric pressure of θ''. Specimens were homogenized, quenched and

Fig. 2
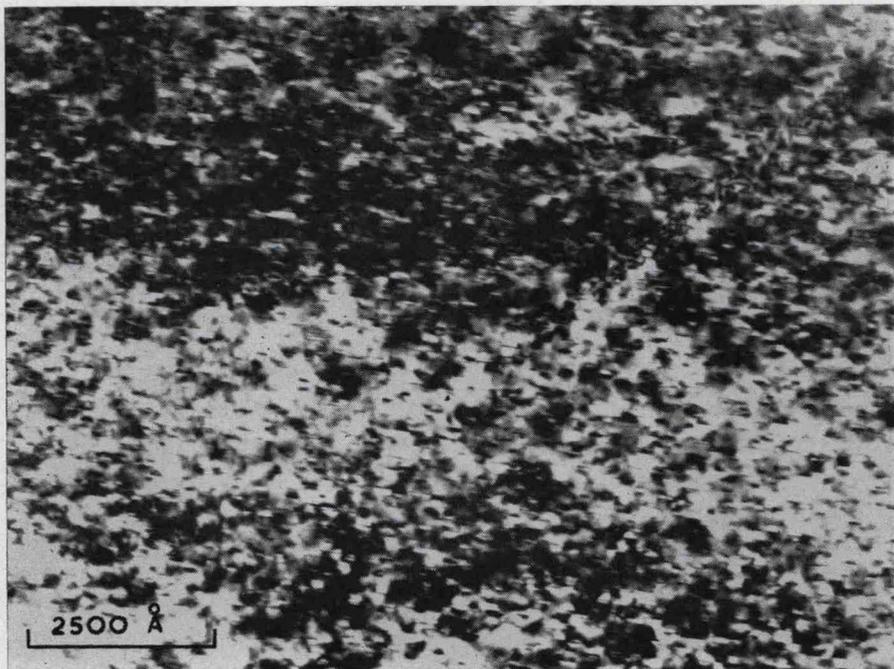
The standard θ'' result. The ageing conditions were: 170°C, atmospheric pressure, 4 hr.

aged at room temperature for 24 hr at atmospheric pressure. Then followed an ageing treatment of 4 hr at 170°C at atmospheric pressure to produce the standard amount of θ'' precipitation with no other type of precipitation present (fig. 2). The θ'' precipitation appeared to occur evenly in the specimens and the diameters of the θ'' precipitates were measured and a histogram constructed for the standard result (fig. 3). The mean θ'' diameter as determined from the measurements was 165 Å. Several specimens were given the standard ageing treatments of 4 hr at 170°C and the range of diameters produced were shown by the Student's t test, which will be briefly mentioned later, to come from the same population of diameters.

Fig. 3
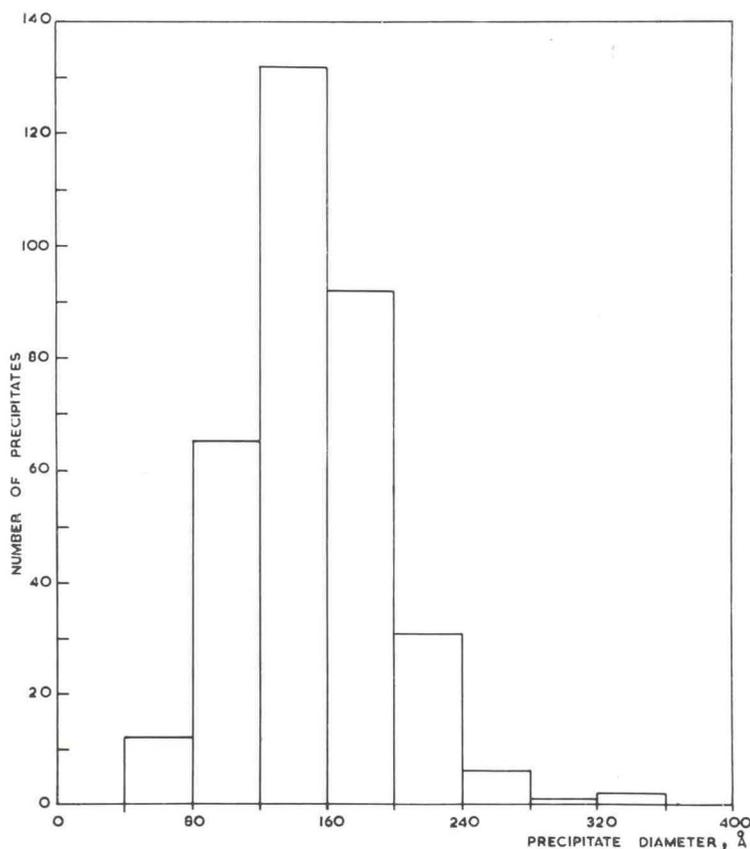
Histogram of the distribution of θ'' diameters in a specimen which had been aged under the standard conditions.

3.2. *Formation of θ'' Precipitates under Hydrostatic Pressure at 170°C*

Specimens which had been homogenized, quenched and aged at room temperature and atmospheric pressure for 24 hr were further aged at 170°C at various hydrostatic pressures for times such that the standard θ'' result

was obtained.   To compare the sizes of the θ'' precipitates formed under pressure with the standard θ'' result for a particular experiment, the diameters were measured and the mean precipitate diameter and the standard deviation from the mean of the precipitate diameter distribution were obtained.   These values were then compared with the corresponding values obtained from the standard result using the 'Student's t test'.   If the agreement was not within the required limits of error the ageing time was adjusted accordingly.   The Student's t test is a statistical method for comparing two sets of data in order to determine the probability that they come from the same population. t is defined as:

$$t = \frac{(\bar{x}_1 - \bar{x}_2)(n_2 n_1)^{\frac{1}{2}}}{(n_1 \sigma_1{}^2 + n_2 \sigma_2{}^2)^{\frac{1}{2}}},$$

where, in the present work:

> $\bar{x}_1 =$ mean of the standard set of data,
> $\bar{x}_2 =$ mean of the trial set of data,
> $n_1 =$ number of readings in the standard set of data,
> $n_2 =$ number of readings in the trial set of data,
> $\sigma_1 =$ standard deviation from the mean for the standard set of data,
> $\sigma_2 =$ standard deviation from the mean for the trial set of data.

The details of the t test are given by Weatherburn (1961).   If $t \leqslant 2$, then the probability that the trial set of data comes from the same population as the standard set of data is at least 95%.   This was the criterion used for the comparison of the results obtained under different ageing conditions.   It was also used to check that the micrographs which were taken were representative of each result.

The results are summarized in fig. 4.   The error bars were obtained by taking the shortest and longest times of ageing within which the standard θ'' result was still obtained.   Pressure did not appear to affect the actual density of precipitates for the standard result, nor was there any apparent change in the observed contrast at the precipitates.

It is very probable that the imposition of pressure is slowing down the diffusion of copper atoms to the precipitates and the following is applicable:

$$D = D_0 \exp\left(-\frac{\Delta H}{RT}\right),$$

where D is the diffusion coefficient of copper in aluminium, D_0 is the frequency factor and ΔH is the enthalpy change.   This may be written:

$$\ln D = D_0 \exp\left[-\left(\frac{\Delta U + P \Delta V}{RT}\right)\right],$$

where $\Delta U =$ activation energy for the diffusion process at atmospheric pressure, P is the pressure and ΔV is the activation volume.   From diffusion theory (see, for example, Wert and Thompson 1964):

$$\bar{x}^2 = 2Dt.$$

Fig. 4
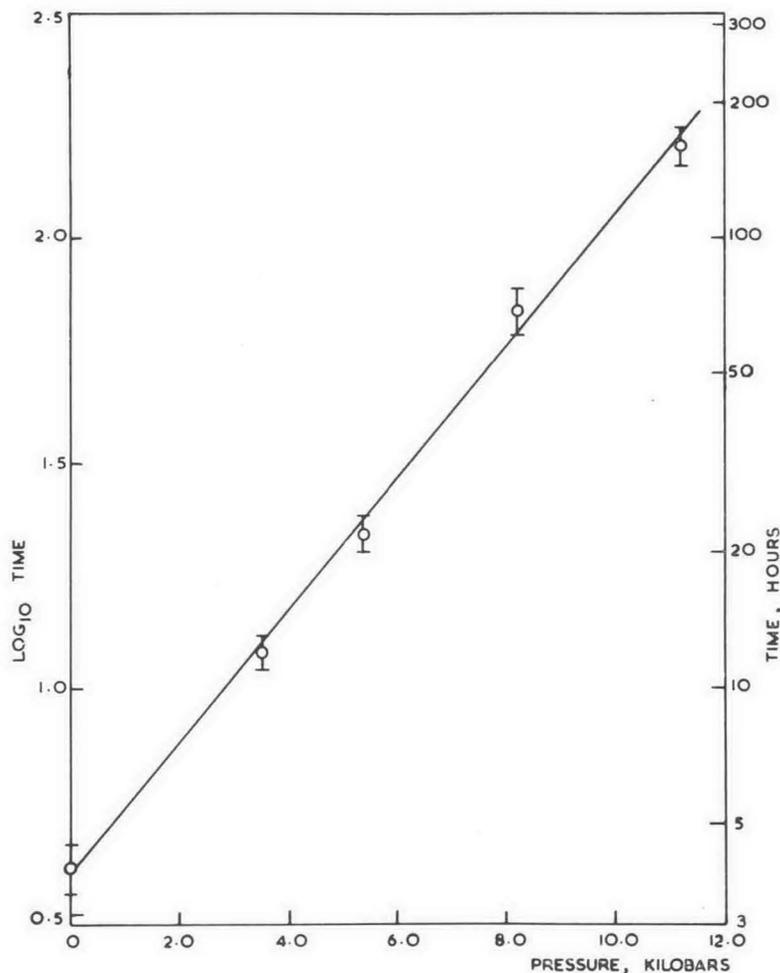
Variation with pressure of the time required to obtain the standard θ'' result.

where $\bar{x}^2 =$ mean square distance travelled by an atom in time t. Hence, if $\bar{x}^2$ is a constant, as is assumed in the present experiments :

$$D = \frac{\alpha}{t},$$

where α is a constant. Thus

$$\ln t = \frac{P\Delta V}{RT} + \frac{\Delta U}{RT} + \ln \frac{\alpha}{D_0}.$$

Thus at constant T and if D_0 and ΔV are independent of pressure, then the slope of $\ln t$ versus P will have a gradient of $\Delta V/RT$. From fig. 4 an activation volume ΔV for the diffusion process in the formation of θ'' precipitates

of $12\cdot4 \pm 0\cdot4\,\text{cm}^3\,\text{mole}^{-1}$ is obtained.   This can be compared with

$$10\cdot02\,\text{cm}^3\,\text{mole}^{-1},$$

which is the molar volume of aluminium.   In work on the effect of pressure on self-diffusion, D_0 is not independent of pressure but the correction to the activation volume due to this factor is less than 10%.   For instance, Beyeler and Adda (1968) found that the uncorrected activation volume for vacancies

Fig. 5
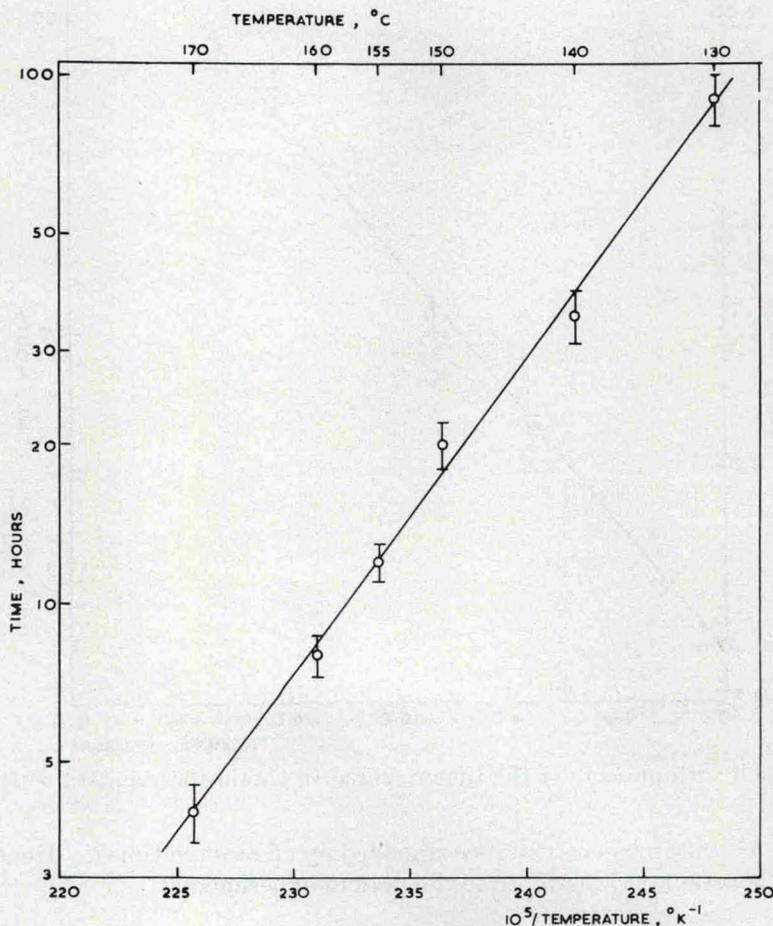
Variation with temperature of the time required to obtain the standard θ'' result.

in aluminium was $12\cdot5\,\text{cm}^3\,\text{mole}^{-1}$, and when the correction for the variation of D_0 with pressure was made, the activation volume became $12\cdot9\,\text{cm}^3\,\text{mole}^{-1}$, a correction of less than 4%.

To obtain the apparent activation energy for the formation of the θ'' precipitates, specimens were homogenized at 540°C, quenched to 0°C, aged at room temperature for 24 hr and then further aged at temperatures in

the range 130°C–170°C at atmospheric pressure for times such that the standard θ'' result was obtained. The results are shown in fig. 5. By applying the above formula at atmospheric pressure and varying temperature:

$$\ln t = \frac{\Delta U}{RT} + \ln \frac{\alpha}{D_0},$$

and the slope of $\ln t$ versus $1/T$ will be $\Delta U/R$.

From fig. 5 the activation energy for the θ'' precipitation is $27\cdot45 \pm 1\cdot15$ kcal mole^{-1}, i.e. $(1\cdot19 \pm 0\cdot05\,\text{ev})$ for the atomic activation energy.

3.3. *Formation of θ' Precipitates at 220°C*

The next series of experiments was concerned with the effects of pressure on the formation of θ' precipitates. The experimental method was the same as that for the investigation of θ'' precipitates and a standard θ' result was obtained. This standard result was obtained by homogenizing a

Fig. 6
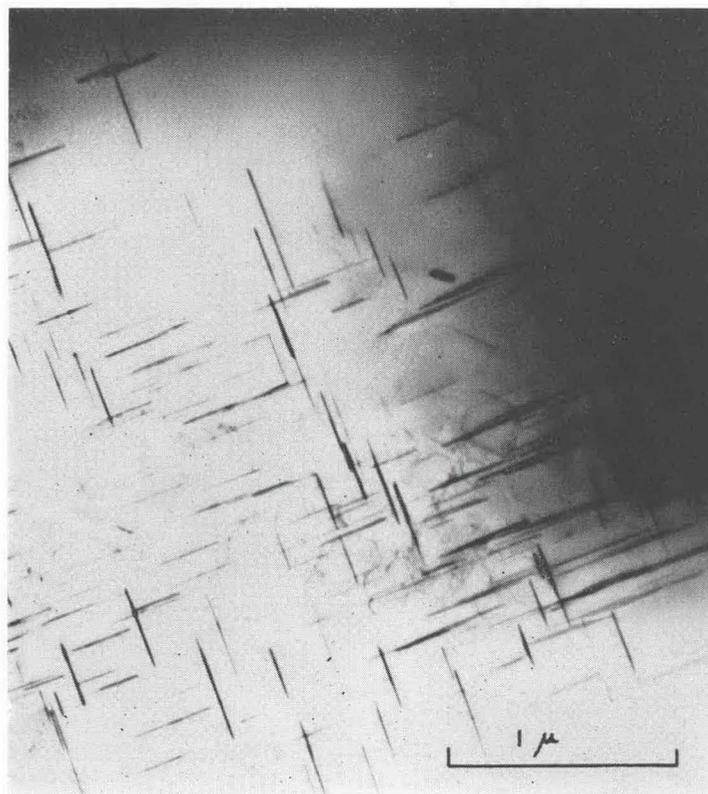
The standard θ' result. The ageing conditions were: 220°C, atmospheric pressure, 1·5 hr.

specimen, quenching, ageing for 24 hr at room temperature at atmospheric pressure and then ageing at 220°c for 1·5 hr at atmospheric pressure (fig. 6).

The distribution of θ' diameters obtained from the micrographs is shown in fig. 7 and the mean diameter was 2700 Å. Unlike the θ'' precipitates the θ' precipitates were not uniformly distributed throughout the specimens but occurred in wide bands with a lower density of θ' precipitates in between. It is possible that the θ' precipitates formed preferentially at dislocations but there was no direct evidence for this. The micrographs used for the measurement of precipitate diameters were taken at the high density regions. The standard result was for incomplete precipitation, since if the ageing times were longer than 1·5 hr at 220°c the θ' precipitates increased further in size.

Fig. 7
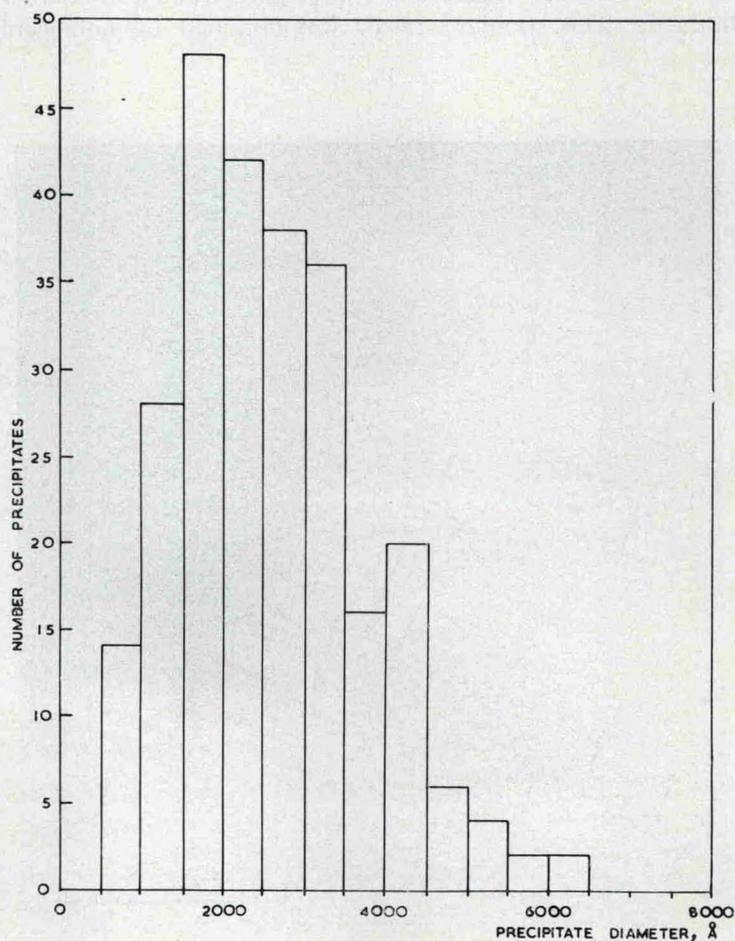
Histogram of the distribution of θ' diameters in a specimen which had been aged under the standard conditions.

3.4. *Formation of θ′ under Hydrostatic Pressure at 220°C*

Specimens which had been homogenized, quenched and aged at room temperature and atmospheric pressure for 24 hr were further aged at 220°C under various pressures such that the standard θ′ result was obtained. The Student's *t* test was again used.   The results are shown in fig. 8 which gives an activation volume for diffusion of copper in aluminium of $12·3 \pm 0·6$ cm^3 mole^{-1} for the formation of θ′ precipitates, which is effectively the same activation volume as for the θ″ formation.

To obtain the apparent activation energy for the formation of θ′ precipitates, the standard θ′ result was obtained by ageing specimens in the

Fig. 8
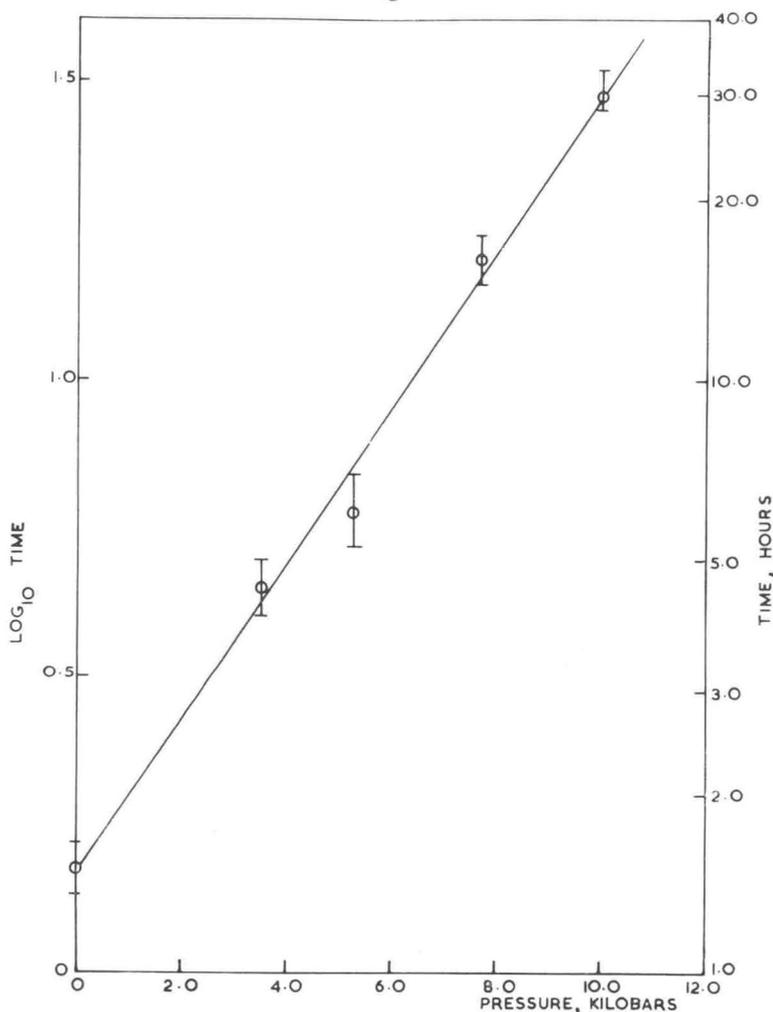
Variation with pressure of the time required to obtain the standard θ′ result.

temperature range of 210°c to 240°c at atmospheric pressure for various times. Temperatures of less than 210°c could not be used as some θ'' precipitates were also formed and ageing temperatures above 240°c produced such a rapid growth of θ' precipitates that the times to obtain the standard θ' result could not be accurately measured. The results are shown graphically in fig. 9 from which an activation energy of $27 \cdot 45 \pm 1 \cdot 85$ kcal mole^{-1} ($1 \cdot 19 \pm 0 \cdot 08$ ev) was obtained. This value is the same as was obtained for the activation energy for θ'' formation at 170°c.

Fig. 9
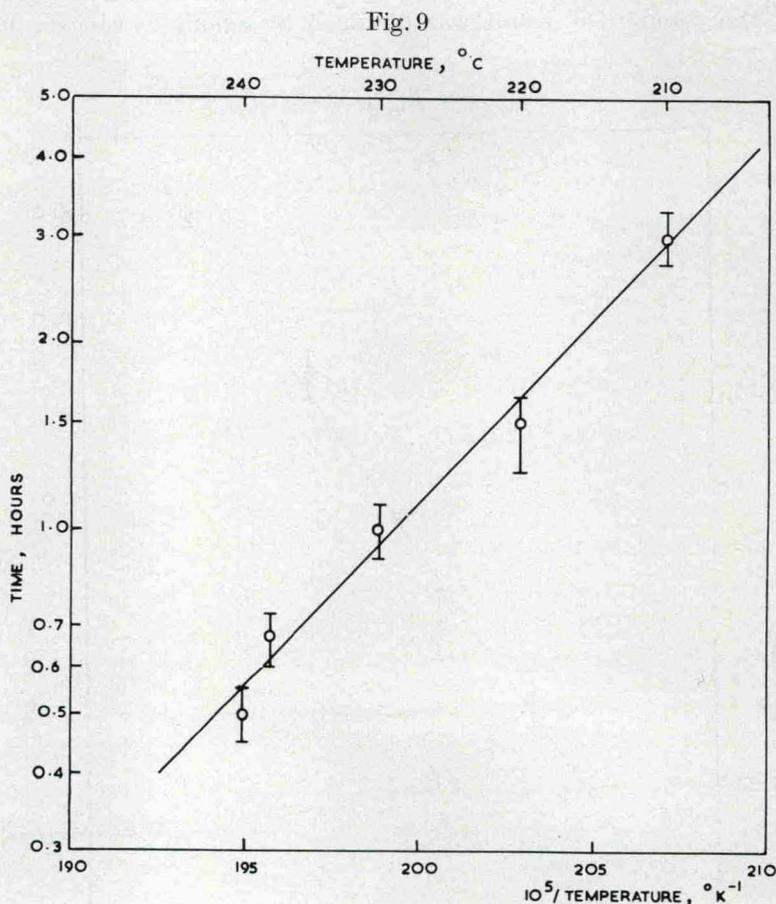
Variation with temperature of the time required to obtain the standard θ' result

§ 4. Conclusions

The conclusions of this work are :

1. Because the activation energies and activation volumes for the formation of both θ'' and θ' precipitates are the same, the formation of the two types of precipitate is controlled by the same diffusion process.

Turnbull and Cormia (1960) suggested that the low measured activation energy for the formation of G.P. zones can be accounted for by vacancy traps at the zones.   If vacancy traps are also present at θ'' and θ' precipitates of depth about 0·67 ev (assuming an activation energy of migration of 0·52 ev) to account for the low measured activation energy (1·19 ev) compared with the reported activation energy of copper in aluminium (1·4 ev), then the traps are of the same type at the θ'' and θ' precipitates.   It is considered extremely unlikely that the low activation energy can be explained by either grain boundary diffusion or diffusion along dislocations in the present work.

2. It has been mentioned that Beyeler and Adda (1968) obtained an uncorrected value of 12·5 cm^3 $mole^{-1}$ for the activation volume for self-diffusion in aluminium and this value is within the experimental errors for the values obtained for θ'' and θ' formation.   A direct comparison of the activation volumes for θ'' and θ' formation and that for self-diffusion in aluminium cannot be made because present theories (Le Claire 1962 and Corless and March 1961) have considered very dilute alloys which Al-4% Cu certainly is not.   However, the magnitude of the measured activation volumes and the fact that they are the same for both types of precipitate show that pressure is inhibiting the diffusion of copper to the precipitates and not inhibiting the nucleation of the precipitates.

3. The magnitude of the measured activation volumes shows that the vacancy concentration is at thermal equilibrium or not greatly in excess of it.   This would lend some credence to the same sort of suggestion to that which has been put forward by Stoebe and Dawson (1968) for self-diffusion in aluminium, that the migration energy component of the activation energy for the diffusion of copper in aluminium is, for some reason, temperature dependent and the activation energy is, in fact, about 1·2 ev at 200°c. Then there would be no need to postulate vacancy traps at the precipitates. Obviously further diffusion work on copper in aluminium at various temperature ranges would have to be done to resolve this point.

REFERENCES

BEYELER, M., and ADDA, Y., 1968, *J. Phys., Paris*, **29,** 345.
BUTUZOV, V. P., 1957, *Soviet Phys. Crystallogr.*, **2,** 533.
CORLESS, G. K., and MARCH, N. H., 1961, *Phil. Mag.*, **6,** 1285.
CURTIN, H. R., DECKER, D. L., and VANFLEET, H. B., 1965, *Phys. Rev. A*, **139,** 1552.
DE SORBO, W., TREAFTIS, H. N., and TURNBULL, D., 1958, *Acta metall.*, **6,** 401.

GOLIBER, E. W., MCKEE, K. H., KASPER, J. S., TILLYARD, J. E., CAHN, J. W., and PHILLIPS, V. A., 1959, General Electric Research Report, No. WADC–TR–59–747.

HALL, T., 1958, *Rev. scient. Instrum.*, **29,** 267.

HANNEMAN, R. E., and STRONG, H. M., 1965, *J. appl. Phys.*, **36,** 523; 1966, *Ibid.*, **37,** 612.

HARVEY, J. S., KAUFMAN, L., KULIN, S. A., LEYENAAR, A., and UDIN, H., 1960, Wright Air Development Center Technical Report, No. 59–655.

HILLIARD, J. E., and CAHN, J. W., 1961, *Progress in Very High Pressure Research*, edited by F. P. Bundy, W. R. Hibbard, and H. M. Strong, (John Wiley), p. 109.

KING, J. H., 1965, *J. scient. Instrum.*, **42,** 374.

LE CLAIRE, A. D., 1962, *Phil. Mag.*, **7,** 141.

LLOYD, E. C., HUTTON, U. O., and JOHNSON, D. P., 1959, *J. Res. natn. Bur. Stand. C*, **63,** 59.

NICHOLSON, R. B., THOMAS, G., and NUTTING, J., 1958, *Br. J. appl. Phys.*, **9,** 25.

PHILIPS, V. A., 1961, *Acta metall.*, **9,** 216.

STOEBE, T. G., and DAWSON, H. I., 1968, *Phys. Rev.*, **166,** 621.

TURNBULL, D., and CORMIA, R. L., 1960, *Acta metall.*, **8,** 747.

WEATHERBURN, C. E., 1961, *A First Course in Mathematical Statistics* (Cambridge University Press).

WERT, C. A., and THOMPSON, R. M., 1964, *Physics of Solids* (McGraw-Hill), p. 54.