THE COIL SPRING FEDERATION RESEARCH ORGANISATION

The Effect of Grain Boundary Precipitate on the Age Hardening Characteristics of Copper-Beryllium

Report No. 105

by

J. K. Wynn, M.Met.

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Summary

A study of the high temperature grain boundary precipitate in a commercial Cu-Be alloy has been carried out, and a time-temperature-transformation diagram plotted in the range 360°C - 500°C.

Tests were carried out to study the effects of this grain boundary precipitate on the mechanical and age hardening properties of the alloy. Four sets of age hardening curves were determined as follows:-

a) Solution treated
b) Solution treated + 10% grain boundary precipitate
c) Cold worked
d) Cold worked + 10% grain boundary precipitate

The effect of the grain boundary precipitate on the solution treated material, was to lower the hardness by about 40 Vickers points in all cases. The effect of the grain boundary precipitate on the cold worked material was to lower the hardness by about 70 Vickers points.

Tensile tests were then made on alloys with and without grain boundary precipitate, the results showed that with 10% grain boundary precipitate the ultimate tensile stress, and 1% Proof stress, were about 10% lower than in alloys similarly aged without grain boundary precipitate. No difference in elongation % was detected for the treatments studied.

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THE EFFECT OF GRAIN BOUNDARY PRECIPITATE ON THE AGE HARDENING CHARACTERISTICS OF COPPER-BERYLLIUM

by J.K. Wynn, M.Met.

1. INTRODUCTION

Copper beryllium is one of the more troublesome alloys that spring manufacturers use. The difficulties range from inconsistency in the behaviour of the material, to warping on heat treatment. There is no direct evidence to say why the springs warp whilst ageing, but a few tentative suggestions have been put forward. It is known that if a 2% Cu-Be alloy is slack quenched from 800°C, a certain amount of precipitate nucleates at the grain boundaries. This precipitate is thought to be softer than the matrix after ageing, and its presence may affect the elastic and tensile properties of the material. It may also play a large part in the distortion of the springs which occurs during subsequent heat treatment.

Precipitation occurs in Cu-Be alloys during ageing in two distinct ways:-

a) simultaneously throughout the grains at a uniform rate, in submicroscopic form (i.e.) a normal age hardening precipitate).

b) in the grain boundaries spreading inwards and consuming the interior of the grains (this precipitate has a lamellar or pearlitic structure).

Bumm,[1] Guinier and Jacquet[2] Guy Barrett and Mehl.[3]

The relative amounts of the two kinds of precipitate depend strongly on the ageing temperature and amount of beryllium in solution, and also on other less understood factors, Beck.[4]

The mechanism of precipitation hardening in copper beryllium has been studied by Geislet et al,[5] Guinier and Jacquet,[2] Gruhl and Wasserman[6] and Bassi.[7] It seems clear from this work that the hardening is caused by the formation of zones, in a similar manner to Al-4% Cu.

There has been little detailed work published concerning the "pearlitic" form of precipitation, although it is well known that additions of cobalt to the binary alloy tend to suppress it. A considerable amount of theoretical work has been published concerning the kinetics of this type of precipitation, Zener,[8] Fisher[9] and Turnbull.[10]

It was decided to investigate the effect of this grain boundary precipitate on the age hardening characteristics of one particular commercial alloy of composition 1.77% Be 0.24% Co. This alloy is of slightly lower Be content than many industrial alloys. The objects of the work were:-

1) To study the kinetics of this precipitation reaction during cooling by plotting a T-T-T curve, and carrying out some rate of growth analysis.

2) To determine the effect of this grain boundary precipitate on the mechanical properties of the alloy after age hardening. This was done by plotting ageing curves for solution treated and cold worked material, both with and without grain boundary precipitate. Tensile tests were also carried out to study its effects on the ultimate tensile strength, % elongation, etc.

2. APPARATUS AND EXPERIMENTAL PROCEDURE

A. Isothermal Study

The technique used for determining the T-T-T curve was that mainly developed by Bain, i.e. quench from the solution temperature into a salt bath, hold for a predetermined time then quench into water.

Ten different isothermal temperatures were studied in the range 360 - 500°C, and from these it was possible to plot the T-T-T diagram (Fig. 1).

The specimens were polished down on emery papers using paraffin as a lubricant, the final polish being obtained with 0 - $\frac{1}{4}$ µ diamond dust. The etchants used were ammoniacal copper sulphate, and ammoniacal hydrogen peroxide for aged and unaged specimens respectively.

B. Age hardening investigations

The ageing treatments were carried out in salts baths which were controlled to within ± 2°C by the use of electronic controllers. Four sets of age hardening curves were determined as follows:

a) Solution treated and aged 250 - 400°C.
b) Solution treated + precipitate, and aged 275 - 400°C.
c) Cold worked and aged 300 - 350°C.
d) Cold worked + precipitate, and aged 300 - 350°C.

C. Tensile Testing

A series of specimens were machined down to standard test piece No. 11 (Hounsfield). These were then heat treated and aged in two distinct groups:

a) Solution treated and aged at 325°C.
b) Solution treated + precipitate and aged at 325°C.

After pulling the test pieces values for the ultimate tensile strength, 1% Proof Stress and % elongation were obtained.

3. RESULTS

General features of the isothermal study

The T-T-T curve was determined in the range 360 - 500°C. As can be seen in Fig. 1 the nose occurs at about 470°C and the general shape (i.e. C) is maintained throughout the transformation.

It was observed that precipitation had taken place in three distinct ways, according to the temperature zone in which the transformation had been carried out.

a) At low temperatures, below 390°C, the general structure is that of an aged alloy with a limited amount of precipitate at the grain boundaries, Fig. (a). The general form of the grain boundary precipitate is spheroidal and the amount does not increase appreciably with time. The small white patches are believed to be a beryllium cobalt compound.

b) In the temperature range 400°C - 500°C precipitation occurs almost exclusively at the grain boundaries, Fig. (b). This grain boundary precipitate has a lamellar or pearlitic form with branching occurring between the lamellae, Fig. (c). In the upper range of this zone ($\simeq$ 470°C) precipitation does occur to some extent in the interior of the grains, but is mainly confined to the grain boundaries.

c) At temperatures above 500°C precipitation starts in the grain boundaries but after a short time occurs randomly throughout the sample. At long transformation times the structure is rather coarse, with no trace of the original lamellar grain boundary precipitate nodules, these having broken up and spheroidised, Fig. (d). It was decided to study further the kinetics of precipitate (b) to see which growth mechanism it obeyed, and also to find a value for the activation energy of diffusion for Be in Cu. From the calculations made, it seemed most likely that the growth mechanism for the lamellar grain boundary precipitate in Cu - Be alloys, is similar to that proposed by Zener for the growth of pearlite from austenite. The calculated value for the activation energy for diffusion of Be in Cu agreed very well with published results.

Nature of Age Hardening Curves

Four sets of age hardening curves were determined as follows:

a) Specimens heated 2 hours at 800°C, water quenched, then aged in the range 250 - 400°C. The curves are shown in Fig. (2). It appears that the optimum ageing temperature is 300°C - 325°C with hardnesses over 350 V.P.N. being obtained within reasonably short ageing periods.

On examination of the microstructures it was revealed that only slight precipitation at grain boundaries occurred even after ageing for 96 hours, see Fig. (e).

b) A heat treatment was selected to give about 10% grain boundary precipitate before ageing. Specimens were heated for 2 hours at 800°C quenched into a salt bath at 440°C, held for 5 minutes then water quenched. These were then aged in the range 275°C - 400°C and curves determined as in Fig. (3). These curves on the whole are about 40 Vickers points lower than curves (a) Fig. (2).

c) Samples heated 2 hours at 800°C then water quenched. They were then swaged down from .25" diameter to .156" diameter, a reduction in cross sectional area of 72%, and aged at 300°C, 325°C, 350°C, (Fig.4). The most striking feature of these curves is the higher maximum hardness attained in comparison to heat treatment (a) and the rapid rate of overageing, (Fig. 6). On examination of the microstructure, Fig.(h) it is seen that a considerable amount of precipitate has come down in the overaged alloy, much more than in the overaged alloy for heat treatment (a), Fig. (e).

d) Samples were heated for 2 hours at 800°C, quenched into a salt bath at 440°C, held for 5 minutes, then water quenched. They were then swaged down from .25" to .156" diameter, and aged at 300°C, 325°C, 350°C. The age hardening curves for heat-treatment (d) are on the whole about 70 Vickers points below those for heat treatments (c), Fig.5.

The microstructures for treatment (d) reveal that much more precipitate has come down in the overaged condition than in any other overaged alloy of treatments (a), (b), or (c), see Figs. (e,g,h,i).

Tensile Testing

The heat treatments given to the samples were:

a) Heated for $1\frac{3}{4}$ hours in a salt bath at $800^{\circ}C$ then quenched quickly into water; aged for 2, 8 and 48 hours at $325^{\circ}C$.

b) Heated for $1\frac{3}{4}$ hours at $800^{\circ}C$, quenched into a salt bath at $440^{\circ}C$, held for 5 minutes then water quenched. Ageing followed at $325^{\circ}C$ for 2, 8 and 48 hours.

The results listed in table (1) indicate that there is no significant difference in the % elongation figures for the different heat treatments. The ultimate tensile strength and 1% Proof stress are greater in the cases where there is no lamellar grain boundary precipitate.

4. DISCUSSION OF RESULTS

Factors which may influence the nature of the C curve

Although no direct evidence is available for factors which may influence the shape of the T-T-T curve, much speculation can be made as regards the effects of Be content, grain size, and possible alloy additions.

The composition of the alloy studied was 1.77% Be and 0.24% Co but alloys of higher Be content may be used to obtain greater hardness values on ageing. If the Be content was increased up to 2% then the supersaturation ratio would increase also, this would cause increases in the rate of nucleation and the rate of growth of the lamellar grain boundary precipitate nodules. Hence by raising the Be content the T-T-T curve is moved to the left, increasing the amount of grain boundary precipitate obtainable with a slack quench. It seems logical therefore, to use only the minimum percentage Be needed to give the required hardness values.

If the solution temperature was rather low, the grain size would be small, this would give a greater grain boundary area, and hence the rate of nucleation should increase. However, in the normal solution treating range $770^{\circ}C$ - $820^{\circ}C$ it is unlikely that grain size variations radically alter the rate of nucleation so this effect can be ignored.

Cobalt is added to Cu - Be alloys to reduce the amount of grain boundary reaction that occurs on subsequent ageing. By so doing it increases the resistance of the alloy to overageing and promotes high hardness values. This is particularly true in the higher Be alloys where the high supersaturation seems to promote rapid growth of the grain boundary precipitate if no cobalt is present.

Another element with an action similar to cobalt is desirable to prevent the formation of isothermal grain boundary precipitate at such short times on slack quenching, i.e. move the T-T-T curve to the right.

Age Hardening Curves

It must be stated that the 1.77% Be in the alloy used was somewhat lower than in normal industrial alloys, hence the hardness values obtained may appear slightly low.

In the solution treated and aged curves nothing unusual occurred, the optimum ageing temperature being 300 - 325°C. Only a very little lamellar grain boundary precipitate could be observed even after 96 hours ageing. This may be due to:

a) The cobalt present in the alloy
b) The rather low Be content

Cobalt definitely prevents to a great extent the outgrowths of grain boundary precipitate which occur on ageing, but it is likely that if there had been more Be in the alloy, more grain boundary precipitation would have occurred. The solution treated + 10% precipitate curves followed similar paths to the solution treated curves, being generally 40 Vickers points lower and displaced to the right. The reason why the curves are of lower hardness is because there is 10% of a very soft phase mixed with 90% of a harder phase. It is not due to the general depletion of Be in the alloy because of the formation of the grain boundary precipitate, as was clearly shown by microhardness testing. Tests were carried out at levels corresponding to the maximum macrohardness on the solution treated and solution treated + 10% grain boundary precipitate specimens, both values for maximum hardness were approximately equal. This discounts the idea that the Be % is reduced generally throughout the alloy to form the grain boundary precipitate, it is probably only reduced in areas near to the grain boundaries.

The cold worked and aged curves all show higher maximum hardnesses and greater rates of overageing than the equivalent solution treated curves. The microstructures are interesting because in the overaged state considerable amounts of precipitate are visible, whereas in the solution treated and overaged alloy only a very little grain boundary precipitate was visible. The cold working probably sets up strains, etc., in the metal which aid the diffusion process and cause more rapid growth of the grain boundary precipitate in the cold worked alloys.

Microhardness tests were carried out on the cold worked alloys to see whether the grain boundary precipitate was the main cause of rapid overageing, or whether it was just natural overageing after coldworking. The results showed that the grain boundary precipitate, and natural overageing process, work together to produce the rapid overageing effect observed.

The cold worked + 10% grain boundary precipitate ageing curves follow approximately the same lines as the cold worked ones. They are generally 70 Vickers points lower but reach the maximum hardness after approximately the same ageing time. A possible reason why the cold worked + 10% grain boundary precipitate alloys are lower in hardness than the others is as follows. The cold working sets up strains in the metal which increase the volume diffusion coefficient, speeding up the rate of growth of the grain boundary precipitate. The 10% grain boundary precipitate already introduced into the alloy could act as nucleation centres, and hence increase the rate of nucleation, which also speeds up the formation of this grain boundary precipitate. An alloy containing a large percentage of this soft grain boundary precipitate will naturally have a lower hardness than one without it. It is a fact that these cold worked + 10% grain boundary precipitate alloys do show much more grain boundary precipitate after overageing than any of the other alloys examined. It appears, therefore, that the lower hardnesses may be due to the growth of the grain boundary precipitate and that the rapid overageing is due to:

a) Natural overageing
b) Excessive growth of the grain boundary precipitate

Tensile Testing

The specimens were all aged to give reasonably high hardness and ultimate tensile strength values. Naturally the elongation figure is expected to be low, and on the specimens tested the grain boundary precipitate introduced had no detrimental effect on the % elongation. It seems clear, however, that the grain boundary precipitate does affect the figures for the ultimate tensile strength and 1% Proof stress, these generally being 10% lower than in alloys with no grain boundary precipitate after the same ageing treatment. This drop in the ultimate tensile strength and 1% Proof stress is in accordance with the fall in hardness for the specimens containing the 10% grain boundary precipitate, as is shown in Table (1).

Conclusions and Suggestions for Future Work

CONCLUSIONS

1. After carrying out isothermal transformations in the range 360°C - 500°C, it was found that the T-T-T curve, for the high temperature precipitate in Cu-Be is C shaped. Three distinct types of precipitate were observed as follows:

   a) At temperatures above 520°C a rather coarse precipitate throughout the whole microstructure.

   b) At temperatures between 400°C - 500°C, a nodular lamellar precipitate which starts at the grain boundaries and spreads into the grains.

   c) At temperatures below 390°C, a normally aged microstructure with a little lamellar precipitate at the grain boundaries.

2. The grain boundary precipitate influences the age hardening characteristics of Be-Cu as follows:

   a) Solution treated + 10% grain boundary precipitate specimens are generally 40 Vickers points lower than the solution treated ones after the same ageing treatment.

   b) Cold worked + 10% grain boundary precipitate specimens are generally 70 Vickers points lower than the cold worked ones after the same ageing treatment.

3. The effects of cold working the solution treated alloy then ageing are as follows:

   a) To increase markedly the amount of grain boundary precipitate that occurs on ageing. This increase in precipitate is probably one of the reasons why the cold worked alloys overage so rapidly.

   b) To decrease the ageing time needed to reach the maximum hardness.

   c) To increase the maximum hardness obtainable.

4. The results of the tensile testing showed that the grain boundary precipitate reduces the ultimate tensile strength and 1% Proof stress of the alloy after ageing. The amount these values are reduced depends upon how much grain boundary precipitate is present.

No difference in the % elongation was observed for specimens with and without grain boundary precipitate after the same ageing treatment.

5. Using laboratory techniques it is possible to water quench Cu-Be from the solution temperature (800°C) and obtain a microstructure devoid of lamellar grain boundary precipitate. In industrial practice it may not be easy to avoid this grain boundary precipitate especially if the beryllium content is high. If the quench for any reason is slack lamellar grain boundary precipitate may form, and the hardness values, tensile properties etc., will be lower than expected. It is essential therefore to quench efficiently from the solution temperature. If the alloy has to be cold worked after the solution treatment it is even more essential that the quench should be efficient.

<u>Suggestions for future work</u>

1. The work already accomplished only gives a limited picture of the processes occurring, and must be extended to alloys of higher Be content. A start has already been made with an alloy containing 1.87% Be and 0.14% Co, but alloys with greater amounts of Be should also be studied.

2. More detailed information for the cold worked material is required, particularly data from tensile tests.

3. The effect of lamellar precipitate on the elastic moduli and elastic hysteresis etc., should be investigated.

4. The effect of additions of further alloying elements on the "hardenability" of the basic Cu-Be-Co alloys would seem to be a worthwhile long term investigation.

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TABLE 1

Treatment	Hardness V.P.N.	U.T.S. t.s.i.	1% P.S. t.s.i.	E%
a) $1\frac{3}{4}$ hours at 800°C, water quenched, then aged 2 hrs at 325°C.	367	76.2	70.7	7
b) $1\frac{3}{4}$ hours at 800°C, water quenched, then aged 8 hrs at 325°C.	381	77.0	71.2	6
c) $1\frac{3}{4}$ hours at 800°C, water quenched, then aged 48 hrs at 325°C	357	71.2	68.2	6
d) $1\frac{3}{4}$ hours at 800°C, quenched into salt bath at 440°C, held 5 mins., water quenched, then aged 2 hrs at 325°C.	332	67.4	64.9	7
e) $1\frac{3}{4}$ hours at 800°C, quenched into salt bath at 440°C, held 5 mins. water quenched, then aged 8 hrs at 325°C	344	69.6	67.4	7
f) $1\frac{3}{4}$ hours at 800°C, quenched into salt bath at 440°C, held 5 mins. water quenched, then aged 48 hrs at 325°C.	321	64.6	58.4	10

Fig. 1.

Illustrates the T-T-T curves determined.

Fig. 2.

Gives the age hardening curves for the alloys in the solution treated condition, at the temperatures 250°C, 275°C, 300°C, 325°C, 347°C, 396°C.

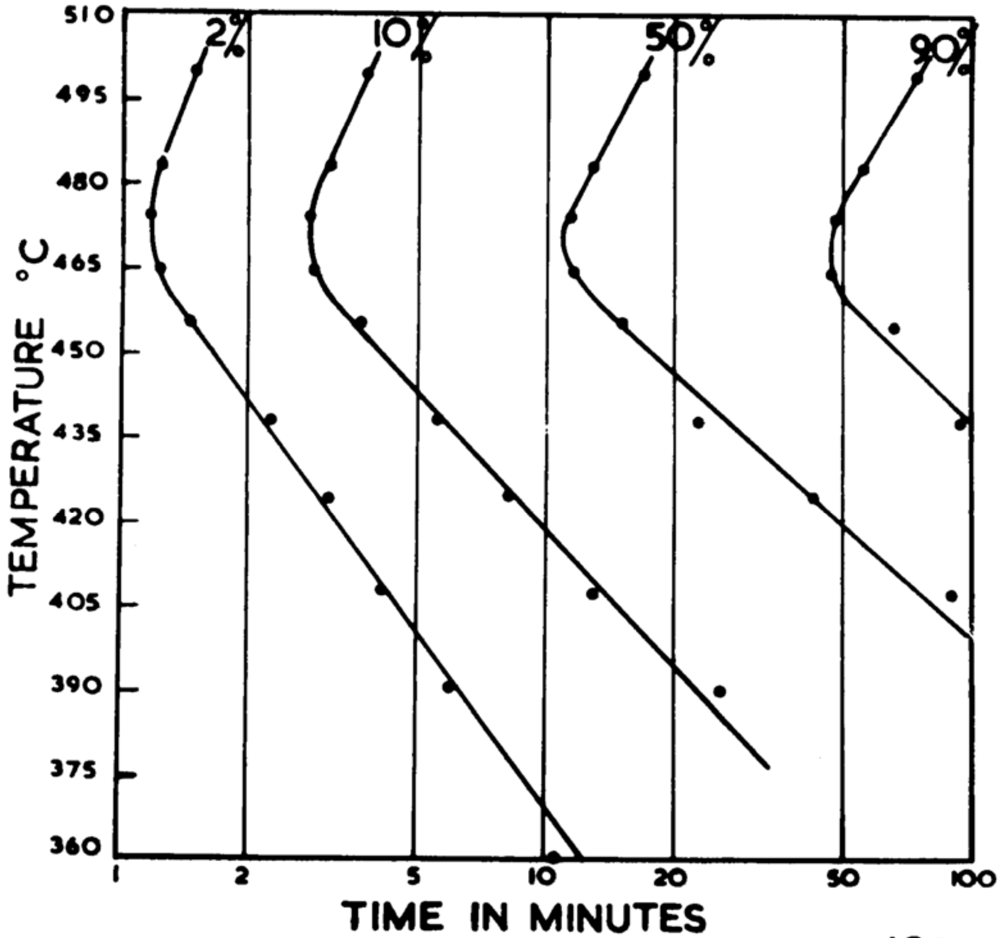

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Figure 1.

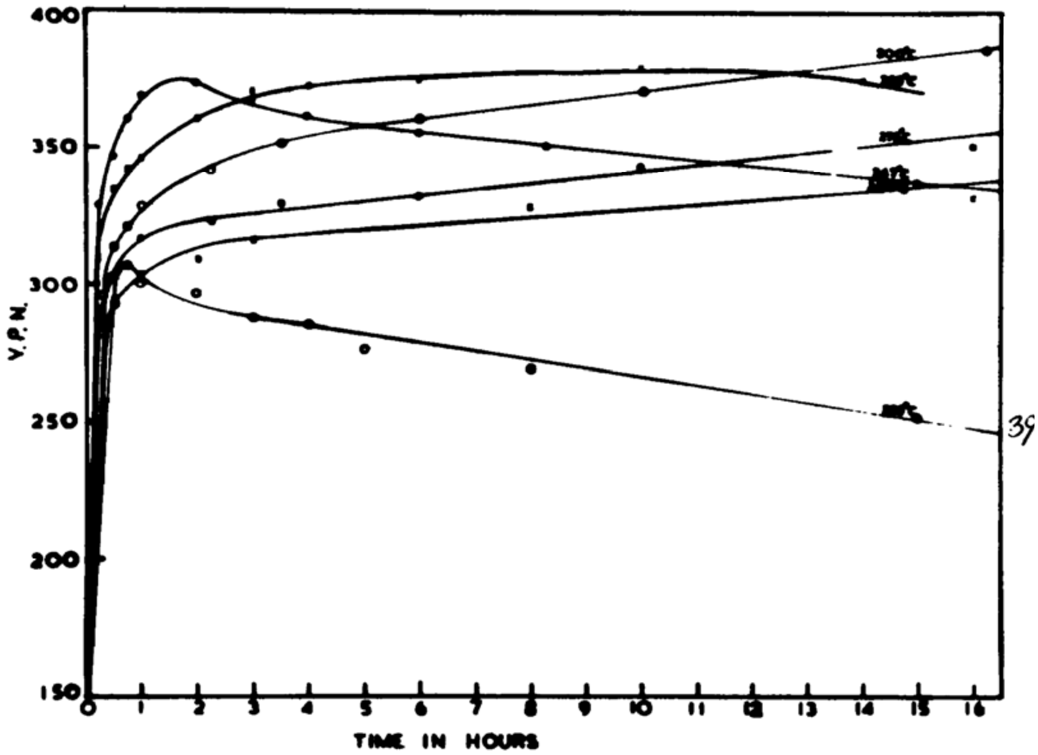

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Figure 2.

Fig. 3.

Gives the age hardening curves for alloys in the solution treated + 10% grain boundary precipitate condition, at the temperatures 275°C, 300°C, 325°C, 347°C, 396°C.

Fig. 4.

Gives the age hardening curves for alloys in the cold worked condition, at the temperatures 300°C, 325°C, 350°C.

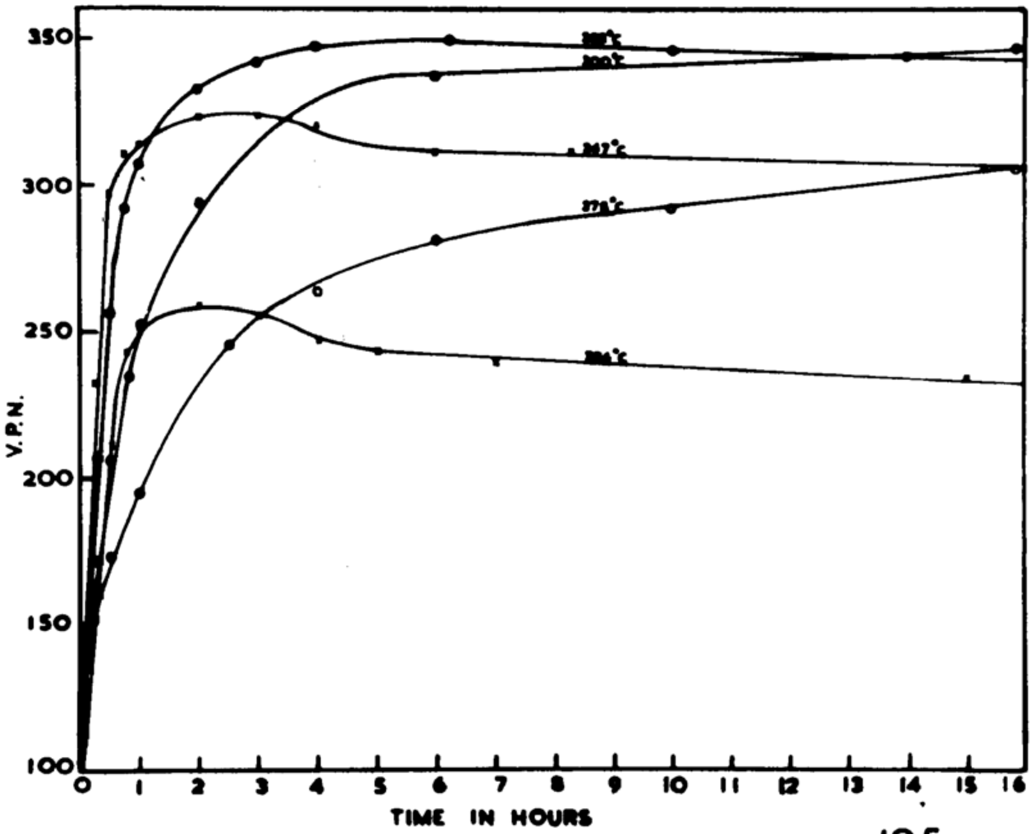

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Figure 3.

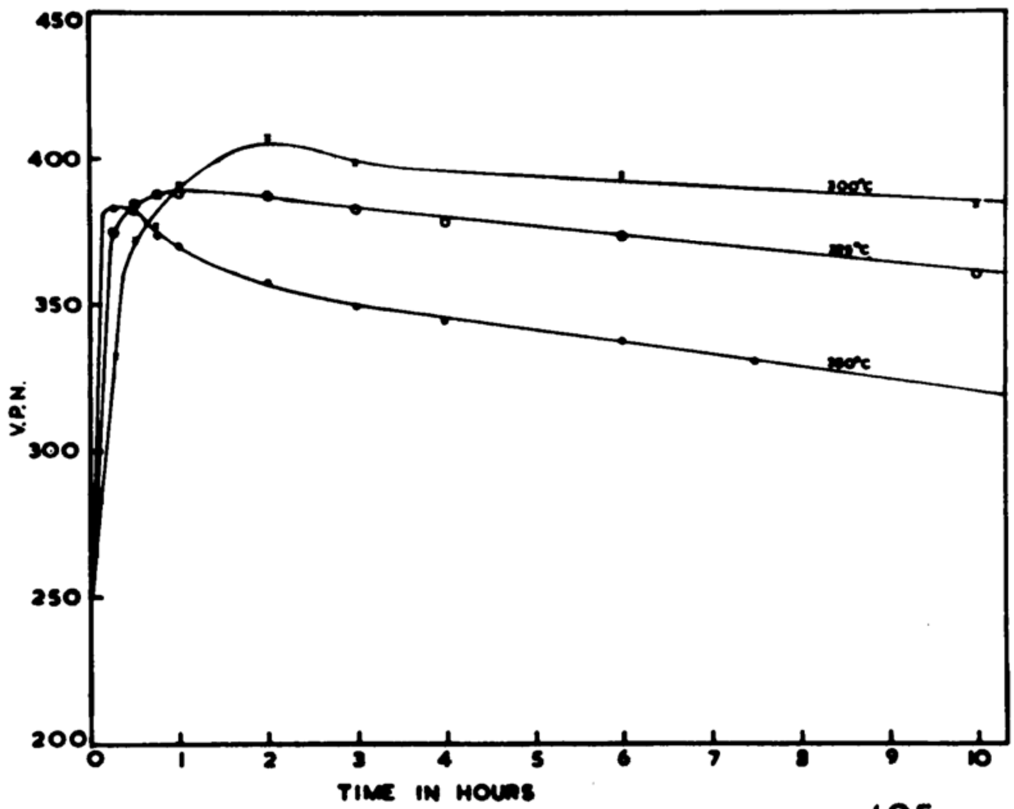

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Figure 4.

Fig. 5

Shows a comparison between the cold worked and cold worked + 10% grain boundary precipitate curves at 300°C.

A. 2 hours at 800°C, water quenched, swaged down from .25" diameter to .156" diameter then aged at 300°C.

B. 2 hours at 800°C, quenched into salt bath at 440°C held for 5 minutes then water quenched, swaged down from .25" diameter to .156" diameter, then aged at 300°C.

Fig. 6

Shows a comparison between the solution treated and cold worked age hardening curves at 300°C.

A. 2 hours at 800°C water quenched, swaged down from .25" to .156" diameter then aged at 300°C.

B. 2 hours at 800°C, water quenched, then aged at 300°C.

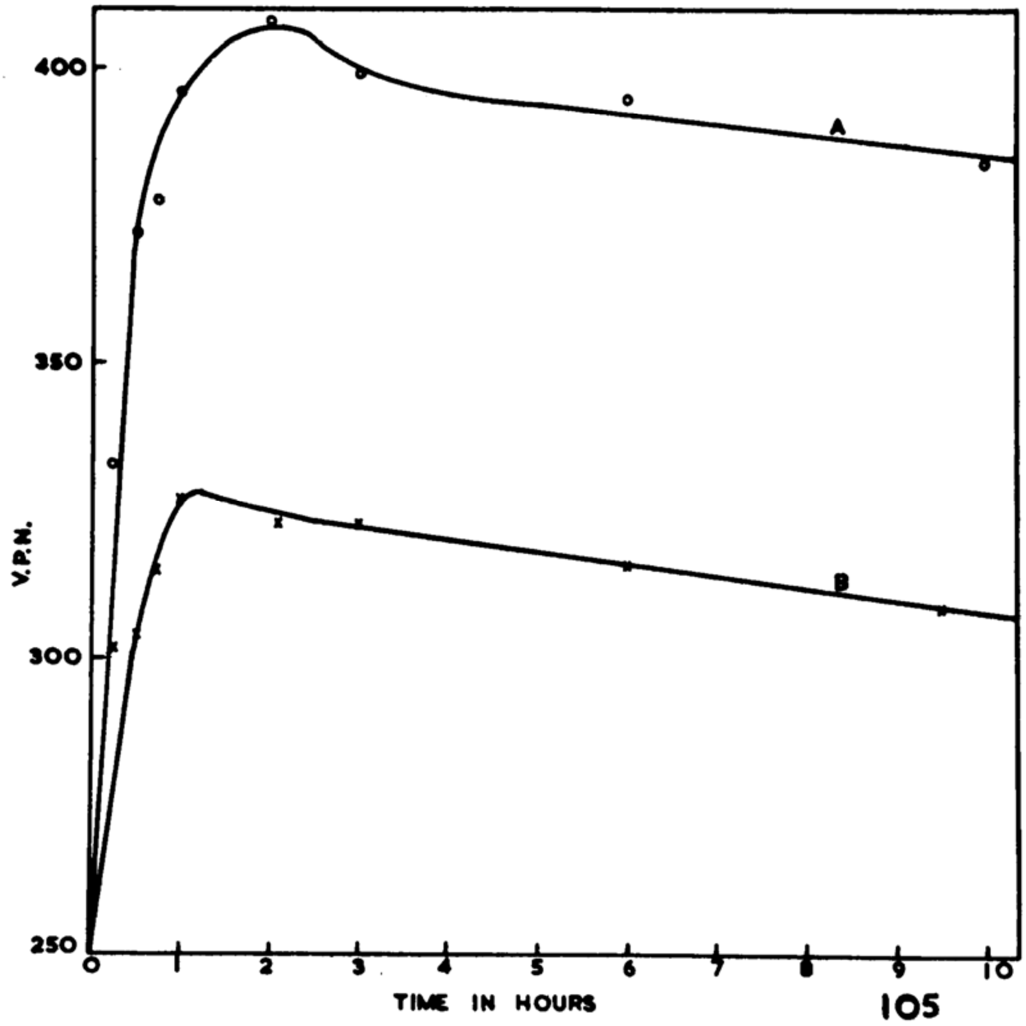

Figure 5.

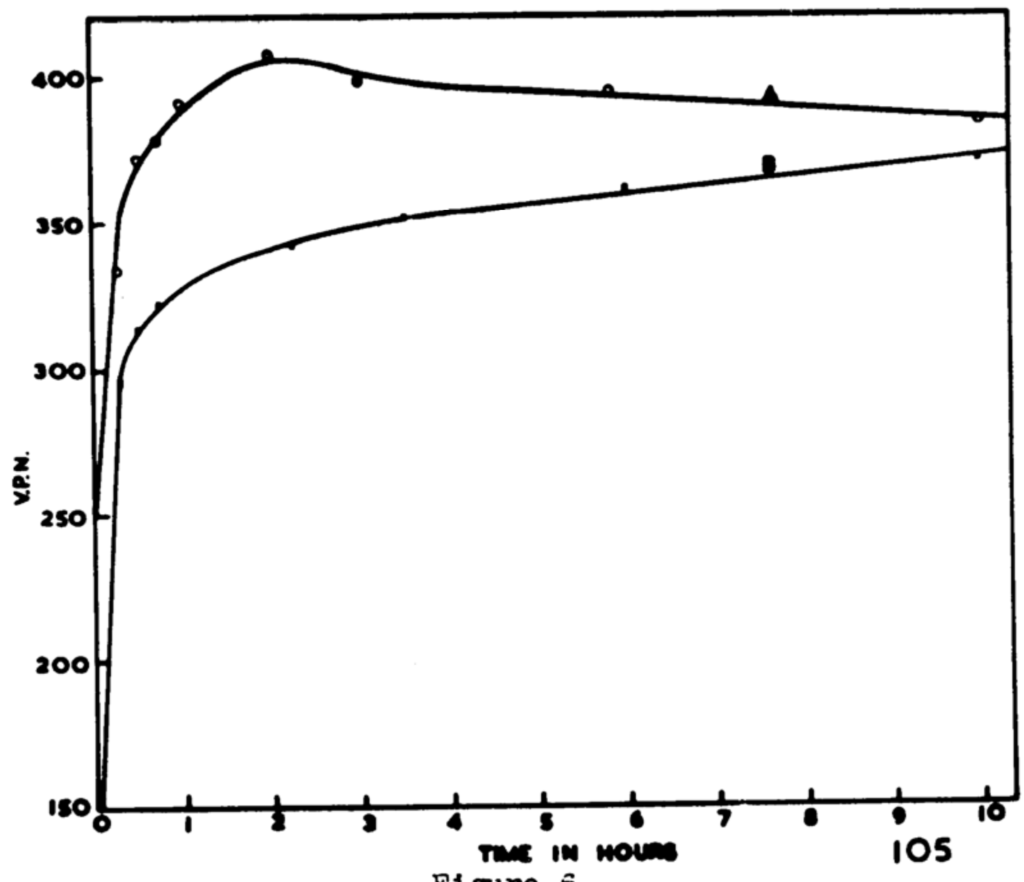

Figure 6.

Fig. (a)   Magnification 400x

<u>Treatment.</u> Held for 2 hours at 800°C, quenched into salt bath at 360°C, held for 45 minutes then water quenched.

Etchant. Copper, Amm. Sulphate.

Fig. (b).   Magnification 850x

<u>Treatment.</u> Held 2 hours at 800°C, quenched into salt bath at 407°C, held 30 minutes, then water quenched.

Etchant. Ammoniacal hydrogen peroxide.

Fig. (c).   Mangification 2000x

<u>Treatment.</u> Held 2 hours at 800°C, quenched into salt bath at 483°C, held 5 minutes then water quenched.

Etchant. Ammoniacal hydrogen peroxide.

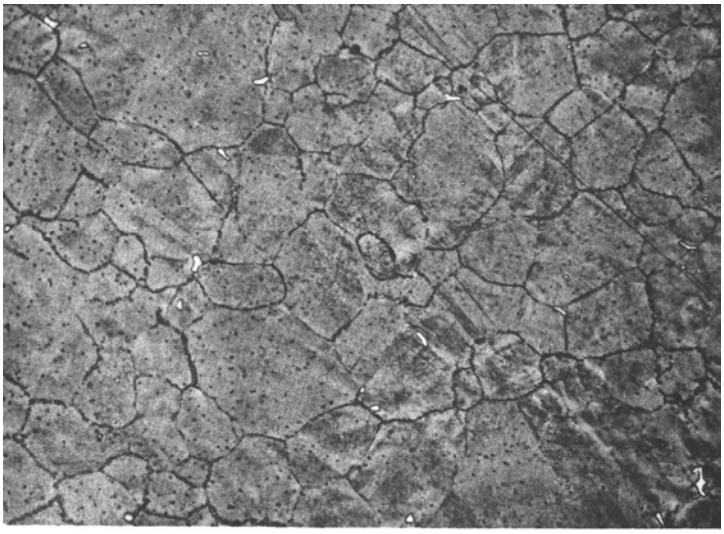

Figure (a).

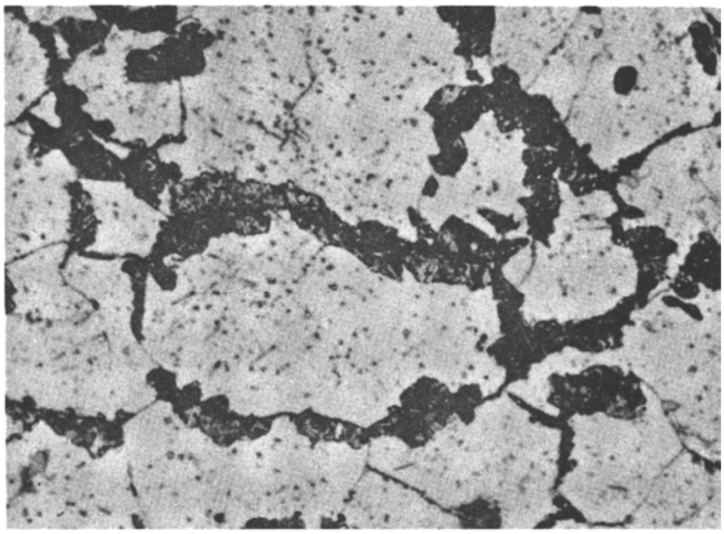

Figure (b).

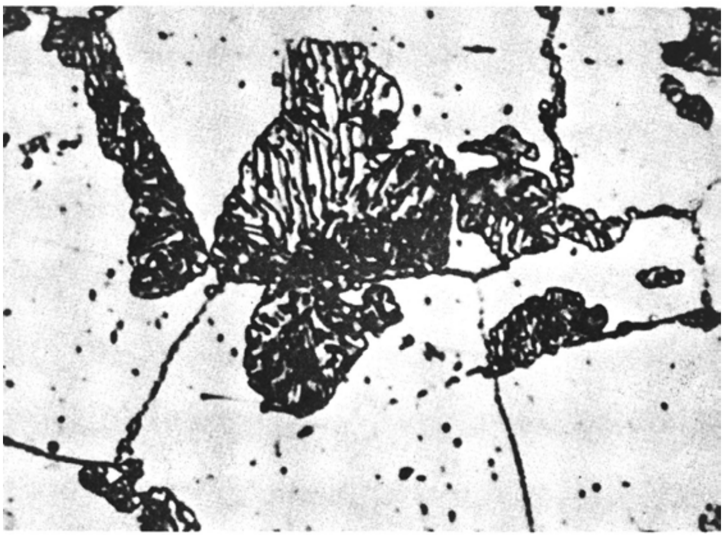

Figure (c).

Fig. (d). Magnification 400x

<u>Treatment</u>. Held 2 hours at 800°C, quenched into salt bath at 520°C, held for 3 hours then water quenched.

Etchant. Ammoniacal hydrogen peroxide.

Fig. (e). Magnification 400x

<u>Treatment</u>. Held 2 hours at 800°C, water quenched, then aged 96 hours at 300°C.

Etchant. Copper Amm. Sulphate.

Fig. (f). Magnification 400x.

<u>Treatment</u>. Held 2 hours at 800°C, quenched into a salt bath at 440°C, held for 5 minutes, and water quenched, then aged 6 hours at 300°C.

Etchant. Copper Amm. Sulphate.

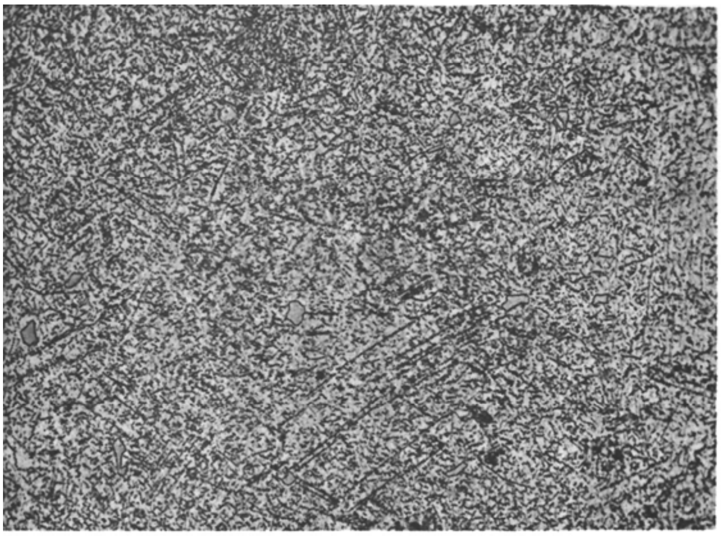

Figure (d).

Figure (e).

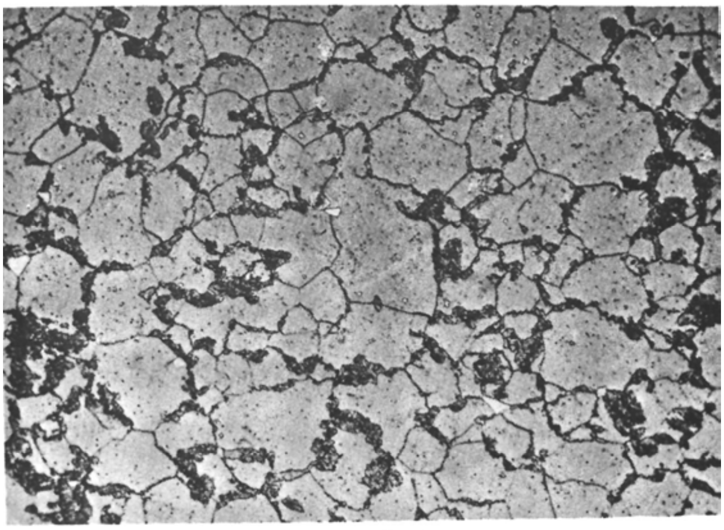

Figure (f).

Fig. (g). Magnification 400x

Treatment. Held 2 hours at 800°C, quenched into salt bath at 440°C, held for 5 minutes and water quenched, then aged for 96 hours at 300°C.

Etchant. Copper Amm. Sulphate.

Fig. (h). Magnification 400x

Treatment. Held 2 hours at 800°C, water quenched. Swaged down from .25" to .156" diameter then aged for 96 hours at 300°C.

Etchant. Copper Amm. Sulphate.

Fig. (i). Magnification 400x

Treatment. Held for 2 hours at 800°C, quenched into salt bath at 440°C, held for 5 minutes, water quenched. Swaged down from .25" to .156" diameter then aged for 94 hours at 300°C.

Etchant. Copper Amm. Sulphate.

Figure (g).

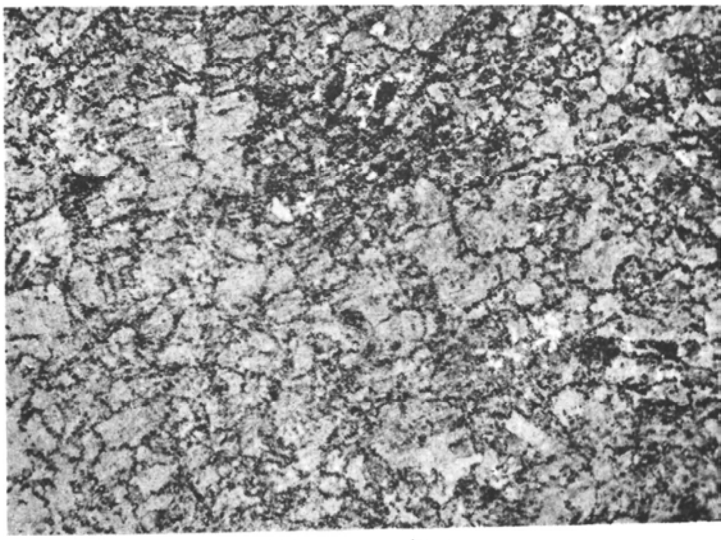

Figure (h).

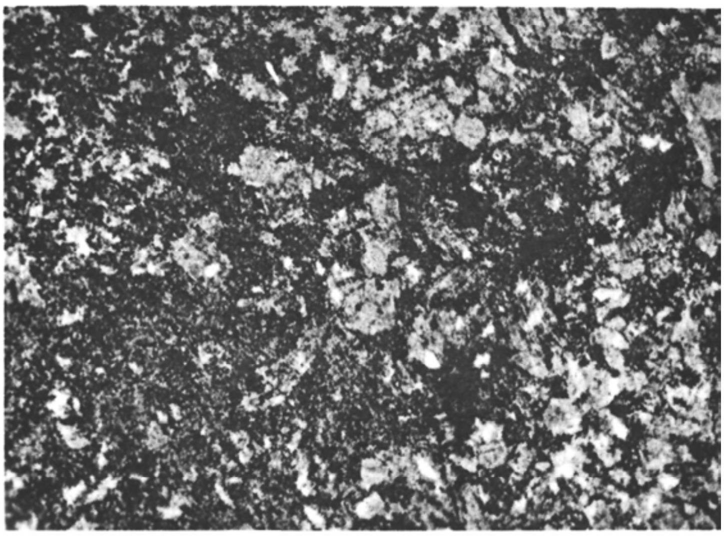

Figure (i).