Effect of Low Temperature Annealing on Cold-rolled Sheets of Phosphor Bronze

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ABSTRACT: The mechanical properties of copper-alloy sheets that were cold-rolled and then given low temperature anneal show anomalies, especially with respect to bending plasticity; phosphor bronze sheets are among the typical examples. In the present work effect of low temperature (10–350°C) annealing on cold-rolled sheets of phosphor bronze was studied by means of bending plasticity measurement and hardness measurement. The Vickers hardness number versus annealing temperature curve (annealing time=const=1 hour) show at least four maxima; the maximum that occurs just prior to recrystallization is probably related with polygonization, the two maxima that precede the above-mentioned maximum are related with the precipitation hardening, and the maximum that occurs at or near the room temperature is the most difficult to interpret, and is possibly related with the re-arrangement of internal stress. Details of the bending plasticity measurement are described.

§ 1. Introduction

In 1935 improvement of the spring material for precision instruments was undertaken in this Institute (which was Aeronautical Research Institute at that time), and the method of measuring the plasticity of copper-alloy sheets was critically reviewed in the author's laboratory. Finally the bending plasticity measurement to be described in § 2 was adopted as the most adequate method. During the period 1942–1945 financial aid was given by the Nippon Kôkû-Gijutsu Kyôkai (Japan Society of Aeronautical Techniques) in order to improve the spring characteristics of phosphor brnoze sheets manufactured in Japan. A manuscript describing all the results obtained by the author before March 1945 was submitted (in July 1945) to that Society for publication in Japanese. However the event that occurred subsequently did not allow to publish it, so some data were published in Japanese fragmentarily[1-3] afterwards. Shortage of paper in Japan seems to be away recently, so the above-mentioned manuscript is now translated into English, revised in some points and supplemented by experimental results obtained after 1945, and is presented here.

In 1936 Haase and Pawlek[4] showed that precipitation took place in Cu–Sn alloys with Sn content greater than 5% that were cold-worked and then annealed. Neglecting the effect of phosphorus, ordinary cold-rolled phosphor bronze sheets also should show precipitation-hardening, when they are annealed at adequate temperature.

With the aid of X-ray technique only, it is difficult to investigate the details of the temperature condition of the precipitation-hardening in cold-rolled phosphor bronze sheets, so that in the present work study of adequate mechanical properties was employed for this purpose.

§2. Experimental Procedure

a. Sample Alloys. The alloys used in this study are listed in Table I. Cu-Sn alloys without P were not easy to prepare, so that only one kind of this alloy (No. 10) was studied. All the other alloys examined were phosphor bronze. The alloys were annealed for 30 minutes at about 500°C and then reduced by cold-rolling to the final thickness of 0.5 mm.

Two methods of examining the mechanical properties of the sheets were employed: namely, the bending plasticity test and the measurement of the Vickers hardness number. They will now be described separately.

Table I. Composition of the Sample Alloys.

No.	Sn %	P %	Cu %
1	0.00	0.00	99.92
2	1.74	0.3	bal
3	4.0	0.2	bal
4	4.5	0.2	bal
5	4.5	0.6	bal
6	6	0.2	bal
7	7	0.2	bal
8	7.5	0.2	bal
9	8	0.15	bal
10	8	0.00	bal
11	10	0.2	bal

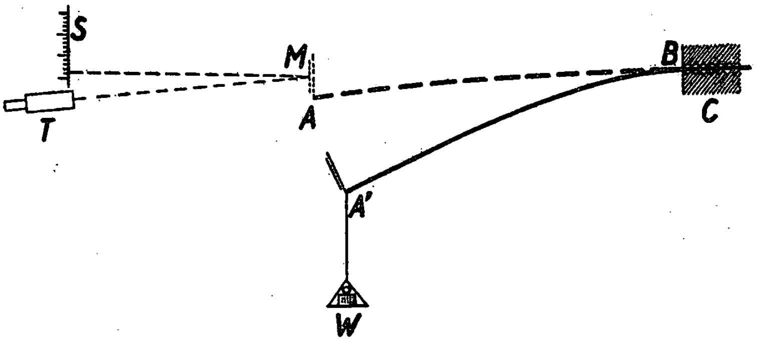


Fig. 1. Schematic illustration of the arrangement for measuring the bending plasticity of the test piece.

b. Bending Plasticity Measurement. The arrangement for measuring the bending plasticity[1] is sketched schematically in Fig. 1. The test piece 10 mm in width, about 190 mm in length and 0.5 mm in thickness was cut from the sheet to be examined and clamped horizontally at one end B by a chuck C. The other end A was loaded with a weight W for one minute and then unloaded. One minute after unloading, the angle ($\Delta\theta$) between the tangent at A to AB before and after loading was measured by means of telescope T and scale S and mirror M. The mirror M was a galvanometer mirror with a negligible weight and was fixed at A. We will denote the span length of the loaded and unloaded test piece by L_W and L_0 respectively. L_0 was usually 160 mm.

The test piece was cut from the sheet in such a way that the direction of AB coincided with the direction of rolling or with the direction perpendicular to the direction of rolling. The former will be denoted by $\parallel$, while the latter will be denoted by $\perp$.

In order to obtain results of measurement with negligible scatter, it was necessary to get wide rolled sheets and to reject about 50 mm wide margins on both sides.

The arrangement of mounting the mirror is shown schematically in Fig. 2. One end A (Fig. 1) of the test piece is inserted through E (Fig. 2) and is fixed by the screw

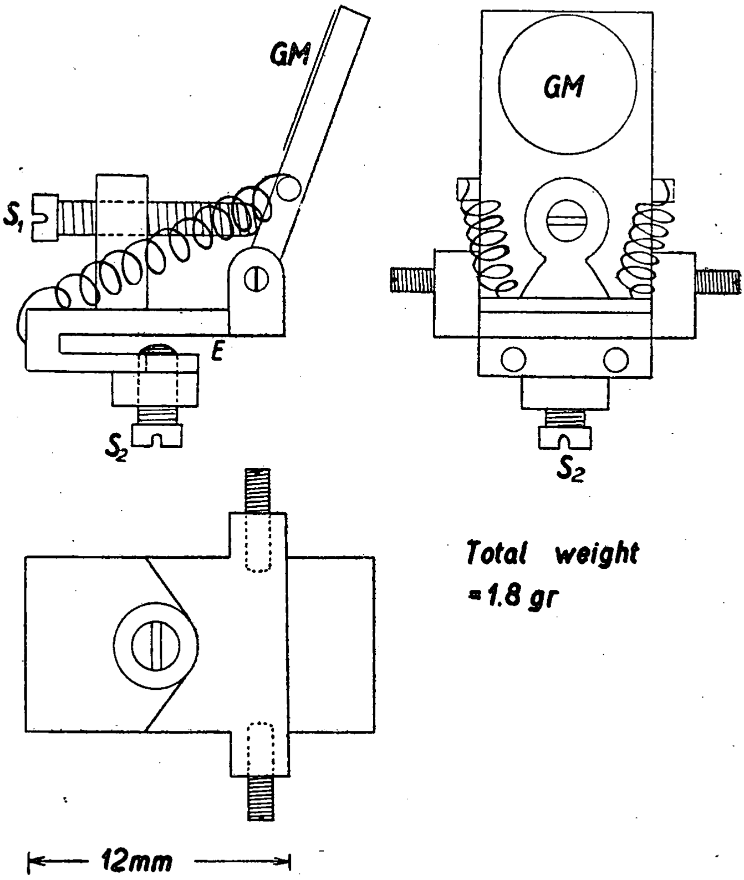
S_2. The inclination of the mirror is adjusted by the screw S_1 so that the image of the scale S may enter the telescope T. Except the screws S_1 and S_2 and the piano wire, the mount is made of duralumin, the total weight being 1.8 grams. We have therefore to keep in mind the fact that a dead weight of 1.8 grams was always given to the test piece. $\Delta\theta$ will be expressed in radians.

For each test piece the angle $\Delta\theta$ was measured by increasing W successively from zero to about 150 grams. The origin of $\Delta\theta$ was such that $\Delta\theta=0$ before the first loading. By plotting $\Delta\theta$ versus the maximum fiber stress ($\sigma_{\max}$) at B, a curve is obtained.

$\sigma_{\max}$ was calculated by the usual formula

$$\sigma_{\max}=\frac{6WL_W}{bt^2}$$

where b and t are the breadth and thickness of the sample respectively. This formula is valid only when the test piece is homogeneous. Since this is true only approximately in cold-rolled sheets⁽⁶⁾, the above-mentioned formula is appro-



GM: galvanometer mirror. S_1: screw (steel). S_2: screw (steel).

Fig. 2. Detail of the mechanism of mounting the mirror.

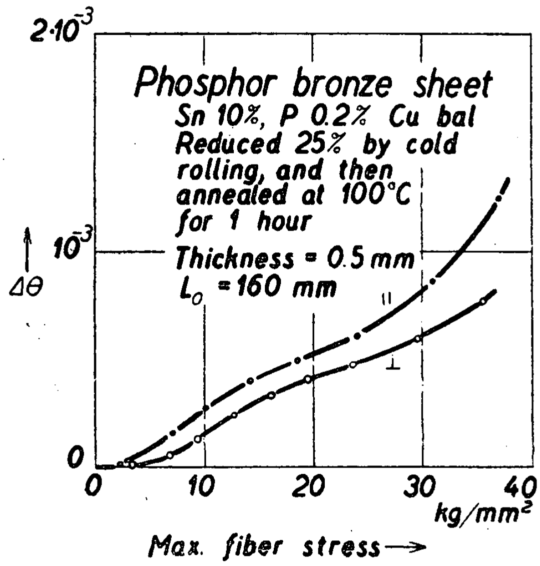


Fig. 3. Plot of $\Delta\theta$ versus the maximum fiber stress in the indicated sample of phosphor bronze sheet.

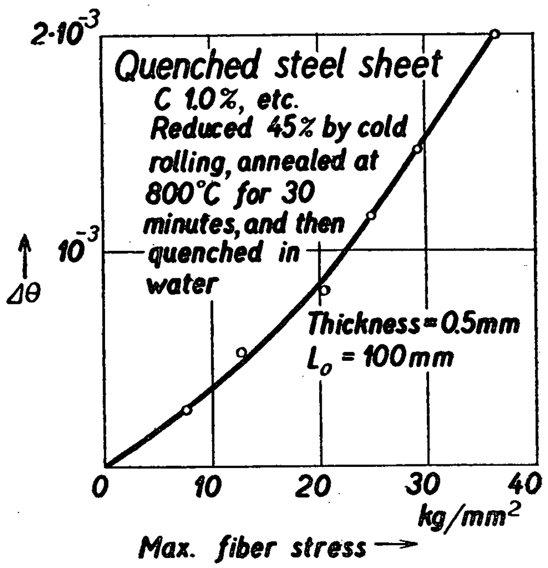


Fig. 4. Plot of $\Delta\theta$ versus the maximum fiber stress in quenched steel sheet.

ximate in our case.

Figs. 3 and 4 show two examples of the plot of $\Delta\theta$ versus $\sigma_{\max}$. The value of $\Delta\theta$ for $\sigma_{\max}=30\,\mathrm{kg/mm^2}$ is obtained from this curve by interpolation and has approximately the best accuracy; this value will hereafter be denoted by $\Delta\theta_{30}$. In every case at least three test pieces were examined under the same condition, and the final $\Delta\theta_{30}$ was obtained by taking the mean. The value of $\Delta\theta_{30}$ published in the present paper would be accurate to within about 4%; only for the as-rolled condition the error would exceed 4%.

The value of $\Delta\theta$ is of course a function of the time during which test piece was given a cantilever loading. Before March 1955 the time of loading was always one minute, but afterwards 5 minutes' loading was adopted, since this was found to give more consistent result. Only the No. 2 alloy sheet was tested after August 1955.

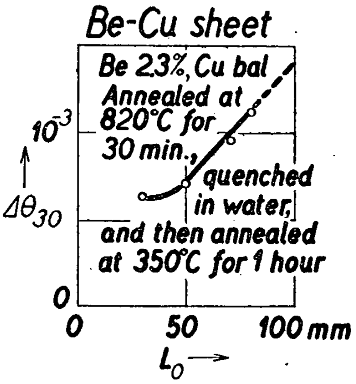


Fig. 5. Plot of $\Delta\theta_{30}$ versus L_0 in Be-Cu sheet.

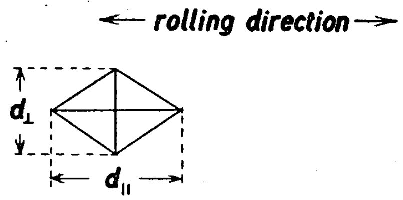


Fig. 7. Schematic illustration of an imprint in the measurement of the Vickers hardness number of a cold-rolled sheet.

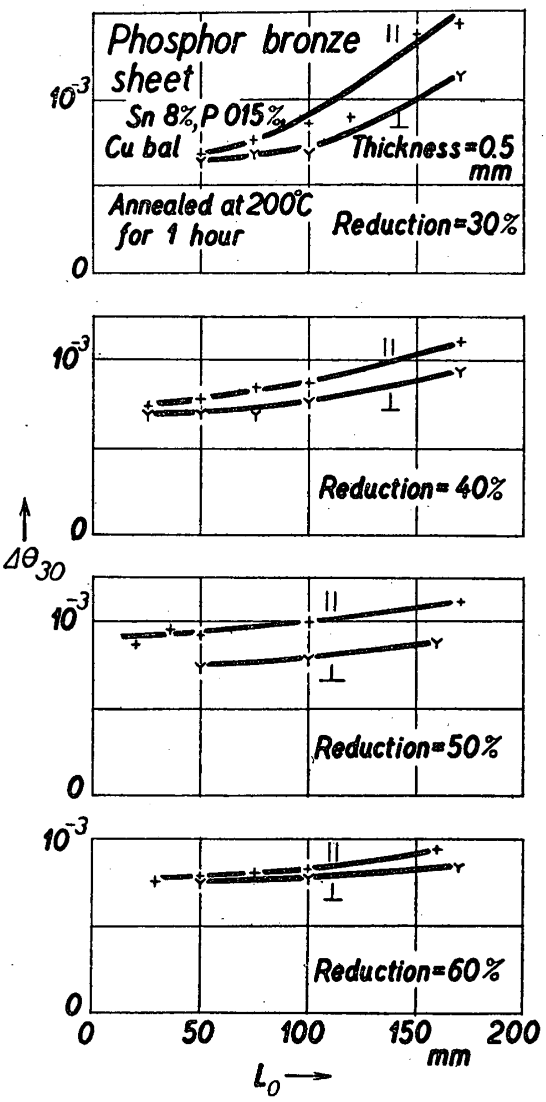


Fig. 6. Plot of $\Delta\theta_{30}$ versus L_0 in phosphor bronze sheet.

Figs. 5 and 6 show curves plotting $\Delta\theta_{30}$ versus L_0. When extrapolated to $L_0=0$, they do not pass through $\Delta\theta=0$, which seems to indicate that the rigorous physical meaning of $\Delta\theta$ is rather complicated.

c. Hardness Measurement. The Vickers hardness number (VHN) was measured[5], setting the sample in such a way that one of the diagonals of the impression made by the diamond indenter coincided with the rolling direction of the sample (see Fig. 7). The length of the diagonal parallel to the rolling direction is denoted by $d_{\parallel}$ and the length of the other diagonal by $d_{\perp}$.

The usual definition of VHN is

$$\mathrm{VHN} = [2P \sin(\omega/2)]/d^2,$$

where ω is the angle between opposite faces of the pyramidal penetrator, P is the load and $d=(d_{\parallel}+d_{\perp})/2$. However, in the present experiment it was found convenient to introduce

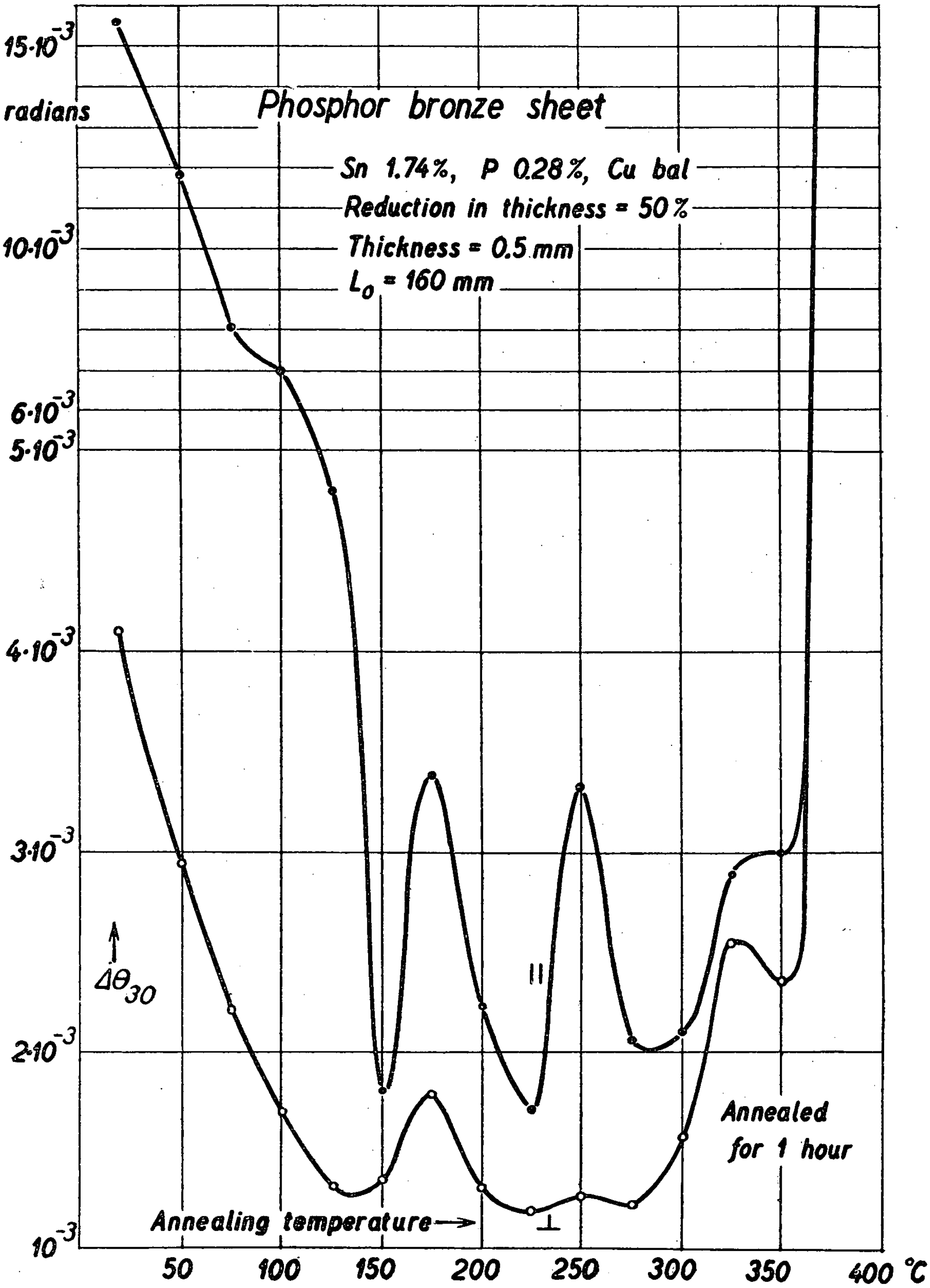


Fig. 8. Effect of annealing for 1 hour on $\Delta\theta_{30}$ in phosphor bronze sheet with 1.74% Sn.

$$\mathrm{VHN}_{\parallel}=[2P\sin(\omega/2)]/d_{\parallel}^{2},$$
$$\mathrm{VHN}_{\perp}=[2P\sin(\omega/2)]/d_{\perp}^{2}.$$

These two VHN's do not follow the usual definition of VHN strictly, but they have the advantage that the larger the reduction in thickness by cold rolling, the larger is their difference $\mathrm{VHN}_{\perp}-\mathrm{VHN}_{\parallel}$, and that their difference vanishes approximately when the sample is recrystallized. The usual VHN is obtained approximately by taking the mean of $\mathrm{VHN}_{\parallel}$ and $\mathrm{VHN}_{\perp}$.

For each sample at least twenty impressions were given, then the sample was turned 90°, and then at least twenty impressions were given again. The final VHN's were obtained by taking the mean.

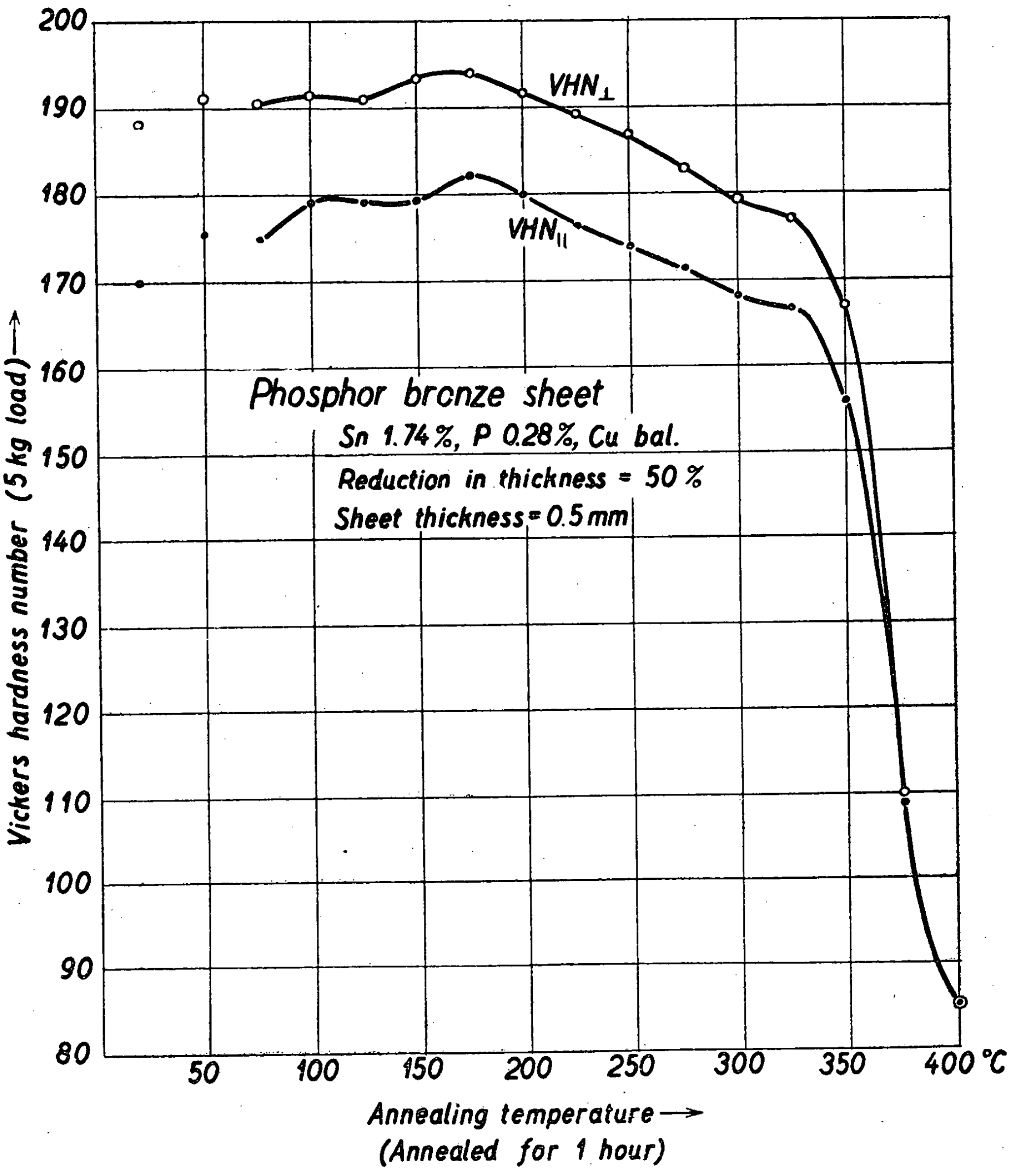


Fig. 9. Effect of annealing for 1 hour on VHN in phosphor bronze sheet with 1.74% Sn.

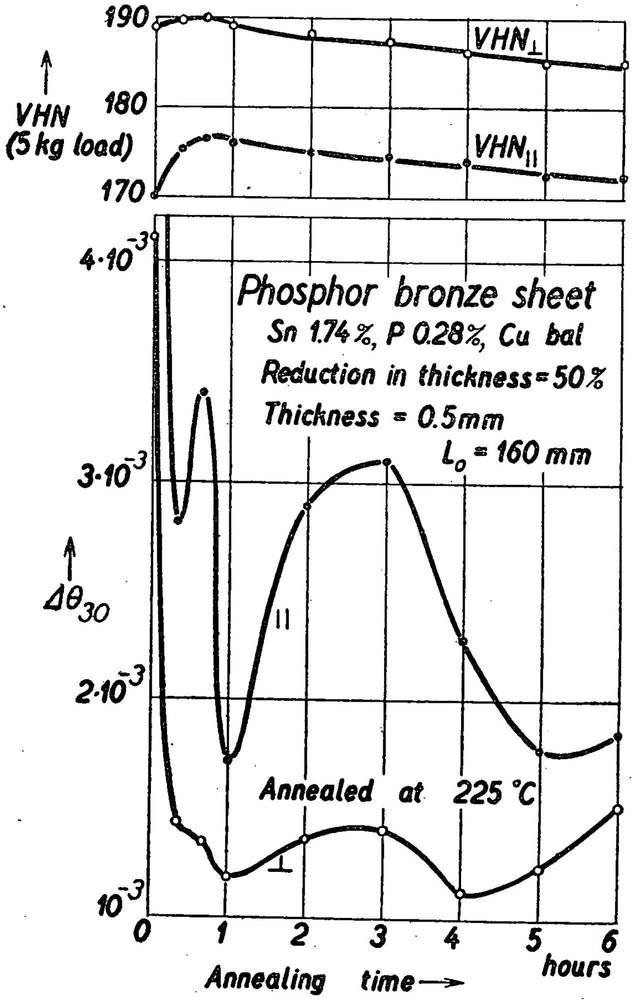


Fig. 10. Effect of annealing at 225°C on VHN and $\Delta\theta_{30}$ in phosphor bronze sheet with 1.74% Sn.

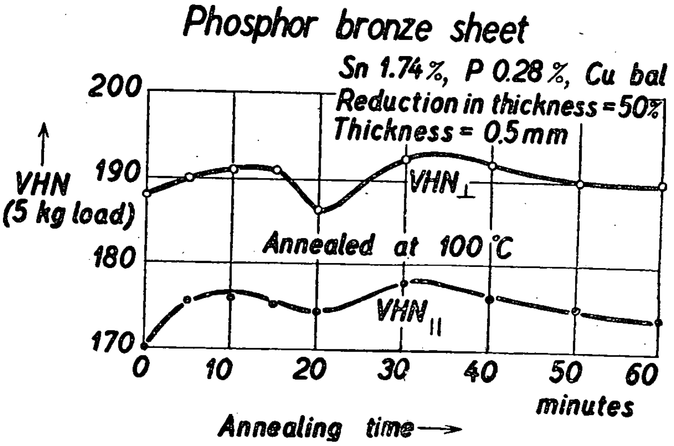


Fig. 11. Effect of annealing at 100°C on VHN in phosphor bronze sheet.

§ 3. Result of Measurement

The sheet to be examined was cut into many test pieces; different pieces were annealed at different temperatures, the annealing time being 1 hour in each case. Figs. 8 and 9 show the result of measurement of $\Delta\theta_{30}$ and VHN respectively as a function of annealing temperature in the case of 1.74% Sn phosphor bronze sheet. $\Delta\theta_{30}$ is minimum for annealing at 225°C (for 1 hour). Then several samples were prepared by annealing them for various duration at constant temperature 225°C.

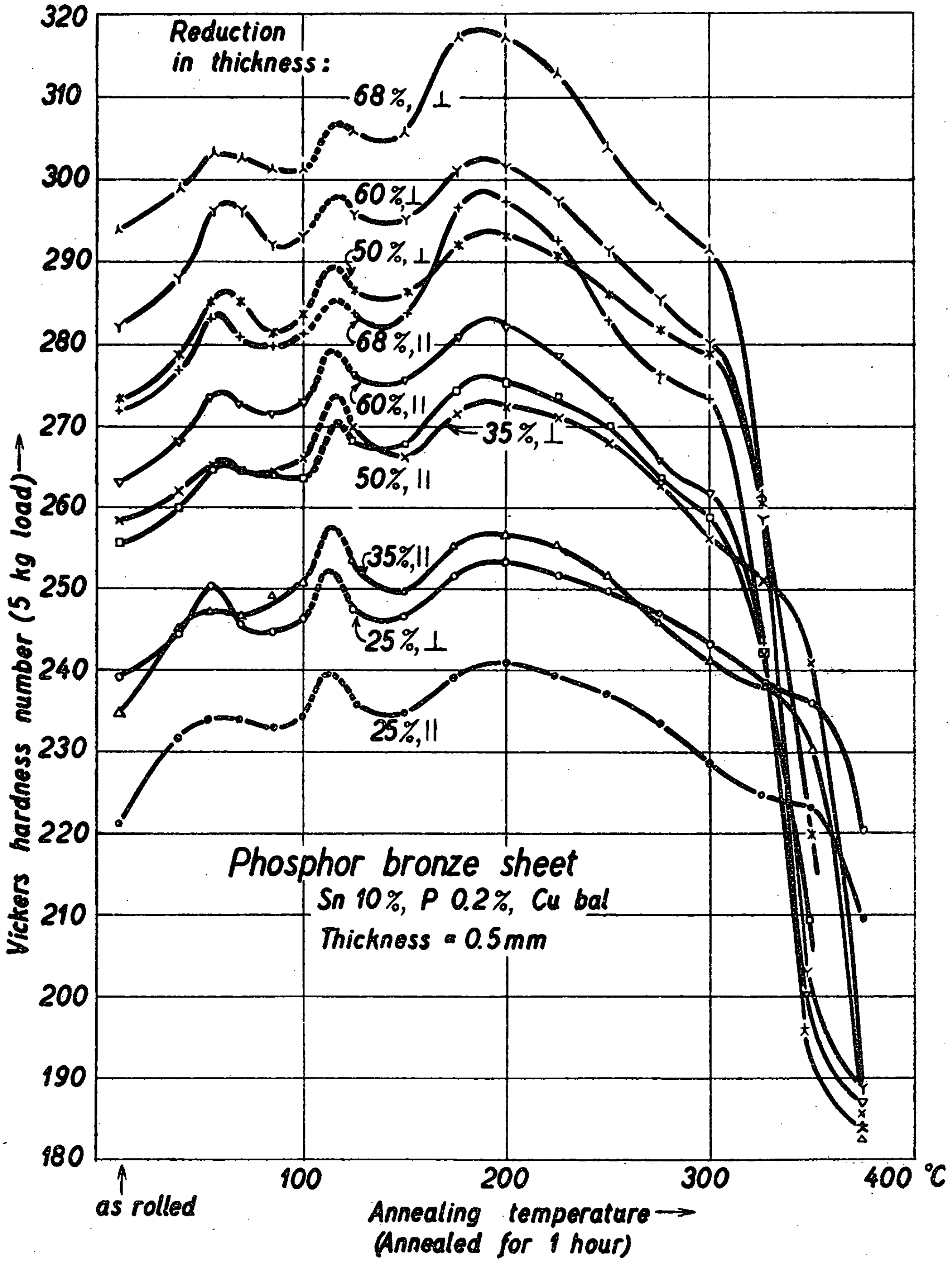


Fig. 12. Effect of annealing for 1 hour on VHN in phosphor bronze sheet with 10% Sn. || and ⊥ mean $\mathrm{VHN}_{\parallel}$ and $\mathrm{VHN}_{\perp}$ respectively.

The result of measurement is shown in Fig. 10. Finally the plot of VHN versus annealing time (annealing temperature=100°C) is shown in Fig. 11. Similar curves obtained for the samples Nos. 3–9 were published previously[2], so they will not be repeated here.

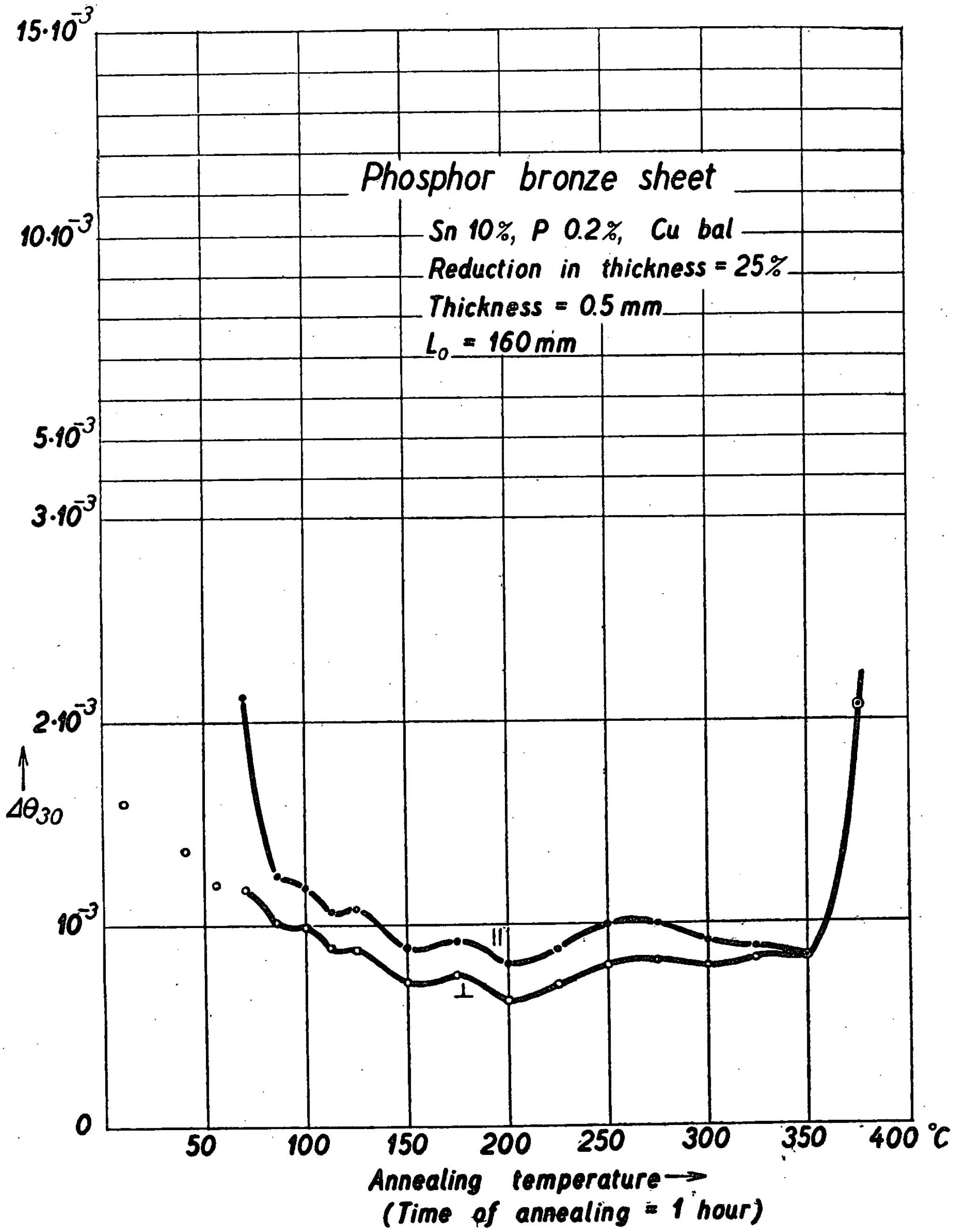


Fig. 13. Effect of annealing for 1 hour on $\Delta\theta_{30}$ in phosphor bronze sheet with 10% Sn.

Change of VHN with the annealing temperature is expected to be large in 10% Sn phosphor bronze sheet. This was indeed found to be the case, as shown in Fig. 12. Fig. 13 is a curve plotting $\Delta\theta_{30}$ versus the annealing temperature for the sheet that was 25% reduced by cold-rolling. Figs. 14 and 15 were obtained for the same alloy.

Figs. 16 and 17 show experimental result for the 8% Sn alloy sheet. They are qualitatively the same as in the case of 8% Sn phosphor bronze sheet, although the minor details are different.

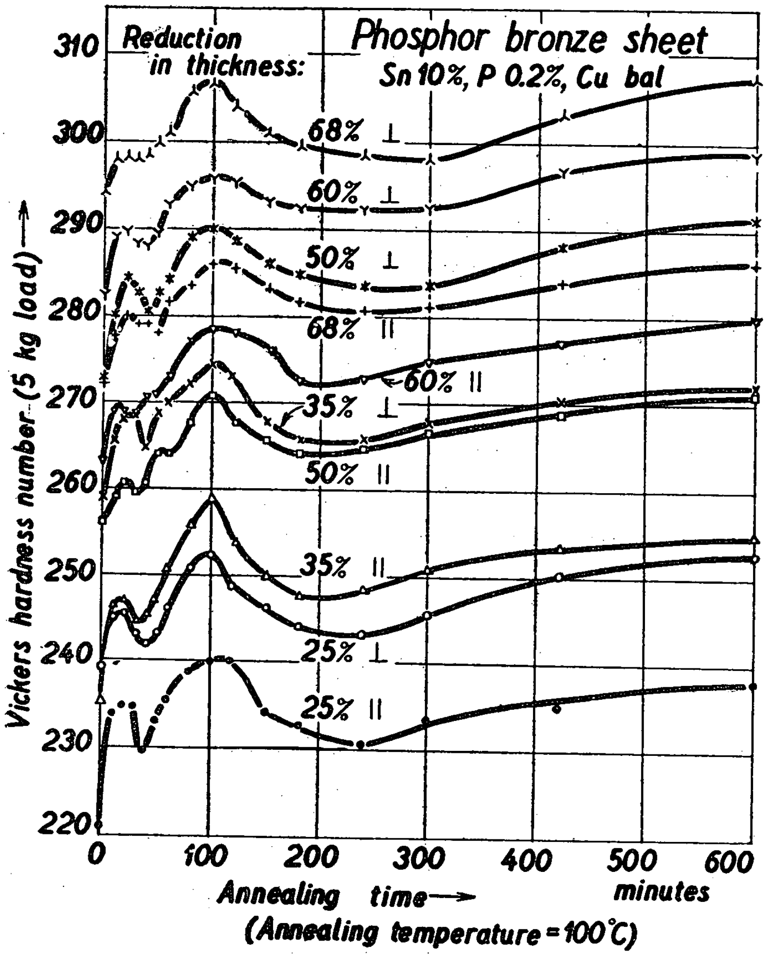


Fig. 14. Effect of annealing at 100°C on VHN in phosphor bronze sheet with 10% Sn. The same notation as in Fig. 12 is used.

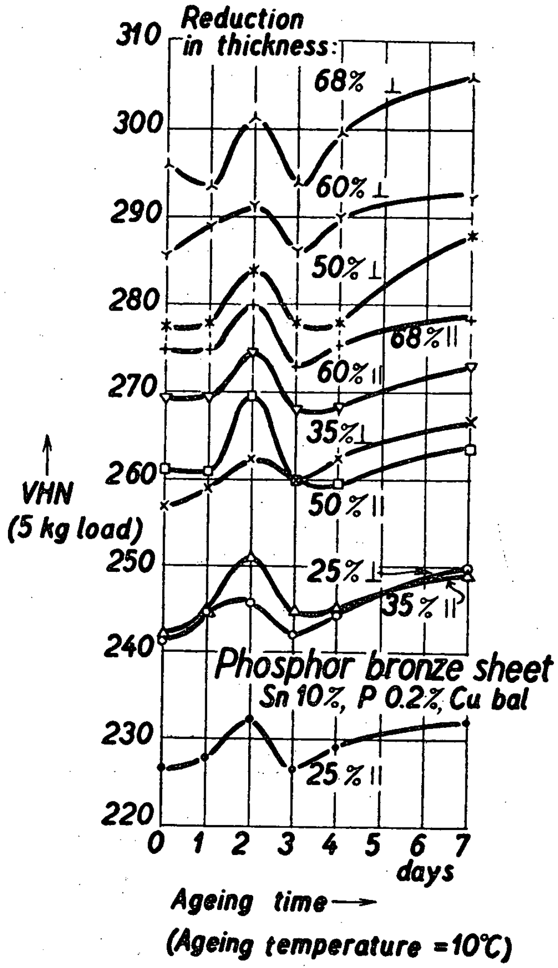


Fig. 15. Effect of ageing at 10°C on VHN in phosphor bronze sheet with 10% Sn. The same notation as in Fig. 12 is used.

Finally it was felt desirable to make some measurements on pure copper sheet. In this case $\Delta\theta_{30}$ was large for all samples and it was impossible to get reliable results; therefore the present paper is concerned with hardness measurements only (Figs. 18 and 19).

§4. Discussion of the Result

Fig. 20 shows schematically the essentials of Figs. 12, 13, 18 and 19. It was found that all the other phosphor bronze sheets that were tested in the present work show qualitatively similar behaviour with respect to $\Delta\theta_{30}$ and VHN.

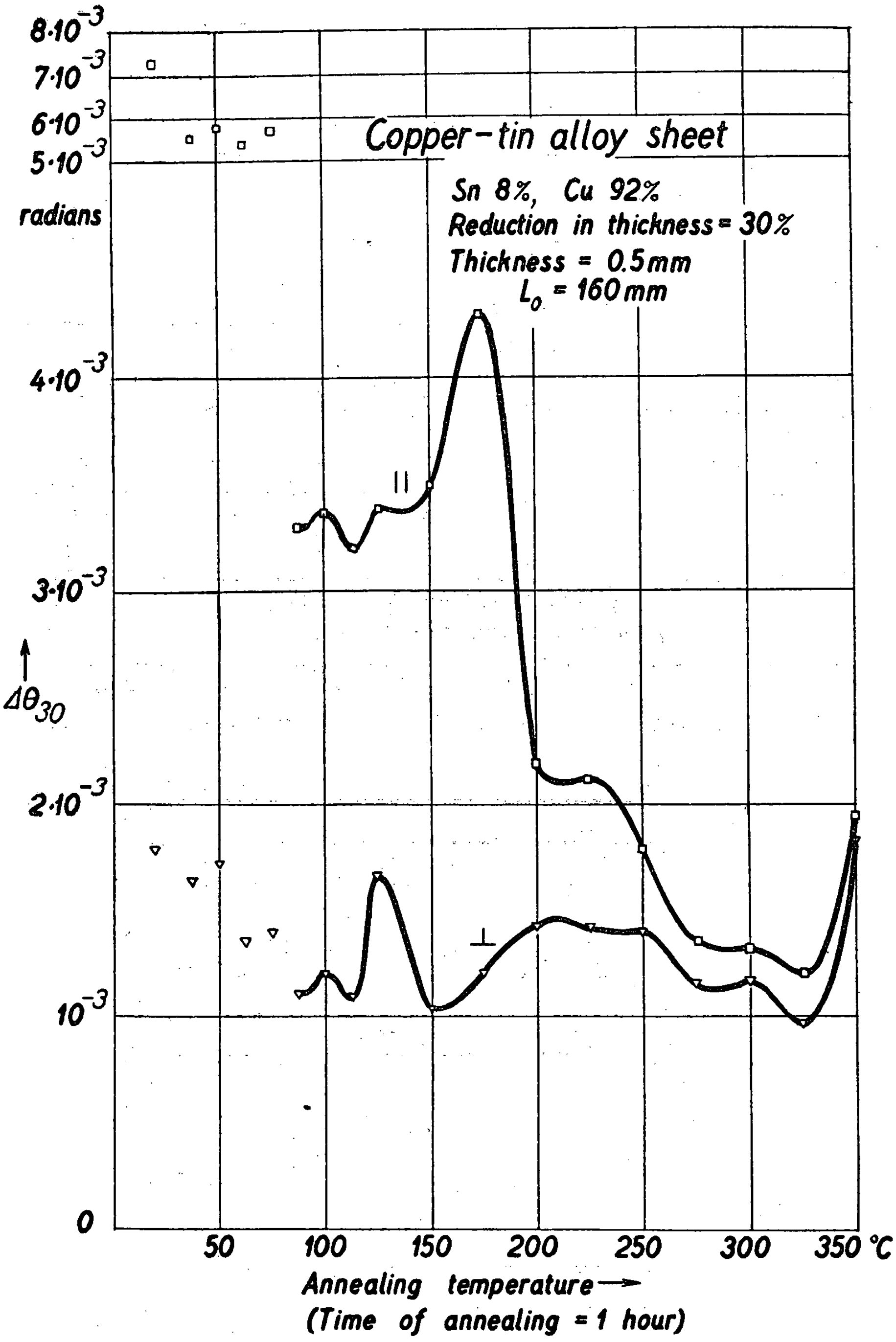


Fig. 16. Effect of annealing for 1 hour on $\Delta\theta_{30}$ in Sn-Cu alloy sheet.

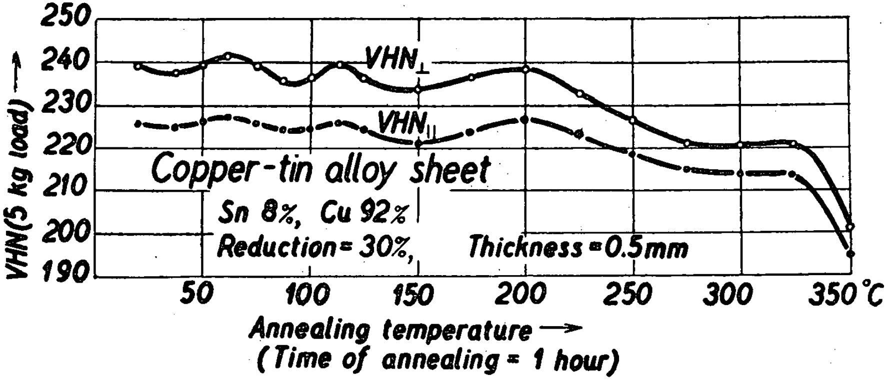


Fig. 17. Effect of annealing for 1 hour on VHN in Sn-Cu alloy sheet.

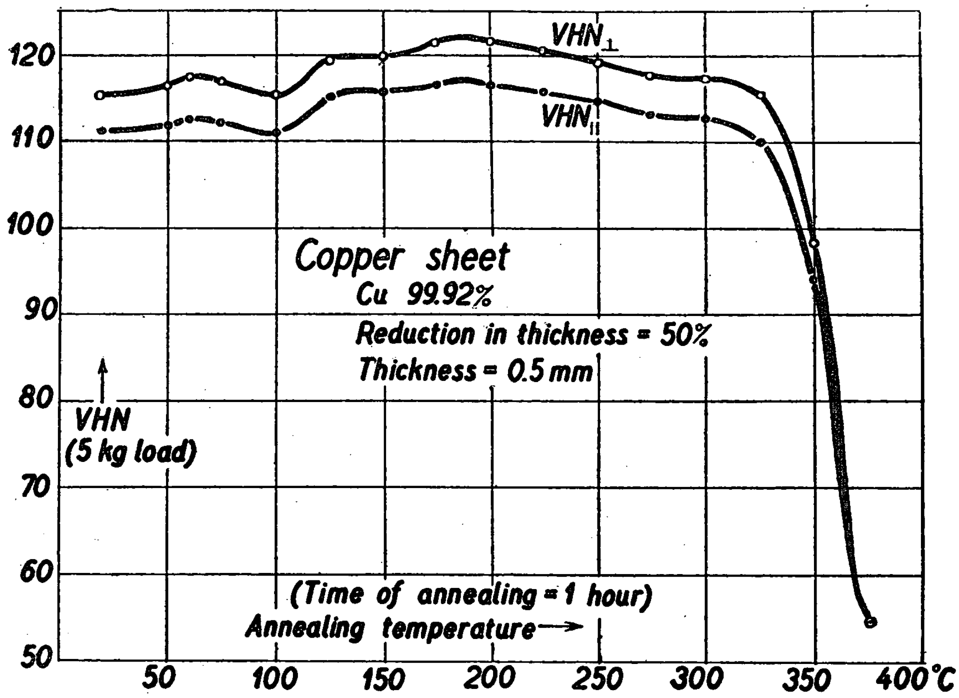


Fig. 18. Effect of annealing for 1 hour on VHN in pure Cu sheet.

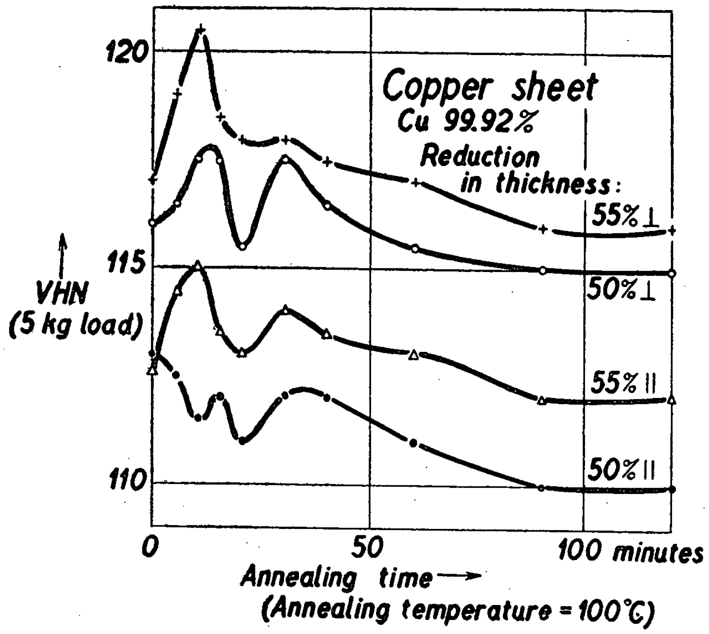


Fig. 19. Effect of annealing at 100°C on VHN in pure Cu sheet. ∥ and ⊥ mean VHN∥ and VHN⊥ respectively.

Fig. 20 shows that the VHN plot has at least four maxima. The one denoted as R corresponds to the state just prior to recrystallization and has nothing to do with the precipitation-hardening. During the period 1938–1945 very many kinds of copper-alloy sheets were prepared and measured, and it was found that all of them show the phenomenon that is denoted by R in Fig. 20, so it must be of very general nature. Crussard et al[5] studied polygonization in cold-worked metal, and Fig. 5 in their paper shows a small maximum of elastic limit at the stage of polygonization.

One would, therefore, be permitted to identify the phenomenon occurring at R of Fig. 20 with polygonization.

P_1 corresponds to the final precipitation stage that was detected for the first time by Haase and Pawlek using X-ray technique[4]. In addition to P_1 there is another stage P_2 in the precipitation-hardening mechanism in phosphor bronze sheets. This stage is not conspicuous in microstructure and Debye-Scherrer pictures but can be detected only by the very sensitive method (investigation of mechanical properties) that was adopted in the present investigation. As Fig. 20 shows, there is at least one hardening phenomenon (which we will call P_3) that occurs at a temperature very near the room temperature. The existence of P_3 is clear in Fig. 14. The number of VHN maxima at P_3 is very difficult to determine, however. The maximum P_3 was also detected by Mishima[7] in cold-rolled sheets of brass with the Zn content in the range 10-30%.

Turning now to the $\Delta\theta_{30}$ plot in Fig. 20, each of P_1, P_2 (and probably P_3) and R shows approximately a minimum instead of maximum. Denoting the internal stress and the sum of the area of grain boundaries per unit volume by σ_i and A respectively, $\Delta\theta_{30}$ in Fig. 20 can be phenomenologically and roughly represented by $\Delta\theta_{30}=F(\sigma_i)/G(A)$, where $F(\sigma_i)$ and $G(A)$ are monotonously increasing functions of σ_i and A respectively. When any precipitation occurs, the surface area of the precipitants should be included in A.

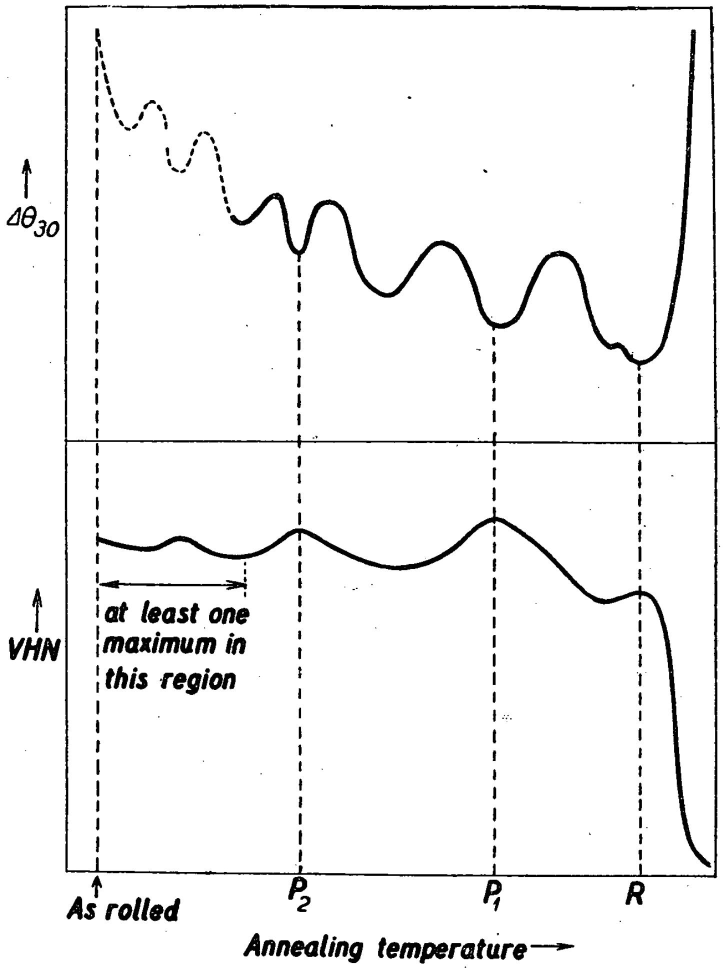


Fig. 20. Schematic representation of $\Delta\theta_{30}$ and the Vickers hardness number as functions of annealing temperature in the case of cold-rolled phosphor bronze sheet.

In the case of one phase alloy sheet, we might expect Fig. 20 to be replaced by Fig. 21, since there should be no precipitation hardening. The case of pure copper sheet (Fig. 18) is roughly represented by Fig. 21, but the existence of P_1 and P_2 and P_3 is evident in Figs. 18 and 19. Since only 99.92% pure Cu sheet was available to the author, it was not possible to find reason for the existence of P_1 and P_2 in our sample. Probably we might assume that they have the origin in the impurity.

In the case of copper sheet, P_3 consists of at least two maxima in Fig. 19.

Many other measurements that correspond to Fig. 19 in copper sheets were performed, and it was found that Fig. 19 is merely an example and that the form of the curve changes from one sample to another. All these facts would probably be explained by assuming that the P_3-stage is connected with something like irregular internal stress caused by the cold-rolling. Such an internal stress would be changed materially by a small addition of heat or by merely keeping the sample at room temperature for a finite length of time. This makes precaution desirable, and any measurement concerning the stage P_3 must be performed as soon as the sample is cold-rolled.

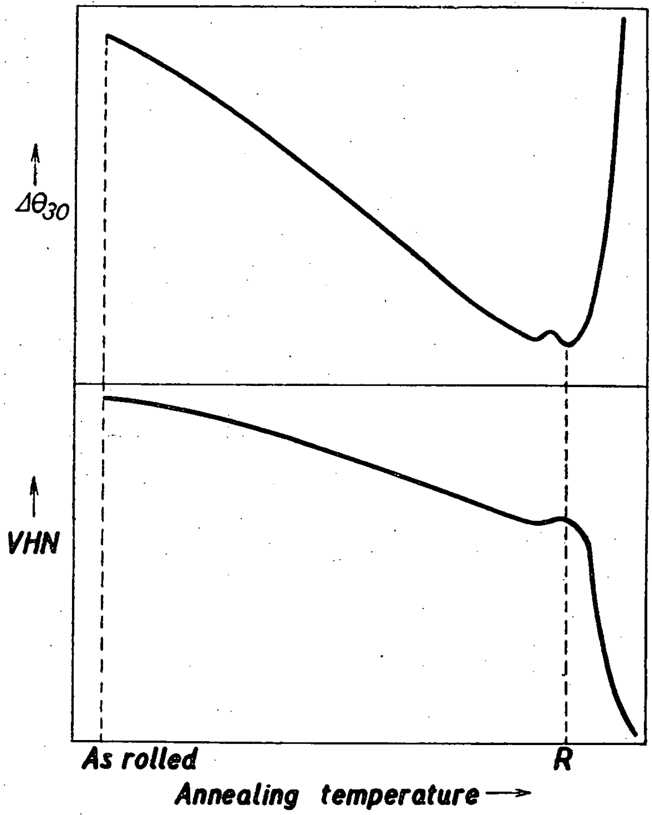


Fig. 21. Ideal relationship between $\Delta\theta_{30}$ or VHN and the annealing temperature in one phase metal sheet that was cold-rolled.

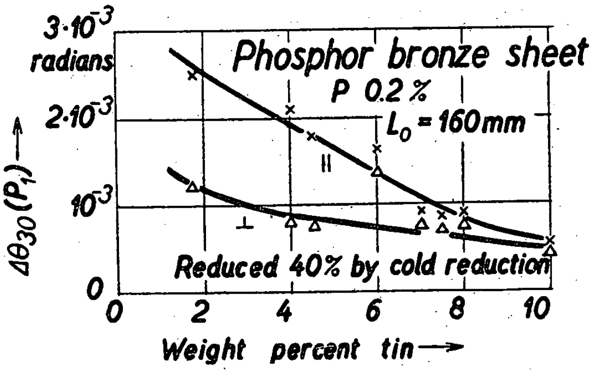


Fig. 22. Plot of $\Delta\theta_{30}(P_1)$ versus the tin content in phosphor bronze sheet.

Finally, Fig. 22 is a plot of $\Delta\theta_{30}(P_1)$ versus the Sn content for phosphor bronze sheets that were reduced 40% in thickness by cold-rolling and then annealed at the temperature of P_1 for 1 hour. Similar curves for reduction other than 40% were plotted, and it was found that each of them is qualitatively similar to Fig. 22. The curve seems to show a small maximum at Sn 6%, but its explanation has hitherto been not met with success.

As a practical problem, it may be remarked that in order to prepare good phosphor bronze sheet used as spring material of precision instruments the sheet must be annealed at about 500°C (intermediate annealing temperature) for 30–40 minutes prior to final cold-reduction. The spring is improved by annealing it at the temperature of P_1 or at the temperature slightly lower than R for 1 hour.

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2) K. Murakawa: Rep. Inst. Sci. Tech. Univ. Tokyo **1** (1947) 60; **6** (1952) 197.
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4) C. Haase u. F. Pawlek: Z. f. Metallkde **28** (1936) 73. Cf. also A.E. Owen and J. Iball: Jour. Inst. Metals **57** (1935) 267.

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