TITLE:

On the Age-hardening of Aluminium-rich Al-Zn alloys

AUTHOR(S):

Nishimura, Hideo

On the Age-hardening of Aluminium-rich Al-Zn alloys.

By

Hideo Nishimura.

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INTRODUCTION.

The author had already observed the age-hardening of the aluminium-rich Al-Zn alloys after quenching in water at 400°C. in 1920. Since that time he had no opportunity of investigating the subject. But now he can fortunately publish the results of the investigation which was made to determine the age-hardening of these alloys and the cause of hardening.

MATERIALS EMPLOYED.

The alloys were made from electrolytic zinc and aluminium of 99.4% purity. The analyses are given in table 1.

TABLE 1.

	Cu	Fe	Si	Pb	Zn	Al
Aluminium.	0.11	0.40	0.16	—	—	balance.
Electrolytic zinc.	0.0017	0.004	—	0.017	99.97	—

PREPARATION OF SPECIMENS.

The specimens whose analyses are given in Table 2, were made for the determination of the range of the composition which hardens after quenching. For this purpose aluminium was melted in a magnesia crucible heated in an electric furnace with precautions not to heat over 720°C, After the fusion zinc was added, the contents stirred with the addition of a small quantity of zinc chloride, and then poured into a chill mould ($\frac{1}{2}'' \times 1'' \times 2''$).

The specimens thus obtained were machined to a plane surface and heated for 2 days at 400°C. in an electric furnace, in order to remove the surface strain of machining and the heterogeneity of casting. After the cooling Brinell measurements were made.

The results are given in Table 2 and plotted in Fig. 1. Considering these curves, it is plain that the annealing showed a marked influence upon the hardness of cast metals ; i.e. the alloys below 16% zinc became softer, and the alloys between 16% and 28% zinc were harder after annealing. This is due to the cooling in the furnace which was comparatively rapid and had a somewhat quenching effect on the alloys containing between 16% and 28% zinc.
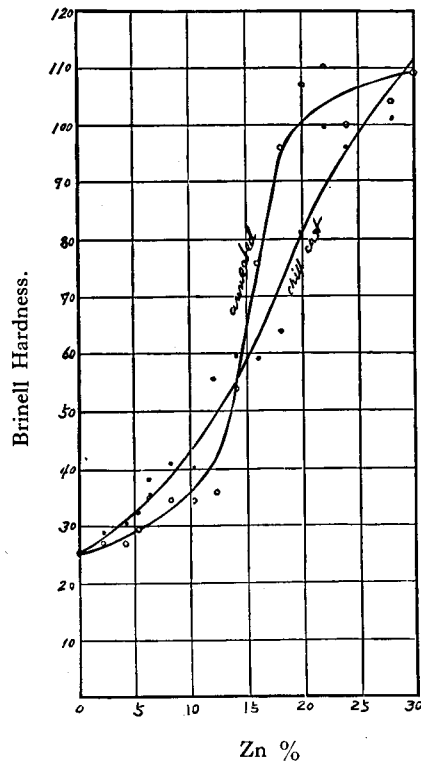
Fig. 1.

Zn %

TABLE 2.

No.	Composition Zn% (Analyzed).	Brinell Hardness. (500 Kg. pressure, 10 m.m. ball, 30 sec.)	
		Chill cast.	Annealed at 400°C. for 2 days.
Z 0	—	26.5	—
Z 1	2.16	29.0	26.8
Z 2	3.85	30.5	27.2
Z 3	5.04	32.5	29.7
Z 4	6.43	38.5	35.5
Z 5	8.46	41.7	34.5
Z 6	10.15	40.3	34.5
Z 7	12.87	55.5	35.8
Z 8	14.20	59.7	54.5
Z 9	16.11	59.0	75.5
Z10	18.87	64.0	96.0
Z11	19.80	81.0	107.5
Z12	22.52	99.5	110.0
Z13	24.25	96.0	100.0
Z14	28.47	101.0	104.0
Z15	30.43	111.0	109.0

MEASUREMENT OF HARDNESS.

(A)   Experimental method.

For this experiment an electric tube furnace was used and an iron tube was introduced into the furnace, as shown in Fig. 2.

Fig. 2.
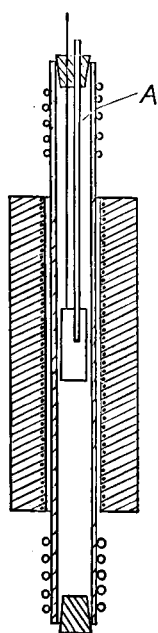
The temperature was measured with a thermo-couple, made of platinum and platinum-rhodium wires. When the furnace was heated to the desired temperature, the specimen previously introduced at A was lowered to the central part of the furnace. This would cause the cooling of that part. After the desired temperature was recovered, the furnace was kept at that temperature for 30 minutes, and then the specimen was quenched in ice water. According to this operation, the duration of heating was kept always constant for the experiments.

The hardness was measured with the Brinell Tester, using 500 Kg. pressure and 10 m.m. ball.

(B)   Determination of age-hardening range.

The Brinell hardness of the quenched specimens was measured immediately after quenching, 2 hours after, 20 hours after and so on.

The results are summarized in Table 3 and are plotted in Fig. 3.

In the figure it is seen that the alloys containing above 5% zinc showed the age-hardening and the hardening occurred rapidly in the first 20 hours and then gradually. These hardening effects are more noted in Fig. 4.

The upper curves of the figure show the relation between zinc content and hardness measured immediately after quenching and 165 hours after. The lower curves give the Brinell numbers of hardening (Brinell numbers immediately after quenching minus Brinell numbers after 165 hours), and the degree of hardening

$$\left(\frac{\text{Brinell numbers of hardening}}{\text{Brinell numbers immediately after quenching}} \times 100 \right)$$

TABLE 3.

| No.	Quenching temperature.	Brinell hardness.							Hardening number.	Hardening degree.
		Immediately after.	2 hrs. after.	20 hrs. after.	50 hrs. after.	75 hrs. after.	120 hrs. after.	165 hrs. after.		
Z 1	500°C.	27.5	28.0	28.0	27.5	27.5	28.0	28.0	—	—
Z 2	,,	28.4	27.5	28.4	27.5	29.5	28.5	28.5	—	—
Z 3	,,	30.5	32.0	35.0	35.0	34.5	36.5	36.0	4.9	16.0
Z 4	,,	34.8	36.0	41.0	43.5	43.0	45.0	48.5	10.2	28.8
Z 5	,,	36.5	43.0	43.0	40.5	45.5	45.0	50.0	12.0	32.9
Z 6	,,	36.0	39.5	45.0	45.0	49.0	43.0	49.0	9.6	26.6
Z 7	,,	40.2	46.5	54.8	56.5	59.5	57.0	57.5	17.4	43.3
Z 8	,,	47.5	50.5	59.5	61.5	62.0	67.0	64.0	16.8	35.3
Z 9	,,	49.5	62.2	64.0	65.0	69.0	65.0	65.0	16.5	33.3
Z10	400°C.	56.0	69.5	70.0	70.0	66.5	69.0	69.0	13.0	23.2
Z11	,,	69.5	73.0	76.5	80.5	80.5	78.0	78.5	10.5	15.1
Z12	,,	75.5	81.0	81.0	82.0	80.5	80.0	86.5	6.5	8.6
Z13	,,	79.0	80.0	82.5	85.5	86.0	89.5	90.5	8.9	11.3
Z14	,,	85.0	89.0	92.5	97.5	93.0	97.0	101.0	11.3	13.3
Z15	,,	92.0	92.5	97.0	97.5	98.0	103.0	100.0	6.1	6.6

Fig. 3.

Hours.
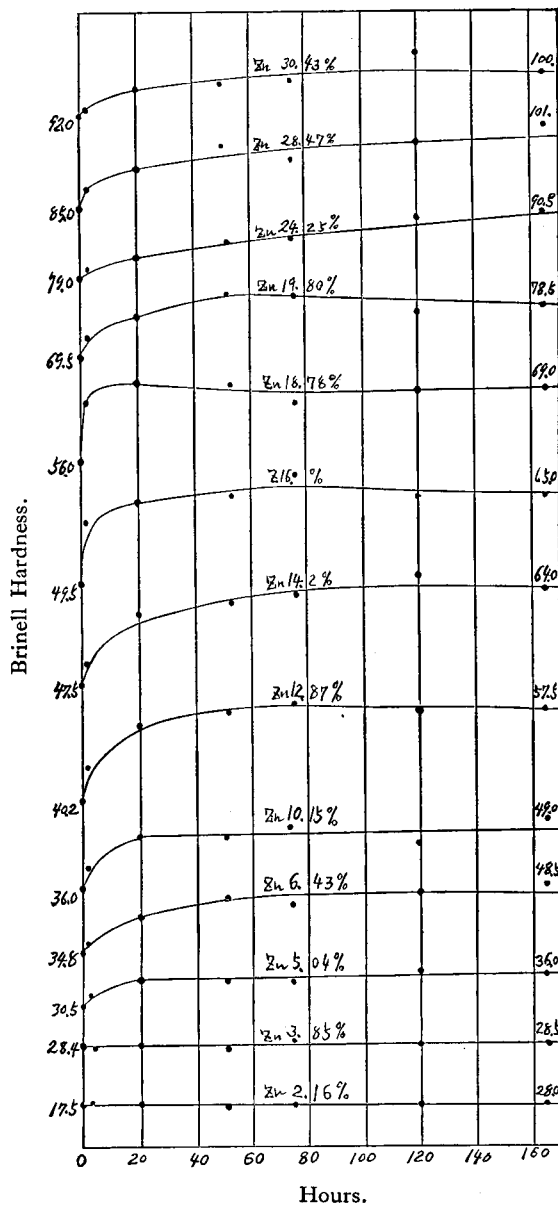
Fig. 4.
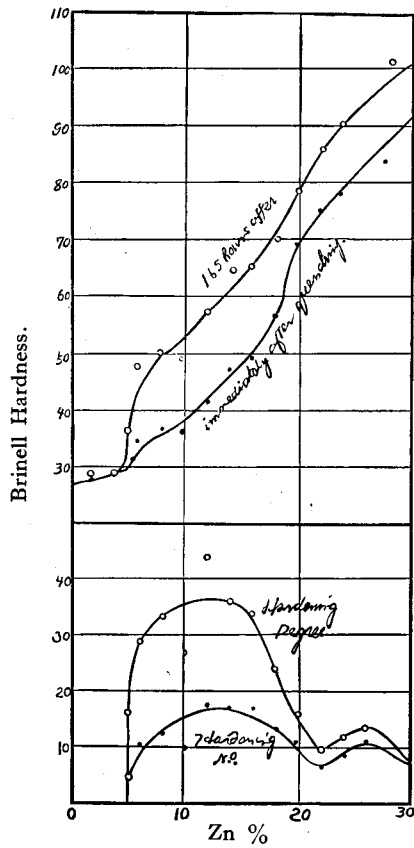
Fig. 5.
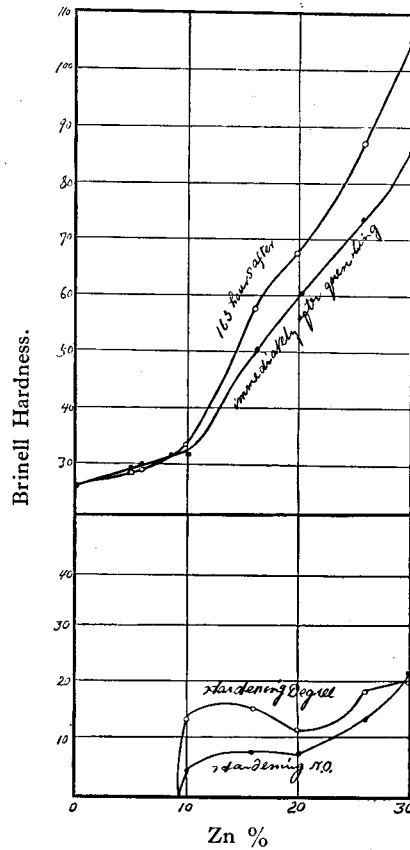
A glance at these curves shows that the curve of hardening degree makes an abrupt change at 5% zinc and shows a maximum at 12% zinc and then decreases until a minimum point at 20% is reached. On further raising the content of zinc the variation of hardening becomes very slight, even though it has a maximum at 26% zinc.

The results above obtained are summarized as follows :—

(i) The aluminium–rich Al–Zn alloys which contain zinc 5% above, showed the so–called age–hardening phenomena when they were quenched at 400°C. or 500°C. in ice water.

(ii) This hardening occurred rapidly at first and then gradually.

(iii) The degree of hardening varied with the content of zinc. Therefore zinc must be the main factor of this hardening.

TABLE 5.

No.	Composition Zn %.	Brinell hardness.		Hardening number.	Hardening degree.
		Before heating.	After heating for 30 minutes at 100°C..		
Z 3	5.04	28.7	29.5	—	—
Z 4	6.43	30.2	30.0	—	—
Z 6	10.15	32.3	32.3	—	—
Z 9	16.11	43.0	49.5	6.5	15.1
Z11	19.80	59.0	74.5	15.5	26.3
Z13	25.49	70.0	100.0	30.0	42.9
Z15	30.43	76.5	109.0	32.5	42.5
Z16	39.90	100.0	120.0	20.0	20.0

Fig. 6.
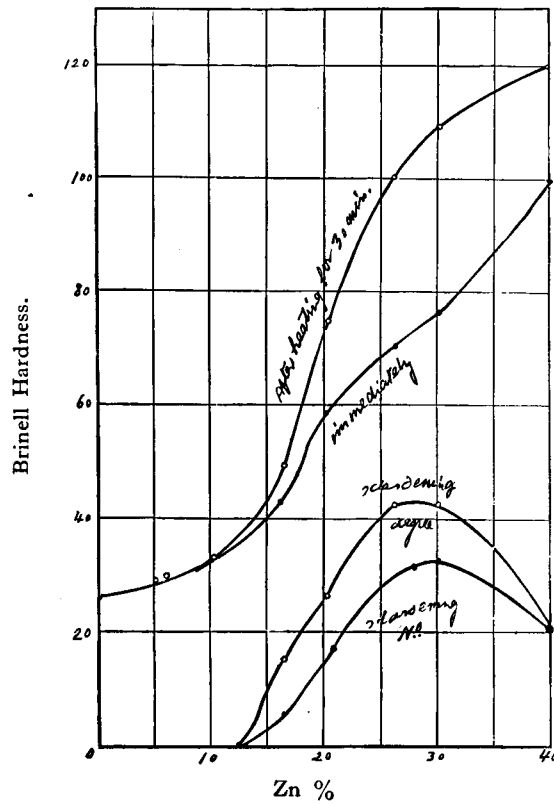
Fig. 7.
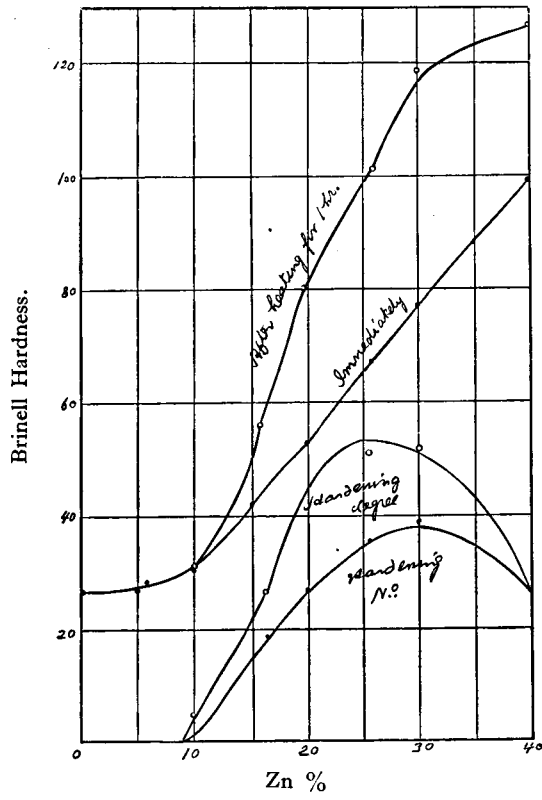
Fig. 8.
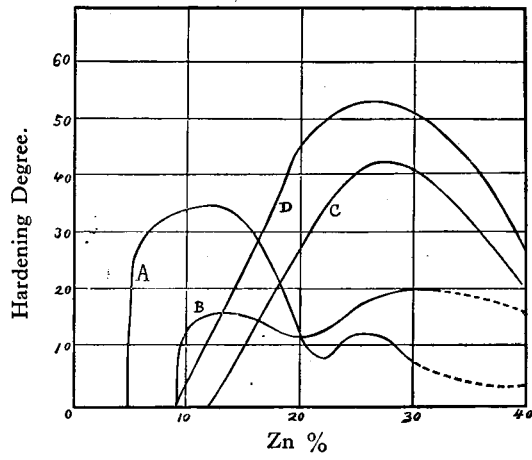
TABLE 6.

No.	Composition.	Brinell hardness.		Hardening number.	Hardening degree.
		Before heating.	After heating for 1 hour at 100°C.		
Z 3	5.04	28.0	28.0	—	—
Z 4	6.43	29.5	29.5	—	—
Z 6	10.15	30.0	31.5	1.5	4.5
Z 9	16.11	44.5	56.5	17.5	26.9
Z11	19.80	52.5	80.0	27.5	52.4
Z13	25.49	67.0	191.0	34.0	50.8
Z15	30.43	78.5	119.5	41.0	52.2
Z16	39.9	100.0	126.5	26.5	26.5

Tables 5 and 6, Figs 6 and 7 give the results of the experiments. Owing to this experiment, the hardening which occurs gradually at room temperature was much accelerated by tempering, and its effect was more evident when the heating was prolonged. It is, however, to be noted that the hardening of the alloys containing less than 20% zinc was somewhat insignificant.

In Fig. 8, the hardening degrees obtained with various methods of treatment are summarized for comparison.

(a) When quenched in ice water and aged for 165 hours at room temperature.

(b) When quenched in boiling water and aged for 165 hours at room temperature.

(c) When quenched in ice water and tempered for 30 minutes at 100°C.

(d) When quenched in ice water and tempered for one hour at 100°C.

The theoretical treatment for this phenomenon is given later.

(E) Effect of long heating at 130°C.

The specimens above employed were put into the automatic regulating electric oven and heated for 3 weeks at 130°C. After cooling the Brinell Tests were made, and the results are given in Table 7.

Fig. 9.
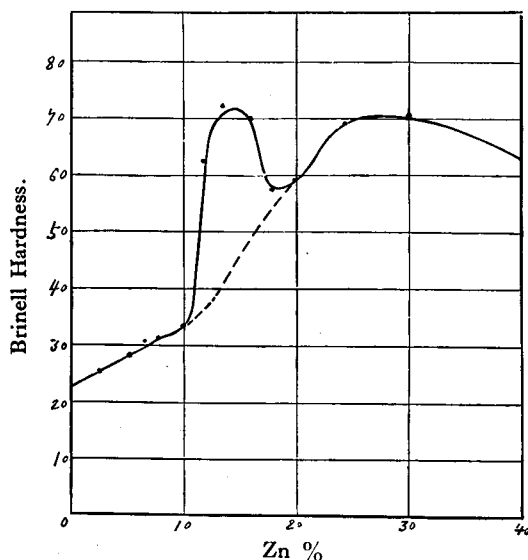
In Fig. 9 the hardness curve is found to rise slowly as the zinc content increases, and changes rapidly at 10% zinc, until it reaches a maximum in the neighbourhood of 15%. Then it falls to a minimum at 20% and again rises to 30%.

An examination of the curve shows that the alloys between 10% and 20 % zinc attain the conditon of equilibrium with difficulty. If the equilibrium condition has been reached, hardness would be plotted as shown by the dotted line in the figure.

TABLE 7.

No.	Composition Zn. %.	Brinell hardness.
Zn 1	2.16	25.5
Zn 2	3.85	27.5
Zn 4	6.43	30.5
Zn 5	8.47	31.0
Zn 6	10.15	33.5
Zn 7	12.87	63.0
Zn 8	14.20	74.0
Zn 9	16.11	70.0
Zn10	18.78	58.0
Zn11	19.80	59.5
Zn13	24.25	69.5
Zn15	30.43	71.5
Zn16	39.90	64.0

Fig. 10.

Minutes.
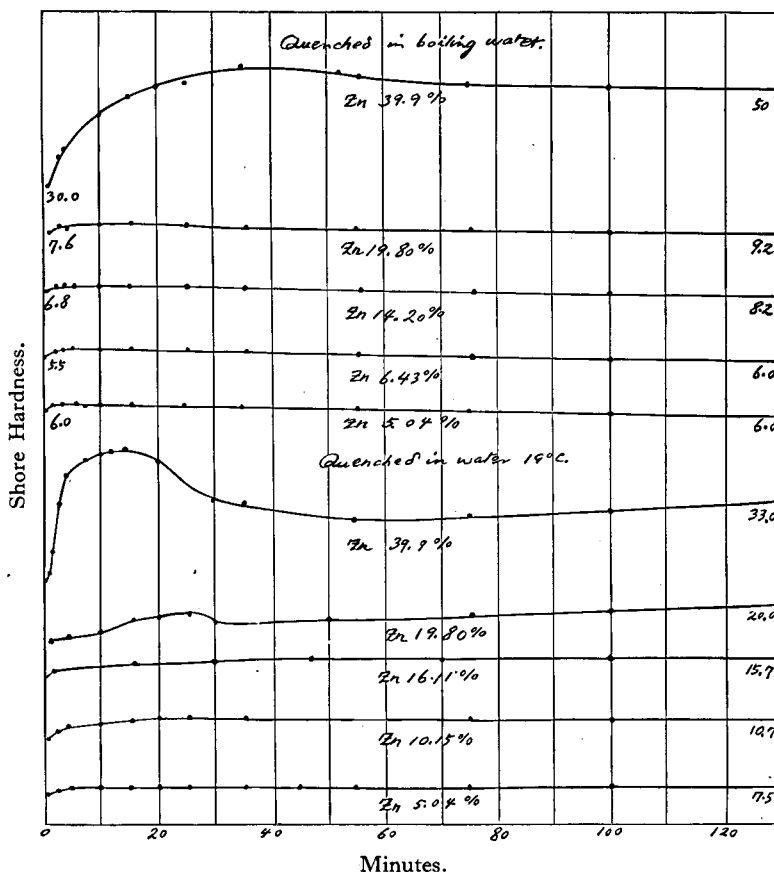
(F)   Hardness in short time after quenching.

Further experiments were made to determine the variation of hardness in a short time after quenching. The experiment was carried out in the same way, i.e., the specimens heated for at 400°C. were quenched in water at 19°C. and in boiling water respectively. Quickly after quenching the hardness was measured with the Shore Screloscope, using the magnifying hammer.

The hardness–time curves are plotted in Fig. 10. Be it observed that the alloy 40% zinc hardened in the first fifteen minutes and then became somewhat softer. Again its hardness rose slowly. The alloy 20% zinc showed the same hardening effect, and its degree was slight. However,

the alloys containing less than 20% zinc hardened rapidly in 20 minutes after quenching and then gradually without any softening. The alloy containing 5% zinc showed no change of hardness.

A glance at the results shows that the hardening effect of quenching was less marked when boiling water was employed as the quenching bath. This agrees with the fact already proved.

MEASUREMENT OF THERMAL EXPANSION.

(A) Method of measurement.

Test specimens 0.5 cm. diameter and 7 cm. long were prepared and treated similarly as mentioned above. These specimens which had been heated at 400°C. for 30 minutes and quenched in cold water, were aged at room temperature. After 1 week the thermal expansions was measured with Prof. Honda's dilatometer. Heating and cooling were carried out at the rate of 3°C. per minute.

(B) Results of experiment.

Fig. II shows the results of the experiment. According to the experiment the alloy 28% zinc was found to expand continuously at a lower temperature and at about 130°C. the rate of expansion was observed to slacken, until it was accelerated in the neighbourhood of 250°C. After the temperature reached 300°C., the expansion followed the normal course. On cooling, however, the irregularity of expansion was hardly observed.

Although the alloy with 20% zinc showed a similar change of expansion, the specimen containing 16% zinc began to expand rapidly at about 160°C. With regard to the alloys 12 and 8% zinc no peculiarity in expansion was found during heating and cooling. Nevertheless it is noted that the heating and cooling curves do not concide with each other.

In order to measure the thermal expansion for the specimens which have attained equilibrium, the above test pieces were heated for 2 weeks at 130°C., and after cooling the experiment was carried out with a heating and cooling rate of 2.5°C. per minute. The results are given in Fig. 12.

We see in the figure that the test pieces containing 20% zinc or more showed similar changes of expansion, i.e. a slight retardation of expansion began to take place in the neighbourhood of 200°C., and they expand rapidly at about 300°C. and this expansion continued until the temperature reached 350°C. On cooling, some irregularity was observed between 250°C. and 240°C., but it was very slight.

On the other hand, the alloys less than 20% zinc showed no special change of expansion on heating and cooling. They were almost reversible and some change of direction is noticed in the curves of expansion.
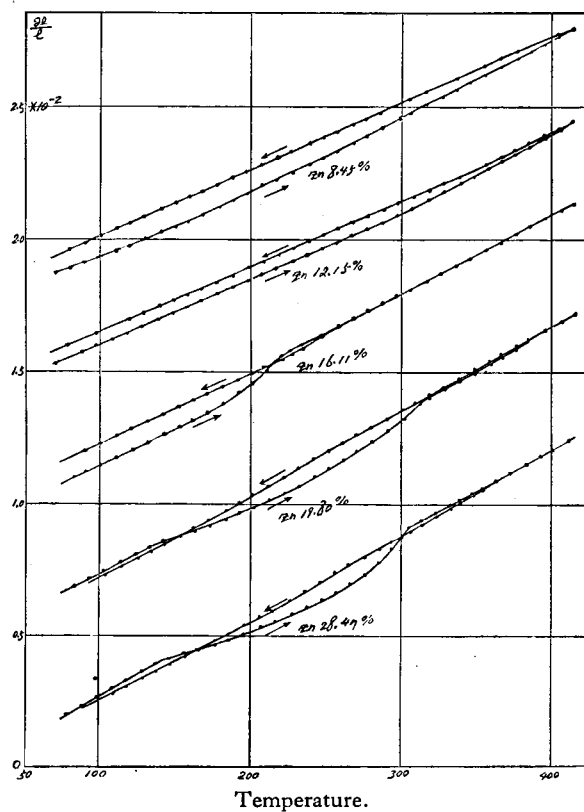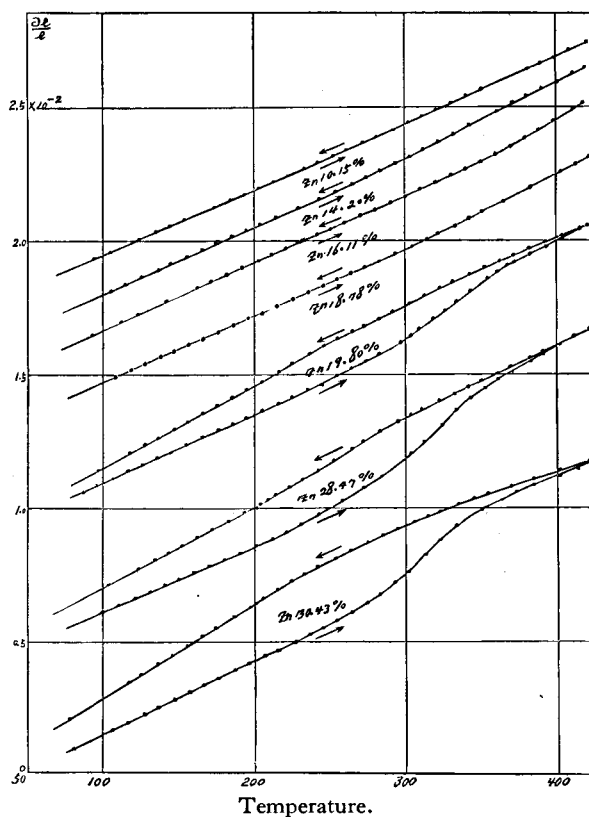
Fig. 11.

Temperature.

Fig. 12.

Temperature.

THERMAL ANALYSES.

(A) Method of analyses.

The specimens 1 cm. diameter and 3 cm. long, which had been heated at 240°C. for 1 week and cooled in the furnace were employed, and for the analysis a differential method was adopted, using a copper piece of the same dimensions as the neutral body. The temperature difference between the test specimen and the neutral body was read with deflection of a mirror galvanometer made by the Leeds and Northrup Co., and the temperature of the specimen was measured with a platinum and platinum rhodium couple. The rate of heating and cooling was 5°C. per minute. The results are described in the following paragraph.

(B) Results of experiment.

In Fig. 13 it is noted that the alloy 24% zinc showed a slight absorption or development of heat in the neighbourhood of 260°C. With regard to the alloy 28% zinc some change was already observed at about 200°C. on heating, and the heat absorption reached a maximum at 280°C. On cooling, however, the reaction was somewhat retarded as may be seen in the figure. On the other hand, the alloys less than 20% zinc showed no irregularity in thermal curves.

Considering these results with the measurement of thermal expansion the rapid change of expansion at about 290°C. agreed with that of the thermal analysis. Contrary to the former, however, the thermal analysis showed the change on cooling distinctly.

Fig. 13.
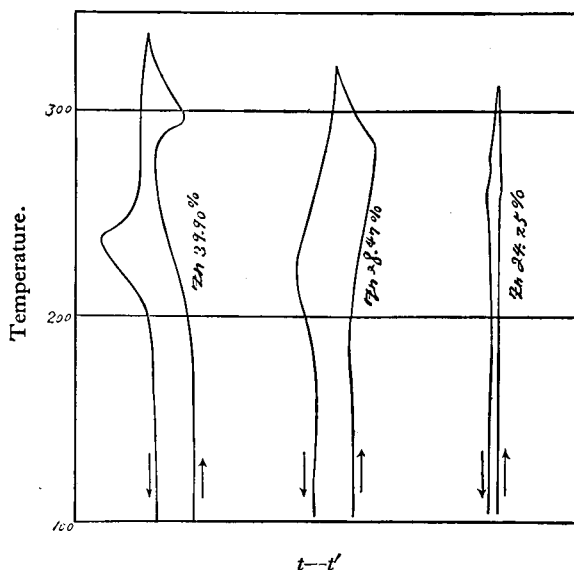
MEASUREMENT OF ELECTRICAL RESISTIVITY.

(A) Experimental method.

The test specimen was a cylindrical bar, 15 cm. in length and 6.5 mm. in diameter, which was prepared by casting.

As shown Fig. 14 (a), the specimen was connected at e and f with a Leeds and Northrup Potentiometer. The distance between e and f was taken as 10 cm. and the connecting device after Broniewski[1] at e and f are shown in Fig. 14 (c). As the source of current secondary batteries were employed.

The resistivity was calculated the potential difference between e and f and the current.

<center>(B) Results of experiment.</center>

Resistivities measured at room temperature of cast and annealed specimens are given in Table 8. Annealing was carried out at 380°C for 2 days, and then cooled in the furnace.
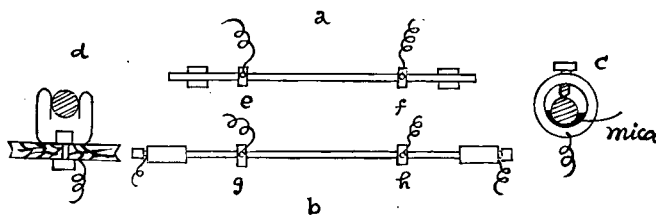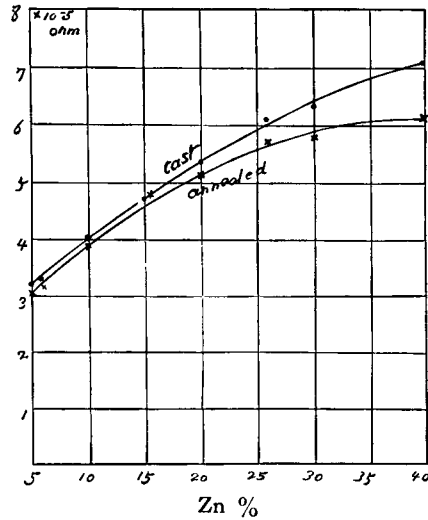
<center>Fig. 14.</center>

<center>TABLE 8.</center>

No.	Composition Zn %.	Resistivity (10^{-5} ohm).	
		Cast.	Annealed.
Z 3	5.04	3.18	3.03
Z 4	6.43	3.20	3.06
Z 6	10.15	4.05	3.93
Z 9	16.11	4.84	4.84
Z11	19.80	5.33	5.03
Z13	25.49	6.35	5.76
Z15	30.43	6.37	5.80
Z16	39.90	7.12	6.19

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[1] Witold Broniewski; Introduction a l'étude des alliages, page 117.

Fig. 15.

In Fig. 15 the results are plotted against the concentration of zinc, and it is seen that the difference between the resistivity of the alloys less than 16% zinc was very slight in both cast and annealed state. However this difference became more distinct with the increase of the zinc content.

Furthermore, experiments were carried out on the specimens quenched at 400°C. in water, in order to observe the change on heating. A specimen was connected with the potentiometer as shown in Fig. 14 (b) and heated in an electric tube furnace, passing CO_2 gas to avoid oxidation.
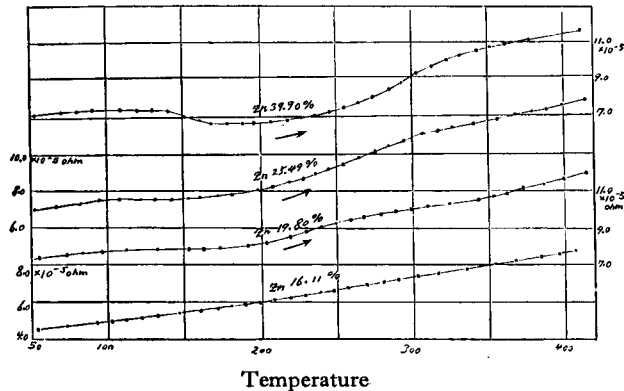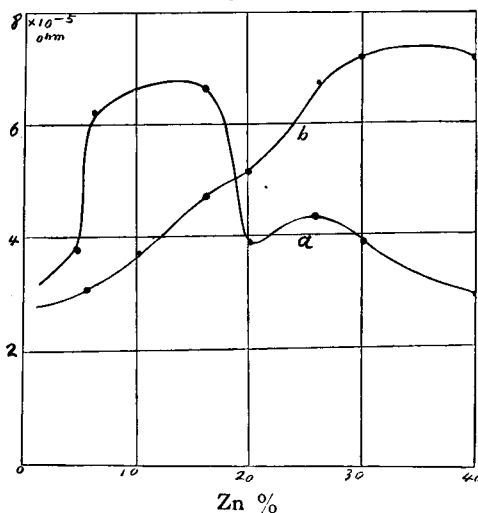
Fig. 16.

Temperature

Fig. 17.

Zn %

We see the results in Fig. 16. In the experiment the alloy less than 20% zinc did not show any marked change in resistivity. Nevertheless, on the specimens containing more than 20% zinc a retardation of the increase of resistivity was observed to begin at about 100°C. As the temperature rose, resistivity increased slowly, but in the neighbourhood of 200°C. it changed to rapid increase until 360°C, was reached.

Then the specimens above employed were put in an electric oven and heated at 110°C. for 5 weeks. After cooling, their resistivity was measured at room temperature.

Table 9 gives the results.

TABLE 9.

No.	Composition Zn %.	Resistivity (10^{-5} ohm).	
		Annealed at 100°C. for 5 weeks.	Quenched at 400°C.
Z 1	2.16	3.30	—
Z 3	5.04	3.81	—
Z 4	6.43	6.27	3.06
Z 6	10.15	6.58	3.71
Z 9	16.11	6.67	4.78
Z11	19.80	3.87	5.12
Z13	25.49	4.37	6.77
Z15	30.43	3.87	7.18
Z16	39.90	2.91	7.22

According to the curve a in Fig. 17 the variation of resistivity against the concentration of zinc is found to agree almost with that of hardness in Fig. 9. This verifies the similarity of change in resistivity and hardness.

Fig. 17 b shows the relation between concentration and resistivity which was measured immediately after quenching. Compared with the former results, the resistivity of the alloys less than 10% is higher in the annealed condition, but this relation is reversed for the specimens containing more than 20% zinc.

Accordingly we can conclude that the alloys less than 20% zinc attain equilibrium with much difficulty.

Thus we summarize as follows:

(1) Electric resistivity varies with the zinc content in both cast and annealed state. Nevertheless, prolonged heating at 110°C. showed an irregularity in the resistivity concentration curves. This proved the difficulty of attaining equilibrium for the alloys between 5 and 20% zinc, and this relation coincides with that of the hardness obtained by prolonged heating.

(2) Electric resistivity measured on quenched specimens varied with the temperature even as did the thermal expansion.

MICROSCOPICAL STUDY.

(A) Polishing and etching reagent.

For the microscopical study a piece of suitable size was taken and polished by hand on emery paper of grades 0, 00, 000. Finally it was finished on a wet flannel, using calcined magnesia as polishing powder.

Then we tried to develop the figure with caustic soda solution, hydrofluoric acid or concentrated nitric acid, but to our disappointment all in vain. After numerous attempts, however, we found a solution of sodium picrate to be most suitable in our study.

This solution was made as follows ;

Picric acid	2	grams.
Caustic soda	25	grams.
Water	75	cubic centimeter.

This reagent is generally employed in the detection of cementite in iron and steel. When it is used, it should be diluted with 10 parts of water.

The specimen was etched slowly and the figure was distinctly developed. But a black precipitate was deposited sometimes on the specimens in too much immersion. However, this was avoided by shaking in the solution.

(B) Microscopical study.

Microstructures thus obtained are shown in Fig. 18. Fig. (a) is an example of cast metal, which shows a dendritic structure due to chill casting. Figs. (b), (c), and (d) are the micro–photographs of the specimens which were previously annealed at 350°C. for 2 days and then quenched at 400°C. in ice water. They show a homogeneous structure and prove that the samples were formed of a solid solution in the above experiments, when they were quenched at 400°C. or 500°C.

Nevertheless, the Specimens with less than 20% zinc, which had been heated at 110°C. for 22 days, developed a second constituent over the original solution. They were found to be developed along the grain boundaries and slipping or cleavage faces, and their structure was very fine and troostitic. An example containing 16% zinc is shown in Figs. (f) and (g). This change was observed to some extent in the alloy 6% zinc as may be seen in Fig. (e). Accordingly, it is verified that the solubility of zinc in aluminium is less than 6% at 110°C.

On the other hand, an alloy containing 32% zinc treated similarly showed a different type of structure, i.e., the disintegration of the original structure was far advanced. This is seen in Fig. (h), where the white portions of aluminium–rich solution are surrounded by the black portion, which had been developed secondarily, and troostitic parts are also found.
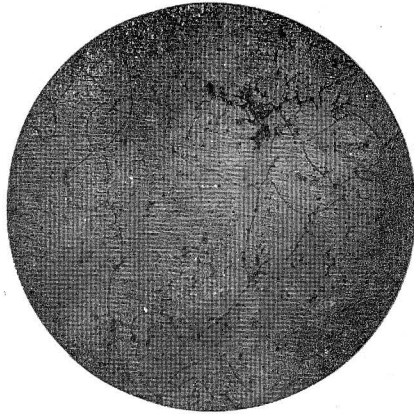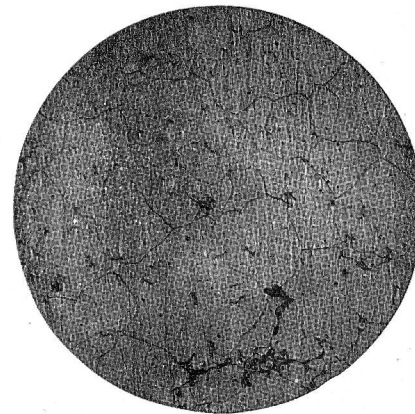
Fig. 18.
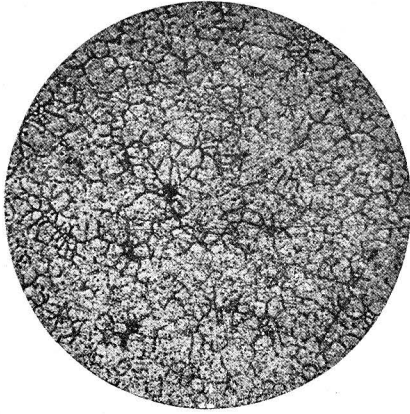
(a)

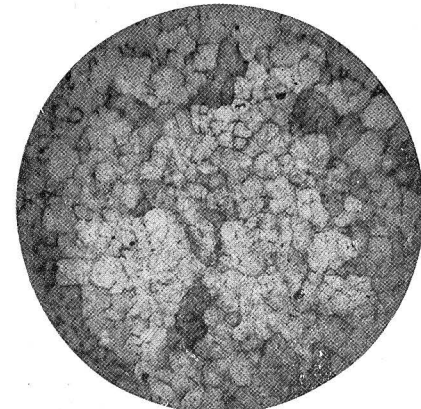Specimen 16.11% Zinc, chill cast. Magnification 110 diameters.

(b)
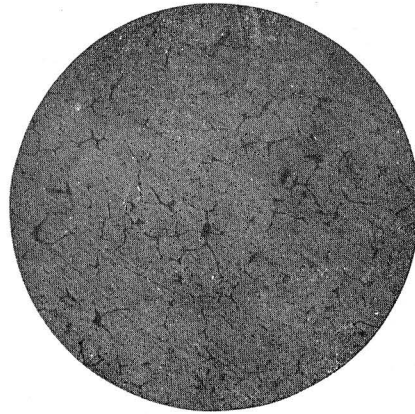
Specimen 5.04% Zinc, quenched at 500°C. in ice water. Magnification 100 diameters.
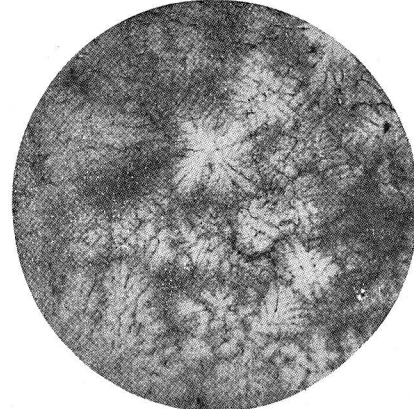
(c)

Specimen 32.0% Zinc, quenched at 400°C. in ice water. Magnification 100 diameters.

(d)

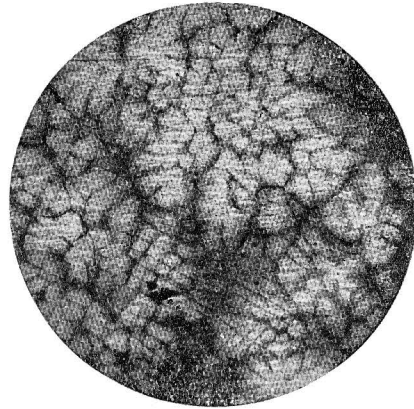Specimen 36.0% Zinc, quenched at 400°C. in ice water. Magnification 100 diameters.

(e)

Specimen 6.43% Zinc, annealed at 110°C. for 3 weeks after quenching at 500°C. Magnification 50 diameters.
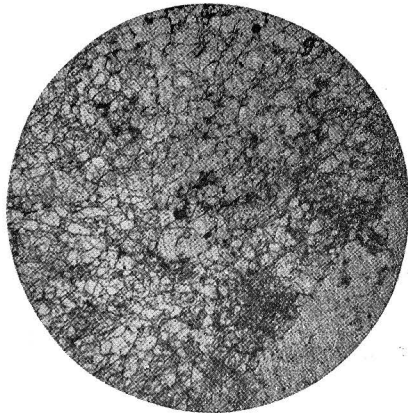
(f)

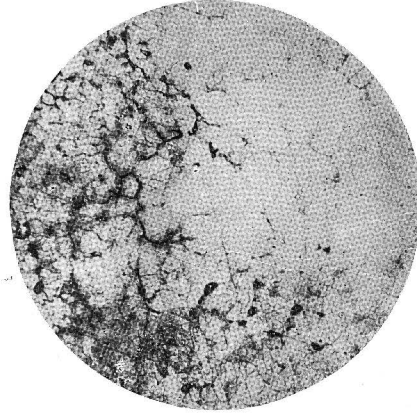Specimen 16 11% Zinc, annealed at 110°C. for 3 weeks after quenching at 500°C. Magnification 50 diameters

(g)
Specimen the same as (f). Magnification 100 diameters.

(h)
Specimen 32.0% Zinc, annealed at 110°C. for 3 weeks after quenching at 400°C. Magnification 500 diameters.

(i)
Specimen 8.46% Zinc, annealed at 320°C. for 50 hours, and then at 110°C. for 3 weeks after quenching. Magnification 100 diameters

(j)
Specimen 12.87% Zinc, ditto. Magnification 100 diameters.
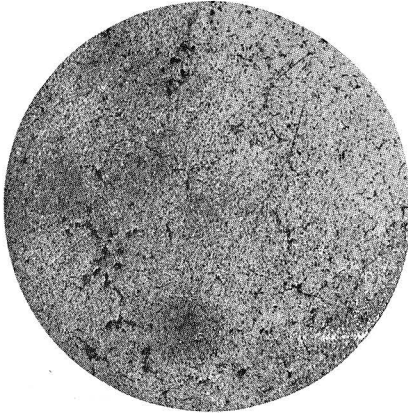
(k)
Specimen 14.2% Zinc, ditto. Magnification 100 diameters.

(l)
Specimen 19.80% Zinc. ditto. Magnification 100 diameters.

(m)

Specimen 28.47% Zinc, ditto. Magnification 100 dimeters.
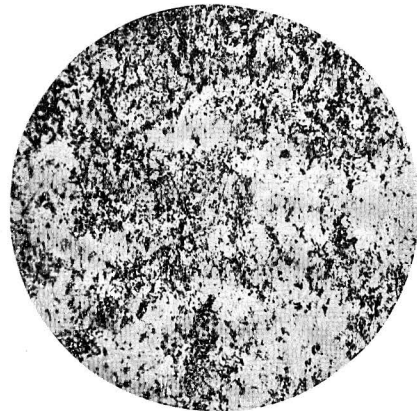
(n)

Specimen 32.0% Zinc, ditto. Magnification 100 diameters.

Fig. 19.

(a)

Specimen 5.04% Zinc, quenched at 500°C. in water.
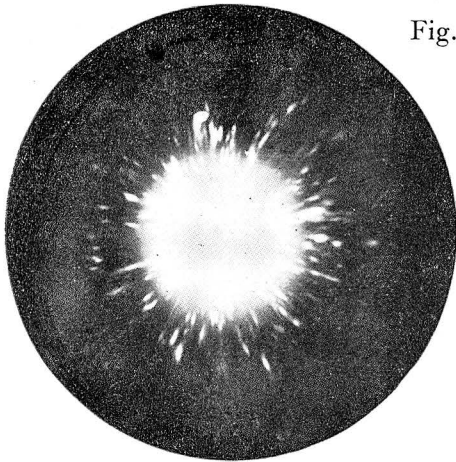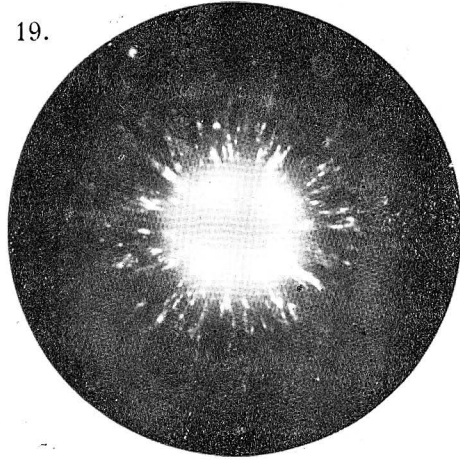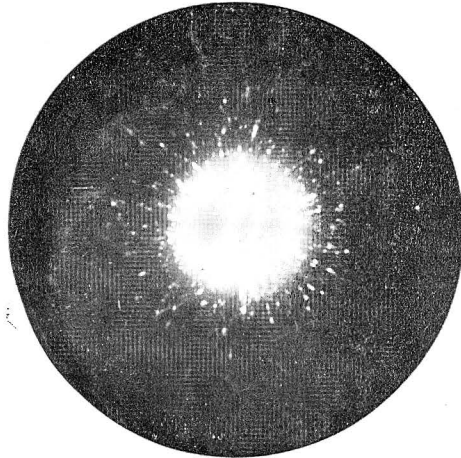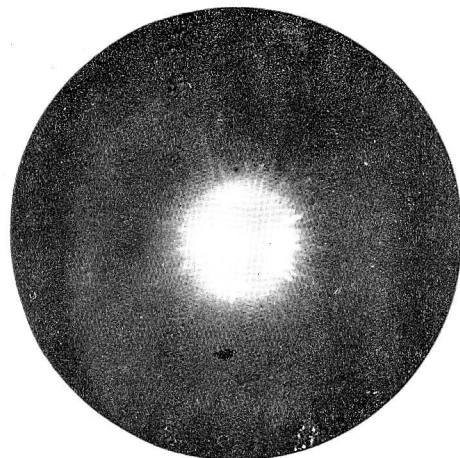

(b)

Specimen 5.04% Zinc, annealed at 110°C. for 3 weeks after quenching.

(c)

Specimen 12.87% Zinc, annealed at 110°C. for 3 weeks after quenching.

(d)

Specimen 39.90% Zinc, annealed at 110°C. for 3 weeks after quenching.

The above treatment was found to be incomplete in attaining equilibrium. Therefore, the specimens previously heated at 320°C. for 50 hours were annealed at 110°C. for 3 weeks. These results are given in Figs. (i) to (n).

On the alloys less than 20% zinc the disintegration was seen to be advanced in a marked degree, and the original solid solution transformed into fine grains, which were surrounded by very fine crystals newly developed. However, on the alloy 20% zinc these finely divided crystals are found to be uniformly distributed.

Figs. (m) and (n) are the examples of the alloys containing more than 20% zinc, and it shows especially that the eutectoid structure is distinct in the black portion.

According to these results we may conclude that the solid solution, which is super–saturated with regard to the solute constituent, disintegrates into fine grains when it precipitates the other constituent, in order to attain equilibrium.

<center>X–ray Analysis.</center>

The phenomena accompanying the age-hardening were almost investigated in the experiments mentioned above. However, we considered that an X-ray analysis might result in some interesting data. Therefore, we had a Laue spot taken on the alloys annealed and quenched. The results are given in Fig. 19.

Figs. (a) and (b) are the patterns taken on the same specimen containing 5% zinc, but one of them was quenched at 500°C. in ice water and the other annealed at 110°C. for 3 weeks after quenching.

These photographs tell us that the prolonged heating gave rise to the disintegration of the original grains, because Fig. (b) is a finer-grained pattern, in comparison with Fig. (a).

Figs. (c) and (d) show the patterns of specimens annealed similarly at 110°C. for 3 weeks. Especially Fig. (d) is a very fine–grained pattern, and can be well distinguished from Fig. (c).

Now we can say all these results gave us the positive proof of the disintegration of crystal grains observed by the microscopical study.

THEORETICAL CONSIDERATION.

(A) Equilibrium diagram of aluminium zinc series.

Concerning the equilibrium diagram, Rosenhain and Archbutt[1] published in the first place an investigation of this series in a fairly complete form. Afterward Bauer and Vogel[2] corrected it, and recently Hanson and Gayler[3] made an investigation concerning the solubility line of the aluminium–rich solid solution and an intermetallic solution. Their investigation, however, dealt entirely with the solubility and the transformation of the β phase. More recently, W. Sander and K. L. Meissner[4] published a short report on the solubility of the aluminium–rich solution and gave a diagram, as shown in Fig. 20.

Comparing the results of our experiments with these diagrams, it seems to us that all of these diagrams are somewhat incomplete. We want
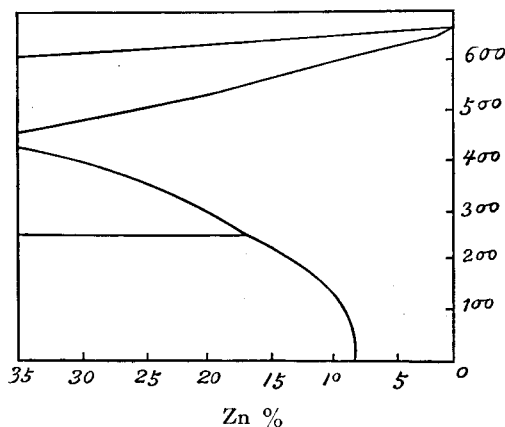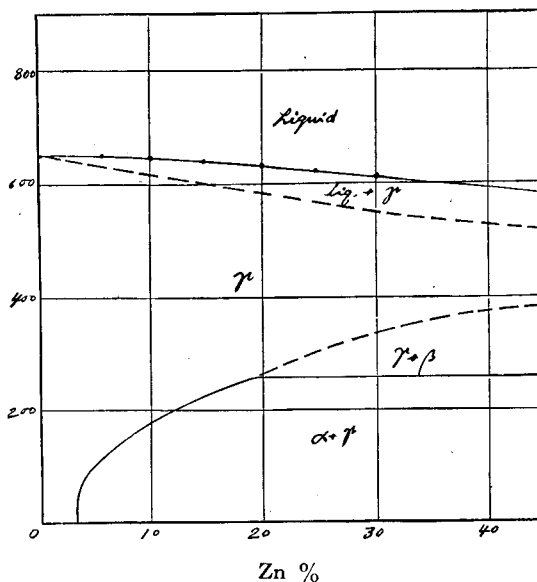
Fig. 20.

Fig. 2I.

Zn %

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[1] J. Inst. Metals, 1911, p. 236.
[2] Mitt. d. Kgl. Mat. prüf. Amts, 1915, s. 146.
[3] J. Inst. Metals, 1922, p. 267.
[4] Z. Metallkunde, 1922, s. 385.

to explain the reason why they are not complete.

Hanson and Gayler did not recognize the age–hardening on the alloys with less than 20% zinc. In our experiment, however, the alloys containing more than 5% zinc showed hardening after quenching.

In this range, Hanson and Gayler did not find the structure consisting of 2 phases, while Sander observed the decomposition of the γ phase at 100°C. on the alloy with 9% zinc. In our X–ray analysis an alloy 5% zinc showed the disintegration of the solid solution at 110°C. in consequence of prolonged heating, and our microscopical study also confirmed this result.

Accordingly it can be concluded that the solubility of the γ phase does not exceed 5% zinc at 110°C., and the age-hardening has much to do with the limit of solubility of the γ phase.

Moreover, it is evident from the measurement of hardness, thermal expansion and electrical resistivity, that there is a demarcation at 20% zinc. Namely, the eutectoid transformation of the β phase was found in those alloys only with more than 20% zinc, on the other hand, the phenomena concerning the alloys with less than 20% zinc were due to the change of solubility of the γ phase.

In considering these points we obtained an equilibrium diagram of the Al–Zn series on aluminium side. It is shown in Fig. 21.

(B) Thermal Expansion and Electrical Resistivity.

In Fig. 11 we see a retardation of expansion measured on the quenched specimens of more than 20% zinc at about 130°C.

Probably this retardation must be due to the separation of the β and the decomposition of the β into α and γ, in consequence of attaining the so–called tempering temperature, because the microscopical study showed that the quenched specimens were apparently formed of one solid solution, that is, the γ phase, and in consequence, heating brought on the separation of the β and the transformation of the β into α and γ at the same time. And the separation of these phases stable at lower temperatures caused the retardation of expansion.

Exceeding 250°C. the transformation of $\alpha+\gamma$ into β began to occur

and proceeded to 300°C. This caused the rapid expansion observed in this temperature range. Indeed, this transformation of $\alpha + \gamma \rightarrow \beta$ must occur in reversible manner on heating and cooling at a definite temperature 256°C. But the rate of reaction must be fairly gradual. With our rate of heating, therefore, it continued to 300°C. It is also confirmed by our thermal analysis and the measurement of electrical resistivity.

On cooling, we observed a slight change at 250°C. This change informs us that the separation of the β from γ and the transformation of the β into $\alpha \times \gamma$ have a tendency to be suppressed on cooling.

The measurement of thermal expansion and electrical resistivity carried out on the alloys with less 20% zinc showed no irreguler change on heating and cooling. It is considered that it takes a longe time to separate α crystals from γ solution, and accordingly the tests gave nothing to be noted.

The tests on annealed pieces containing more than 20% zinc showed similarly the eutectoid transformation of β more distinctly. But on the specimens with less than 20% zinc nothing was specially noted.

In summary it is concluded from the above considerations that the attainment of equilibrium at higher temperatures from the conditions is easy on heating, while the transformation on cooling has a tendency to be suppressed.

Especially the separation of the α crystals from the γ solution was observed to require a long time of heating.

Furthermore, this series of alloys is classified into 2 sorts at 20% zinc.

a) $\gamma \rightarrow \gamma + \beta \rightarrow \alpha + \gamma$

b) $\gamma \rightarrow \gamma + \alpha$
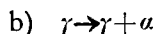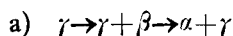
(C) Theoretical study of Age-hardening.

Power of spontaneous crystallisation and hardening.
Quenching is employed as a means of keeping the condition of the quenching temperature at room temperature. But we can not consider that it

is possible to keep the high temperature condition intact at room tempera-
ture by means of quenching. It must be rather treated as a kind of super-
cooling. Tammann[1] investigated the phenomena of the surfusion of liquid,

Fig. 22.
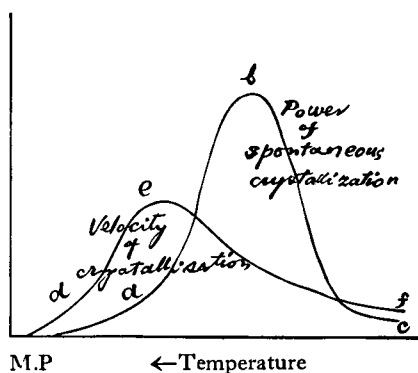
and obtained the relation between
surfusion and the power of spon-
taneous crystallisation or velocity of
crystallisation as shown in Fig. 22,
where the power of crystallisation
means the numbers of centers of
crystallisation to be produced per
unit time in unit volume. We con-
sider this relation holds in the case
of a super-cooled solid.

It is well known that the alloys, which show age-hardening exist at
higher temperatures in solid solution and at lower temperatures they are
over the limit of solubility with regard to the second phase or phases.
Accordingly, the solubility of that solid solution must vary in great degree
with the temperature.

Now we consider the phenomena of quenching in Fig. 23, referring
to those points. In the figure CB shows a solubility line of a solid solution a.
When an alloy x is cooled rapidly to the temperature w by quenching
at z, the solid solution can exist in a super-cooled condition super-saturated
with β, according to the temperature w. If the temperature w is in the
range of spontaneous crystallisation the separation of the β phase has to
occur, even if its velocity is small. In the range of spontaneous crystallisa-
tion, the power of crystallisation should vary with the temperature and its
maximum region would exist at a certain range of temperature. Besides,
this range must vary with the composition of x.

Furthermore, we have to take into consideration the quantity of β
to be separated, that is, the degree of super-saturation. The more β be
separated, the more would the centres of crystallisation be produced.

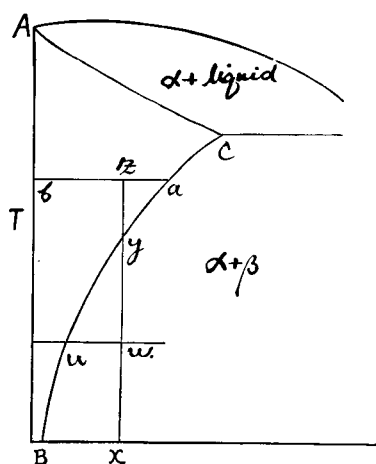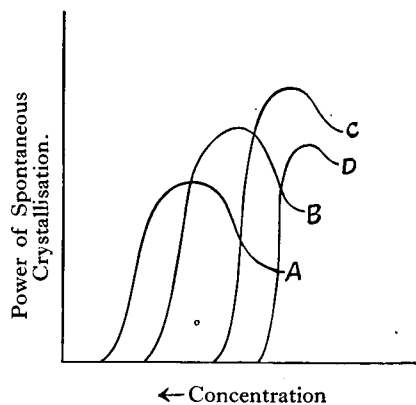[1] Tammann : Aggregatzustände, s. 223.

Fig. 23.

Fig. 24

←Concentration

Granted that the quenching temperature is constant, the power of spontaneous crystallisation depends mostly on the degree of super-cooling z w and the degree of super-saturation u w, and the velocity of crystallisation is in most part the function of the temperature.

With this conception, the relation between the power of spontaneous crystallisation and the concentration is plotted in Fig. 22. At a certain temperature this relation is shown by a curve A, and the curve varies A, B, C, ..., as the temperature rises. Above a certain temperature the power of spontaneous crystallisation may decrease, but on the other hand the velocity will be more powerful. Curve D shows such a case.

As described already, age-hardening is due to the cause that an alloy in the super-cooled state desires to attain equilibrium at lower temperature. Therefore, this degree of hardening should agree with that of the spontaneous crystallisation of the super-cooled phase. Nevertheless, age-hardening is a phenomenon, when the spontaneous crystallisation is not powerful and occurs gradually.

On this concideration, the results of hardness measurement in our experiment will be easily explained. Of course, it is somewhat complicated, because these alloys are classified into 2 parts at 20% zinc.

In Fig. 8 we see the curves A and B which show the degree of hardening ; in one case, specimens were quenched in ice water, and in the

other in boiling water. Either curves are divided into 2 branches at 20% zinc, and each branch has a maximum.

For the alloys less than 20% zinc curve B shows that the hardening commences at a higher percentage of zinc, compared with A. It proves that the solubility of γ solid solution is greater at higher temperatures as seen in the equilibrium diagram.

In the case B it can be also considered that the velocity of crystallisation was fairly high. Consequently, the relation between A and B correspond to C and D in Fig. 22.

In the alloys containing more than 20% zinc, however, transformation occurs at 2 steps, namely, the separation of β from γ and then the decomposition of β into α and γ. Comparatively these reactions must take place so easily and they want to attain equilibrium so rapidly, that the hardening may be small.

Furthermore, the relation between A and B is seen to be reversed, corresponding to A and B in Fig. 22.

In Fig. 8 we see also the curves C and D, which show the effect of tempering. It is noted here that the tempering accelerated the rate of spontaneous crystallisation and the effect is much influenced by the duration of heating. In this case each curve has only a maximum, but it was due to heating in a short time.

Probably in a prolonged heating 2 branches would be obtained, as we see in Fig. 9.

In summary, we conclude that the phenomena of age-hardening are due to the spontaneous crystallisation of the super-cooled solid solution, and the degree of hardening depends upon the degree of super-cooling and super-saturation.

MECHANISM OF HARDENING.

Age-hardening was considered to be due to the spontaneous crystallisation, which takes place gradually at room temperature. However, this assumption did not explain the mechanism of hardening. Many theories about

this question have been put forward by many authors. Above all Jeffries and Archer's slip interence theory[1], Merica's modification of Jeffrie's theory[2] and Honda's β theory are important[3]. Besides these theories investigations upon the phenomena of ageing have been published, most of all concerning duralumin[4]. With regard to duralumin, the cause of ageing is said to be due to the solubility of $CuAl_2$ or Mg_2Si in aluminium, or the combined action of these compounds.

From our experiment it is evident that ageing does not always concern a compound. The only question is the solubility of a solid solution.

Then arises the question how the separation of a second phase from a super-cooled solution gives rise to age-hardening.

According to Honda's theory aluminium solid solution transforms into a hard state called β.

But it is well known that aluminium has no allotropic transformation. Moreover, in our experiment ageing was observed when the addition of zinc exceeded a certain amount, and the degree of hardening has a maximum at a certain percentage of zinc. The maximum also varied with the temperature of quenching bath. To our regret Honda's theory did not give us any explanation of these facts.

With regard to the mechanism of hardening, we would wish to divide it into 2 kinds:

(1) Separation of a second phase.

(2) Disintegration of grains, due to the separation of a second phase.

It is evident that the disintegration of grains gives rise to hardening, because fine-grained materials are harder than coarse grained.

For the reason why the separation of a second phase in finely dispersed condition causes hardening, we desire to adopt that the separated crystals are in colloidal order. But we do not know whether these dispersed particles

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1 Chem. Met. Eng. 1921, vol. 25, p. 1001.
2 Op. Cit. 1922, vol. 26, p. 881.
3 Sci. Rep. Tohoku Imp. Univ., vol. 11, No. 4.
4 Bull. Am. Inst. Min. Eng. 1919. No. 151, p. 1031. The eleventh report of the alloy research committe. Metal Industry (London), vol. 22, No. 12, p. 281. Zeit. Metllkunde, 1922, Heft 222, s. 4.

act as key particles or the increase of cohesion. We recognise only that the particles at critical dispersion give rise to the maximum hardening.

SUMMARY.

(1) The phenomena of age-hardening were observed on the Al-rich Al-Zn alloys, when the zinc content exceeded 5%, and these alloys were divided into 2 kinds at 20% zinc, according to their properties.

(2) Al-Zn series showed an eutectoid transformation at 256°C, and this transformation was observed on the alloys containing more than 20% zinc. The solubility of zinc in aluminium was found to be less than 5% at 110°C. Owing to these facts, the equilibrium diagram on the aluminium side was obtained.

(3) It was found that age-hardening did not always concern a compound. The question is the solubility of a solid solution.

(4) Age-hardening was considered to be due to the spontaneous crystallisation of a super-cooled solid solution. With this conception, the phenomena of hardening were explained.

(5) As the mechanism of hardening it was found that the separation of a second phase in finely divided perticles gave rise to hardening on the one side, and on the other the disintegration of the grains.

ACKNOWLEDGMENT.

(Dec. 10th, 1923.)