論 説

本邦に於ける金屬材料研究の最近の發達 (其 2)

（萬國工業會議に於て發表）

本 多 光 太 郎

RECENT PROGRESS IN JAPAN IN THE FIELD OF THE SCIENCE OF METALS. (II)

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§6. Equilibrium Diagrams of Non-Ferrous Alloys.

(a) *Antimony-Bismuth system.* Previous investigations showed that this system is isomorphous, but strangely enough, the liquidus curve on the bismuth side is given as a horizontal line. B. Otani[63] studied therefore the equilibrium diagram of this system by means of the electric resistance method with an extremely slow heating and cooling of the specimen and obtained the liquidus and solidus lines which form a smooth loop as shown in Fig. 21.

(b) *Aluminium-Zinc system.* The equilibrium diagram of this system has for long been a subject of many investigators. Recently T. Tanabe[64] and T. Ishihara[65] made also the investigation of this system and obtained a similar result ; Fig. 22 shows Ishihara's result with the omission of a line at 340°, which, according to him, is the line of the same nature as the A_2 line in iron; but the existence of this line is not certain ; because other investigators have failed to observe it.

Fig. 21.
Antimony-Bismuth

(c) *Aluminium-Calcium system.* Scarecely any determination of the equilibrium diagram of this system has been undertaken. K. Matsuyama[66] first thoroughly studied this system, his result being shown in Fig. 23.
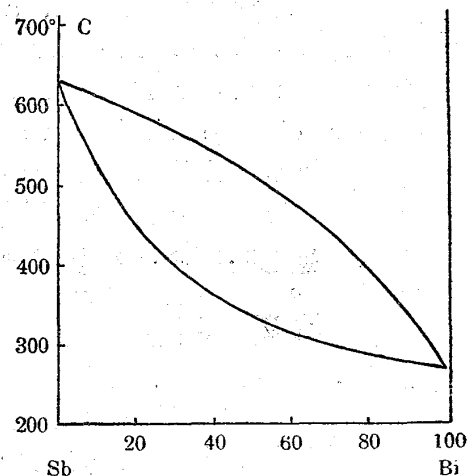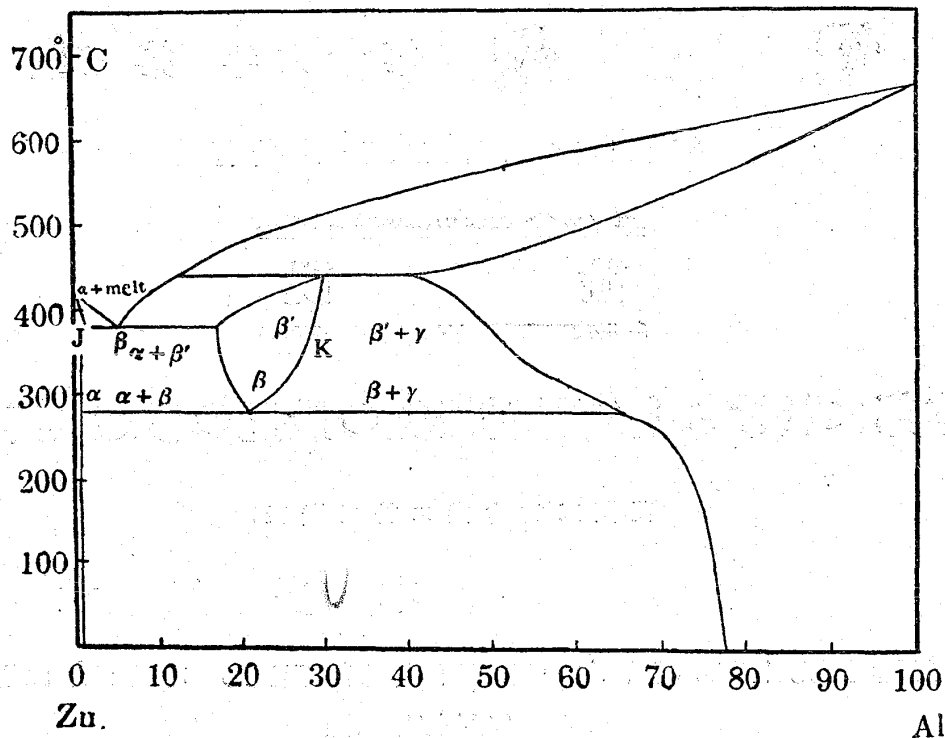
Fig. 22.

Aluminium - Zinc.

(d) *Copper-Zinc system.* Since brass belongs to this system, the determination of the equilibrium diagram has been a favorite subject of many investigators; the results of all the recent investigators agree with each other, except in one point, that is, a transformation at 460°. Some investigators maintain this transformation to be a non-phasic change similar to the A_2 change in iron, while others assume it to be an allotropic change taking place in the β phase. H. Imai[67] and T. Matsuda[68] were the first to take the first view, which has now been confirmed by the X-ray analysis. The transformation extends over a wide range of temperature. At every point of this range, it is only a function of temperature, and not a function of time, unlike any changes of phase, and hence it seems to the present writer that there is no room for doubt as to the correctness of the first view. The second view has been supported by M.L.V. Gayler[69], T.L. Haughton, W.T. Griffiths[70], Iitsuka[71], O. Bauer and M. Hansen[72], but it is to be noted that they ignore the important result of X-ray analysis and attach too much a weight on the thermal change, which may possibly occur whenever the rate of increase of specific heat changes even in the
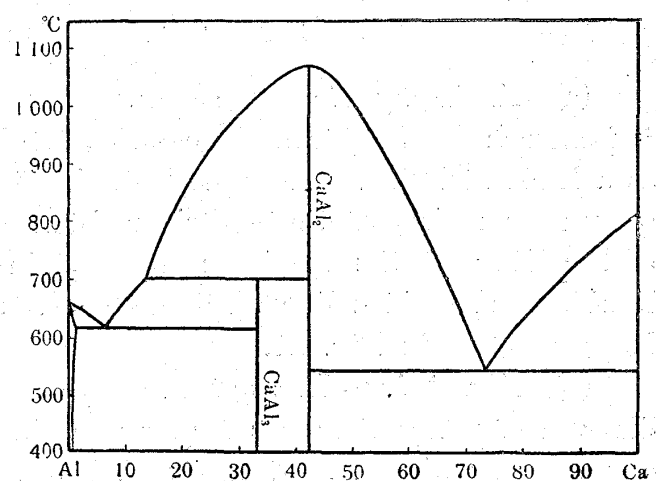

Fig. 23.

Aluminium - Calcium.

absence of any change of phase.　Fig. 24 is the diagram based on Imai's determination.
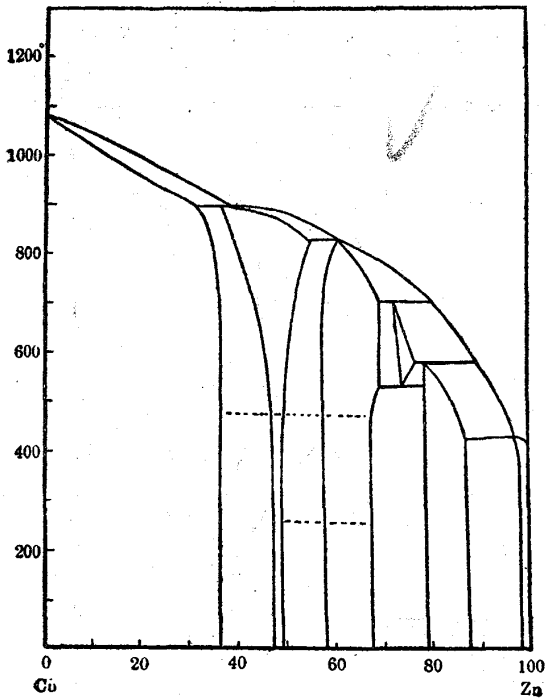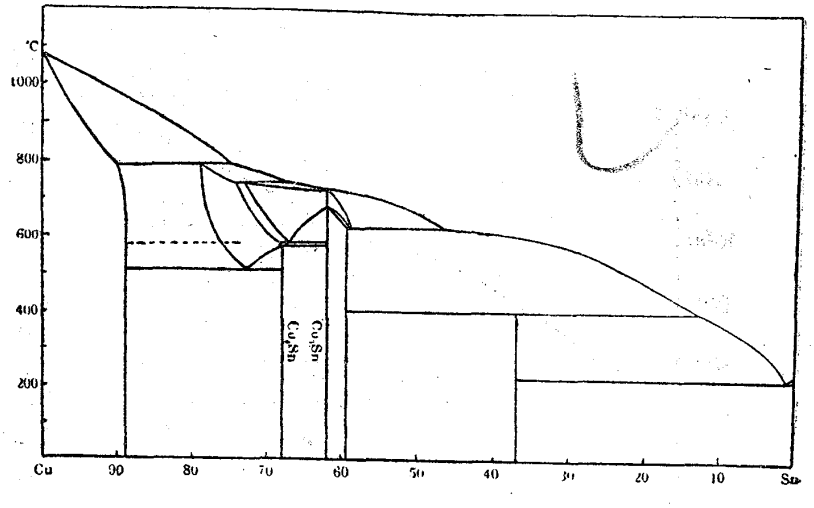

Fig. 24.
Copper-Zinc.

Fig. 25.
Copper-Tin.

The equilibrium diagram of the ternary alloys of copper-zinc-cobalt system in the copper-zinc rich side was investigated by D. Iitsuka[73].

(e) *Copper-Tin system*.　This system has also been investigated by many scientists such as Heycock and Nevill[74], E. S. Shepherd and E. Bluch[75], Bauer and Vollenbruck[76].　T. Isihara[77] and T. Matsuda[78] also studied the same diagram by using several methods, such as electric resistance, thermal expansion, therma-analysis and microscopic observation.　The revised diagram is based on the result by T. Isihara is given in Fig. 21.　According to Y. Matsuyama's result[79], the intermetallic compound Cu_2Sn exists even in the molten state, showing that in the vicinity of this concentration, the diagram shown by Fig. 25 is very probable.
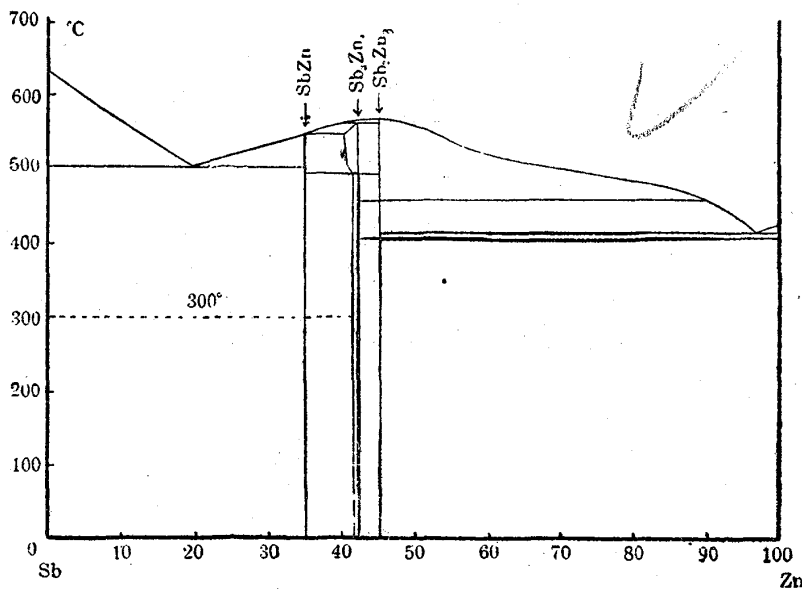
Fig. 26.
Antimony-Zinc.

(f) *Antimony-Zinc system*.　T. Takei[80] revised the equilibrium diagram of this system obtained by previous investigators.　His diagram, slightly modified according

to the view of the present writer, is given in Fig. 26.

(g) *Aluminium-Chromium system*. This system was recently investigated by M. Goto and G. Dogané[81];. the diagram is found quite different from that previously proposed by Hindrich, as shown in Fig. 27.

Fig. 27.
Aluminium-Chromium.

Fig. 28.
Aluminium-Manganese.
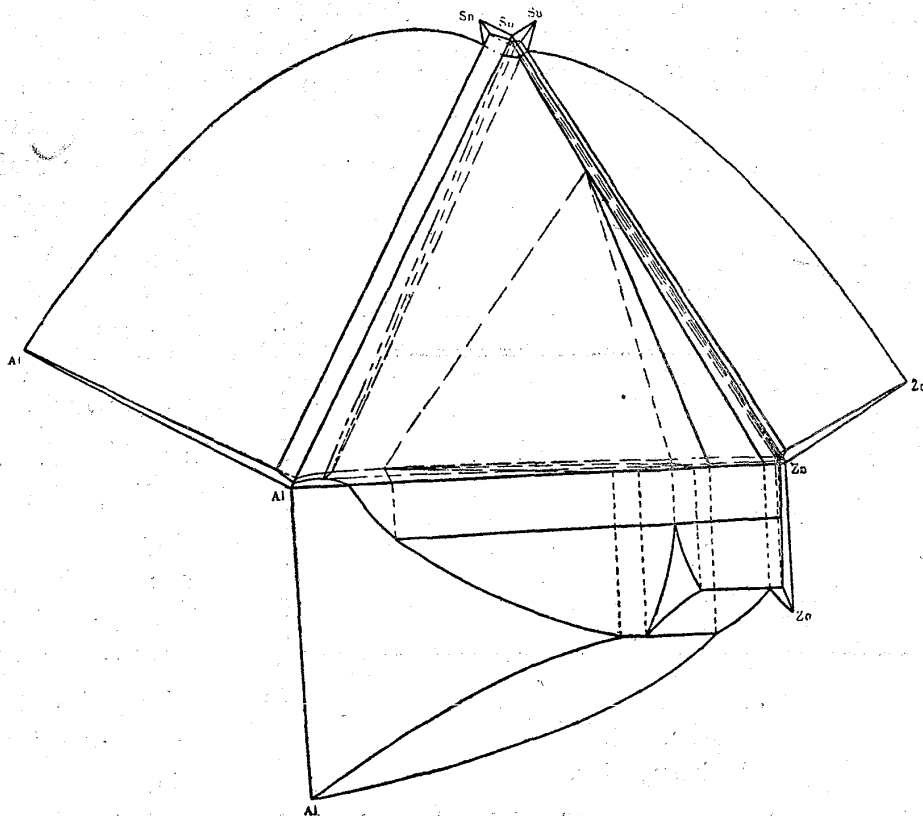
Fig. 29.
Aluminium-Tin-Zinc.

(h) *Aluminium-Manganese system.* The equilibrium diagram of this system was investigated by M. Goto and T. Mishima[82] and T. Ishiwara[83], the result of the last investigator is shown in Fig. 28.
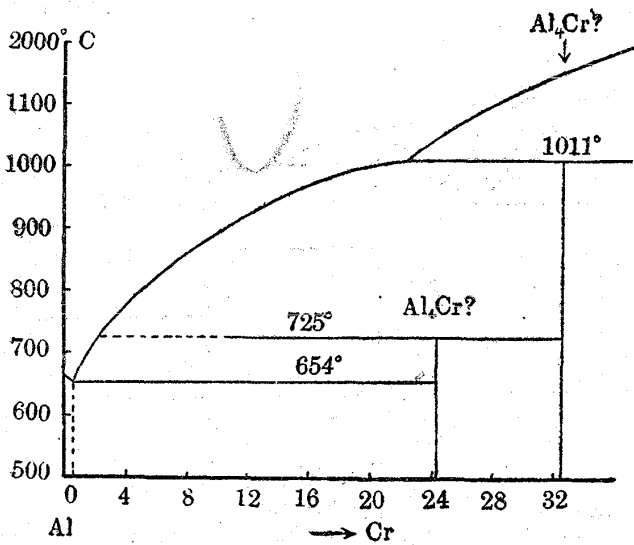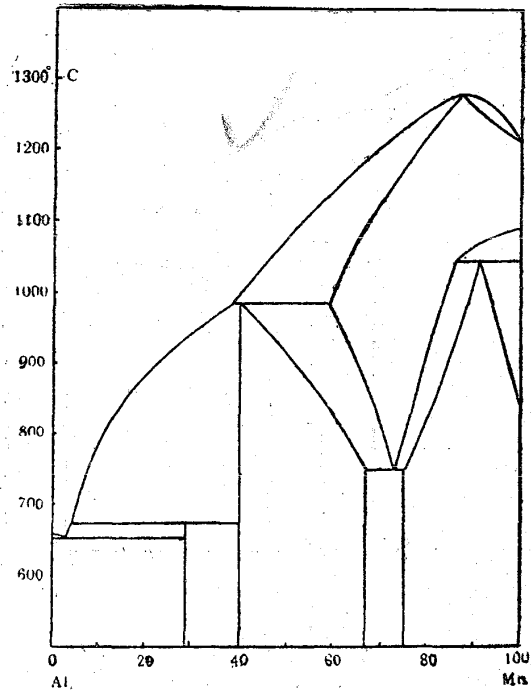
(i) *Aluminium-Tin-Zinc system.* The equilibrium diagram of this ternary system was completed by H. Nishimura and D. Suzuki[84]; the result is graphically given in Fig. 29.

(j) *Aluminium-Copper-Zinc system.* H. Nishimura[85] also investigated the equilibrium diagram of this system at the aluminium-rich side and obtained the result shown in Fig. 30.
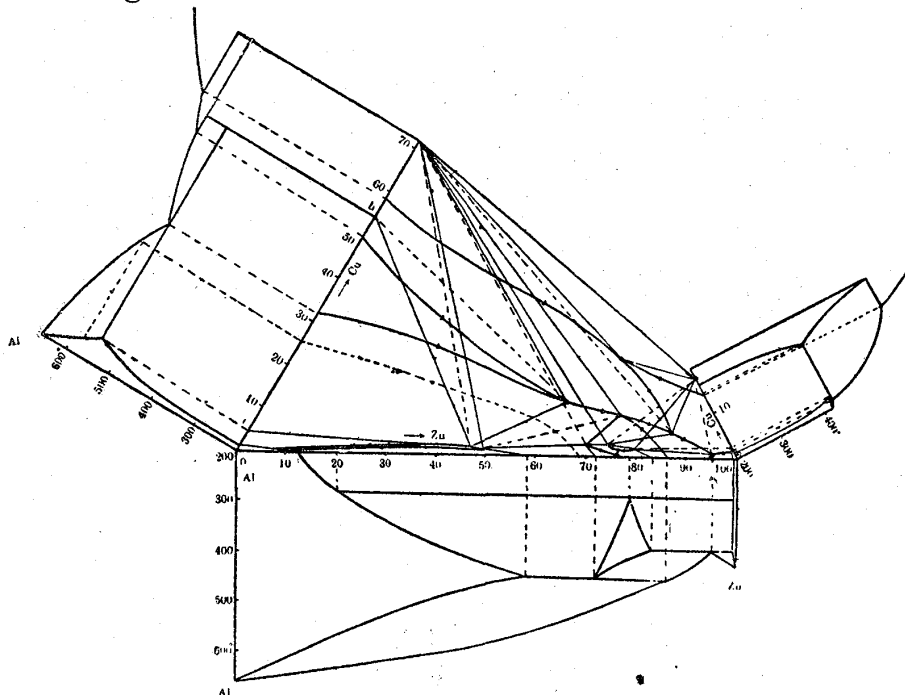
Fig. 30.
Aluminium-Copper-Zinc.
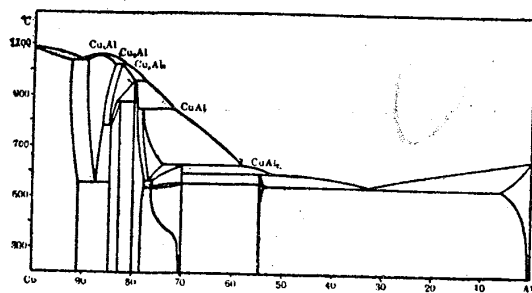
Fig. 31.
Aluminium-Copper.
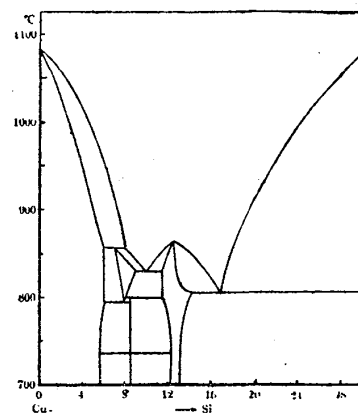
Fig. 32.
Copper-Silicon.

(k) *Aluminium-Copper, Copper-Silicon and Aluminium-Copper-Silicon systems.* The equilibrium diagram of the binary system aluminium-copper was determined by M. Tasaki[86] and that of the system copper-silicon by K. Matsuyama[87] their results
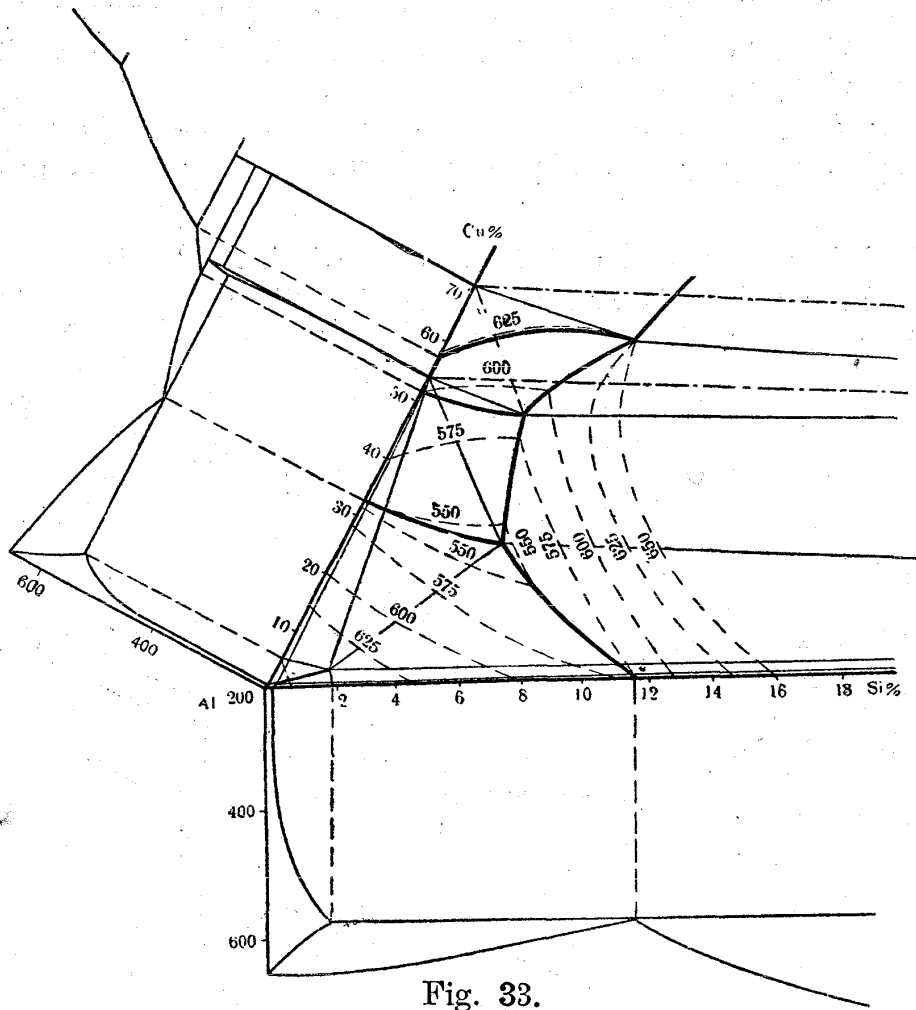
Fig. 33.

Aluminium-Copper-Silicon.
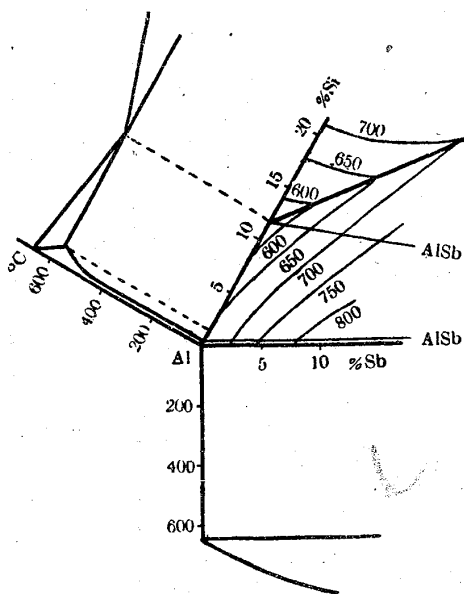
Fig. 34.
Aluminium-Antimony-Silicon.
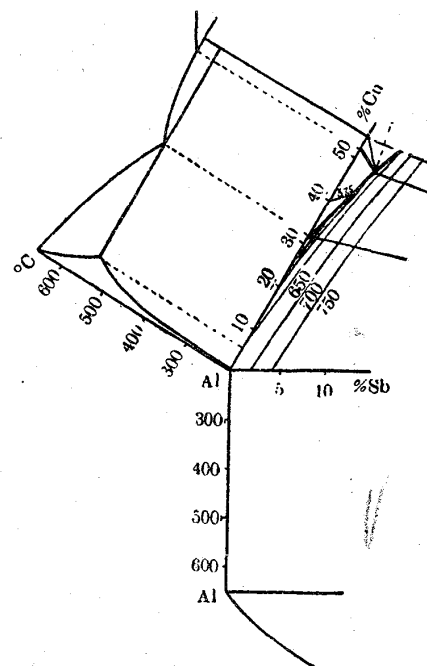
Fig. 35.
Aluminium-Antimony-Copper.

are shown in Figs. 31 and 32. The equilibrium diagram of the ternary system at the aluminium-rich side was investigated by M. Goto and T. Mishima, and also by T. Hisatsune[87]; the result of the last investigator is shown in Fig. 33.

(1) *Aluminium-Antimony-Silicon and Aluminium-Antimony-Copper systems.* The equilibrium diagrams for these ternary alloys on aluminium-rich side were obtained by T. Matsukawa[88] as shown in Figs. 34 and 35.
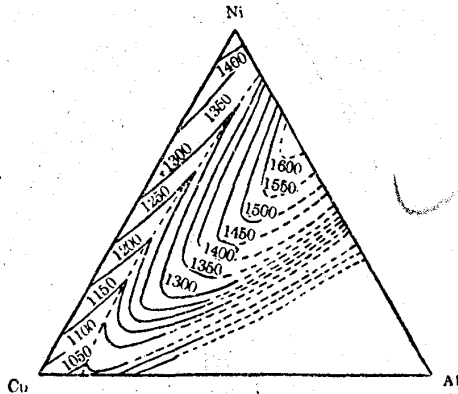
Fig. 36.

Aluminium-Copper-Nickel. Isothermal Liquidus Curves.
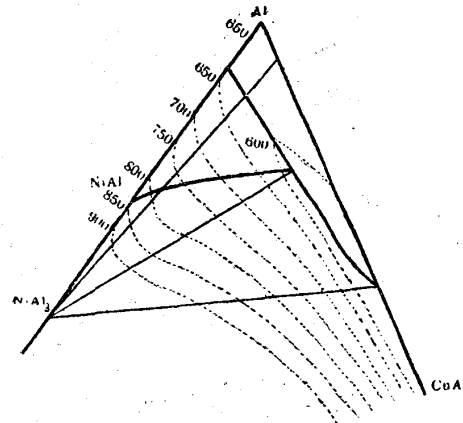
Fig. 37.

Aluminium-Copper-Nickel.

(m) *Aluminium-Copper-Nickel system.* The copper-nickel side of the equilibrium diagram of this system was investigated by I. Iitaka[89] with the result shown in Fig. 36; the aluminium side of the same diagram was determined by M. Goto and T. Mishima[90] and afterwards by H. Nishimura[91]; their results are given in Figs. 37 and 38.
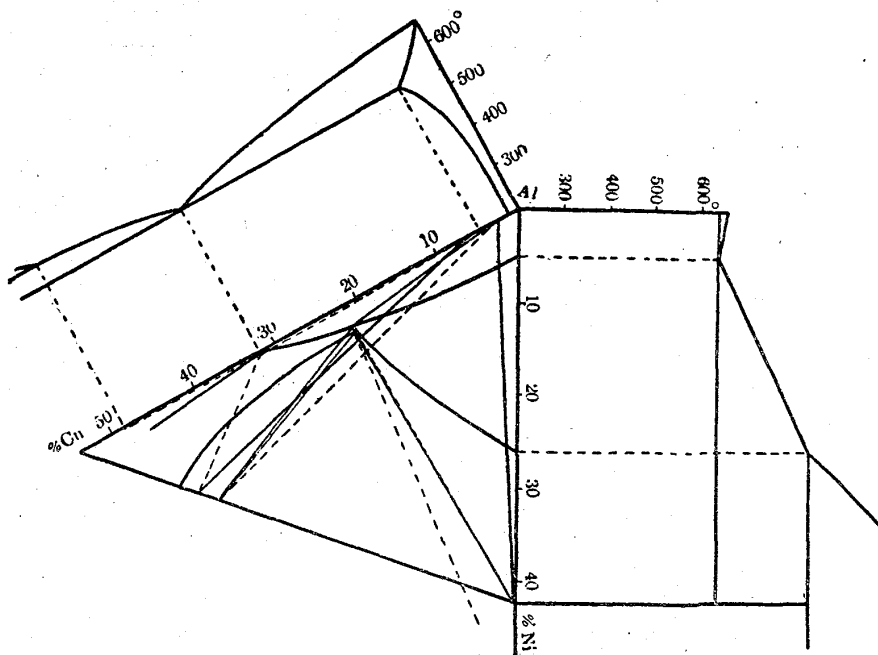
Fig. 38.

Aluminium-Copper-Nickel.

(n)　*Aluminium-Copper-Silver, Aluminium-Copper-Iron, and Aluminium-Silicon-Silver systems*.　The aluminium rich sides of these ternary systems were investigated by M. Goto and T. Mishima[90] with the results shown in Figs. 39, 40, 41.
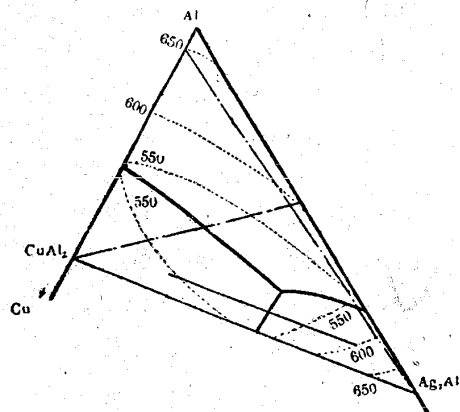
Fig. 39.
Aluminium-Copper-Silver.
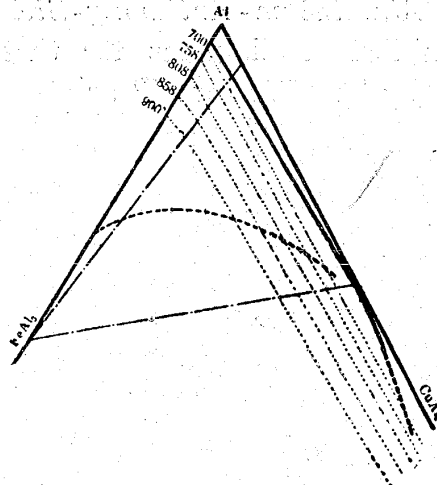
Fig. 40.
Aluminium-Copper-Iron.
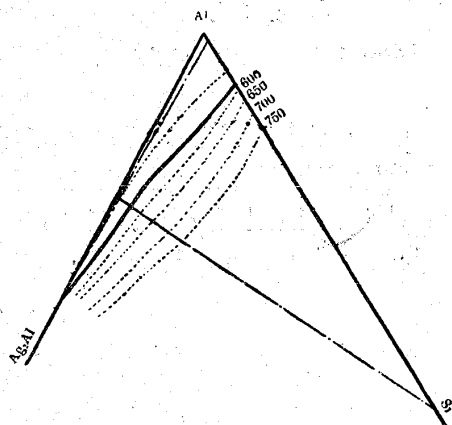
Fig. 41.
Aluminium-Silicon-Silver.
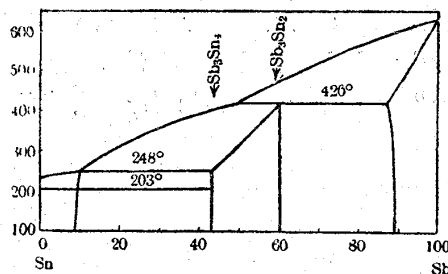
Fig. 42.
Tin-Antimony.
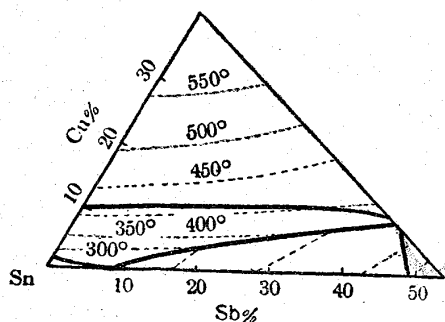
Fig. 43.
Tin-Antimony-Copper.
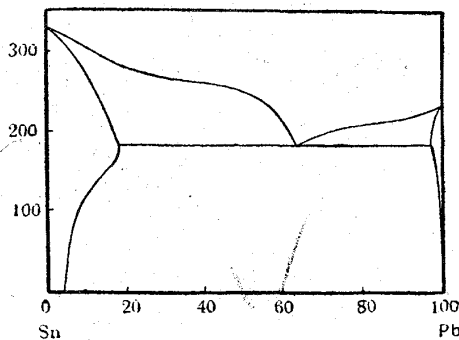
Fig. 44.
Tin-Lead.

(o)　*Tin-Antimony and Tin-Antimony-Copper systems*.　The equilibrium diagrams of these systems were investigated by S. Yoshioka[92] wtih particular reference to the white metal; his diagrams are given in Figs. 42 and 43.　He also measured the

hardness, the tensile strength and the resistances to pressure and impact.

(p) *Tin-Lead system.* H. Abé[93] made a new determination of the equilibrium diagram of this system and explained the abnormal thermal change occurring at 150° or just below the eutectic horizontal 182° as due to the abrupt diminution of the solubility of tin in lead accompanying the fall of temperature, Fig. 44.
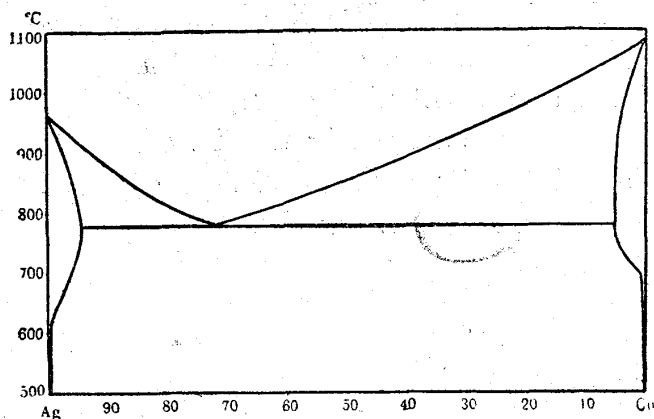
(q) *Silver-Copper system.* The equilibrium diagram of this system was investigated by T. Hirose[94] with the result shown in Fig. 45.

(r) *Antimony-Cadmium system.* T. Murakami and T. Shinagawa[95] recently determined the equilibrium diagram of this system, which is shown in Fig. 46.

(s) *Copper - Manganese system.* Quite recently T. Ishiwara[96] determined the equilibrium diagram of this system, which is considerably different from those hitherto published. Fig. 47 shows his result.

Fig. 45.
Silver-Copper.
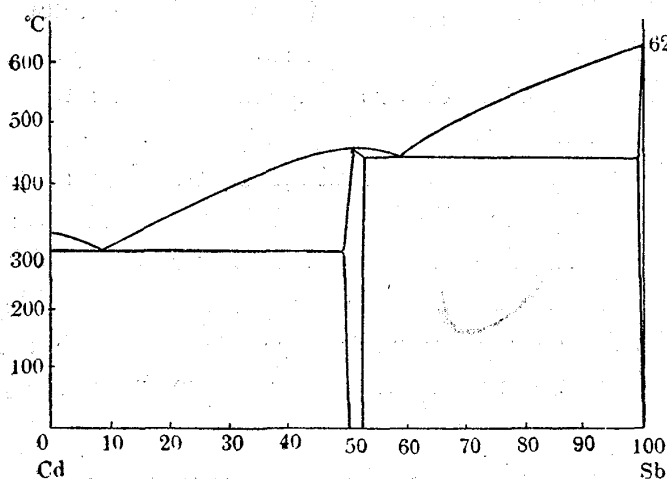
Fig. 46.
Cadmium-Antimony.
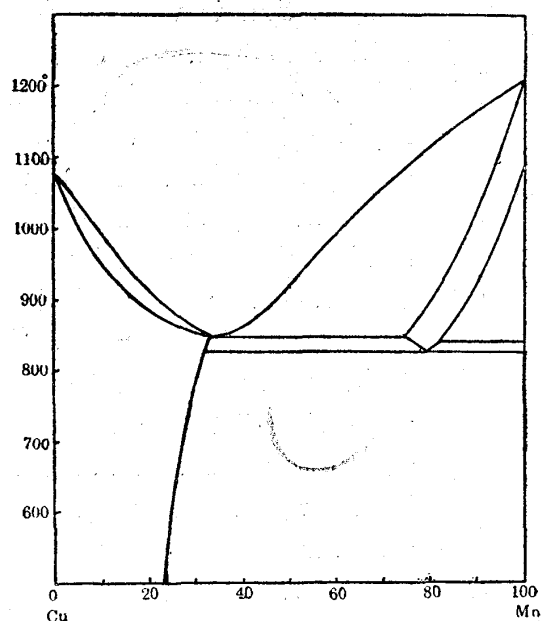
Fig. 47.
Copper-Manganese.

§ 7. Mechanical Properties of Metals and Alloys.

(a) *Work of rupture of a test-piece.* Three years ago, the present writer[97] discussed theoretically the work of rupture of a test-piece or the energy required for breaking it in the case of a tensile or bending test, and analysed it into three parts :—

(1) The energy required for a simple breaking of the specimen without any

deformation, W_1,

(2) The energy of deformation required up to the point of breaking, W_2;

(3) The kinetic energy of the specimen possessed at the instant of breaking, W_3.

The first part of energy, W_1. is the surface energy acquired by the new surfaces of separation and is shown theoretically to be very small as compared with the total energy of rupture; it is a potential energy P_1. The second part of energy, W_2, is the principal one and consists in the work of deformation, of which a small fraction remains, after the break, within the specimen as the potential energy of interstrain, P_2, and the remaining part is given out as the heat energy H_2; that is, $W_2 = P_2 + H_2$. The third part, W_3, is the kinetic energy and is finally converted into heat H_3; it is also a very small quantity. Hence for the total energy, W, we have

$$W = W_1 + W_2 + W_3 = P_1 + P_2 + (H_2 + H_3),$$

or

$$W - (H_2 + H_3) = P_1 + P_2 > 0.$$

Hence the following conclusions may be drawn:—

(1) The work required for breaking a specimen depends chiefly on the degree of deformation, which the specimen undergoes up to the point of its breaking. For the same material, the work required for a simple breaking without any deformation is very small and the work of rupture increases with the degree of deformation.

(2) In the case of an impact notched-bar test, the deformation of the specimen diminishes as the depth of the notch increases, or as the tip of the notch is sharpened, and therefore the work of rupture varies in the same way.

(3) The quantity of heat generated at the time of breaking must be somewhat smaller than the total work required.

(4) The work of rupture divided by the area of the section of the bar at the notched portion is called "notch toughness." This quantity was introduced from the conception that the work required for breaking is proportional to the sectional area; but as the work of the simple breaking is much less than the work of deformation, this conception cannot be a sound one and hence the notch toughness is by no means an appropriate measure of toughness.

(b) *Indentation hardness of metals.* K. Takahashi and the present writer[98] have shown that Brinell's method of measuring the hardness of metals from the diameter of impression after the load is taken off, is not proper, but that the diameter of impression should be measured with the load on. In soft metals, the hardness as measured by these two methods do not differ much from each other, but in hard metals, such as quenched steels, the hardness as given by the latter way of measurement is about half of that given by the former. They have also shown that a more reasonable method is to take as the measure of hardness the work required for producing an indentation of unit volume of impression, the measurement being of course made with the load on.

K. Takahashi[99] also studied Meyer's relation between the pressure P and the

diameter of indentation d in the Brinell test, that is, the relation given by

$$P = ad^n,$$

where n and a are two constants, and found that this relation is not satisfied for very low pressures of 5~100 Kg., in the range of which a and n decrease with pressure, n tending to 2 as the load is diminished.

S. Kokado[100] worked out theoretically the problem of the ball indentation and obtained an expression of load in terms of the angle of indentation and two constants which characterise the stress-strain relation. From this expression he deduced Meyer's law: $P=ad.^n$ He also obtained an expression for the Brinell hardness and showed that in order to have the same hardness number for a given metal, a load proportional to the square of the radius of the ball is to be applied. This law has already been confirmed by many investigators.

Similarly S. Kokado obtained an expression for the hardness number, which is defined as the work required to produce a unit volume of indentation. He also deduced two laws for the work done, W, which are found by C. Edwards; this is,

$$W = ad^n, \quad \text{and} \quad W = a'V^{n'},$$

V being the volume of indentation. He also obtained an expression for the Shore hardness.

K. Ito[103] investigated the relation between the hardness and the temperature for 20 metals and alloys in the range of temperatures from—50° to 150°, and found two simple laws, which connect on one hand the hardness H and the temperature t and on the other the melting point T_m (absolute scale) and the temperature coefficient α of hardness; that is,

$$H_2 = H_1 e - \alpha(t_2 - t_1) \qquad \text{for metals and alloys,}$$
and
$$T(\alpha + 0.00145) = 2.50 \qquad \text{for metals,}$$

where 1 and 2 refer to the two temperatures of observation.

(c) *Impact test at low and high temperatures.* R. Yamada[104] made the determination of the absorbed energy for carbon and special steels in the case of notched bar and tension impact tests at low temperatures extending down to —185°. The brittleness of steels increases rapidly with the fall of temperature. Sorbitic steels are much tougher than pearlitic steels. Nickel steel and nickel-chromium steel are tougher than plain carbon steels, and the increase in brittleness with the fall of temperature is comparatively small. The absorbed energy is nearly proportional to the bending angle, at which the break takes place; hence the straight line representing the relation between these two quantities almost passes through the origin (Fig. 48). This shows that the absorbed energy is chiefly spent in the deformation of the test-piece, the energy of the simple breaking without any deformation being very small.

Fig. 48.

Absorbed energy-bending angle curve.

K. Sasagawa[103] also made the determination of the absorbed energy at high

temperatures in the case of impact bending and tension tests; the apparatus used by him was specially constructed so as to give the impact value accurately at any desired temperature. Steels of different carbon concentrations and several special steels were tested with following results:—The absorbed energytemperature curves for the bending test has generally two maxima and a minimum, the latter of which corresponds to the blue shortness, appearing at 500°~600°. The first maximum is not so conspicuous as the other and this totally fails to be observed in the case of a very low carbon steel and also in some special steels. In the same curves for the tensile test, the first maximum is absent, but the course of the curve above 400° is similar to that of the bending test.

The investigation of the relation between stress and strain in impact test is a very difficult undertaking, so that up to the present, only few determinations have been published. R. Yamada[104] using the same method as that of Körber and Storp[105] with some improvements investigated the stress-strain relation in the notched bar impact test, and obtained the following results: — (1) In the testpiece made of the same material, but of different breadths, the energy absorbed is generally not proportional to the breadth, but in the case where the thickness is small as compared with the breadth, the proportionality between them nearly holds good. (2) In the case where the shape and the depth of the notch remain unchanged, but the dimensions of the cross-section of the test-piece vary in the same ratio, both the energy absorbed and the maximum stress are proportional to the product of the breadth and the square of the effective thickness of the test-piece. (3) In low temperature tests, it was found that as the temperature falls, the maximum stress and the energy absorbed decrease in a similar way. (4) For the same material, the maximum stress in the dynamic test is considerably greater and the amount of bending less, than those in the static test, and the product of these two, or the energy absorbed is greater in the former test than in the latter.

(d) "*Blue shortness*" *in steel and other metals*. T. Inokuty[106] determined the mechanical properties of Armco iron and of steels containing 0.1 to 1.5 percent of carbon, at temperatures ranging from 20° to 1100°, with a special attention to the uniformity of temperature along the test-specimens. This important point has not been given due attention it deserves by many previous experimenters. For all the specimens, a conspicuous maximum in the tensile strength-temperature curve is observed; this phenomenon is known as "blue shortness," the cause of which is attributed to the hardening of steel caused by the deformation during the tensile test. To confirm this view, he[107] also made a similar experiment with aluminium, 4:6 brass, copper, lead, tin and zinc and obtained the expected result.

(e) *Temper brittleness in steel*. In the case of a certain special steel, such as nickel-chromium, or manganese steel, it is observed that, of two specimens, one that is quenched in oil from 850°, tempered at 400°~650° for a certain interval of time, and then again quenched in water, and the other that has undergone the same treatment except that it is finally slowly cooled instead of being quenched in water, the former, i.e. the specimen that is finally quenched shows a much greater resistance in the notched bar impact test than the latter, i.e. the specimen that is finally slow-

cooled. This curious phenomenon is known as "temperbrittleness." R. Yamada and the present writer[108] investigated the cause of the phenomenon and arrived at the conclusion that temper-brittleness is due to the presence of carbides separated at the grain boundaries along the solubility line below tht A_1 point. J. H. Andrew and H. A. Dickie[109] also arrived at the same conclusion.

S. Maita[110] studied recently the same phenomenon and concluded that there is also a second important factor affecting the temper-brittleness. He found, namely, that the temper-brittleness is greatly intensified by heating the specimen above the A_3 point in the process of quenching; during this high temperature heating, grain growth take place and during cooling down to the A_1 point, carbides separate at the boundary, thus increasing the brittleness of the specimen and consequently also the temper-brittleness.

(f) *Effect of cold-working on the physical properties of metals and alloys.* T. Matsuda[111] studied the effect of cold-working on the physical properties of aluminium, copper, brass, aluminium-bronz, etc., and found that by such coldwork, as rolling, drawing and twisting, the electric resistance of metals and alloys becomes greater, and that specimens taken parallel to the direction of rolling have lower strength and higher elongation than those taken at right angles to the said direction. He also found that by annealing at a gradually increasing temperature, the electric resistance of cold-worked metals and alloys decreases in two steps, that is, at about 200° and 320°; the first step corresponds to the release of internal strain and the second to recrystallisation. The length of the cold-werked specimens was also found to vary in two steps in the case of a gradual heating; the change is an expansion in the specimens taken parallel to the direction of cold-working, while contraction is found to take place in cold-drawn rods and in specimens taken from plates at right angles to the direction of rolling.

T. Ishigaki[112] measured the hardness and the density in iron and steel, which were cold-worked by stretching and compression. The hardness always increases by cold-working, at first rapidly and afterwards gradually, tending to an asymptotic value. In the case of stretching, the density is decreased by cold-working, its amount increasing with the degree of cold-working; while in the case of compression, the density first decreases; reaches a minimum, increases to a maximum and then again decreases. He also studied the effect of heating at a gradually increasing temperature.

It is generally believed that elastic constant increases by cold-working, although Körber and Dreyer[113], Körber and Rohland[114] have found it to decrease. R. Yamada and the present writer[115] undertook a new series of experiments and found that the elastic constant is decreased by cold-working. They explained this decrease of the elastic constant from the law of atomic force as commonly used,

(g) *Fatigue of metals.* In this series of experiments of fatigue test, Y. Fuji[116] confirmed that steels are enbrittled by the application of a heavy repeated stress, and that on the other hand, the breaking strength and proportional limit are rather improved, and again, that by the repeated stress, the slipping takes place in the crystals themselves as well as at the grain boundary, and also the boundary of slag particles.

He also found that the fatigue of the material is recovered by a high temperature annealing for a suitable interval of time.

T. Matsushita, K. Nagasawa and K. Komatsu[117] made also fatigue tests by using Matsumura's repeated impact test machine for carbon and alloy steels, which were quenched and temperd at different temperatures and obtained the relation between fatigue and tempering temperature and that between fatigue and applied load. They showed also that the elastic limit is maximum at a tempering temperature of 400°, and recommended for machine parts a lower tempering temperature than is usually adopted in practice. It has also been shown, that by repeated impacts, fatigue begins to take place below the ordinary elastic limit, and steadily progresses, until finally failure takes place.

Y. Asakawa[118] investigated magnetically the degree of fatigue of test pieces. Two magnetising coils of the same dimensions were placed horizontally and parallel to each other, and a magnetizing current was passed through those coils in series. Two secondary coils of the same dimensions were placed in each of these magnetising coils and connected in series, but in an opposite sense, a sensitive galvanometer being included in the circuit. When no specimen was placed in each of these coils, the induced current flowing through the secondary just canceled each other. Two test-pieces made of the same material and having the same dimensions were placed in each of the secondary coils; then on magnetization the galvanometer showed no deflection. When, however, one of these specimens is taken out, subjected to a certain number of repeated stresses placed again in the secondary coil and magnetized, a certain amount of deflection of the galvanometer is obtained. These processes were repeated with an increasing number of repeated stress, until the test-piece was finally broken. The deflection-stress number curve gives the progress of fatigue or the degree of fatigue. In this way he determined the fatigue degree for different carbon steels and obtained very interesting results. (Fig. 49). By the same method he also investigated the recovery of the strained specimen caused by annealing.

Fig. 49.

Number of impacts.

The degree of fatigue F was also determined for different steels by means of a Charpy machine and by using the relation proposed by the present writer:

$$F = \frac{W_0 - W}{W_0},$$

where W_0 is the absorbed energy of an unstrained specimen and W that of the same specimen which has undergone a certain number of repeated stress. This method is not only convenient for measuring the fatigue degree, but also the fatigue recovery by annealing.

1, 2, 3, 4, 5 are different specimens taken from the same material.

Electric resistance

1
2
3
4
5

0 2 4 6 8 10 12 14 16 18 20 22 24 26 28

Skin stress Kg/mm².
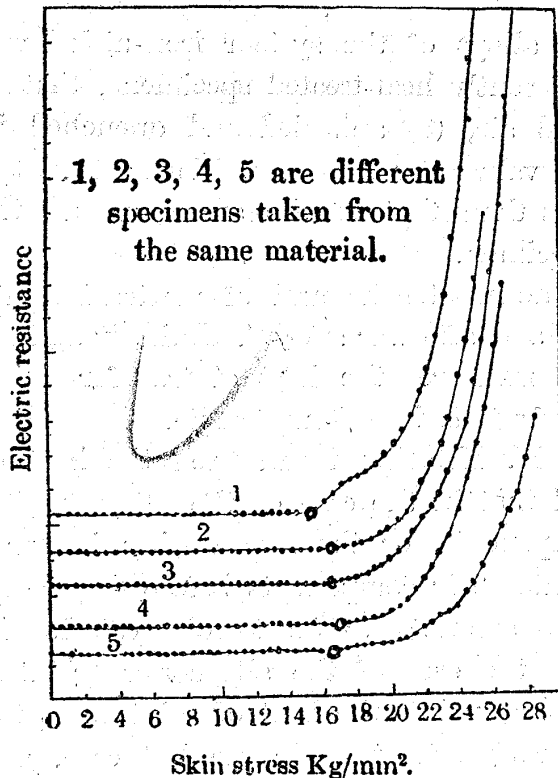
Fig. 50.

A 0.69% Carbon steel.

(h) *Endurance limit.* The usual method of determining the endurance limit requires a very long time and consequently is not very convenient; M. Ikeda[119] recently devised a new rapid method by which the endurance limit can be determined in three hours only. The following is his method: —A repeated stress is given by Ono's rotating beam bending test machine, and the electrical resistance between two points of a test-piece which obtains after a definite number of repetition of stress, is measured by means of an ammeter and a potentiometer, this process being repeated for different magnitudes of stress. Up to a certain magnitude of stress the electric resistance remains constant and then begins to increase (Fig. 50). The stress at which the resistance begins to increase, is found quite distinct, and hence is taken as the endurance limit: this value is always a little less than that obtained by the ordinary method. The relation between the endurance limit and the hardness is found to be expressible by a straight line passing through the origin of coordinates; this shows that a material having zero hardness has no endurance limit, and that the inclination of this line to the abscissa is a characteristic constant of the material.

M. Suzuki[120] used Moore's machine of the reversed flexure rotating spring type and applied the above method for determining the endurance limit. He also confirmed that the endurance limit as obtained by the new method is about 10 percent less than that obtained by the usual method.

§ 8.　Miscellaneous.

(a) *Specific heat and heat of transformation.* The specific heat of steel containing different amounts of carbon and of cast iron at ordinary temperature was measured by the present writer[121] with forged, normalised and annealed specimens. It was found that the specific heat of the annealed specimens increases linearly with the content of carbon, and that internal strain increases the specific heat of these steels

by 2~3 percent.

In a series of papers, S. Umino[122] published his results of measurement of the specific heat of steels containing 0.09~2.84 percent of carbon at temperatures ranging from 23° to 1250°. From these results he deduced the heat of the A_1 transformation. He also determined the heat of transformation and that of fusion of iron, nickel, cobalt and several other metals.[123] Recently he also measured the specific heat of some slags at high temperatures.[124]

The specific heat of a complete series of alloys of the system iron-nickel was determined by M. Kawakami[125] with three differently heat-treated specimens, that is, (1) annealed, (2) annealed and cooled in liquid air, (3) annealed and quenched in water. The specific heat has slightly different values for these conditions; thus the specific heat of the martensitic specimen is less than that of the annealed and the latter is greater than that of the austenitic specimen.

The heat of transformation of austenite into martensite and of martensite into pearlite were first measured by N. Yamada,[126] and afterwards dy S. Umino[122] and M. Kawakami.[127] Quite recently M. Kawakami[128] measured the heat of transformation from austenite into α-martensite and also that from α into β-martensite.

(b) *Heat of mixture in molten metals.* M. Kawakami measured the heat of dissolution of many binary alloys, and showed that in the case of the alloys which form no intermetallic compounds of their components, or those possessing intermetallic compounds, which, however, break up into their components before they reach the liquidus line, the atomic heat of dissolution amounts to 50 to 600 calories in most cases and rarely to 800 calories, but in the case of the alloys having intermetallic compounds existing up to their melting point, the heat of mixture at the concentration of the compounds is 10 to 30 times greater than in the last case, and sometimes even exceeds 6000 calories. This result is very important in confirming the fact that an intermetallic compounds existing in the solid phase up to its melting point exists also as such in the molten state.

(c) *Law of depression of freezing point.* It is well known that in the case of the ordinary solution, the law of depression of freezing point holds good exactly and is used for the determination of the molecular weight of a solute. In the case of alloys, it is generally believed that the above law does not generally hold, although Heycock and Neville[130] have already shown that for binary alloys which form a simple eutectic with each other, this law is fairly well satisfied. In the case of binary alloys forming a solid solution, there has as yet appeared no paper dealing with the confirmation of the law of depression or the elevation of the freezing point. T. Ishigaki and the present writer[131] showed that in the case of the binary alloys of the simple eutectic type, which has no solubility on both sides of the pure components, the law of depression first given by Van't Hoff, that is,

$$\delta T = - \frac{RT^2 C}{m\lambda}$$

holds good exactly, where δT is the depression of freezing point, R the gas constant, T the melting point of the solvent in the absolute scale, C the concentration of the

solute, m the molecular weight and λ the latent heat of fusion. They also showed in the case of the eutectic alloys having a limited solubility on the both sides of pure components, or in alloys having a complete solubility between pure components, the more general law deduced by M. Planck, that is,

$$\delta T = - \frac{R T^2 (C_l - C_s)}{m \lambda},$$

where C_l and C_s are the concentrations of the liquidus and the solidus phases corresponding to a given temperature, holds good exactly. Thus the freezing point may be depressed or elevated according as $C_l \gtrless C_s$. They also showed that the above law is satisfied in the case of an allotropic transformation taking place in a solid phase, for example, in the case of the A_3 and A_4 transformations in iron-carbon system, or in iron-nickel system.

(d) *Properties of molten metals and alloys.* Y. Matsuyama[132] investigated several properties of molten metals and alloys, such as surface tension, electric resistance, density and solidification shrinkage, and obtained many interesting results, amongst which the following may be mentioned:—

In the case of alloys which have no intermetallic compounds, or those possessing compounds which however, break up before they reach the liquidus line, the surface tension, electric resistance or density plotted against the concentration forms a smooth curve, showing no break, but in the case of the alloys which have intermetallic compounds existing up to their melting point, sharp breaks at the concentration of the compounds are observable, indicating that even in the molten state, these intermetallic compounds exists as such, the same conclusion which is arrived at in section (b).

(e) *Volume change during solidification of metals and alloys.* H. Endo[133] made use of a thermobalance for measuring the volume change during solidification of metals and alloys. The sample is placed in a small silica vessel suspended from one arm of the thermobalance and dipped in a suitable liquid medium. During cooling, the molten sample solidifies, the volume change takes place and consequently the bouyancy of the medium acting on the sample varies; this change is continually observed by means of the thermobalance, and from the discontinuous change of

Metals	$\dfrac{\delta V}{V}$	Metals	$\dfrac{\delta V}{V}$
Hg	3.75%	Cd	4.74%
Pb	2.57	Pb	3.44
K	2.81	Al	6.26
Na	2.53	Ag	5.00
Sn	2.80	Au	5.17
Bi	−3.32	Cu	4.05
Sb*	−0.95	Mn*	1.69
Tl	3.23		

Alloys	Composition (%)	$\dfrac{\delta V}{V}$
Al—Si—Fe	87.5 : 12　: 0.5	3.47%
Al—Cu—Fe	66.9 : 33.2 : 0.4	4.81
Al—Cu—Mg—Si—Fe	92.5 : 4.4　: 1.5 : 0.5 : 0.45	5.06
Cu—Al	87.1 : 12.9	4.27
Cu—Sn	62　: 38	3.57
Cu—Zn	60.6 : 39.4	2.89
Pu—Sb - Sn*	79　: 16　: 5	2.06
,,　,,　*	76　: 16　: 8	2.06
,,　,,　*	92　: 4　: 4	2.61
Pu—Sb – Sn—Cu*	83.7 : 11.8 : 4　: 0.5	2.04

bouyancy-temperature curve, the total change of volume during solidification can be obtained. The above table contains the result of measurement by H. Endo and also that* recently obtained by Y. Matsuyama.[134]

The last four alloys are type-metals commonly used; contrary to the general belief, these alloys contract during solidification.

(f) *Occlusion of gases in metal and alloys.* A. Sievert[135] was the first to make the most important investigation on this subject. Recently K. Iwase[136] carried out the same experiments and obtained the following results:—

Hydrogen is dissolved in iron, copper, zinc, antimony, tin and aluminium; nitrogen is dissolved in iron, copper, aluminium, silumin and cast iron, but not in zinc, tin and antimony; CO and CO_2 are dissolved in iron, copper and cast iron, but not in zinc, tin and antimony. In these metals and alloys, the solubility of gases in the liquid state is much greater than that in the solid state, and its temperature coefficient differs from each other for these states. In iron, this coefficient differs also for α and γ states.

(g) *Physical constants of metals and alloys.* Y. Okubo and the present writer[137] measured the coefficient of thermal expansion from ordinary temperature up to 400° for aluminium, magnesium and several typical aluminium alloys used in different countries in the world; they also determined the same constant for the systems nickel-iron and cobalt-iron. H. Masumoto and H. Nara[138] measured also the same constant for alloys of the systems nickel-cobalt and iron-cobalt.

The measurement of thermal and electrical conductivities was also made by H. Masumoto[139] for several typical aluminium alloys used in aeroplanes and air-ships in their cast, annealed, quenched and aged conditions. He also measured the same constant for alloys of the system nickel-cobalt,[140] carbon steel and cast iron of different concentrations of carbon.[141]

A. Osawa[142] measured the lattice constant for the whole series of iron-nickel alloys, and confirmed that for specimens annealed at 1150°, a bodycentred cubic lattice is found for pure iron as well as in the alloys containing up to 35 percent of nickel and a face-centred cubic lattice for the alloys containing from 27 percent of

nickel up to pure nickel. Hence the heterogeneous field, in which these two kinds of lattice are found mixed together, extends from 27 to 35 percent of nickel. When these heterogeneous alloys are once dipped in liquid air, the heterogeneous range is slightly displaced towards a higher percentage of nickel. Further, from the lattice constant of the iron-nickel alloys, he calculated the density of these alloys and compared it with that directly observed; the agreement between them is very satisfactory.

S. Sekito[143] determined the lattice-constant of several series of solid solutions of aluminium, tin, zinc, manganese and nickel in copper in the range of respective solubilities. He found that the lattice constant of these alloys follows the substitution law of Vegard, and that the density of these alloys calculated from the lattice-constant agrees satisfactorily with that experimentally found.

The lattice constant of a series of iron and nitrogen alloys was investigated by A. Osawa and S. Iwaizumi.[144] The existence of the two compounds Fe_4N and Fe_2N has been confirmed; the former is a cubic crystal having 3.80 Å as the lattice constant; the iron atoms in the lattice have a face-centred distribution, one nitrogen atom being present in each elementary cube. The latter compound belongs to the hexagonal system; the iron atoms form a hexagonal close-packed lattice with lattice constants $a = 2.743$ Å and $c/a = 1.59$, one nitrogen atom being present in each elemetary parallelopiped lattice.

(h) *Mechanism of crystal growth by annealing.* .T. Sutoki[145] studied experimentally the mechanism of crystal growth in aluminium and in tin containing 1.5 per cent of antimony, the former being strained and annealed and the latter merely annealed. Based on his results of experiment, he explains the mechanism of the crystal growth in the following way:—

For crystal growth a suitable internal stress must be given before annealing; because this pretreatment gives rise to a small number of relatively stable nuclei for crystallization and during annealing the growth starts from these nuclei as centres. The grain growth takes place from the concave side of the grain boundary forward; it continues so long as it is surrounded by a large number of microcrystals. Minute gaps in grain boundaries or slip planes formed by the initial strain favors the growth of the crystal, these serving as a " Spielraum " for the rebuilding of the crystals. If several large crystals are in contact with each other, their boundaries are nearly plane so a considerable extent and consequently these crystals cannot grow by further heating.

(i) *Single crystals of metals.* Large single crystals of iron, nickel and cobalt measuring over 10 cm in length were obtained by S. Kaya and the present writer,[146] and the magnetization for different orientations of the specimens in varying magnetising field was thoroughly studied, and many important results were obtained. The magnetostriction of these ferromagnetic substances was also measured by Y. Mashiyama and the present writer[147] and by Z. Nishiyama.[148]

K. Yamaguchi[149] investigated by means of the X-ray analysis the deformation caused by tension in the case of single crystals of copper and aluminium. T. Sakao[150] studied by the same means, the mode of destruction of the single crystal of aluminium by tension. K. Tanaka[151] examined the orientation of single crystals zinc and
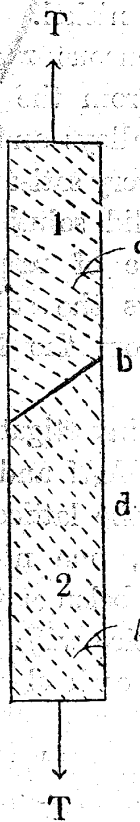
aluminium caused by straining and annealing.

K. Yamaguchi[152] investigated the elongation caused by tension in different portions of a test-piece consisting of large crystals, and showed that the rate of elongation in portions which contain grain boundaries is much less than that of the portion consisting of a single crystal. This result seems at first sight to confirm the long held view that the grain boundary is stronger than the grain itself; but as is shown below, this fact may be explained in another way: Thus in the annexed figure, let us suppose that a test-piece in the form of a plate consists of two large crystals 1 and 2, the boundary of which is line ab, and that the parallel lines in the plate denote the direction of slip planes in these crystals. Suppose also that the plate is gradually stretched lengthwise by a tension P, the angle between the tension and the slip planes being α and β and $\alpha < \beta$. Let the stress by which the crystal 2 just begins to slip, be T_2; then the effective stress along the slip plane ad will be $T_2 \cos \beta \sin \beta$ and the slip takes place everywhere below line ad, but not yet tn the crystal 1, where the effective stress $T_2 \cos \alpha \sin \alpha$ is less than the value $T_2 \cos \beta \sin \beta$. The stress which is just sufficient io cause a slip in the crystal 1, is T_1, such that $T_1 \cos \alpha \sin \alpha = T_2 \cos \beta \sin \beta$. Assuming the boundary to have the same strength as the crystal itself, it is concluded that stress T_2 cannot cause any slip in the triangular portion abd; for in order that slip may take

Fig. 51.

place in this portion, the slip must also occur in the adjacent triangular portion abc and therefore a greater stress is required. This stress T_2' is given by

$$T_2' \cos \beta \cos (\alpha - \beta) \sin \alpha = T_1 \cos \alpha \sin \alpha = T_2 \cos \beta \sin \beta;$$

$$\therefore \quad \frac{T_2'}{T_2} = \frac{\sin \theta}{\cos (\alpha - \beta) \sin \alpha} > 1$$

$$\text{and} \quad \frac{T_2'}{T_1} = \frac{\cos \alpha}{\cos \beta \cos (\alpha - \beta)} > 1.$$

Thus the slip in the portion $adbc$ requires a much larger stress than that in portions below line ad or above line bc. The ratio of the stresses depends chiefly upon the value of $\cos (\alpha - \beta)$, or the difference between two angles α and β. Thus, it is realised why in the vicinity of the grain boundary the rate of elongation is small, or, in other words, why the grain boundary is apparently stronger than the crystals themselves.

In specimens consisting of minute polycrystals, the state of things explained above prevails at a great number of points within them, so that the strength as a whole is greatly increased as compared with that of the specimen consisting of a single crystal. Thus, for the explanation of an important fact that the strength of a material increases as the grain size diminishes, we can dispense with the very improbable assumption that the grain boundary is much stronger than crystals

themselves.

　(j)　*Orientation of microcrystals in metals*.　The orientation of microcrystals in rolled platinum plate was investigated by S. Tanaka[153] by means of the X-ray analysis. He also examined the orientation of microcrystals both in rolled and beaten gold foils, finding that in the case of rolled gold foils, microcrystals are chiefly so arranged that face (110) is parallel to the face of rolling and the normal to face (211) is parallel to the direction of rolling, while in the case of beaten foils, face (100) is arranged parallel to the surface of the foil, the orientation in other respects being at random.　H. Hirata and H. Komatsubara[154] studied the orientation of microcrystals of electrically deposited silver and found that the crystals have a tendency to deposit themselves iu a fibrous form, the diagonal axis of the cubic crystals being parallel to that of the fibre.　S. Tsuboi[155] also carried out the same investigation with silver deposited with different electrolytic solutional pressures and obtained the same result as that of the last two investigators, except that the (112) axis is, in this case, parallel to the direction of growth.　He[156] also examined the orientation of microcrystals in compressed magnesium and aluminium plates, and found that in the case of magnesium, the principal axis of the hexagonal crystal tends to take the direction of compression, and that in the case of aluminum, the (110) axis takes the direction of compression.　A similar investigation was also made by H. Hirata[157] with bismuth and antimony deposited by electrolysis.　F. Fujiwara[158] studied also the orientation of microcrystals in the case of drawn wires of aluminium and copper, and confirmed that the trigonal axes of the crystals are arranged nearly parallel to the axis of the wire, leaving the orientation in other respects rather at random.

　The arrangement of microcrystals in a rolled tungsten plate or a rolled molybdenum strip was studied by T. Fujiwara[159]; he found that face (110) is perpendicular to the direction of rolling and face (100) is nearly parallel to the surface of the strip. He also found that in the case of the molybdenum strip, the tensile strength in the direction of rolling is greater by about 20 percent than that in the direction inclined at 45° or 90° to that of rolling.

　(k)　*Corrosion of iron and steel*.　K. Inamura[160] investigated several factors which affect the corrosion of iron, such as the action of distilled water, city water and sodium chloride solution on Armco iron.　It was found that in the absence of air, the water appears to have no appreciable action upon the iron, and that even though it contains sodium chloride, water free from oxygen and carbon dioxide has no action.　He[161] also studied the relation between the corrosion-loss and the concentration of various corroding reagents with copper, 7:3 and 6:4 brasses.　H. Endo[162] has been studying for several years the corrosion of iron and steel; in his first paper, he gives the results of experiments on the action of water, light, temperature, oxygen, acids and salt solutions on the corrosion of iron, and also the mechanism of iron passing into the passive state in solutions of $K_2Cr_2C_7$, K_2CrO_4, $KClO_3$ and $KMnO_4$.　In the second paper[163], the results of his experiments on the corrosion of steels containing various amounts of carbon, cobalt, nickel, chromium, manganese, molybdenum, vanadium, tungsten, copper, titanium, phosphorus, silicon

and sulphur, in hydrochloric, sulphuric and nitric acid solutions are described. The same measurement was also made by Y. Uchida and M. Saito[164]. The relation between the rate of dissolution of hardened steels in a sulphuric acid solution and the degree of tempering was also studied by T. Matsushita and K. Nagasawa[165]

The effect of cold-working on the corrosion of iron and steel was also studied by H. Endo[166]. The specimens were subjected to strains different both in respect of its strength and its kind, and were then submitted to the action of a dilute sulphuric acid. From the results obtained, he concludes that if the stress is so large as to give rise to a permanent deformation of the specimen, its effect, which consists in the promotion of the corrosion, begins to appear and increases with the amount of deformation.

T. Harada[167] investigated the corrosion of aluminium-rich alloys which contained a small quantity of other elements, such as copper, manganese, iron, nickel, cobalt, silicon, magnesium, tin, zinc, in solutions of 0.5 percent hydrochloric, nitric and sulphuric acids, caustic soda and ammonia water. Sea water, water saturated with carbon dioxide, a 3% sodium sulphite solution were also used as corroding media.

The corrosion of different typical light alloys were studied by N. Sekimura[168]. The corrosion and other physical and mechanical properties of different kinds of rustless steel, which are widely used in our country and in abroad, was thoroughly investigated by Y. Kawakami[169].

(1) *Plasticity of metals.* H. Shoji[170] constructed a sensitive differential dilatometer and measured the plastic elongation of different metals, such as cadmium, lead, tin, gold, zinc, silver, aluminium and copper in the form of a wire under constant loads of different magnitudes. With a given load exceeding the elastic limit, the elongation increases at first rapidly and then gradually, its rate of increase tending to a constant value, as the time elapsed after loading increases. From the elongation-time curve the initial velocity of elongation, v, can be calculated for different loads; from the initial velocity-load curve, the elastic limit, w_0, was estimated for different metals. If the applied load w diminished by w_0 be denoted by w', then v and w' were found to satisfy the following relation :

$$v = a \, w' \, e^{bw'}$$

where a and b are two constants characteristic of a metal. The same relation holds good also for the final velocity of elongation.

A similar measurement[171] was also made by H. Shoji and Y. Mashiyama at high temperatures with cadmium lead and tin.

H. Shoji gave a new definition for the plasticity of metals, P, as given by the expression

$$P = \frac{1}{w_0} \frac{dv}{dw},$$

and calculated from his results of experiment this constant for the initial and final velocities.

In a recent paper, H. Shoji[272] made a theoretical investigation on the plasticity of metals, assuming the principle of superposition, and gave a change to his former

definition of the plastic constant; thus he defined the plasticity of a metal by two constants p and w_0:

$$p = \frac{v}{w - w_0} \text{ and } w_0,$$

and calculated these constants for cadmium, lead, tin, zinc, silver, aluminium and copper from the results of his former experiments.

(m) *Cementation of iron.* As regards the mechanism of cementation, there have been two theories; in one theory, carbon is assumed at high temperatures to diffuse into iron in the form of a gas, such as CO, CH_4 and CN, and in the other, it is considered to be capable of direct penetration into iron. G. Takahashi[173] found by a direct experiment that even at very high temperatures, these gases cannot diffuse through iron, although hydrogen gas can do so. According to the X-ray analysis, above 900°, carbon atoms diffusing into iron is found in the interspace of the iron lattice, that is, at the centre of the face-centred cubic lattice, scattered here and there according to the law of probability. This shows directly that carbon atoms themselves can diffuse into iron.

Takahashi also showed that the prevailing theory regarding the energetising action of carbonates on cementation, that is,

$$MCO_3 \rightarrow MO + CO_2; \qquad CO_2 + C \rightarrow 2CO; \qquad 3Fe + 2CO \rightarrow Fe_3C + CO_2,$$
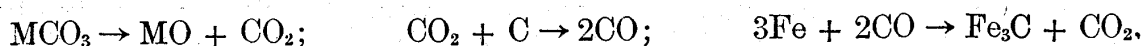
is untenable; because (1) the energetising action is great even at temperatures where carbonates do not yet decompose, (2) in the presence of CO gas and carbonates, the action is accelerated without the presence of carbon, and (3) the cementation by a mixture of carbon and carbonates is far greater than that in the current of CO gas even in the absence of carbonates. Hence he proposed a new theory, in which he assumes that the energetising action of carbonates is to decompose CO gas and to set free nascent carbon atoms, these atoms directly diffusing into iron. He also investigated the effect of other alloying elements on the cementation of iron.

The effect of occluded oxygen gas on cementation was investigated by K. Inouye.[174] In solid steel, oxygen is found in the form of FeO, MnO or in that of solid solution, and increases with the carbon content. In steels containing a considerable quantity of oxygen, grain growth takes place during annealing and yields an abnormal steel, while those containing a small quantity of oxygen yield a normal steel. The cementation is generally deeper in the former case than in the latter.

(n) *Ghost lines in steel ingots.* S. Maita[175] investigated by a long series of experiments special modes of segregation known as "corner ghost" and "thready ghost"; the former is usually found in the inside of polygonal ingot corners and even in that of round ingots. According to his results of experiments, the corner ghost is formed by a quick cooling in the first period of solidification, in which the external crystallised zone is being formed from the molten steel. Thus the quick cooling causes some deformation in the external solidified zone and there gives rise to some internal fissure or loose structure, which is later filled up by the fluid segregate, and in this way the corner ghost is finally formed.

On the other hand, if the molten steel solidifies with a moderately slow cooling,

the thready ghost will be formed by virtue of the development of a local segrega-
tion, which takes place at the boundary of growing crystals, and which direction is
bent upwards on account of its bouyancy.

(o) *Spontaneous hardening of light alloys at ordinary and high temperatures.*
Spontaneous hardening of light alloys occurring at ordinary or high temperatures is
called " age-hardening " or " temper-hardening " respectively. Both kinds of harden-
ing are of the same nature. Spontaneous hardening is always observable in alloys
which posses a eutectoid or a phase change and which have been quenched from a
temperature lying above that of the eutectoid or the transformation. It also occurs
in those alloys, in which the solubility of one component in the other rapidly increases
with the rise of temperature. I. Igarasi[176] measured the aging effect in a 0.9%
carbon steel, aluminium-copper alloys, aluminium-zinc alloys, aluminium-magnesium
alloys, duralumin, aluminium-copper-magnesium alloys, all of which have been
quenched. H. Nishimura[77] investigated the age-hardening of aluminium-rich zinc
alloys by means of the hardness measurement and microscopic observation, the thermal
expansion, thermal analysis and electric resistance methods having also been utilized.
Similar experiment with 6:4 brass was made by N. Ishikawa.[178]

T. Tanabe[179] carried out an extensive investigation of the temper-hardening of
various aluminium alloys containing copper, magnesium, silicon, zinc, iron, nickel
and manganese, in amounts actually found in practice. Their mechanical properties
and the solubitity in acids under different conditions of heat-treatment, were also
investigated. As the result of these investigations, he obtained an excellent wrought
alloy.

As regards the age or temper-hardening, we have a number of theories; but all
of them may be classified into two:—

(1) Hardening is caused by the precipitation of fine, or even colloidal particles
of a dissolved substance from a solid solution.

(2) It is caused by some change taking place in the solid solution.

The present writer supports the second theory; because the idea of " the critical
size " as used by the supportors of the first theory is too arbitrary, and because there
are two important facts which confirm that the precipitation of the dissolved substance
takes place in the range where the hardness decreases rapidly during tempering, but
not in the hardening range, as is usually assumed to be by the supportors of the
first theory. Thus, (1) quite recently S. Kokubo[180] found in the case of aluminium-
copper alloys by means of a very sensitive thermal analysis that in the range of
temperature, where the hardness or electric resistance increases by tempering, a small
heat absorption is observable, and in a higher temperature range where the hardness
or the electric resistance decreases, a conspicuous heat evolution corresponding to the
heat of precipitation is observable; (2) since in aluminium-copper alloys, the tempered
specimen has less resistance than the quenched one, the precipitation of the compound
from the solid solution must be accompanied by the diminution of the resistance.
According to the view of the present writer, the perfectly annealed aluminium-copper
alloy (α) consists of a mixture of the compound Al_2Cu and an aluminium solid solution
dissolving a small quantity of the compound, the copper atoms entering within the

aluminium lattice by simple replacement; the quenched alloy (γ) consists of a super-saturated solid solution, and the temper-hardened alloy (β) is also a solid solution, in which copper atoms are displaced within the aluminium lattice into such positions *as are favorable for precipitation as the compound Al_2Cu*, that is to say, to a more unstable position. The change $\gamma \rightarrow \beta$ is therefore the change from a solid solution into another more unstable one, and the change $\beta \rightarrow \alpha$ is the precipitation of the compound from the latter, more unstable solid solution. During the first change, $\gamma \rightarrow \beta$, a hardening due so lattice disforsion occurs and a small quantity of heat is absorbed, while during the second change, $\beta \rightarrow \alpha$, softening occurs and a considerable amount of heat is evolved. This view explains all observed facts very satisfactorily.

(p) *Abrasion in carbon steels.* In all previous investigations on the abrasion of metals, the wear has been measured without fixing the value of the coefficient of friction between two abrasing surfaces; but, as a matter of fact, it depends consider-ably upon the coefficient of friction, so that the results of thise previous measure-ments cannot be compared with each other. R. Yamada and the present writer[181] were the first to measure the wear of carbon steels and several metals against a carborundum disc, fixing the coefficient of friction at a constant value. They found that the wear is proportional to the work done, and that it increases more rapidly than the coefficient of friction does. M. Suzuki[182] measured the relative abrasion for six hypo-eutectoid carbon steels of different carbon contents and different structures by means of a special apparatus designed by himself, the measurement being always made fixing the coefficient of friction at a constant value. He found as the result of his experiments two important laws for the relative abrasion of different steels. That is,

$$W_{nm} = K \frac{W_{Nm}}{W_{Nn}} \quad \text{and} \quad K = a\mu^2,$$

where　W_{Nm}=specific abrasion of a substance, m, with respect to the given sub-stance N,

W_{Nn}=specific abrasion of a substance, n, with respect to N.

W_{nm}=relative abrasion of a substance, m, with respect to n,

μ　=coefficient of friction,

a　=a constant, which remains invariable for a series of substances having a similar property.

By this formula, the magnitude of the relative abrasion between any two substances in the same series, for which the above laws, are applicable, can be calculated, if their specific abrasions, with respect to a given substance can be known.

Adopting for the unit of work a kilogram-meter and for the unit of weight-loss by abrasion a milligram, Susuki found for a the following values:

1.　For rolled structure,　　　　　$a = 13.4 \times 10^{-3}$
2.　,, annealed ,, ,　　　　　　$= 12.6$,,
3.　,, sorbitic ,, ,　　　　　　$= 10.5$,,
4.　,, troostitic ,,　　　　　　$= 6.3$,,
5.　,, martensitic,,　　　　　　$= 1.6$,,

Thus for the above five structures, the resistance to abrasion is in the following ascending order: Rolled, annealed (pearlitic), sorbitic, troostitic and martensitic structures.

Reference to the Papers.

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