

鐵 と 鋼 第十六年 第二號

昭和五年二月二十五日發行

論 說

本邦に於ける金屬材料研究の最近の發達 (其 1)

(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. (I)

By *Kotaro Honda*, *Rigakuhakushi*, *Director of the Research Institute for Iron, Steel and Other Metals, Tohoku Imperial University, Sendai.*

The present communication contains an outline of the recent progress of the science of iron, steel and other metals made in our country in a period of last six years, that is, from 1923 to the present year. The contents of the paper are divided into the following sections:

1. Research institutes and laboratories,
2. Methods of investigation,
3. Properties of iron and steel,
4. Properties of cast iron,
5. Equilibrium diagrams of ferrous alloys,
6. Equilibrium diagrams of non-ferrous alloys,
7. Mechanical properties of metals and alloys,
8. Miscellaneous.

§ 1. Research Institutes and Laboratories.

Important institutes and laboratories for metallurgical researches in our country, which form a public institution or belong to some private factories, are enumerated below:—

1. Research Institute for Iron, Steel and Other Metals, Tohoku Imp. Univ., Sendai.
2. Metallurgical Laboratories belonging to the Imperial Universities in Tokio, Kyoto, Sendai and Kyushyu.
3. Research Laboratory of Imperial Steel Works, Yawata, Kyushyu.
4. Research Laboratories of the Naval Department, Tsukiji, Tokyo; Kuré and Hiro, Hiroshima.
5. Institute of Physical and Chemical Research, Tokyo.

6. Research Laboratory of Nippon Steel Works, Muroran, Hokkaido.
7. Research Laboratories of Sumitomo Electric Wires and Steel Works, Osaka.
8. Research Laboratory of Tokyo Electric Co., Kawasaki.
9. Research Laboratory of Mitsubishi Shipbuilding Co., Nagasaki.
10. Research Laboratory of Nippon Special Steel Works, Omori, Tokyo.

Besides these, there are a large number of laboratories of smaller scale belonging to technical colleges, or to factories of metal industry. The scientific papers which are issued annually from these institutes and laboratories, amounts to over 70. This number does not much differ from the one given out from each of the countries, Germany, England, America and France.

§ 2. Methods of Investigation.

Ten years ago, the methods of metallurgical investigation were largely restricted to such ones as chemical analysis, thermal analysis and microscopic observation, but in recent years, several physical methods, such as electric resistance method, thermal expansion method, as well as magnetic and X-ray analyses, have been introduced into metallurgical investigation. By virtue of the last method, the science of metals has become very exact and we are now in a position to discuss atomistically different phases occurring in alloys.

(a) *Electric resistance method.* In this method the electric resistance of a specimen is measured at a gradually rising or falling temperature, and from the abnormal change of resistance with respect to the temperature, the change of phase occurring in the specimen can be detected. The resistance is measured by passing a constant current through the specimen and observing the difference of potentials at two points of the specimen by means of a potentiometer. This method is not only applicable in detecting a change of phase taking place in the solid phase, but also in determining the liquidus and solidus lines of a system of alloys.

Usually, thermal analysis constitutes the means of determining the temperatures of the change of phase, but this method cannot be accurate enough for estimating their exact locations; because heat, when it is once evolved, takes a certain time to diffuse towards the outside of the specimen and hence, although the beginning of the heat evolution can be known, its end is hardly recognizable, so that the whole course of the heat evolution during a transformation cannot be determined with certainty. It is to be noted that the electric resistance method or other methods which are based on the change of physical properties, enable us to trace the whole course of the transformation with a greater accuracy.

The first extensive application of the electric resistance method for the determination of the equilibrium diagram of different alloys has been made in our Institute.¹⁾

(b) *Thermal expansion.* The thermal expansion of a test specimen is measured at a gradually rising or falling temperature, and from the abnormal course of the expansion-temperature curve, the change of phase in a specimen can be ascertained. Although this method is applicable to the case of the phase change in a solid only, it often furnishes us very important data; for example, we owe to this method much

of our knowledge regarding the mechanism of tempering of carbon steel. The application of this method to metallurgy has first been made by P. Chevenard.

(c) *Magnetic analysis*. This method consists in detecting a transformation in a metal by measuring the magnetic intensity or susceptibility at a gradually rising or falling temperature. This method enables us not only to detect the various constituents in an alloy, but also furnishes us some information concerning their physical state. For example, it is very convenient in deciding whether carbon in steel or cast iron exists as cementite or graphite, or whether it is present in a free state or in a solid solution.

This method is not only very convenient for detecting a change of phase in ferromagnetic metals and alloys,²⁾ but also in other substances, that is, paraand diamagnetic metals and alloys,³⁾ provided we use, instead of the magnetometer method, a torsion balance or an electromagnetic method, which is very convenient for measuring a small magnetization. Thus, the A_3 and A_4 transformations in iron have been successfully followed by a change of susceptibility during heating and cooling and the exact location of the transformation points in the equilibrium diagram has been established. Again, since the magnetization of steel changes abruptly at the liquidus and solidus points, their temperatures can be exactly determined by magnetic analysis. This method is also due to our institute.

(d) *X-ray analysis*. A. Westgren was the first to apply this method to the metallurgy of iron and steel. The method is very important for studying the equilibrium diagram of alloys. Thus, specimens of different concentrations are prepared and their X-ray spectrum taken; from the distribution and the intensity of spectral lines, it can be known whether the component metals form chemical compounds, or whether in a certain range of concentration they form a solid solution, again whether they are present in the state of a mechanical mixture. The constitution of a system of alloys at ordinary temperature is thus ascertained from these data. Based on this knowledge of constitution, it is now easy to study the change of the constitution at high temperatures by means of different methods above referred to, that is, thermal analysis, microscopic observation, electric resistance, thermal expansion, and magnetic analysis. In this way the equilibrium diagram of the system is accurately determinable.

Another important application of the X-ray analysis is the estimation of internal stress in cold-worked or quenched steels. A cold-worked specimen is undergoing an internal stress, and therefore its spectral lines will be somewhat broadened. Similar remark holds also for quenched steels. Hence from the broadening of these lines the change of the lattice constant and consequently the magnitude of the internal stress can be estimated.

All these methods of investigation are of great importance in the investigation of metals and alloys, but they have each their own merits and demerits, and hence it becomes very important to choose from among these methods some ones that are best suited for our particular purpose.

Besides the above methods, we have three others. The first is to avail of thermoelectricity for finding the transformations in metals and alloys by its abrupt

change during heating or cooling. The second is what has first been used by M. Chikashige⁴⁾ in studying the equilibrium diagram of binary alloys, and consists in measuring the intensity of reflected light from these samples. The intensity-concentration curve shows generally a maximum and rarely a minimum, at the concentration of a compound. It shows a break at the saturation concentration of a solid solution, and a conspicuous minimum at the concentration of a eutectic.

The third method which measures the thermo-ion emitted from a sample at different high temperatures, is very sensitive for detecting a small change taking place in a specimen. The test of the method is now going on our Institute for confirming different allotropic and other changes in iron and steel at high temperatures.

§ 3. Properties of Iron and Steel.

(a) *Transformation points in iron and steel.* In the determination of the various transformation points in iron and steel by thermal analysis, the heating and cooling cannot be made extremely slow: because in this case, the heat evolution or absorption becomes apparently very small and consequently the determination of the corresponding temperature is rendered inaccurate. Thus by thermal analysis, reversible transformation points cannot be located accurately, and hence in our institute, it has been customary for an accurate location of these points to use the dilatometric, magnetic or electric resistance methods. S. Konno⁵⁾ constructed a very sensitive dilatometer for which a deflection of 1 mm in the scale corresponds to an elongation of 1.75×10^{-5} mm of the specimen, and determined the temperature and the magnitude of the A_1 and A_3 transformations in carbon steels very accurately. S. Sato⁶⁾ improved the above dilatometer so as to be fit for the determination of the change of length at very high temperatures, and determined the temperature as well as the magnitude of the A_3 and A_4 transformations in pure iron; he also showed that the change of length accompanying these transformation almost coincides with that deduced from the X-ray data. Quite recently Tomoo Sato⁷⁾ determined the reversible A_1 , A_3 and A_{cm} points in iron and steel by using magnetic and dilatometric methods, and obtained the following results:—

A_1 point: 726°C for all kinds of steel.

Carbon content	A_3 point
Electroly. iron	903°C
0.04%	880
0.12	845
0.22	815
0.32	788
0.39	773
0.45	764
0.62	744
0.74	734

Carbon content	A_{cm} point
0.92%	786°C
1.07	863
1.12	885
1.24	941
1.33	984
1.55	1080

(b) *The A_2 transformation in iron and steel.* 15 years since the present writer⁸⁾ has continued to frequently expound his view that the A_2 transformation or the magnetic change in iron and steel does not constitute any change of phase, or expressed atomistically, it is not related to any change of atomic configuration in the iron lattice, but is a gradual change occurring within the atoms themselves, accompanying the rise of temperature. This view has been confirmed by X-ray analysis.

Since the A_2 transformation is a continuous change extending from the lowest temperature up to 790° , it is not rational to designate, the temperature, at which the rate of change is a maximum, by the name " A_2 point"; hence the present writer has chosen to call the temperature at which the change is completed during heating, or begins during cooling, the A_2 point.

As a matter of fact, the A_2 point in steel really belongs to the iron in steel, which latter consists of a mixture of the iron and cementite, and hence it must have a constant value for all steels possessing the A_2 point.

In the equilibrium diagram of the iron-carbon system,⁹⁾ the present writer has represented the A_2 line, which does not mean any change of phase, by a dotted line to distinguish it from other lines in the same diagram, which does represent a change of phase. Fig. 1 shows a portion of this diagram in the iron side.

In the range of concentration between two points e and a , steel consists, at the temperature, of a mixture of two constituents—iron and α -austenite; this latter is only weakly magnetic, its intensity of magnetization rapidly decreasing with the rise of temperature, and from 770° upwards it is weakly paramagnetic. This point is named the A'_2 point of α -austenite in analogy with the A_2 point in iron; it remains of course constant between the two points e and a . Between points a and b , austenite varies in its concentration of carbon, but its A'_2 point is found experimentally to be constant; above the concentration shown by b , it has always the same concentration and therefore its A'_2 point is also constant.

(c) *Theory of hardening.* With regard to the theory of hardening, a great diversity of opinions has been prevailing; but thanks to the many valuable informations furnished by X-ray analysis, this problem may now be considered as settled.¹⁰⁾

Above the A_1 point, iron atoms in austenite have a face-centred cubic lattice and carbon atoms in it are present at the centre of unit cube scattered here and there according to the law of probability. During cooling through the A_1 point, iron atoms take a body-centred cubic lattice and carbon atoms precipitate as cementite. Hence the A_1 transformation consists of two changes, that is, (1) the change of atomic configuration from a face-centred cubic lattice to a body-centred, and (2) the precipitation of carbon as cementite from iron lattice; that is,

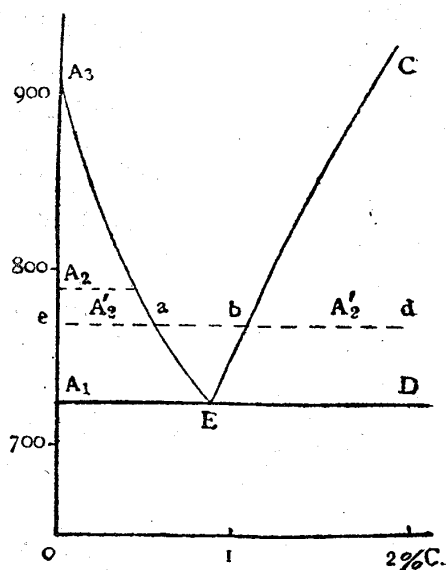


Fig. 1.

Equilibrium diagram of Iron-Carbon System.

A_1 transformation $\equiv (1) \rightarrow (2)$

\equiv a face-centred iron containing carbon atoms within its lattice \rightarrow a body-centred iron containing carbon atoms within its lattice \rightarrow a body-centred iron + cementite,

or, A_1 transformation \equiv austenite \rightarrow martensite \rightarrow perlite.

Thus the A_1 transformation consists of two stepped changes.

If a steel be cooled slowly from its austenitic state, the above two changes take place in an immediate succession and pearlite is obtained at room temperature. In the case of a very rapid cooling, such as quenching in oil or in water, the change from austenite to martensite is so much retarded that it begins to take place at a temperature below 300° , and when this change is completed, the steel finds itself nearly at room temperature, and the second change from martensite to pearlite cannot take place because of the great viscosity of iron at room temperature. Thus martensite, the hard constituent, is obtained by the quenching of steel in water or in oil.

According to the recent X-ray analysis,¹¹⁾ martensite has two kinds of lattice; that is, in the outer portion of the quenched steel, where the cooling is very rapid, a body-centred tetragonal lattice with an axial ratio 1.03~1.07 is found, while in the inner portion where the cooling is less rapid, an ordinary body-centred cubic lattice is found. The occurrence of these two kinds of martensite, α and β , may be expected from the above theory of quenching. Thus a face-centred cubic lattice (austenite) may be considered a body-centred tetragonal lattice with an axial ratio $\frac{c}{a} = \sqrt{2}$ and a body-centred cubic lattice a body-centred tetragonal lattice with an axial ratio 1; hence the transformation from austenite to martensite takes place very probably in the order:

Tetragonal lattice ($c/a = \sqrt{2}$) \rightarrow tetragonal lattice ($c/a = 1.03 \sim 1.07$)
 \rightarrow tetragonal lattice ($c/a = 1$);

or, austenite \rightarrow α -martensite \rightarrow β -martensite.

As has been remarked above, α -martensite is found only in the outer portion and β -martensite in the inner portion, of the quenched steel. S. Sekito¹²⁾ investigated the mode of distribution of the martensite from the surface to the interior, and confirmed that the axial ratio of the α -martensite appearing on the surface of the quenched steel diminishes from 1.07 with increasing depth and finally attains the value of unity.

It is a well-known fact that in a rapid cooling of a carbon steel from a high temperature, the A_1 transformation takes place at a lower temperature than is the case with a slow cooling, the extent of the lowering increasing with the velocity of cooling, until it reaches a certain temperature, i.e. about 550° , and that, if the velocity of cooling has a much larger value, the transformation point is discontinuously brought down to about 300° or even lower. If the velocity of cooling has an intermediate value, the two transformations above referred to, usually designated by A_{11}' and A_{12}'' points, take place during a single cooling; as the cooling velocity increases from the lower limit to the upper one, the magnitude of the A_{11}'' trans-

formation increases at the cost of the A_{r1}' transformation. By a thorough study of this phenomenon, T. Kikuta and the present writer¹³⁾ showed that the two transformations are of the same nature, the A_{r1}'' transformation being merely the retarded A_{r1}' transformation.

The structure corresponding to the A_{r1}' transformation is troostitic and that corresponding to the A_{r1}'' is martensitic; in the former case, two stepped changes (1) and (2) before referred to are both completed, while in the latter, the first change (1) is completed and the second (2) is arrested.

T. Matsushita¹⁴⁾ investigated by means of a special apparatus the mode of development of martensite during the period of a rapid cooling and showed it by numerous expansion-time curves.

(d) *Tempering of quenched steel.* Martensite is a structure in which the transformation has been suspended at an intermediate stage, and is consequently unstable.

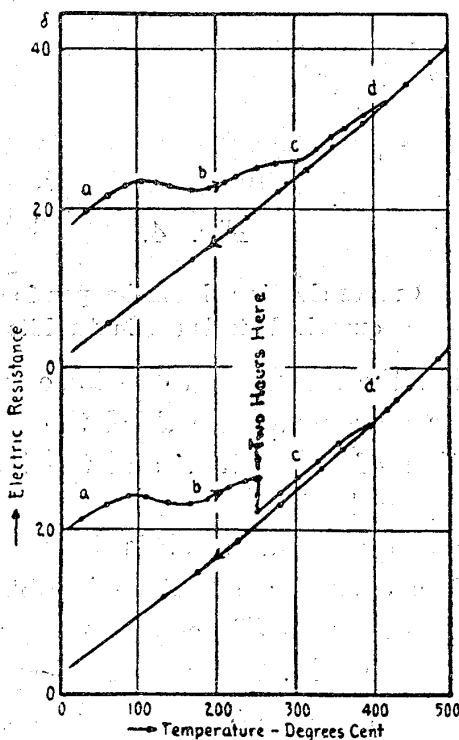


Fig. 2.

Curves showing 2-stepped changes in the electric resistance-temperature relationship (T. Matsushita).

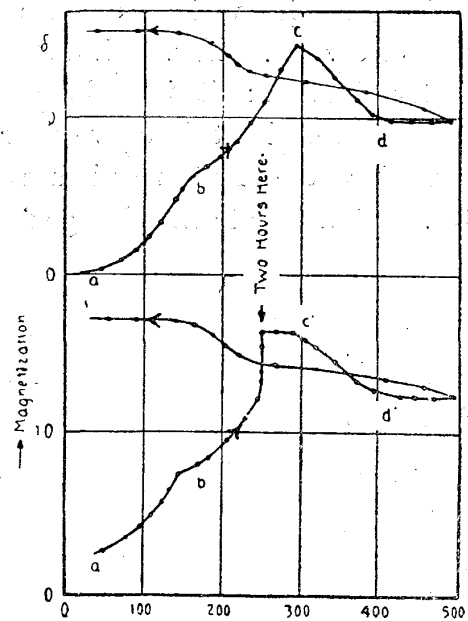


Fig. 3.

Curves showing magnetization-temperature relationship (T. Matsushita).

If a martensitised specimen is heated at a gradually rising temperature, the precipitation of cementite¹⁵⁾ takes place in two steps, that is, in the vicinity of 150° and 270°, as seen from the two succeeding breaks in the electric resistance-temperature curve, or from a similar singularity in the magnetization-temperature curve, given in Figs. 2 and 3. The first break indicates the change of the α into β -martensite and the second the decomposition of the β -martensite. A third break, though inconspicuous, is also noticeable in these curves; that is, the decrease of an electric resistance or that of magnetization, in the range of 300° to 400°; this indicates the building up

of the crystals of cementite from its molecules or colloidal particles of cementite, which is precipitated from martensite.¹⁶⁾ In the expansion-temperature curve of a quenched steel, only the first and third singularities are observable, the second being absent as is evident in Fig. 4.

We have already remarked above that the β -martensite decomposes in the vicinity of 270° , but it is here implied that a very slow decomposition takes place even at a much lower temperature; as a matter of fact, the decomposition of the β -martensite begins below 100° , although its velocity is extremely small; as the temperature is raised, the rate of decomposition increases at first very gradually, but from 200° upwards it does so at a much greater speed.

S. Sato¹⁷⁾ measured very accurately the thermal change occurring during a slow heating of quenched steels which contain different percentages of carbon. Fig. 5 shows an example of his determination; it is a heat evolution-temperature curve. In this curve four maxima are observable; the first maximum indicates the heat-evolution due to the change from α into

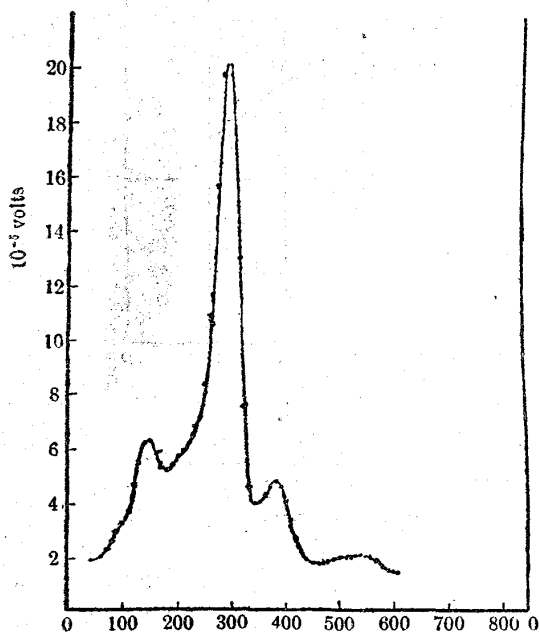


Fig. 5.

1.2% C Steels. Heat evolution-temperature curve (S. Sato),

martensite in its nature, will be obtained. Such a pseudo-martensite¹⁹⁾ is actually obtainable by cooling nickel alloys containing 15 to 30 percent of nickel from the

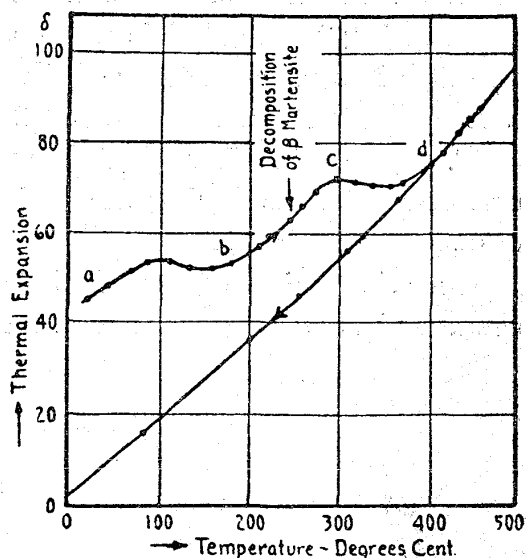


Fig. 4.

Curves showing thermal-expansion of quenched steels (T. Matsushita)

β -martensite, the second that due to tempering of the latter martensite, the third the heat of the formation of cementite, and the last the heat of recrystallisation.

When a quenched steel is tempered at $300^\circ \sim 400^\circ$, a troostitic structure is obtained, while a tempering at $500^\circ \sim 600^\circ$ results in a sorbitic structure. K. Tamaru and the present writer¹⁸⁾ showed, however, that these structures can be obtained by a single quenching of a specimen in a salt bath at a suitable temperature from $300^\circ \sim 500^\circ$.

(e) *Martensite without carbon.* As we have shown above, iron atoms in martensite have a body-centred cubic lattice, carbon atoms occupying the centre of the face of the cube, scattered here and there according to the law of probability. If we suppose that these carbon atoms are replaced by atoms of some other elements, a structure which is similar to

austenitic region. For, in austenite, the atoms have a face-centred cubic lattice, some iron atoms being replaced by nickel atoms, and during cooling they change their lattice from a face-centred to a body-centred; but as nickel atoms themselves have the property of forming a face-centred lattice, some of these atoms may take a face-centred position of the body-centred lattice, other nickel atoms occupying some positions in the same lattice by a simple substitution. In this way a structure which is similar in its property to ordinary martensite will be obtained. T. Matsushita and K. Nagasawa²⁰⁾ recently found that iron alloys containing chromium, vanadium, molybdenum or tungsten in the proportion, which forms an α solid solution at room temperature and changes into the γ at a high temperature, is hardened by quenching from the austenitic region, even though it does not contain any carbon. It has been confirmed by X-ray analysis that this quenched specimen consists of the α iron containing no trace of the γ iron; it is in fact a pseudo-martensite.

(f) *Internal stress in cold-worked or quenched steels.* As we have already remarked, a cold-worked or quenched steel is subject to an internal stress; that is, every small portion of the steel undergoes a tension and exerts a pressure on its neighbouring portion, these tension and compression balancing with each other and thus constituting the internal stress or strain. Consequently different portions of the space-lattice of the strained steel are deformed in various degrees and the spectral lines are broadened. From the broadening of these lines that of the lattice can be calculated and hence the magnitude of the internal stress estimated. In this way S. Sekito²¹⁾ found for copper and for steels of different carbon contents that the maximum internal stress is a little less than their tensile strength. This is quite reasonable; because internal stress cannot naturally increase beyond the breaking stress of the material. A similar result was also obtained in the case of quenched carbon steels.

(g) *Hardness of different structures of steel.* The hardness of austenitic carbon steel and that of cementite are not yet accurately known; K. Tamaru²²⁾ measured the hardness of these substances together with those of martensite, sorbite and troostite in the following way: Many specimens of a 1.69% C steel were prepared and quenched in different media; structures consisting of a mixture of martensite and austenite in varying proportions were thus obtained. Their hardness as well as the area of the martensite in the microphotographs of these specimens were measured. By the extrapolation of the hardness-martensite area curve, the hardness of martensite and that of austenite were estimated to be 720 and 155 in Brinell scale respectively. K. Tamaru also confirmed experimentally that above 0.8 percent of carbon, the hardness of austenitic steel is almost independent of the carbon content.

For the measurement of the hardness of cementite, specimens of steel containing 1 to 5.55 percent of carbon were cast in a thick copper mould with a narrow rectangular hole; the castings thus obtained showed no trace of the decomposition of cementite. The hardness of these specimens was measured by a Rockwell hardness tester. By extrapolating the hardness-concentration curve, the hardness of cementite was found to be 820 in the Brinell scale. We have thus the following table of the hardness of different structures of steel:

Armco iron	austenite	pearlite (0.9% C)	sorbite, (0.9%)	troostite, (0.9%)	martensite	cementite
90 B.N.	155	225	ca. 270	ca. 400	720	820

(h) *Spheroidization of cementite in steels.* On account of the practical importance of the characteristic property of the spheroidized or globularized cementite in steel, i.e. the property that it possesses the smallest hardness and the largest ductility which steel can show at room temperature, a large number of investigations concerning the formation of this structure have been carried out. According to the result of investigation by S. Saito and the present writer,²³⁾ the mechanism of the spheroidization of lamellar cementite is as follows: —

If we heat a lamellar pearlite up to the A_1 point, the lamellar cementite begins to dissolve into the γ iron, but since the degree of dissolution cannot be the same for different portions of the same lamella, the latter is, so to speak, torn assunder into isolated islets as the dissolution goes on. These islets are then rounded into a globular form by virtue of the surface tension acting on the boundary surface of the cementite and thus spheroidization takes place. In this view, the separation of a lamella into isolated islets by a mere prolonged heating below the A_1 point cannot be possible, because here the dissolution of the lamella does not take place at all. If, however, steel be quenched and tempered, or severely forged, cementite is present as fine particles, or the lamella is mechanically destroyed, so that a prolonged heating below the A_1 point results also in the spheroidization of cementite particle by virtue of surface tension.

If a pearlitic steel is gradually heated beyond the A_1 point, the cementite dissolves in γ iron and finally disappears completely. On the other hand, at the moment of the dissolution of cementite at the A_1 point, its concentration in austenite is not uniform; because the diffusion of carbon in austenite requires a certain duration of time. Hence if the steel be cooled from the A_1 point or a little above it, the cementite is first precipitated from the numerous centres of the concentrated portion, the deposits themselves agglomerating by virtue of the surface tension and thus resulting in the formation of numerous globules. If, however, the steel be heated far beyond the A_1 point, the diffusion of cementite in γ iron becomes complete and the concentration becomes homogeneous; hence during cooling through the A_1 point, a pearlitic structure results. Thus, to obtain the spheroidised cementite from a pearlitic steel, the temperature of heating must reach the A_1 point, but must not be raised too high, and hence the occurrence of spheroidisation is limited to a certain range of temperature, as is actually observed. This range depends naturally upon the velocity of the A_1 transformation or that of the dissolution of cementite; when a steel contains other elements, the velocity of the A_1 transformation is diminished, and hence the above range of temperature is widened. S. Saito and the present writer found that in the case of carbon steels, this range is $15^\circ \sim 20^\circ$ for hypo-eutectoid steels and $20^\circ \sim 120^\circ$ for hyper-eutectoid steels. T. Ishihara²⁴⁾ investigated the effect of manganese, chromium and copper on the spheroidising range and found that the range is more or less widened. S. Yokota²⁵⁾ also investigated the same effect very extensively by experimenting on the effect of silicon, nickel, cobalt, tungsten, vanadium, molybdenum, sulphur and phosphorus.

Recently S. Maita²⁶⁾ shortened the time of annealing required for spheroidization by a special heat-treatment. Thus, the specimen is at first quenched from a high temperature above the A_1 point, then is reheated a little above the A_1 point and cooled below this point; it is again heated to the A_1 range and then slowly cooled. In this way, a structure in which fine globular cementites are uniformly distributed and which is consequently very soft, can be obtained. S. Maita applied this process not only to plain carbon steels, but also to special steels; in this way he could impart to various kinds of steel a high elongation, a high impact value and even high elastic limit. Steels thus heat-treated are now called "Niseko steel" and is produced on a commercial scale by the Nippon Seikoshio, Muroran.

§ 4. Properties of Cast Iron.

(a) *Change of volume of cast iron during solidification.* The measurement of the shrinkage of cast iron during solidification is very important both from practical and theoretical points of view. H. Endo and the present writer²⁷⁾ carried out the same measurement. The method consists in measuring the change of bouyancy of a small vessel containing the specimen, which is suspended within an inert liquid, by means of a thermobalance. The same measurement was also repeated recently by Y. Matsuyama, T. Kasé and the present writer²⁸⁾; the result is summarised below:—

(1) In the case of eutectic white cast iron, which contains no graphite when solidified, the solidification shrinkage is 3.7 percent in volume. When the graphite in the solidified cast iron increases, the shrinkage decreases linearly with the amount of graphite and becomes zero at 1.7 percent of graphite. With a further increase of the graphite, the change is an expansion, and in the case when all eutectic cementite is graphitised, the expansion amounts to 3.2 percent in volume.

(2) The amount of the solidification shrinkage which changes from a positive to a negative value, is in quantitative agreement with that deduced from the view that graphite in cast iron is the decomposition product of eutectic cementite; that is, during the solidification of eutectic cast iron, a shrinkage of 3.7 percent takes place, but the decomposition of cementite into austenite and graphite results in an increase of volume, so that the total shrinkage may be positive or negative according to the magnitudes of these two volume changes. This result is very important as regards the equilibrium diagram of the iron-carbon system, as will be shown later on.

In Europe and America it has been usual to measure the total shrinkage of a casting, which consists of the shrinkage during solidification and that after solidification in the temperature range extending down to room temperature, by means of a special dilatometer. Thus, an arm connected with a dilatometer of a high magnification is dipped near one end of a horizontal rectangular mould, and the total shrinkage is recorded on the dilatometer. It is, however, evident that this method cannot give an accurate result, the shrinkage thus obtained being much smaller than the true value. Hence in our Institute, the solidification shrinkage was measured by means of a thermobalance as described above and the shrinkage after solidification by means of an ordinary dilatometer, the sum of these two being the total shrinkage.

In the case of cast iron, these two shrinkages are respectively 3.7 and 5.5 percent, and consequently the total shrinkage amounts to 9.2 percent. On the other hand, the first method of measurement gives only 6.5 percent.

(b) *Growth of cast iron.* It is a well-known fact that if a grey cast iron is repeatedly heated to $800^{\circ}\sim 900^{\circ}$, it grows gradually. This growth was first thoroughly investigated by Carpenter,²⁹⁾ and afterwards by M. Okochi, T. Sato³⁰⁾ and T. Kikuta.³¹⁾ The last three investigators made use of a dilatometer in measuring the growth of cast iron, and much light was thrown on the mechanism of the growth by Kikuta's experiments. Afterwards Andrews³²⁾ and Benedicks³³⁾ used the same method and supplemented Kikuta's theory. According to these investigators the causes of the growth of cast iron are: (1) the expansion due to the decomposition of cementite, (2) minute cracks and fissures formed by repeated heating and cooling through the A_1 range, (3) the formation of silicates through the oxidation of silicon present in a solid solution within iron.

(c) *Graphitization of white cast iron.* The graphitization of white cast iron was investigated by T. Kikuta³⁴⁾ and H. Sawamura³⁵⁾ by using a dilatometer in estimating the degree of decomposition of cementite or of graphitization. Kikuta divided the graphitization into two steps, that is, graphitization above the A_1 point and that in the A_1 range and lower temperatures. For each of these steps, he studied the relation between the graphitization and heating interval at a constant temperature, or that between the graphitization and temperature in a given interval of heating. In this way not only has he succeeded in reducing the heating interval in the malleable cast iron industry, but also improved the quality of the products. Sawamura and Kikuta also investigated the influence of other elements on the graphitization of white cast iron.

D. Saito and H. Sawamura³⁶⁾ found that the graphitization of the first step takes place very easily, when cast iron is first quenched and then annealed; this is probably due to the state of fine division in which the pro-eutectoid cementite finds itself.

Recently H. Sawamura³⁷⁾ investigated the effect of different gases on the first step of graphitization of white cast iron found that the effect on graphitization is strongest in the case of CO_2 , and then those of N_2 , O_2 , CO are in a descending order of their effectiveness. CH_4 , NH_3 , H_2 have the weakest effect.

(d) *Distribution of graphite in cast iron and its strength.* M. Hamazumi³⁸⁾ investigated the relation between the distribution of graphite in grey cast iron and its strength, this distribution being varied by changing the rate of cooling of the cast iron in the mould. He found that a uniformly distributed whirly graphite has the greatest strength. He explained the mechanism of the growth of graphite, especially that of the formation of the whirly graphite. He also investigated the effect of silicon, phosphorous, sulphur, manganese, copper, chromium and tin on the strength of cast iron.

§5. Equilibrium Diagram of Ferrous Alloys.

(a) *Iron-Carbon system.* When a cast iron is cooled from the melt, carbon is present partly as graphite and partly as cementite. As to the formation of graphite we have two controversial theories. In one theory, graphite is considered as a product directly precipitated from the melt, and in the other, the first precipitation product is assumed to be cementite, the graphite being its decomposition product at a high temperature. In the first theory, a double diagram corresponding to the stable and the metastable equilibrium is adopted, while in the second theory, we have a single diagram.

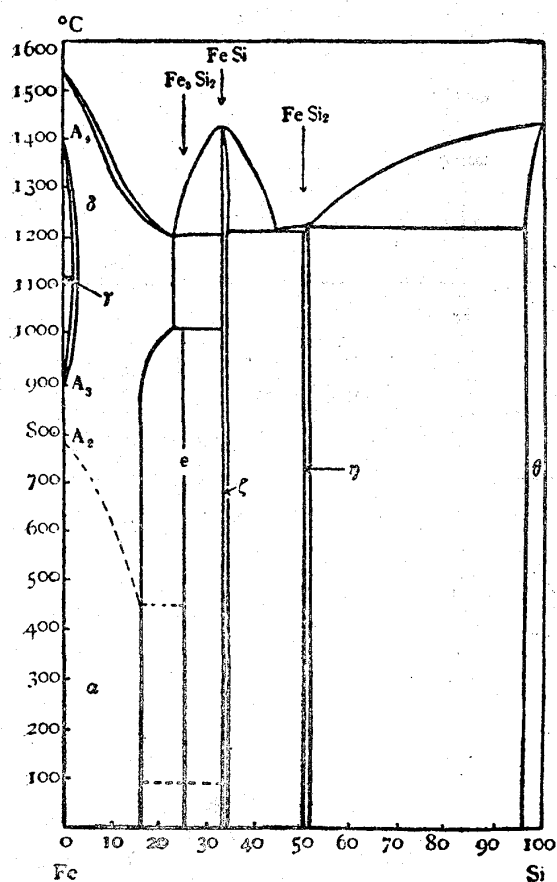


Fig. 6.
Iron-Silicon.

In a paper read before the spring meeting of the American Society for Steel Treating, the present writer³⁹⁾ has shown on the evidence of several experimental facts that the double diagram for iron-carbon system is not only unnecessary, but is unreasonable.

(b) *Iron-Silicon system.* This diagram was largely due to the work of T. Murakami⁴⁰⁾, but the researches of Kurnakow and Urasow⁴¹⁾, Oberhoffer⁴²⁾, Phragmèn⁴³⁾ also contributed to the completion of this diagram, Fig. 6.

An investigation of the structural constitution of the ternary system iron-silicon-carbon was also made by T. Murakami and the present writer⁴⁴⁾.

(c) *Iron-Molybdenum system.* Sykes⁴⁵⁾ made the first thorough investigation of this diagram. Quite recently T. Takei and T. Murakami⁴⁶⁾ improved Sykes' diagram; Fig. 7 shows their diagram.

The study of the equilibrium diagram of the ternary system iron-molybdenum-carbon is now in progress in our Institute.

(d) *Iron-Manganese system.* Tammann's diagram of this system is very simple, but a recent investigation on the same diagram by T. Ishiwara⁴⁷⁾ led to a much more complicated diagram; because manganese itself is now known to have three modifications, α , β and γ , as has recently been confirmed. Fig. 8 shows Ishiwara's result.

(e) *Iron-Zinc system.* The equilibrium diagram of this system has been investigated by many experimenters, but there remain still many points of disagreement. Quite recently Y. Ogawa and T. Murakami⁴⁸⁾ investigated the same diagram and obtained the result shown in Fig. 9.

(f) *Iron-Vanadium system.* The solidus and liquidus lines of this system were

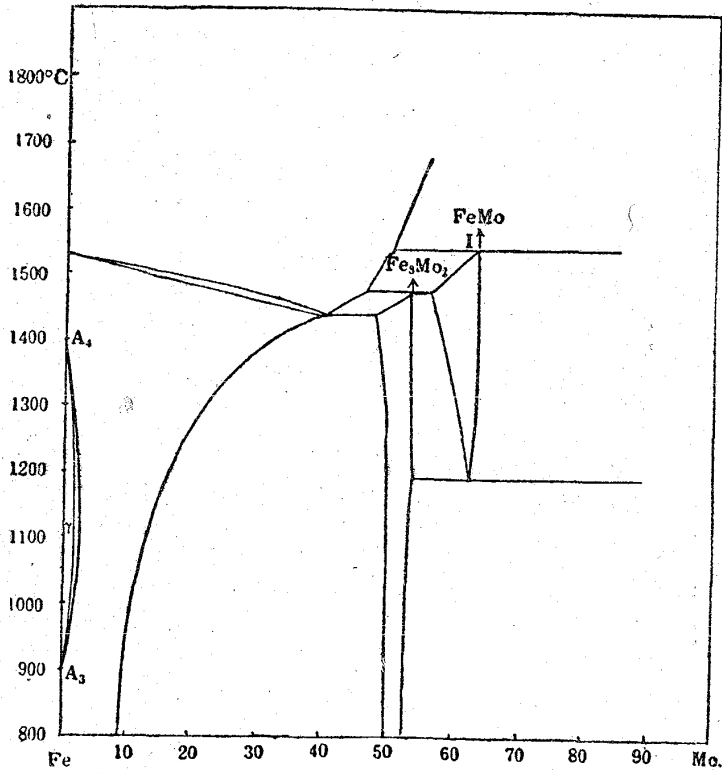


Fig. 7.
Iron-Molybdenum.

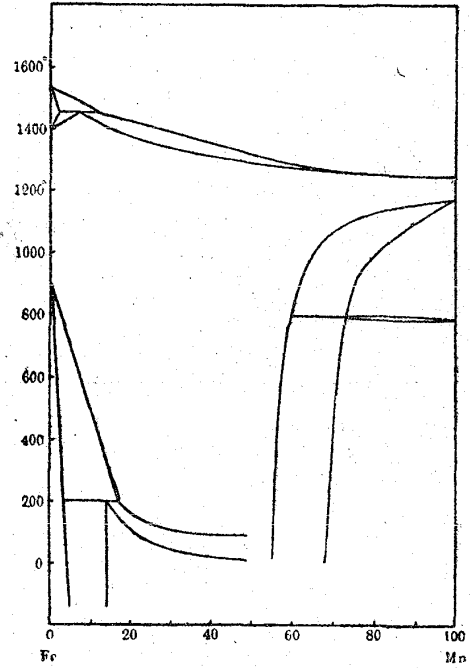


Fig. 8.
Iron-Manganese.

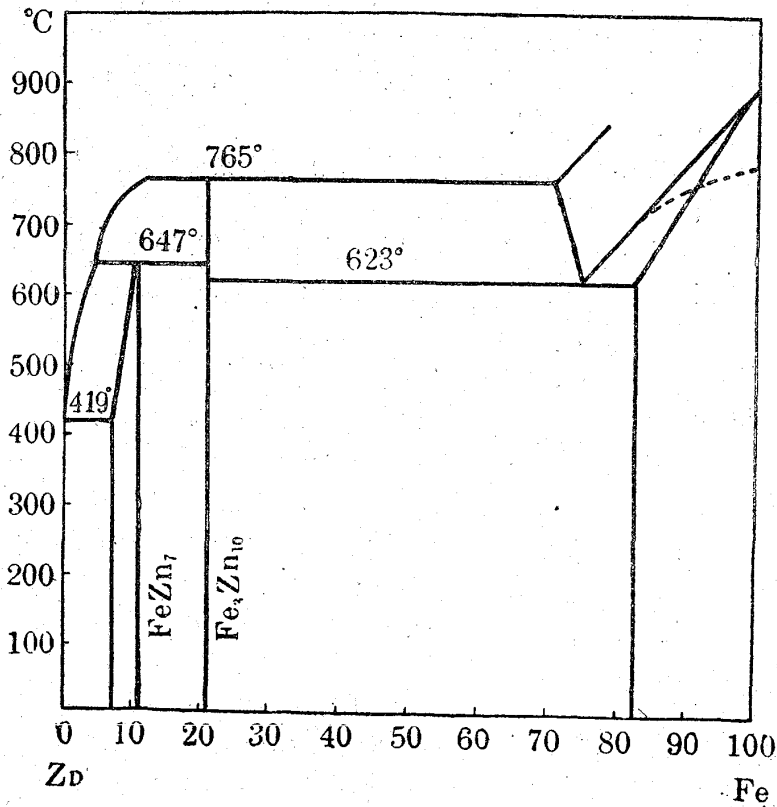


Fig. 9.
Iron-Zinc.

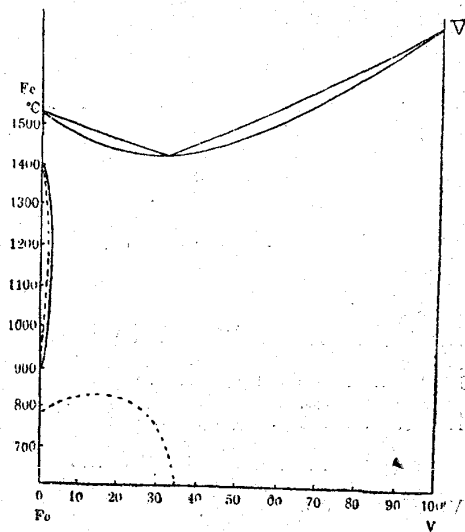


Fig. 10.
Iron-Vanadium.

first investigated by Vogel and Tamman⁴⁹⁾ and the change of the A_3 and A_4 points of iron due to the addition of vanadium by Maurer⁵⁰⁾. Quite recently M. Oya⁵¹⁾ made the determination of the equilibrium diagram of the system using a vanadium of 98 percent purity; Fig. 10 is his result.

He also determined the equilibrium diagram of the ternary system iron-vanadium-carbon⁵²⁾, the result of which is shown in Fig. 11.

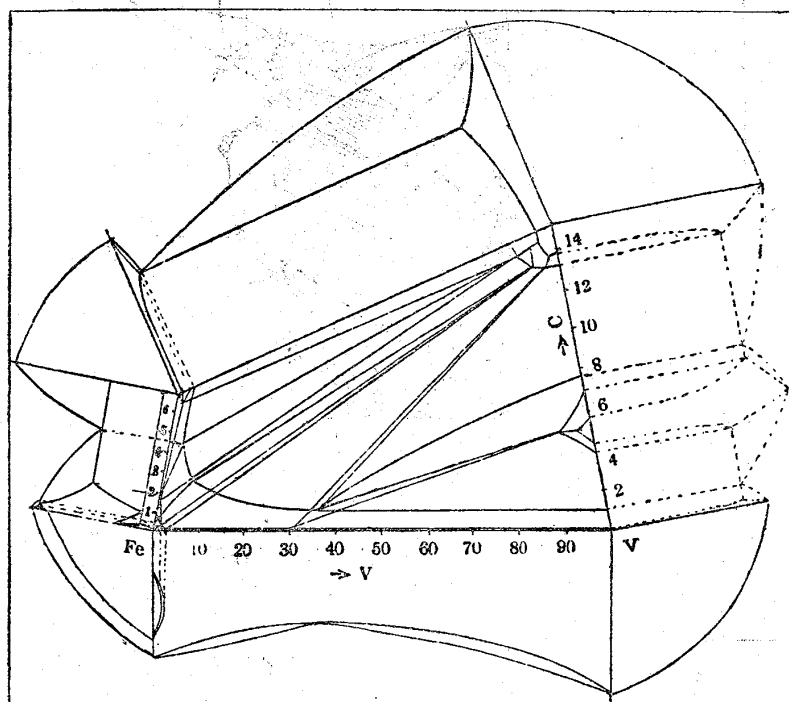


Fig. 11.

Iron-Vanadium-Carbon.

magnetic transformation is in any way connected with the A_3 line, which represents a change of phase. Since, on the other hand, it is actually observed that nickel-iron alloys are heterogeneous between 18 and 28 percent of nickel, the second type of the diagram cannot also be correct.

T. Kasé⁵³⁾ studied the same system and obtained a quite different diagram as shown in Fig. 12. It is a continuous solid solution type with one interruption in the range of 18 to 28 percent of nickel. This diagram, though very simple, not only explains many observed facts, but also the structures in meteorites, i.e. camacite and taenite.

S. Miura and the present writer⁵⁴⁾ determined the actual heterogeneous range of the system by means of a dilatometer.

T. Kasé also determined the ternary system of iron-nickel-carbon⁵⁵⁾, the result of which is given in Fig. 13.

(h) *Nickel-Carbon and Nickel-Copper-Carbon systems.* The equilibrium diagram of the first system nickel-carbon was investigated by T. Kasé⁵⁵⁾ and by T. Mishima⁵⁶⁾ and that of the second system nickel-copper-carbon, by the latter experimenter⁵⁶⁾.

Figs. 14 and 15 show the results given by Mishima.

(g) *Iron-Nickel system.*

The equilibrium diagram of this system has been investigated by many experimenters, and two types of diagram have been proposed. One of them is the eutectic type and the other the continuous solid solution type. The first type of the diagram has been proposed from a misunderstanding that the magnetic transformation of metallic nickel and of high nickel alloys constitutes an ordinary phase change; but as a matter of fact this change is of the same nature as the A_2 change in iron, and hence we cannot consider that the line of the

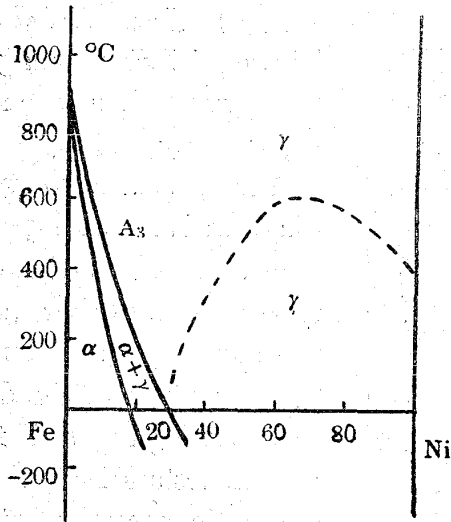


Fig. 12.
Iron-Nickel.

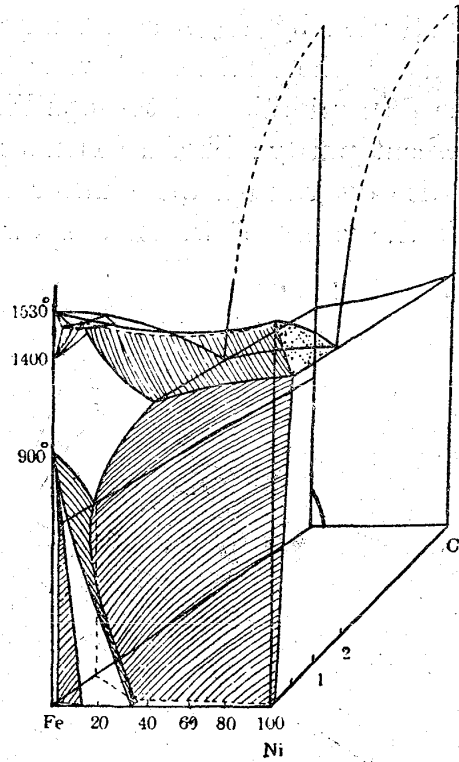


Fig. 13.
Iron-Nickel-Carbon.

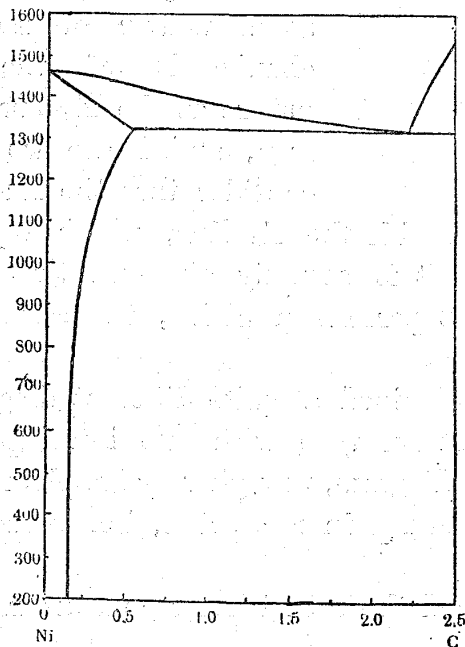


Fig. 14.
Nickel-Carbon

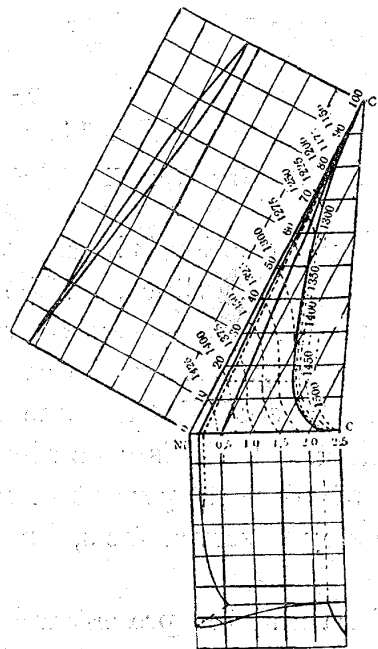


Fig. 15.
Nickel-Copper-Carbon.

It is often found that the cupro-nickel alloy used in coinage is very brittle, the cause of which was studied by T. Hirose⁵⁷⁾. He found that the most injurious element causing the brittleness of the alloy is oxygen in the form of an oxide and that

sulphur comes next to oxygen. The oxygen can be reduced by introducing a piece of magnesium-copper into the molten alloy in the crucible before tapping. The deleterious effect of the eutectic of copper and cuprous oxide can be eliminated by adding a proper amount of arsenic to the alloy.

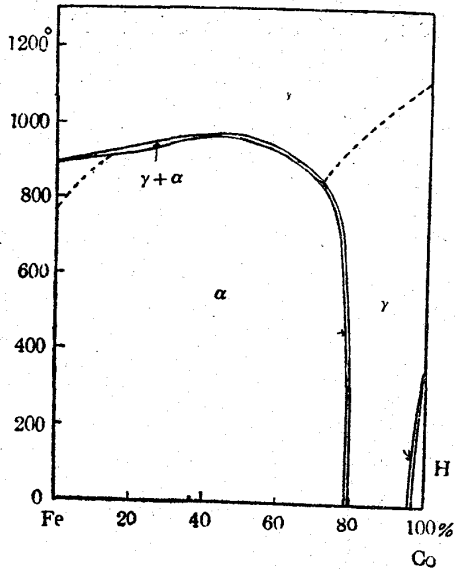


Fig. 16.
Iron-Cobalt.

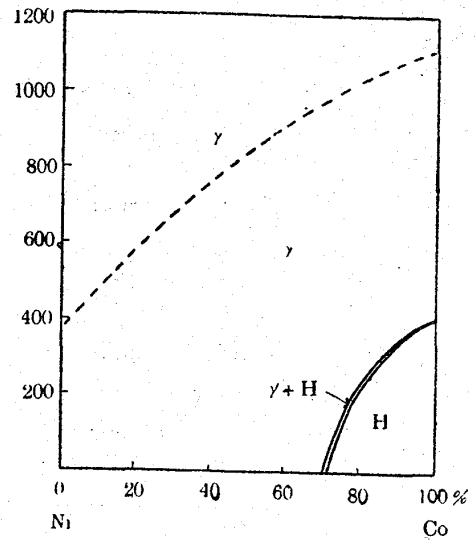


Fig. 17.
Nickel-Cobalt.

(i) *Iron-Cobalt and Nickel-Cobalt system.* H. Masumoto⁵³⁾ found a new transformation in cobalt at 470°, and consequently the equilibrium diagrams of these systems had to be modified. Hence he determined these diagrams and obtained the results shown in Figs. 16 and 17.

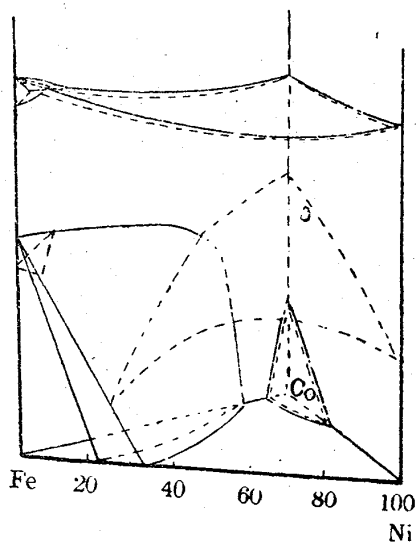


Fig. 18.
Iron-Cobalt-Nickel.

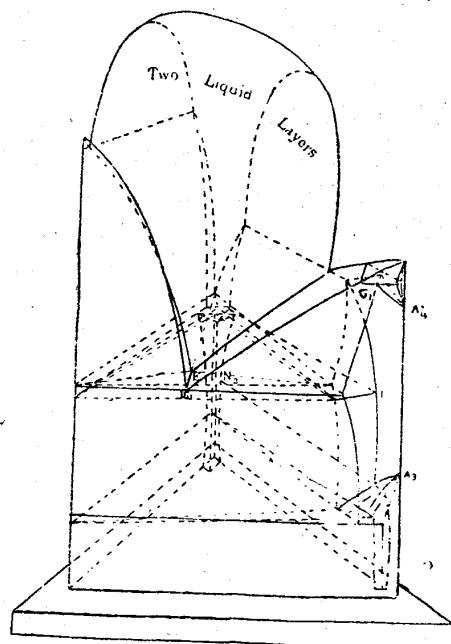


Fig. 19.
Iron-Copper-Carbon.

(j) *Iron-Nickel-Cobalt system.* Based on the new determination of the equilibrium diagrams of three binary systems iron-nickel, iron-cobalt and cobalt-nickel. T. Kasé⁵⁹⁾ determined the equilibrium diagram of the ternary system iron-cobalt-nickel, and obtained a result shown in Fig. 18.

(k) *Iron-Copper-Carbon system.* The equilibrium diagram of this system was investigated by T. Ishiwara, T. Yonekura and T. Ishigaki⁶³⁾, their result is shown in Fig. 19.

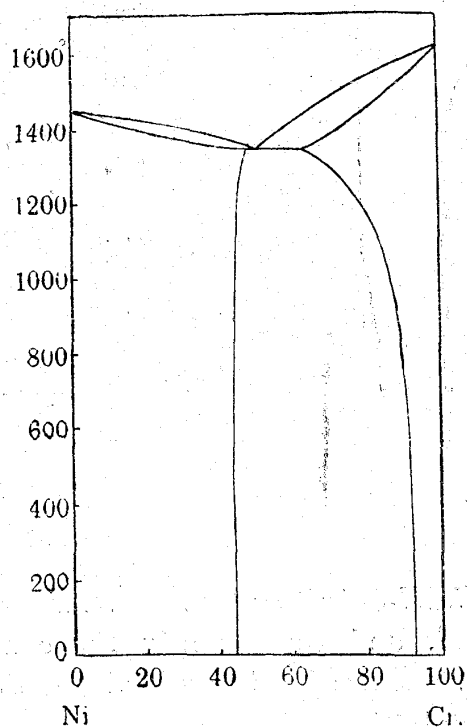


Fig. 20.

Nickel-Chromium.

(l) *Nickel-Chromium system.* In Fig. 20 is shown the equilibrium diagram of this system recently completed by Y. Matsunaga⁶¹⁾, and M. Hamazumi and Nishigori⁶²⁾. It differs from old diagrams in being of a simple eutectic type, on both sides which there is a considerable range of solubility of one component in the other.