

On ? Transformation in Fe-Ni Alloys by Supercooling or Superheating

著者	TAKEUCHI Sakae
journal or publication title	Science reports of the Research Institutes, Tohoku University. Ser. A, Physics, chemistry and metallurgy
volume	1
page range	43-49
year	1949
URL	http://hdl.handle.net/10097/26228

On $\gamma \rightleftharpoons \alpha$ Transformation in Fe-Ni Alloys by Supercooling or Superheating*

Sakae TAKEUCHI

The Research Institute for Iron, Steel and other Metals

(Received September 13, 1948)

I.

Phase boundaries between γ and α in the solid state of Fe-Ni alloys has been undecided due to a marked hysteresis on heating and cooling. In Fig. 1⁽¹⁾ the experimental results are summarized by means of thermal analysis, thermal expansion and magnetic analysis. Marks \triangle , \square , \circ , ∇ , \diamond represent the beginning and finishing temperature of the A_3 -transformation on heating and \blacktriangle , \bullet , \blacktriangledown , \blacklozenge on cooling. It has been hitherto supposed that the A_3 -transformation accom-

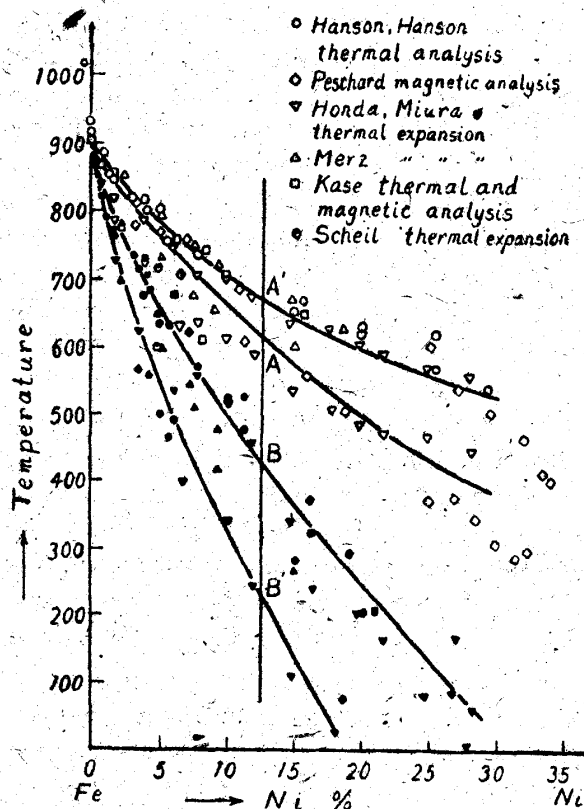


Fig. 1. Observed values of the A_3 -transformation points in Fe-Ni alloys on heating and cooling.

panied with change of concentration would take place in ranges of AA' on heating and BB' on cooling. However, an extra-ordinary long time is required to make diffusion effectively in a case of even low concentration and high temperature with an alloy containing 3% Ni or 5% Ni. It is, therefore, doubtful that variation of concentration is proceeding in the range of AA' or BB' in the ordinary heating or cooling process. A diagram deduced from the above experiments is remarkably different from the results obtained by X-ray analysis^{(2),(3)} on specimens quenched after heating for long hours at a high temperature. This discrepancy may have arisen from a lack of knowledge on the characteristics of the A_3 -transformation in the Fe-Ni alloys. That all phases situated at high temperature can always be supercooled by rapid cooling in the case of small diffusivity, is questionable.

II.

An X-ray analysis was made on small pieces (diameter 1~0.7 mm) quenched after heating for one hour at 1000°C in order to observe whether or not the γ phases of the Fe-Ni alloys containing 10%Ni, 18%Ni, 25% Ni and 27%Ni respectively could be supercooled to the room temperature. X-ray photographs of them reveal Debye rings of the body-centred cubic lattice in every case, and a trace of the face centred lines in addition to the body centred line can be recognized in the case of 27%Ni. Thus, a transition from γ state to α state was so quick that it could not be impeded even by quenching. This fact resembles the case of martensitic

* The 511th report of the Research Institute for Iron, Steel and Other Metals.

transformation in Fe-C alloys.

It must be examined whether or not the temperature of transformation is affected by cooling rate or almost fixed at a given concentration of the alloy with little effect of the cooling rate. The alloys containing 25%Ni and 28%Ni, which were annealed 20 hours at 1000°C and then quenched in ice water for homogenization, were used for the purpose mentioned above. Their thermal expansion curves when they were cooled at a rate of 1~2mm/10° from 1000°C show a sudden expansion at 90°C in the case of 25%Ni and 35°C in the case of 28%Ni. The same specimens, being cooled from 1000°C to 110°C and 50°C respectively, just above the temperatures at which the transformation would occur if they continued to cool down, were kept at these temperature for 24 hours to observe the mode of change, which did not take place. When they were cooled from these temperatures, the similar expansion was observed to begin at the points described above (see curves I in Fig. 2). The alloys, next, were quenched in a molten metal-bath heated at 160°C and 60°C respectively in the cases of 25%Ni and 28%Ni with the aim of giving more rapid cooling in order to avoid precipitation of an

α phase that might happen in slow cooling, and then they were put into a dilatometer heated at the same temperature as the molten metal for observation of transformation temperatures due to cooling therefrom. The result obtained by this method was not so much different from the above measurements in the case of furnace cooling as shown in curves II of Fig. 2. It seems that the transformation temperatures displace by approximately 10° to higher temperature and the progress of transformation is more rapid as compared with the case of furnace cooling.

These results show a most essential feature of the transformation that in spite of such a rapid change that it can not be obstructed even by quenching, it does not occur in the case when the alloy is supercooled to somewhat higher temperature than the transformation temperature, being kept at that point for long hours. Consequently there exist peculiar transformation temperatures depending mainly on concentrations and with little relation to cooling rate. Even in a region of temperature in which diffusion hardly proceeds, transformation is able to occur rapidly. Therefore, such transformation must be a transition of crystal lattice alone γ to α accompanied with no change of concentration. The above experiments were performed in the alloys containing high concentration of Ni in which transformation temperatures are in a range of poor diffusivity. The same conclusions as above can be obtained in the alloys of lower concentration, on quick cooling. The similar phenomenon also takes place on rapid heating, so that contraction of volume on heating is due to the transition of crystal lattice α to γ . If it is the case, we must investigate on the thermodynamical conditions for the occurrence of the lattice transformation, and study the reasons why its temperature must be fixed in each concentration of the alloys.

From the experimental results summarized in Fig. 1 we may expect such a figure as drawn in Fig. 3 as the equilibrium diagram of Fe-Ni alloy, the observations have not yet been performed on the isothermal transformation from which the phase boundaries between γ and α in the equilibrium state can be decided.

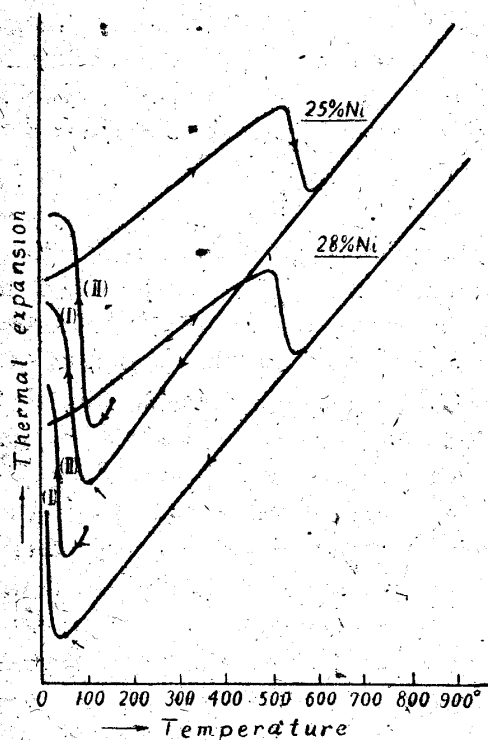


Fig. 2. Thermal expansion in super-cooled state.

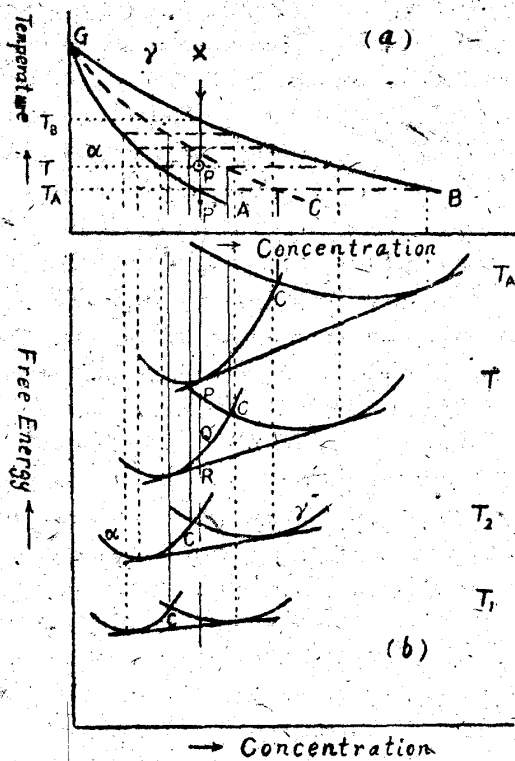


Fig. 3. Relation between free energy and concentration.

III.

We suppose such a type of Fig. 3-a as the true equilibrium diagram of this alloy. The change occurring by supercooling of the alloy from the γ phase to the temperature P in question, is discussed below.

(A) When the point P is outside of a coexisting range of two phases, γ and α , the most stable state α can be attained by only the lattice transformation accompanied with no change of concentration. Hence, its occurrence may be naturally expected at the time when the alloy is supercooled to such a temperature as P'' .

When the point is within the coexisting range the most stable state may be attained by separation into two phases passing through either of the following courses (B) or (C).

(B) Precipitation of the α phase containing lower concentration, and separation into two phases from the supercooled state γ will take place through the process of diffusion.

(C) At first the lattice transformation $\gamma \rightarrow \alpha$ will take place, and then separation into two phases will arise, accompanied with precipitation of γ phase of higher con-

centration from the transformed α state.

We may suppose the above three processes as the changes to happen at the supercooled state of γ . In the case of (A) and (C) occurrence of the lattice transformation is expected. We must consider whether the actual change appears through one or another of the courses (A) and (C). But it is necessary to determine only the course of (B) or (C) within the coexisting region. Fig. 3-b shows the curves of free energy-concentration in the γ and α state at several temperatures, and two phases, having a free energy and a concentration which corresponds to contact points on a common tangent against the curves, are able to coexist each other in the state of equilibrium. Such a state displaced from the equilibrium state as a case of supercooling or superheating can be shown by one point on these curves. In an alloy of a fixed concentration, using the relation between the free energy and temperature shown in Fig. 4 which was derived from the curves in Fig. 3-b, the following was found. A γ state at higher temperature than T_B is more stable as compared with an α state containing the same concentration as the γ state, on the contrary an α state is most stable below T_A . Between T_A and T_B two phases, γ and α , are able to coexist in the most stable state, in which the sum of their free energies is shown as a curve

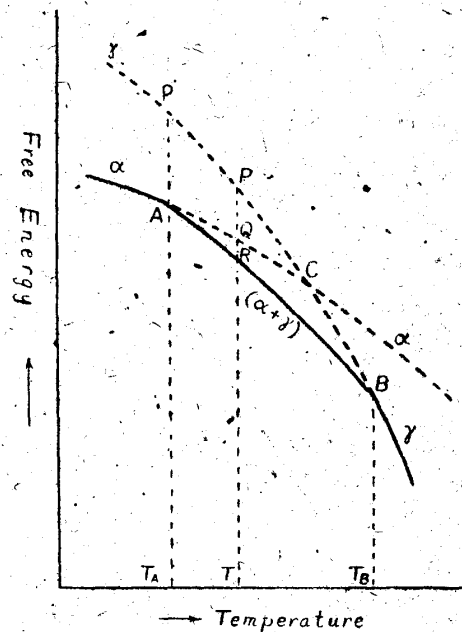


Fig. 4. Relation between free energy and temperature.

ARB. The free energy of the γ state varies along the curve BCP on cooling if no precipitation arises below T_B , until it intersects the curve of α state at a point C at which both states have equal free energy. A trace of such a point C for various concentrations gives the GC line in the diagram of Fig. 3-a. When the γ state is supercooled to a temperature below T_C , the free energy of γ becomes larger than the one of α of the same concentration as γ , therefore above the GC line the α state is more stable as compared with the γ state, below the GC vice versa. It, therefore, is seemingly true that the process (C) mentioned above may give rise at the time when the γ phase is supercooled beyond the GC line or the α phase is overheated beyond the GC, but yet there can also exist another process (B). The actual changes appearing through the process (B) or (C), must be decided experimentally.

IV.

Fig. 5 shows thermal expansion curve of specimens heated or cooled with a tolerable speed to avoid precipitation in such process,

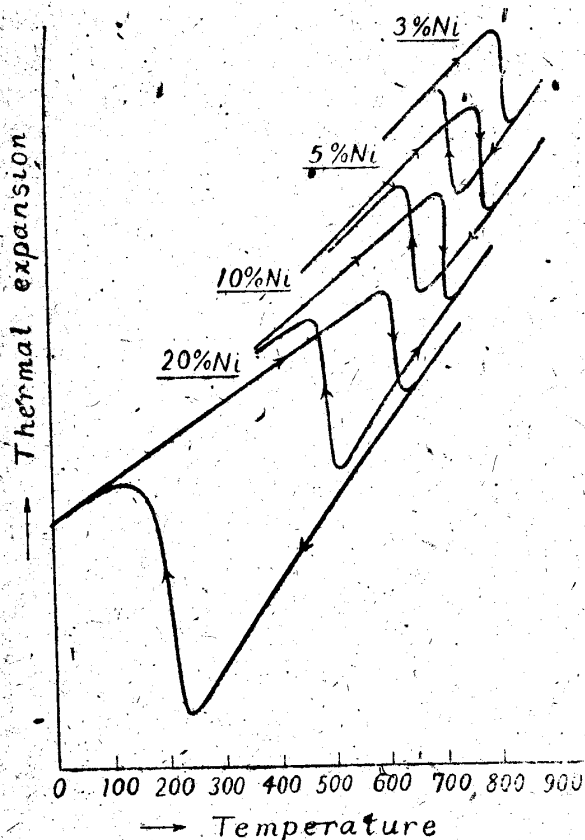


Fig. 5. Thermal expansion curves on heating and cooling with a tolerable speed.

so that the transformation temperature on heating may be defined as well as on cooling. For example, we see an abrupt contraction and expansion to be at 810°C on heating and at 715°C on cooling respectively in the case of 3% Ni, so that the transformation temperatures exist in a region which diffusion may proceed considerably during heating for rather long hours. But no change happened even when the alloy was heated for approximately 20 hours at the temperatures 830°C or 690°C. If the above changes should be caused by the transformation of crystal lattice alone within the coexisting range, the contracted or expanded phase would be in a supersaturated state, so that they would separate into two phases by precipitating α or γ having different concentrations from the original phases during the time they are kept for long hours at the temperature mentioned above. The precipitation of α or γ phase will naturally be accompanied with a gradual expansion or contraction, but in the above experiments no facts were observed to show these phenomena. The similar facts were observed in the case of 5% Ni also in which a sudden contraction occurred at 760°C on heating and a sudden expansion begun at 655°C on cooling. Consequently it can not be considered that the temperatures 810°C and 715°C in the case of 3% Ni and 760°C and 655°C in 5% Ni are within the coexisting region of two phases. We must rather suppose that 810°C and 760°C are outside of the upper limit of the coexisting region and 715°C and 655°C outside of the lower limit. These speculations are justified by lattice transformation on heating or cooling in cases of high concentration such as 10% Ni or 20% Ni. Accordingly there must be at least the coexisting range of two phases between the two temperatures at which the sudden expansion and contraction occur on cooling and heating respectively, and so a process which can be observed within such a temperature interval is nothing but (B) mentioned in the III.

Now, for example, a piece of the alloy of 5% Ni, quenched in ice water after annealing long hours at 1000°C for homogenization, was heated to 730°C, at which the change was observed. A gradual contraction

took place for 50 hours until it terminated, and then the alloy was cooled, but no change occurred until a sudden expansion appeared at 585°C. When the alloy was heated at 700°C, a more gradual contraction continued to occur for 74 hours. On cooling after gradual contraction an anomalous expansion was observed to begin at 460°C. And the higher the heating temperature the larger was the amounts of contraction at 730°C, 700°C and etc. On the contrary every change at 765°C or 650°C was very rapid as mentioned above. Therefore, the contractions at 750°C, 730°C and etc. are not caused by the lattice transformation, but by a transition tending to the equilibrium state by precipitation of phases having higher concentration, which are able to change to α states by the lattice transformation at 585°C or 460°C respectively on cooling. If every change at 750°C, 730°C and etc. was the lattice transformation, $\alpha \rightarrow \gamma$, the amount of every contraction must be equal and such γ phases produced as above must have the same transformation temperature, 650°C contrary to the observed facts.

As it is supposed that the amount of isothermal contraction ΔL is approximately proportional to that of a γ phase precipitated at every temperature, the phase boundaries between γ and α may be determined by measuring the limiting temperatures at $\Delta L = \text{maximum}$ and $\Delta L = 0$, and also at the same time relations between these limiting temperatures and the transformation temperatures of lattice alone may be explained experimentally. It is required to give an impetus to proceed diffusion by an appropriate method to perform further experiments at every temperature within the coexisting range. It is well known that highly cold worked metals and alloys become to have large diffusivity, so that square rods of alloys were prepared in plan of thin plates of 0.5 mm in thickness by cold rolling to a reduction of about 95%. Small pieces of 8 cm in length and 8 mm in width were cut off from the rolled thin plates, then they were bent at approximately right angle along the middle line parallel with their long dimension in order to prevent deformation by external forces. Such a form of the piece of Fe-Ni alloys containing 5%

Ni, 10%Ni and 20%Ni was used for measuring the thermal expansion. Each specimen as mentioned above was heated at a rate of about 3min/10° to the transformation temperature on cooling but after passing it every specimen was heated at a greater rate to the temperature, to avoid precipitation of γ phase in the course of heating, at which the isothermal contraction was measured with the elapse of time. After no contraction being observed, the specimen was cooled to room temperature and variation of thermal contraction was measured in the course of

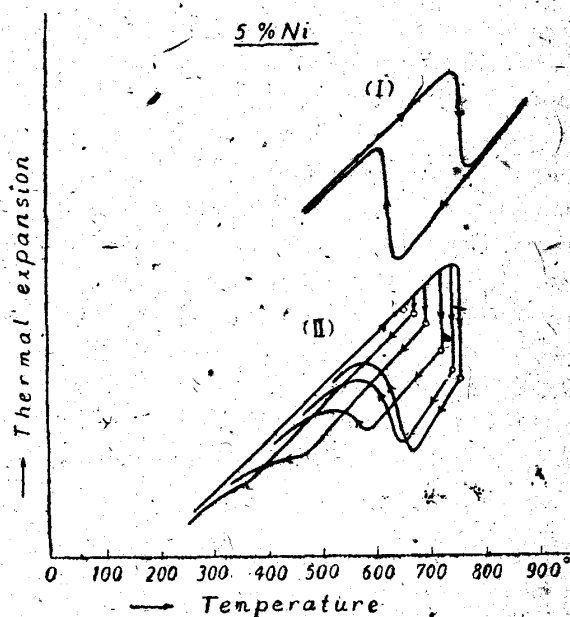


Fig. 6. Isothermal contraction of γ at superheated state.

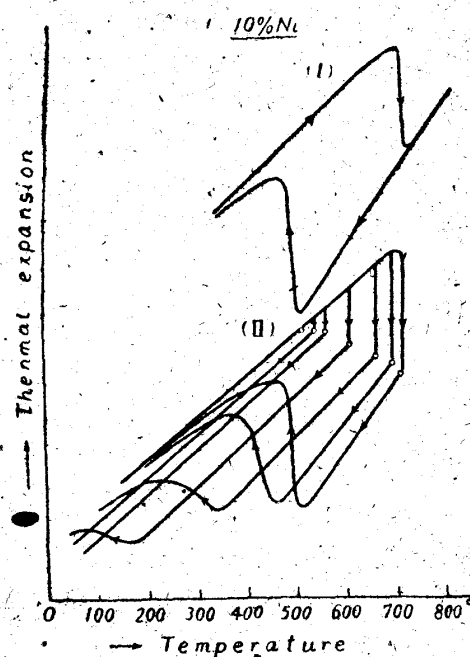


Fig. 7. Isothermal contraction of γ at superheated state.

cooling. These results are shown in Figs. 6 and 7, in which every curve (I) was obtained for specimens quenched in ice-water after annealing 20 hours at 1000°C . The above indicates that transformation of crystal lattice occurs on heating and cooling quickly. The curves (II) were obtained by the method described above. We shall describe, as an example, a case of 10%Ni in detail. Observation on the isothermal change was performed at 680° , 650° , 600° , 550° , 530° and 500°C respectively. Hardly any contraction was recognized at the temperature below 500°C . Since a strain stored in the specimen by cold rolling is released incompletely until it attains these temperatures, a slight contraction may be observed on account of recovery from the strained state during heating for long hours below 500°C . This amount of contraction, therefore, must be subtracted from that of contraction at every temperature mentioned above to obtain the true amount of contraction caused by the transformation. Fig. 8-a shows the variation of ΔL with time plotted at every temperature, the final values of ΔL in the curves of Fig.

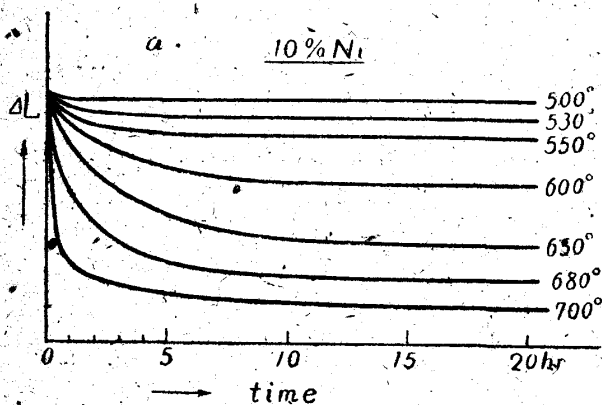


Fig. 8-a. Variation of ΔL with time.

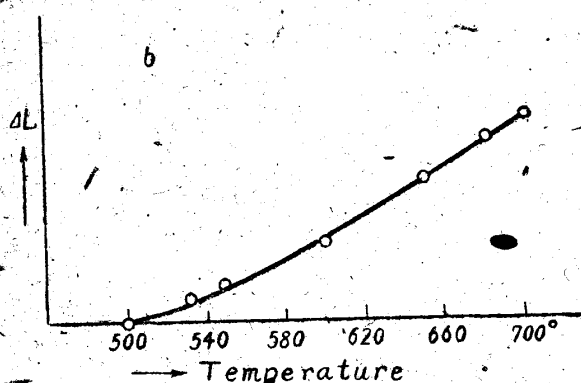


Fig. 8-b. Amounts of contraction at every temperature.

8-a are plotted against temperature in Fig. 8-b, from which we see the limiting temperature reducing ΔL to 0 to be just 500°C , that is the temperature at which the lattice transformation arises on cooling. After when the progress of isothermal change at temperatures, 680° , 650° , 600° and 550°C is almost finished, accordingly the alloys reached approximately the equilibrium state at which the two phases are separated, if they were cooled, an anomalous expansion occurs at 455° , 340° , 170°C and below room temperature respectively. From Fig. 3 it is clear that γ phases produced by isothermal transformation at every temperature contain high concentration of Ni, becoming higher as the heating temperatures are lowered. Results obtained in the case of 5% Ni are quite similar as above, and they are shown in Fig. 6, in which the limiting temperature of $\Delta L=0$ coincides also with the transformation temperature on cooling. In the case of 20% Ni the coexisting range exists in lower temperature. Thus such a isothermal change as in the case of 10% Ni can take place only in the range of comparatively high temperature, near the upper limit of coexisting region due to its small diffusivity. Consequently the lower limit can hardly be determined by the above method. But we may suppose that the temperature of lattice transformation of this alloy on cooling corresponds to its lower limit of coexisting range of two phases as in the case of 10% Ni and 5% Ni.

The upper limit of coexisting range is also determined by the similar method from temperature at which amount of contraction ΔL has a maximum value, and such a temperature too coincides with that of lattice transformation on heating. Fig. 9 shows the phase boundaries between γ and α in the state of equilibrium determined from temperatures of lattice transformation on heating and cooling based on these facts. Thus, we can conclude that only a precipitation of α phases or γ phases is taken place through the process of diffusion when γ phases of the alloy are supercooled or α phases are overheated beyond the GC line on which their free energies of the same concentration of Ni are the same, and the transformation of crystal lattice alone can occur at the time when

they are supercooled or overheated beyond the lower limit or the upper limit of coexisting region of two phases.

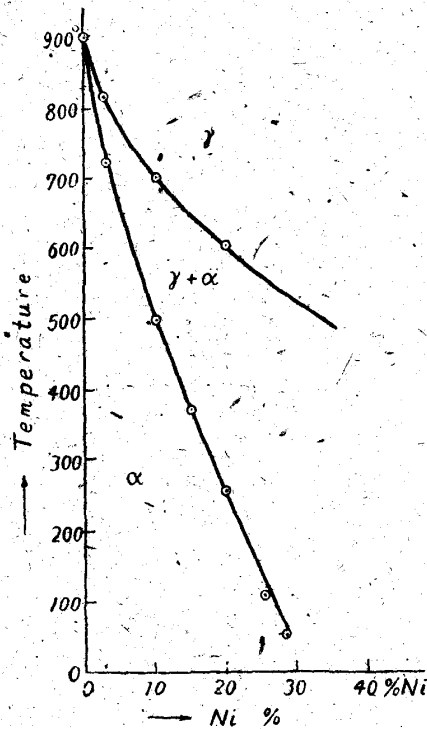


Fig. 9. Phase boundaries between γ and α determined from lattice transformation-temperatures.

In conclusion, the author wishes to express his hearty thanks to Dr. K. Iwase, Prof. of the Tohoku University under whose kind guidance the present investigation was carried out.

Summary.

The characteristics of Fe-Ni alloy, its A_1 transformation and phase boundary between γ and α in the solid state, have been studied. It was concluded that, on cooling or heating with a marked hysteresis, the lattice alone can be transformed without any change of concentration. And such a lattice transformation was found to occur only at the time when the alloy was superheated or supercooled beyond the coexisting region of two phases. The equilibrium diagram of the alloy in the solid state was drawn from the temperature of lattice transformation.

References

- (1) Marsh, Alloys of Iron and Nickel, Vol. 1 (1938), p.
- (2) E. A. Owen, and W. Williams, Nature, 142 (1938), 999.
- (3) A. J. Bradley, Nature, 143 (1939), 518.