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journal or publication title	Science reports of the Research Institutes, Tohoku University. Ser. A, Physics, chemistry and metallurgy
volume	19
page range	35-49
year	1967
URL	http://hdl.handle.net/10097/27346

Structural Diagrams and Phase Reactions of Fe-Cr-N Ternary System*

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(Received March 7, 1967)

Synopsis

Isothermal structural diagrams of Fe-Cr-N system in the range of composition from 0 to 40% chromium and up to 1% nitrogen were described at various temperatures below 1300°C. From the considerations on the phase relationship and the phase reaction, the structural diagrams were also obtained with various cross-sections at 0.1, 0.2 and 0.3% nitrogen, and 7, 13, 18 and 26% chromium. In this ternary system, the existence of the following three invariant reactions was presumed: (1) $L+\alpha \rightleftarrows \gamma+Cr_2N$ at about 1330°C, (2) $\gamma+Cr_2N \rightleftarrows \alpha+CrN$ at about 790°C and (3) $\gamma+CrN \rightleftarrows \alpha+Fe_4N$ at about 760°C.

I. Introduction

In recent years much attention has been paid to the role of nitrogen as a component in heat-resisting alloys. The purpose of the present study is to obtain structural diagrams when nitrogen is added to Fe-Cr alloys which are the basic compositions of heat-resisting alloys.

As to the phase diagrams of Fe-Cr-N system, hardly anything is known, except that Turkdogan et al.[(1)] estimated phase boundaries of α and γ regions at 1200° to 1370°C from the experiment on the equilibrium under various partial pressures of N_2 gas, and that Okamoto et al.[(2)] studied the phase reaction of the liquid surface. Unlike the phase diagram of general alloys, in the diagram of Fe-Cr-N system containing the gas phase the pressure of N_2 must be taken into account, and similar to the cases of Fe-N and Cr-N systems, it is very difficult to make the phase diagram over all compositions. Accordingly, in the present study, examinations were made of these alloys in the composition ranging from 0 to 40% of chromium and from 0 to 1% of nitrogen and at temperatures below 1300°C, in which the equilibrium pressure of nitrogen is less than a few atmospheres.

II. Specimens and experimental methods

The descriptions of the method of preparing the alloys, their chemical compositions and the experimental procedures were omitted here, because the

* The **1299th** report of the Research Institute for Iron, Steel and Other Metals.

(1) E.T. Turkdogan and S. Ignatowicz, J. Iron Steel Inst., **199** (1961), 287.
(2) M. Okamoto and T. Naito, Tetsu-to-Hagané, **49** (1963), 1915.

present work is based on the previous results(3).

As in the previous work(3), the heat-treatments were done by inclosing the specimens in quartz tubes made in conformity with the size of the specimen in order to prevent the evacuation of nitrogen and to obtain homogeneous structure. The structural diagram thus obtained must be close to that projected toward the temperature-concentration plane of the space diagram of the pressure-temperature-concentration. From this point of view, the isothermal sectional diagrams of Fe-Cr-N ternary system were examined below 1300°C, and the vertical sectional diagrams were made of various compositions of nitrogen or chromium.

III. Experimental results and considerations

1. Isothermal structural diagrams

Based on the previous results on microstructures and nitrides(3), the structural diagrams of the isothermal sections at various temperatures in the range of 1300° to 700°C were obtained. Figs. 1 to 8 show the structural diagrams at 1300°, 1200°, 1100°, 1050°, 1000°, 900°, 800° and 700°C, respectively. In making each diagram, the attentions were paid to the following points: (1) Hansen's binary equilibrium diagrams were used for the ordinate of Fe-Cr system and for the abscissa of Fe-N system. (2) The boundary line of the three-phase region in the ternary system is linear and the composition of each phase in the triangle is shown at each apex. According to the previous results(3), the chemical formulas of Cr_2N and CrN were $(Cr_{0.97}Fe_{0.03})_2N$ and $(Cr_{0.95}Fe_{0.05})N$, respectively. Therefore, the boundary lines between $\alpha+\gamma+Cr_2N$ and $\alpha+Cr_2N$, between $\alpha+\gamma+Cr_2N$ and $\gamma+Cr_2N$, and between $\alpha+CrN+Cr_2N$ and $\alpha+Cr_2N$, the the boundary lines between $\alpha+CrN+Cr_2N$ and $\gamma+CrN$ and between $\alpha+CrN+Fe_4N$ and $\alpha+CrN$ were so fixed that their prolongations reach the compositions of $(Cr_{0.97}Fe_{0.03})_2N$ and $(Cr_{0.95}Fe_{0.05})$ N, respectively. The chemical composition of Fe_4N being unknown, the boundary line between $\alpha+Fe_4N+CrN$ and $\alpha+Fe_4N$ was drawn based on an presumption. (3) Each phase boundary was fixed by taking into consideration not only the classification of phase in the micro-structure but also the quantitative relation among phases. The regions without the structural designations ($\alpha+\gamma+Cr_2N$ region in the range 1100° to 1300°C and $\gamma+Cr_2N$ region in the range 800° to 1000°C) were shown by broken lines based on the consideration of the phase relationship. (4) In α phase of the alloys in high chromium range shown by dotted lines in Figs. 1 to 3, the non-equilibrium phase, (Cr_2N), separates finely in spite of an abrupt cooling as described in the previous report(3).

As seen in Fig. 1, the regions of α, $\alpha+\gamma$ and γ occupy quite large field in the diagram at 1300°C, and the regions containing Cr_2N exist when the chromium content is more than 35%. This figure shows that nitrogen expands the γ region of Fe-Cr system, and that the solubility of nitrogen in α coexisting with γ increases with

(3) Y. Imai, T. Masumoto and K. Maeda, Sci. Rep. RITU, **A 19** (1967), 21.

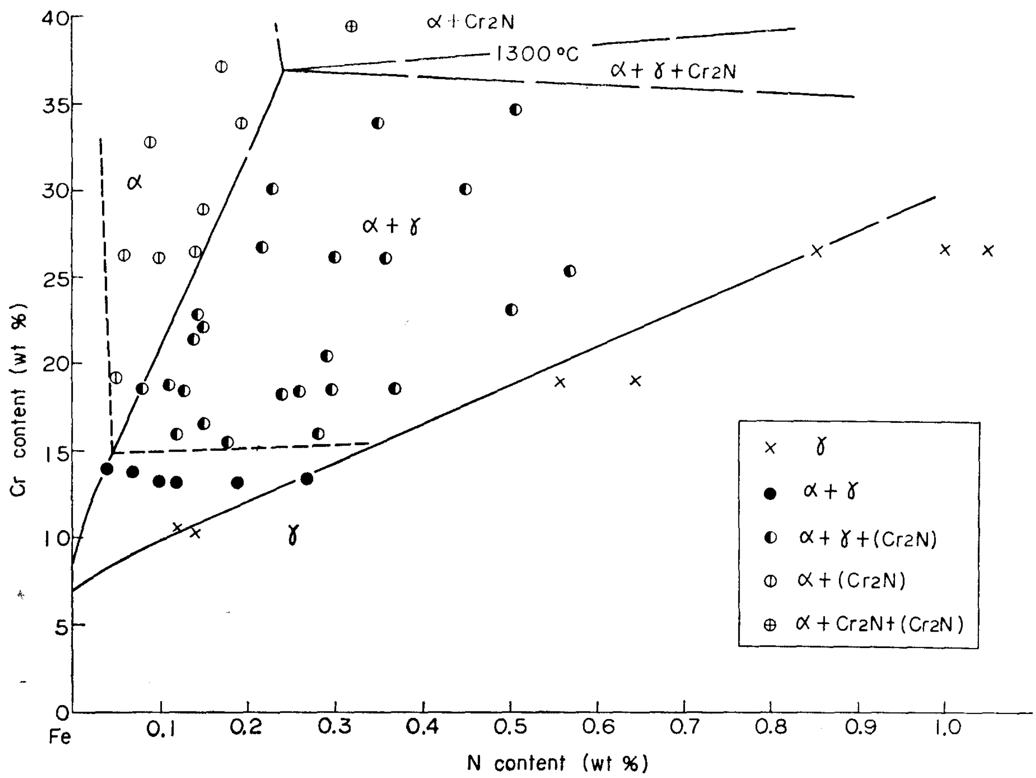

Fig. 1. Isothermal structural diagram of Fe-Cr-N system at 1300°C.

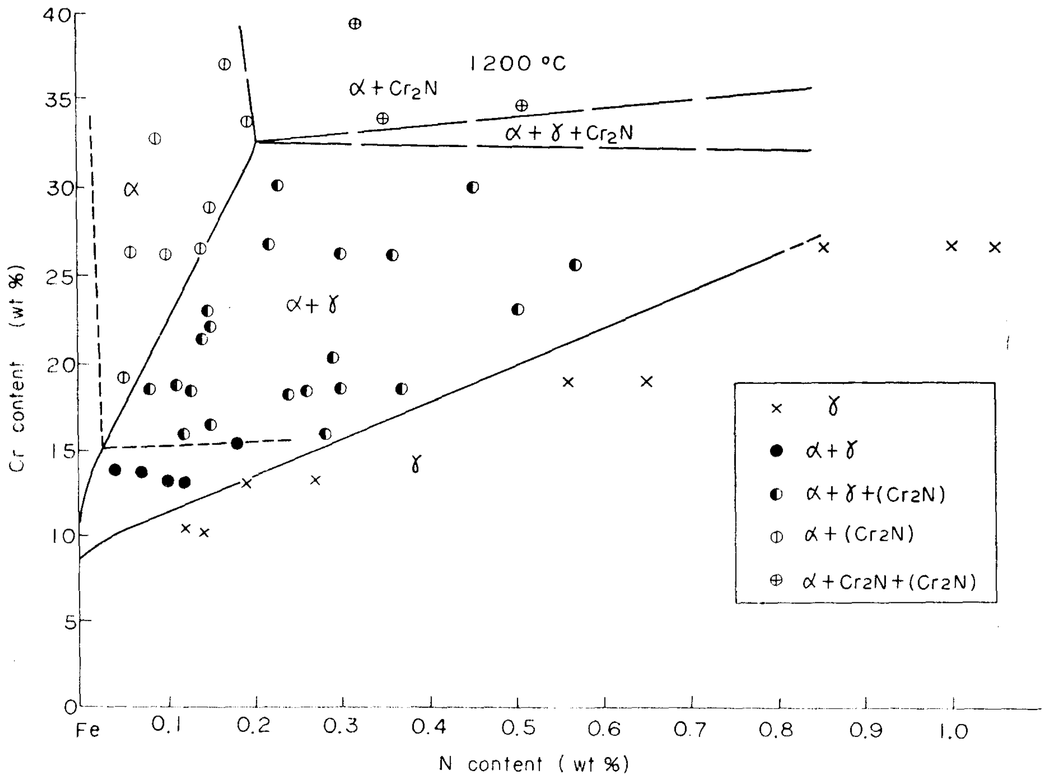

Fig. 2. Isothermal structural diagram of Fe-Cr-N system at 1200°C.

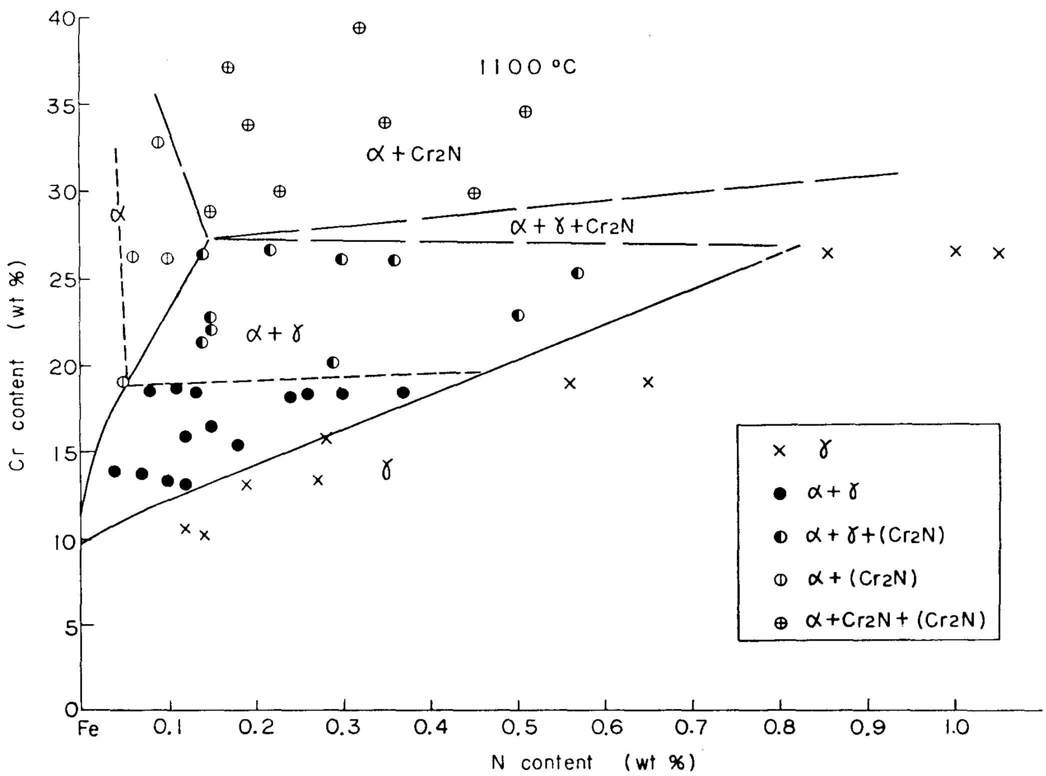

Fig. 3. Isothermal structural diagram of Fe-Cr-N system at 1100°C.

the increase in chromium content, reaching 0.25% of nitrogen with 37% of chromium.

Each of these regions undergoes changes with the fall of temperature; the region of $\alpha+\gamma+Cr_2N$ shifts toward low chromium side, and the region of $\alpha+Cr_2N$ expands in larger field. On the other hand, with the fall of temperature, the solubilities of nitrogen in α and γ are reduced, narrowing α, $\alpha+\gamma$ and γ regions. The solubility of nitrogen in α phase is remarkably reduced between 1100° and 1000°C, becoming less than 0.05%N at 1000°C. The transference of each region, especially of $\alpha+\gamma+Cr_2N$ region becomes pronounced in the temperature range of 900° to 800°C. At 800°C, as shown in Fig. 7, the composition of α phase in the three-phase region of $\alpha+\gamma+Cr_2N$ becomes about 7% chromium content, the region becomes considerably narrow, and the $\alpha+\gamma$ region connects with the $\alpha+\gamma$ region in Fe-N binary system. Below 700°C, the γ phase in the range of compositions of the present case undergoes fully the transformation, becoming all the field of ferrite and nitrides (Fe_4N, CrN and Cr_2N). In Fig. 8, the γ phase ought to be present in low Cr-high N field, but it was impossible to clarify this region in the present study.

Okamoto et al.[2] constructed the isothermal structural diagram of Fe-Cr-N system at 1250°C by nitrogenizing Fe-Cr alloys in NH_3. However, because they considered (Cr_2N) phase separated from α phase during cooling to be an equilibrium phase at that temperature, the $\alpha+\gamma+Cr_2N$ region was broad in field and the

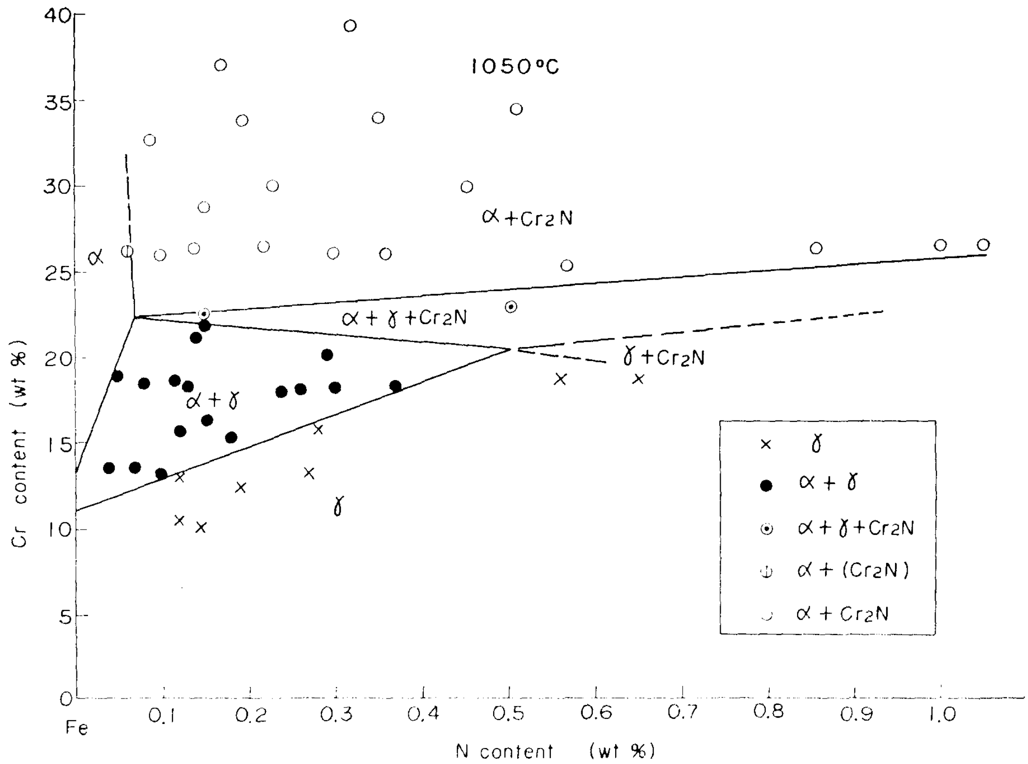

Fig. 4. Isothermal structural diagram of Fe-Cr-N system at 1050°C.

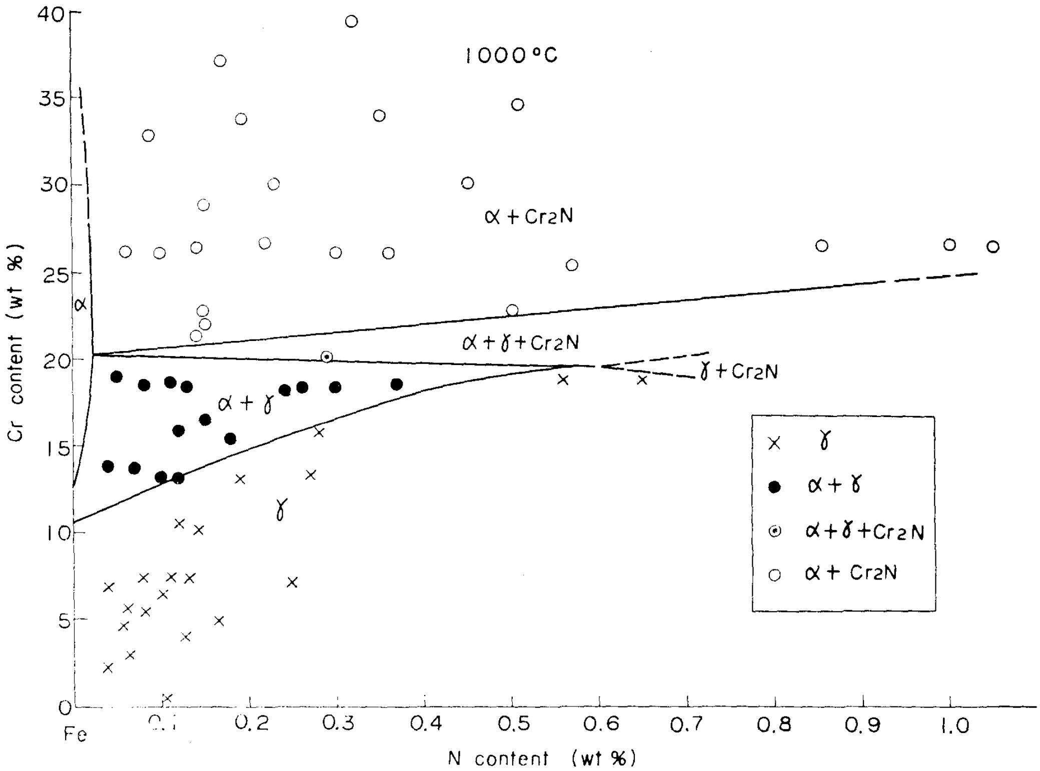

Fig. 5. Isothermal structural diagram of Fe-Cr-N system at 1000°C.

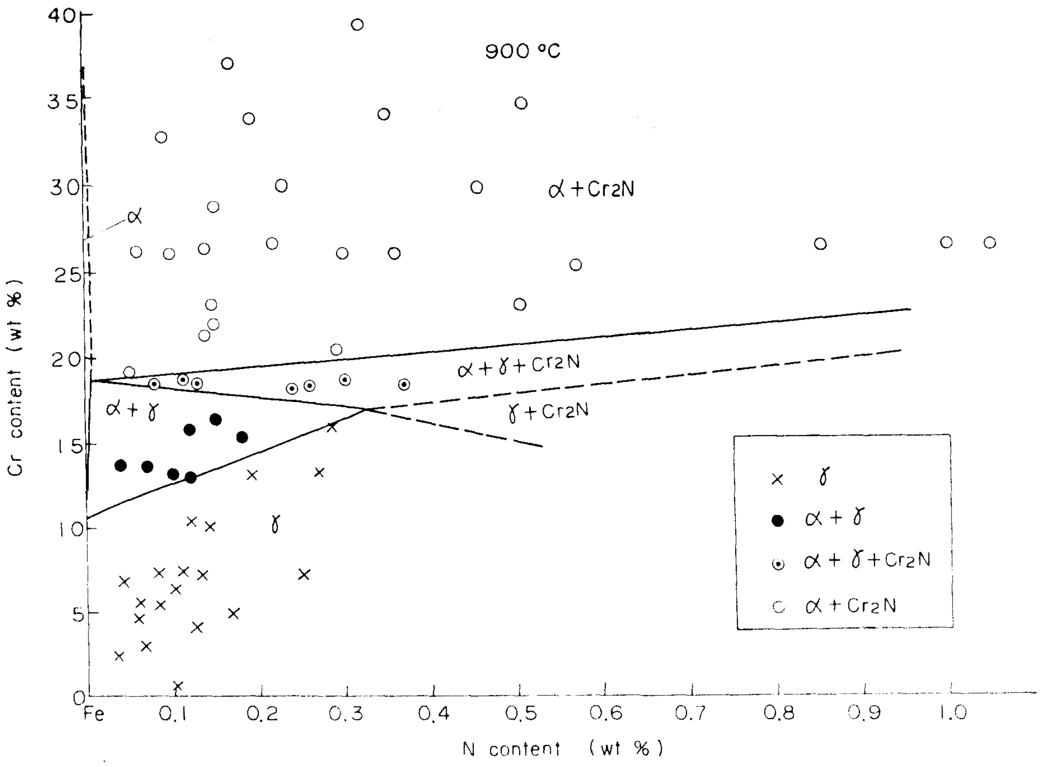

Fig. 6. Isothermal structural diagram of Fe-Cr-N system at 900°C.

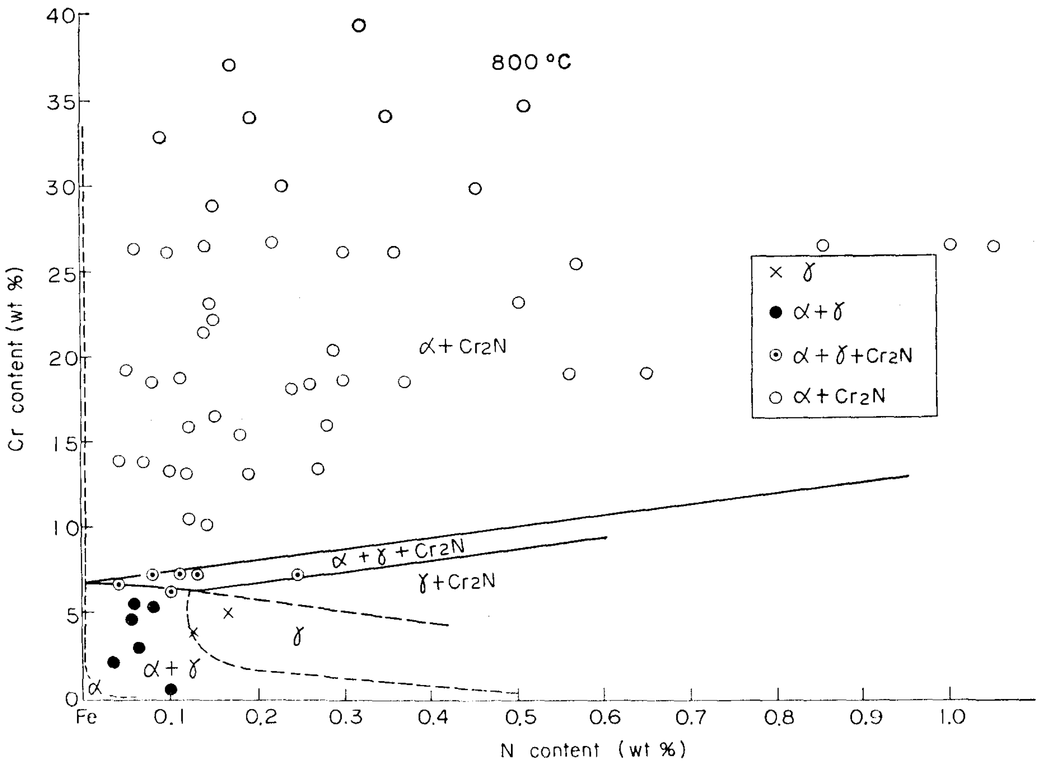

Fig. 7. Isothermal structural diagram of Fe-Cr-N system at 800°C.

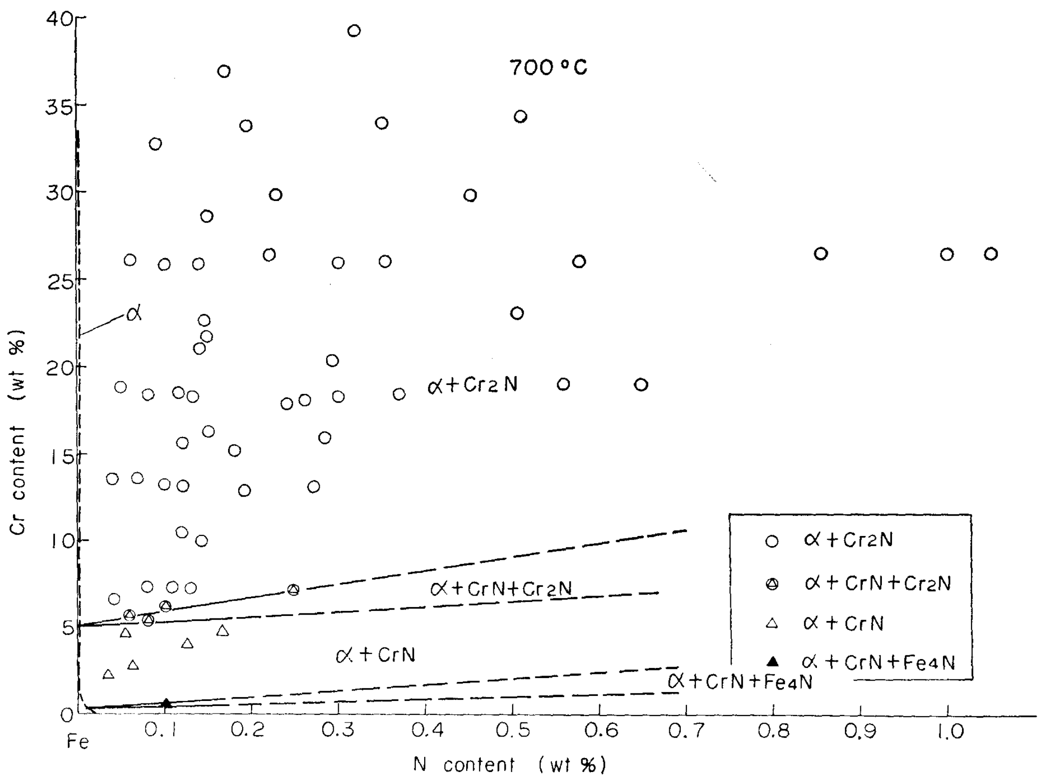

Fig. 8. Isothermal structural diagram of Fe-Cr-N system at 700°C.

prolongation of boundary between $\alpha+\gamma+Cr_2N$ and $\alpha+Cr_2N$ would lead to 1 to 2% of nitrogen content, contradictory to what was expected. If this non-equilibrium phase (Cr_2N) is eliminated out of their phase diagram, the $\alpha+Cr_2N$ region becomes α region and the $\alpha+\gamma+Cr_2N$ region becomes $\alpha+\gamma$ region, closely correspond to the structural diagrams by the present study. On the other hand, Turkdogan et al.(1) found the phase-boundaries of α and γ in Fe-Cr-N system at 1200°C from the equilibrium relation between the N_2 partial pressure and the absorbed nitrogen content. The α, $\alpha+\gamma$ and γ regions obtained in this equilibrium experiment closely correspond to the boundaries shown in Fig. 2.

2. Considerations on phase-reaction

Although the present study dealt mainly with the reaction in solid phase below 1300°C, the phase reaction in the liquid range was presumed in order to explain the phase reaction in solid range.

Okamoto et al.(2) have reported that there are a peritectic reaction $L+\alpha\rightarrow\gamma$ in Fe-N system similar to the case of Fe-C system and a eutectic reaction $L\rightarrow\alpha+Cr_2N$ in Cr-N system, and there ought to be a ternary peritecto-eutectic reaction $L+\alpha\rightarrow\gamma+Cr_2N$ in Fe-Cr-N system at 1328°C, and that the compositions of the four phases participating in this invariant reaction are as follows; L (16% chromium and 0.9% nitrogen), α (37% chromium and 0.05% nitrogen). γ (15% chromium and 0.4% nitrogen) and Cr_2N (11.7% nitrogen).

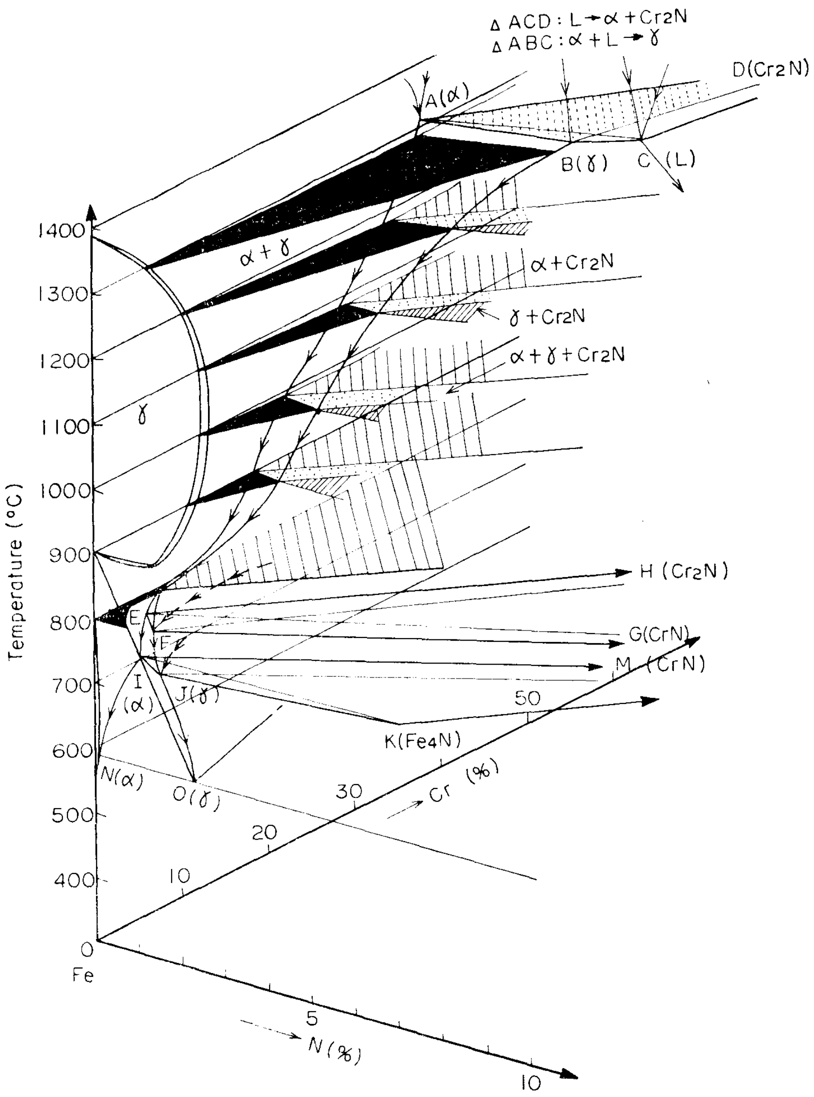

Fig. 9. Schematic space diagram of Fe-Cr-N system.

From the results of the present experiment on the microstructures and the isothermal sectional diagrams, it was estimated that such invariant reaction must be present above 1300°C: Fig. 9 shows three four-phase reaction planes in the space diagram, when the isothermal sectional diagrams in Figs. 1 to 8 is consolidated on the temperature axis. Supposing the ternary peritecto-eutectic reaction plane ($L+\alpha \rightarrow \gamma + Cr_2N$) of the trapezium ABCD at about 1330°C, it will be possible to explain the phase reactions at low temperatures. The compositions of α and γ phases in the invariant reaction assumed from the present experiment is about 39% chromium and 0.25% nitrogen and about 35% chromium and 1.3% nitrogen, respectively, which differ considerably from the values obtained by Okamoto et al.[2] These differences seem to be due to the circumstances that they have included the (Cr_2N) of non-equilibrium phase separated during cooling in the equilibrium diagram.

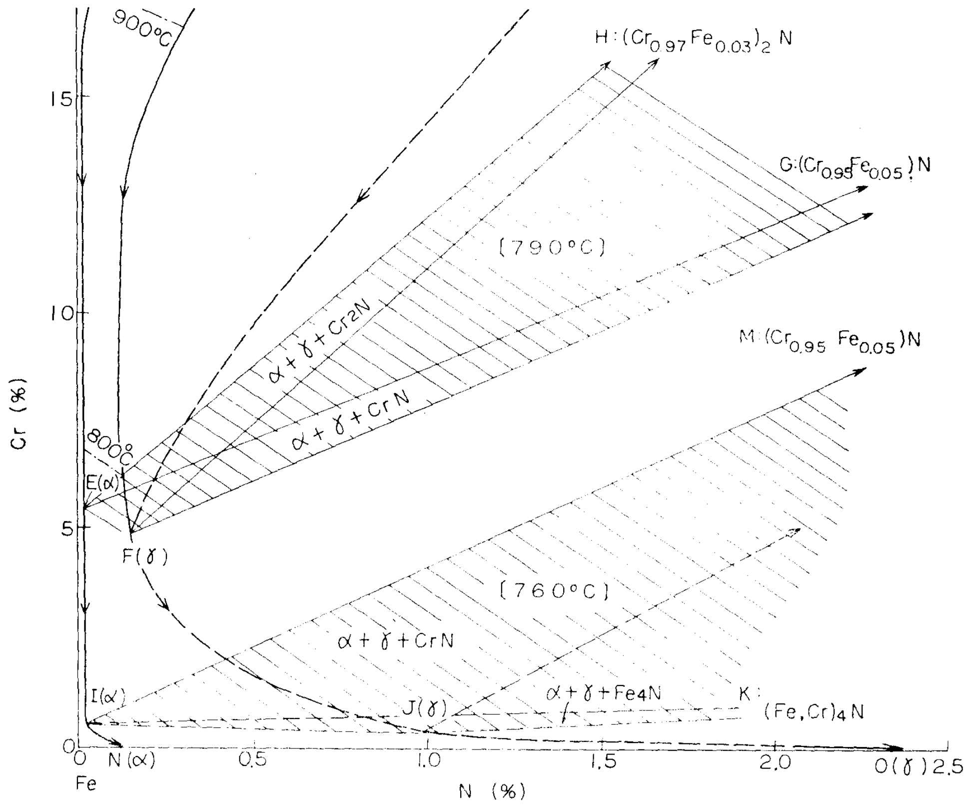

Fig. 10. Tentative reaction diagram in the iron-rich corner of Fe-Cr-N system in temperature range below 900°C.

One of new tie-triangle ABC ($\alpha+\gamma+Cr_2N$) formed after the reaction shifts toward low chromium side with the fall in temperature. It was confirmed that there were two invariant reaction planes at 790° and 760°C, respectively. That is, as seen in Fig. 8, there are two three-phase regions, $\alpha+CrN+Cr_2N$ and $\alpha+CrN+Fe_4N$, and the alloys whose compositions are within these two three-phase regions undergo the following phase reactions with the process of cooling; the former undergoes $\gamma\rightarrow\alpha+\gamma\rightarrow\alpha+\gamma+Cr_2N\rightarrow\alpha+CrN+Cr_2N$ and the latter $\gamma\rightarrow\alpha+\gamma\rightarrow\alpha+\gamma+CrN\rightarrow\alpha+CrN+Fe_4N$. Consequently, it is necessary to presume the existence of two-phase or four-phase region between two three-phase regions in the reactions, such as $\alpha+Cr_2N$ or $\alpha+\gamma+Cr_2N+CrN$ in the former and $\alpha+CrN$ or $\alpha+\gamma+CrN+Fe_4N$ in the latter. In Fig. 10 are shown two four-phase reaction trapeziums based on the transitions of three-phase regions in the isothermal sectional diagrams with the fall of temperature. It is seen from the figure that one of the two tie-triangles to form the four-phase reaction plane $\square$ EFGH is the three-phase region $\alpha+\gamma+Cr_2N$ which has descended from the four-phase reaction plane $\square$ ABCD, and this reaction is conceived to be the eutectoid reaction of $\gamma\rightarrow\alpha+Cr_2N$, considering from the micro-structure and the transition of the tie-triangle with the fall in temperature, while the other tie-triangle $\gamma+Cr_2N+CrN$ is conceived from the considerations of the phase reaction to be a peritectoid reaction $\gamma+Cr_2N\rightarrow CrN$. Consequently, the invariant four-phase reaction plane □ EFGH is formed by two three-phase reaction regions, undergoing the ternary peritecto-eutectoid reaction $\gamma+Cr_2N\rightarrow\alpha+CrN$. The temperature of this reaction plane was estimated to be about 790°C from the microstructural changes. After the completion of the ternary peritecto-eutectoid reaction, it forms two new tie-triangles, EGH ($\gamma+Cr_2N+CrN$) and EFG ($\alpha+\gamma+CrN$). The former descends to room temperature without any change, while the latter leads to the invariant reaction plane □ IJKM. It is conceivable from the microstructure and the phase reaction that the reaction in the IJM region ($\alpha+\gamma+CrN$) is a eutectoid reaction of $\gamma\rightarrow\alpha+CrN$, while the MJK region ($\gamma+CrN+Fe_4N$) is considered from the phase reaction to be the peritectoid reaction of $\gamma+CrN\rightarrow Fe_4N$. Accordingly, the reaction in the IJKM region is the ternary peritecto-eutectoid reaction of $\gamma+CrN\rightarrow\alpha+Fe_4N$. The temperature of reaction plane was estimated to be about 760°C from the micro-structural changes. After the completion of the ternary peritecto-eutectoid reaction, two new tie-triangles, IKM ($\alpha+CrN+Fe_4N$) and IJK ($\alpha+\gamma+Fe_4N$), originate. The former descends to room temperature without any change and the latter shifts to a eutectoid reaction ($\gamma\rightarrow\alpha+Fe_4N$) at 590°C present in Fe-N binary system, completing the decomposition of γ.

3. Vertical sectional diagrams in various compositions

Based on the considerations of the isothermal sectional diagrams and the phase reactions, the vertical sectional diagrams were made of the compositions of 0.1, 0.2 and 0.3% of nitrogen content, and 7, 13, 18 and 26% of chromium content. These diagrams are shown in Figs. 11 to 17. The designations of structural component plotted in the diagrams represent the microstructures of the alloys with the compositions near the given sectional diagram. The (CrN) phase shown in the diagrams is a non-equilibrium phase separated finely in α phase during cooling and it is difficult to suppress its separation.

(i) Vertical sectional diagrams of Fe-Cr-N system at various nitrogen contents

In Figs. 11 to 13 are shown the sectional diagrams at 0.1, 0.2 and 0.3% of nitrogen, respectively. In Fe-Cr alloys containing nitrogen, the γ region extends toward higher chromium side with the increase of nitrogen content. The maximum chromium content to obtain a completely austenitic structure is expressed by the equation, $[Cr\%]=11.0+18.2[N\%]$. The austenite in γ and $\alpha+\gamma$ regions undergoes the phase transition into the structure of ferrite and nitrides (Fe_4N, CrN and Cr_2N) by cooling; For example, in the vertical sectional diagram at 0.1% nitrogen, into $\alpha+CrN+Fe_4N$ in chromium contents less than about 0.5%, into $\alpha+CrN$ in about 0.5 to 5.5% chromium, into $\alpha+CrN+Cr_2N$ in about 5.5 to 6.5% chromium, and into $\alpha+Cr_2N$ in more than about 6.5% chromium. The two invariant reactions considered to be the ternary peritecto-eutectoid reaction are present in the vicinity of about 0.5% and at 5.5 to 6.5% of chromium content, respectively, the former being $\gamma+CrN\rightarrow\alpha+Fe_4N$, and the latter $\gamma+Cr_2N\rightarrow\alpha+CrN$.

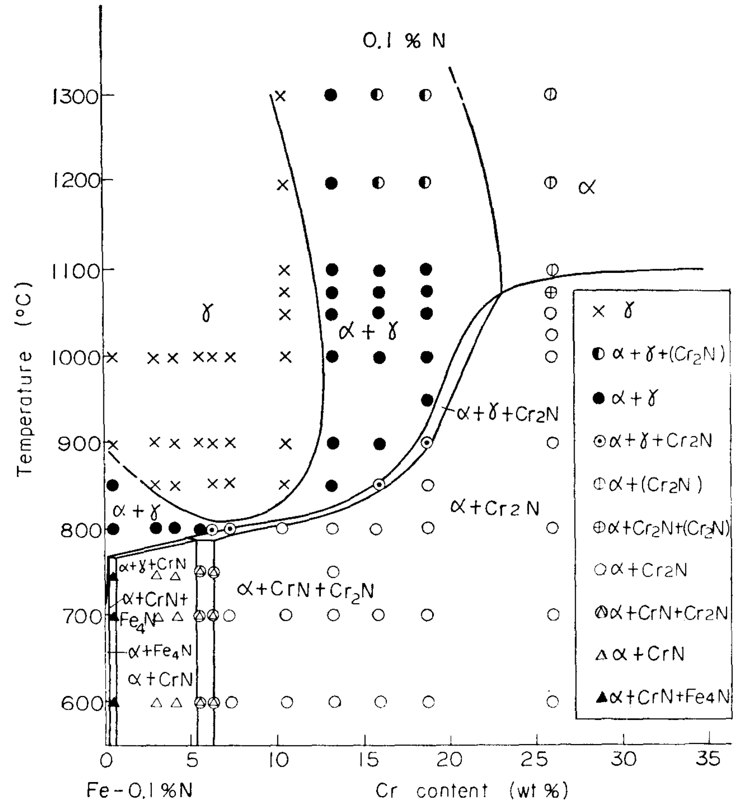

Fig. 11. Section diagram of Fe-Cr-N system at 0.1% N.

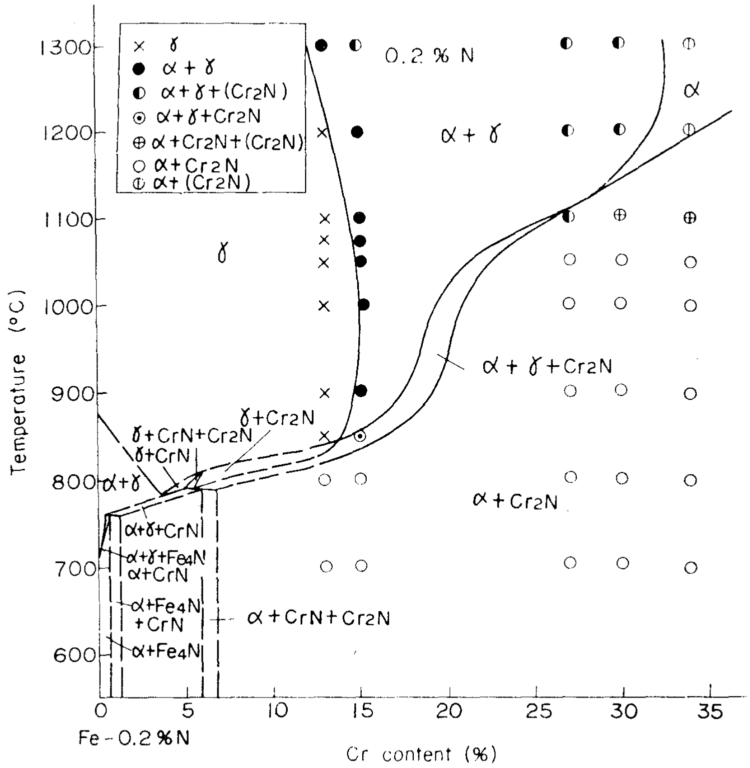

Fig. 12. Section diagram of Fe-Cr-N system at 0.2% N.

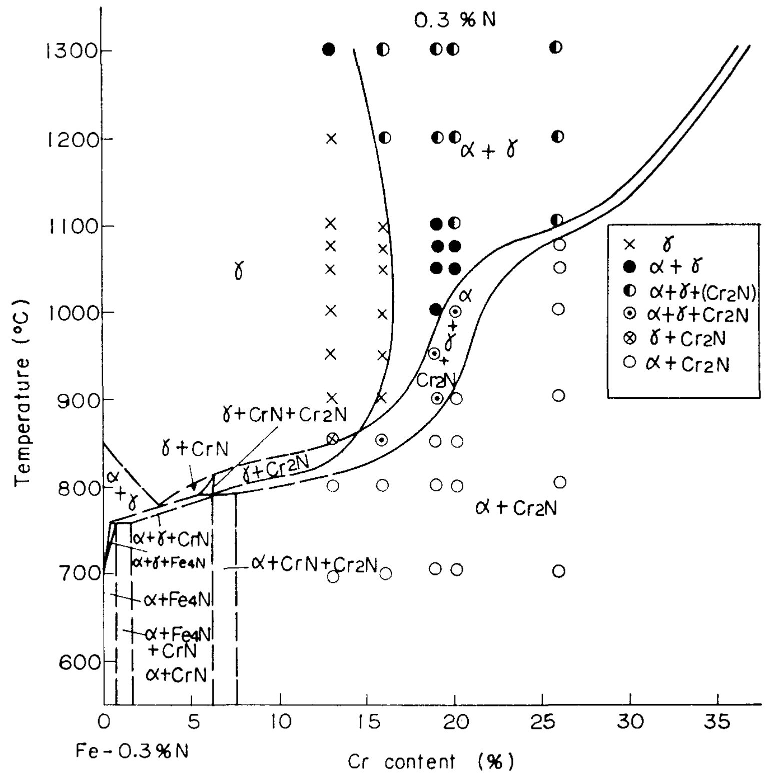

Fig. 13. Section diagram of Fe-Cr-N system at 0.3% N.

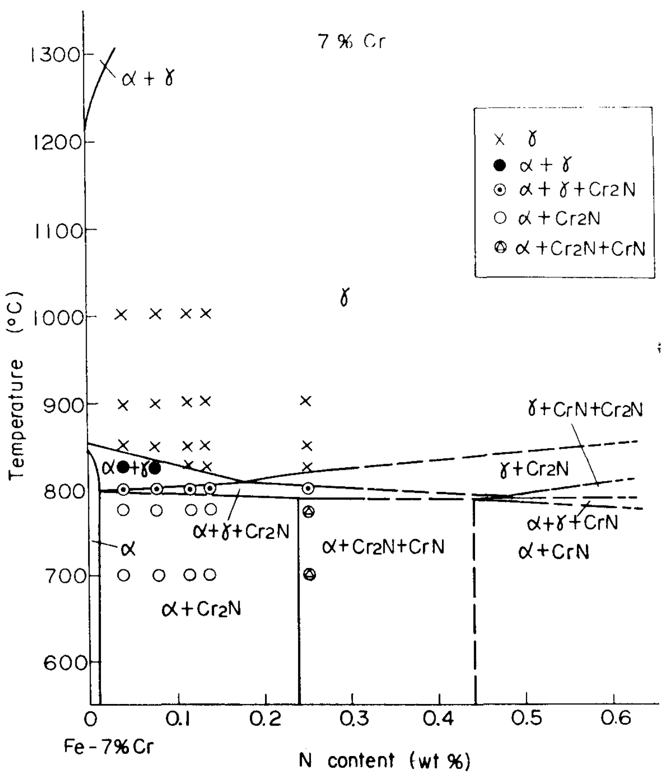

Fig. 14. Section diagram of Fe-Cr-N system at 7% Cr.

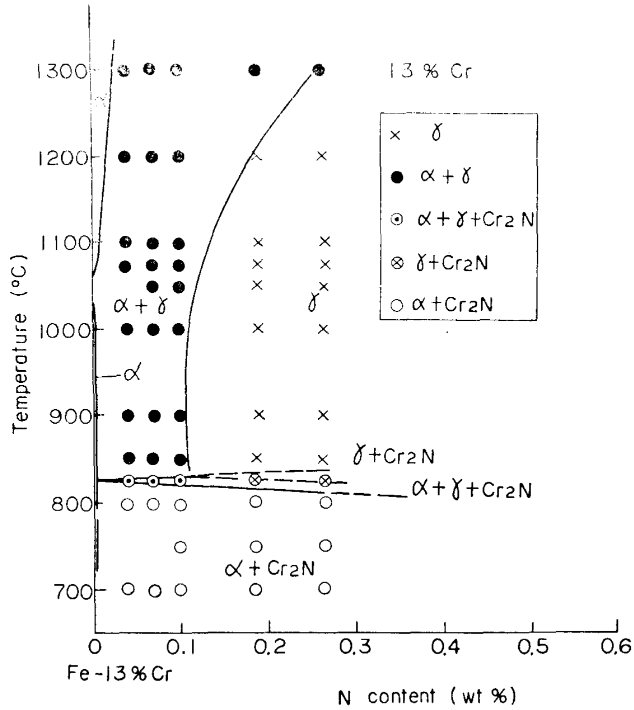

Fig. 15. Section diagram of Fe-Cr-N system at 13% Cr.

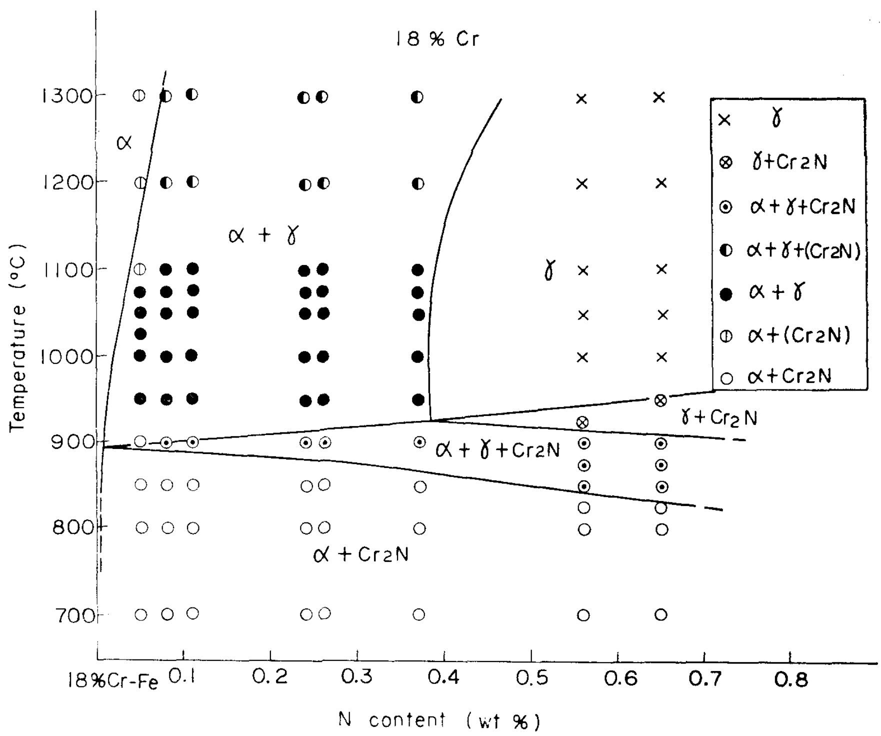

Fig. 16. Section diagram of Fe-Cr-N system at 18% Cr.

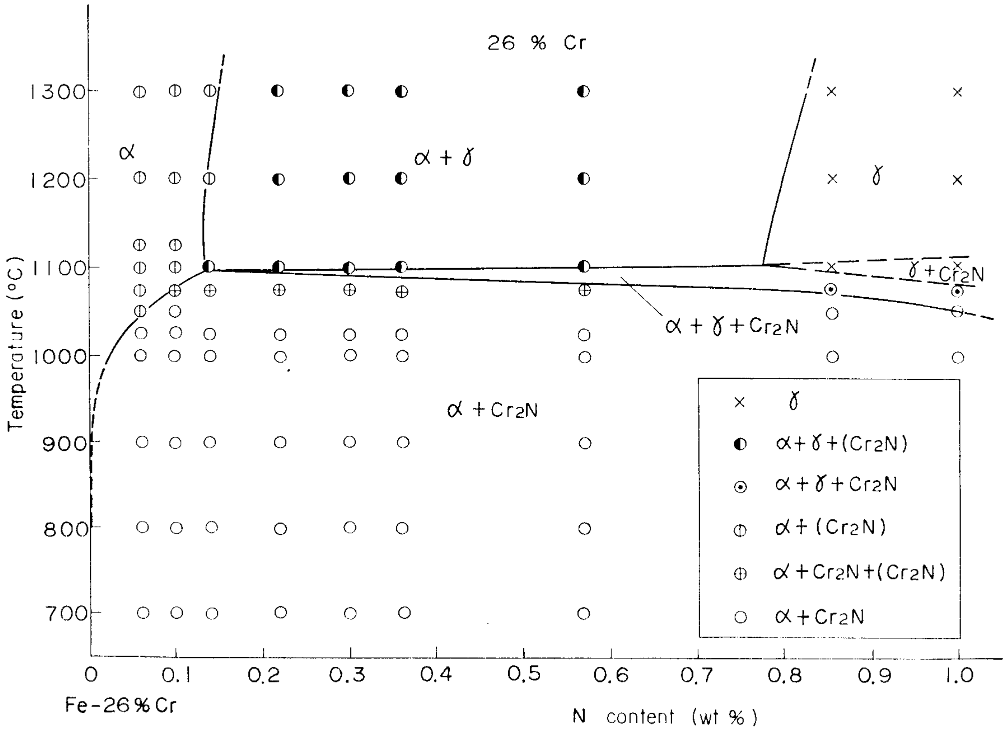

Fig. 17. Section diagram of Fe-Cr-N system at 26 % Cr.

(ii) Vertical sectional diagrams at various chromium contents

Figs. 14 to 17 show the sectional diagrams of Fe-Cr-N system at 7, 13, 18 and 26% chromium contents. As seen in these figures, the boundary between γ and $\alpha+\gamma$ regions shifts toward higher nitrogen content with the increase of chromium content, the minimum nitrogen content of this boundary being expressed by the equation [N%]=[Cr%]/18.2–0.6. The austenite transfers to $\alpha+Cr_2N$ structure through the eutectoid reaction $\gamma \rightarrow \alpha+Cr_2N$ in the $\alpha+\gamma$ region, and through the reactions $\gamma \rightarrow Cr_2N$ and $\gamma \rightarrow \alpha+Cr_2N$ in the simple γ region.

Summary

Based on the previous experimental results on the micro-structures and the nitrides of the alloys of Fe-Cr-N ternary system, the isothermal sectional diagrams below 1300°C were defined in the range of 0 to 40% chromium and with up to about 1% nitrogen. From these results and the assumed phase reaction, the vertical sectional diagrams were described for various chromium contents of 7, 13, 18 and 26% and for various nitrogen contents of 0.1, 0.2 and 0.3%. The results may be summarized as follows:

(1) The isothermal sectional diagrams at high temperatures show that the γ region tends to expand on the high chromium side with the increase of nitrogen content, and that the minimum nitrogen content to obtain a completely austenitic structures is expressed by the equation [N%]=[Cr%]/18.2–0.6. In higher chromium side above this γ region, $\alpha+\gamma$, $\alpha+\gamma+Cr_2N$ and $\alpha+Cr_2N$ regions are present. With

the fall in temperature, $\alpha+\gamma+Cr_2N$ region resulting from the decomposition of γ shifts toward low chromium side, making the γ an $\alpha+\gamma$ regions narrow. The nitrogen solubilities in α and γ are remarkably reduced with the fall in temperature.
(2) The phase reactions in Fe-Cr-N system were considered as follows; at about 1330°C, the peritecto-eutectic reaction, $L+\alpha\leftrightarrows\gamma+Cr_2N$, is present, a new tie-trianlge of $\alpha+\gamma+Cr_2N$ shifts toward low chromium side with the fall in temperature, and at about 790°C the ternary peritecto-eutectoid reaction causes by the connection of two tie-triangles, $\alpha+\gamma+Cr_2N$ ($\gamma\rightarrow\alpha+Cr_2N$) and $\gamma+CrN+Cr_2N$ ($\gamma+Cr_2N\rightarrow CrN$). After the completion of reaction a new tie-triangle of $\alpha+\gamma+CrN$ ($\gamma\rightarrow\alpha+CrN$) shifts further toward low chromium side, and at about 760°C, it together with another tie-triangle of $\gamma+CrN+Fe_4N$ causes a ternary peritecto-eutectoid reaction $\gamma+CrN\leftrightarrows\alpha+Fe_4N$. After this reaction, a new tie-triangle $\alpha+\gamma+Fe_4N$ ($\gamma\rightarrow\alpha+Fe_4N$) descends toward a eutectoid line of Fe-N system at 590°C.