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Structural Diagrams and Phase Reactions of the Quaternary 12%Cr-Fe-C-N System*

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Synopsis

The isothermal diagrams of the 12%Cr-Fe-C-N system in the composition range up to 0.4% carbon and 0.3% nitrogen were studied at temperatures from 1300°C to 700°C. Resorting to the consideration of phase relationship, the phase reaction of 12%Cr-Fe-C-N system was clarified and the sectional diagrams were constructed at fixed contents of 0.1% and 0.2% nitrogen and carbon, respectively. In Fe-Cr-C-N system, the quaternary peritecto-eutectoid reaction ($\gamma + \text{Cr}_{23}\text{C}_6 \rightleftharpoons \alpha + \text{Cr}_7\text{C}_3 + \text{Cr}_2\text{N}$) exists at about 780°C, representing by the hexahedron of five-phase region consisting of α , γ , Cr_{23}C_6 , Cr_7C_3 and Cr_2N . The Cr_7C_3 type carbide detected in the present work is expressed by the formula $(\text{Fe}_2\text{C}_5)\text{C}_{2.4}\text{N}_{0.6}$.

I. Introduction

The respective effect of carbon and nitrogen on the structural constitutions of Fe-Cr alloys have already been clarified.^{(1)~(3)} However, it is important to know their mutual effects of carbon and nitrogen on the constitutions of Fe-Cr alloys, since Fe-Cr alloys used in industry usually contain both nitrogen and carbon. So far, there is only one published work in this system determined by Tisinai et al.,⁽⁴⁾ that is the structural diagram of Fe-Cr-C-N system limited at temperatures above about 1200°C in the range of compositions containing from 21 to 33% of chromium and up to 1% carbon and nitrogen, respectively. At present, the structural diagrams and phase relationships of Fe-Cr-C-N system are left to be clarified. So the structural diagrams and the phase reactions of Fe-Cr-C-N system at 18% chromium have been investigated in the previous paper⁽⁵⁾ and the same system at 12% chromium in the present work.

II. Specimens and experimental methods

The thirty-nine alloys used in the present work were prepared by melting in air

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Table 1. Chemical composition of specimens.

No.	Element (wt%)			No.	Element (wt%)		
	N	C	Cr		N	C	Cr
1	0.007	0.11	12.23	21	0.15	0.12	12.19
2	0.008	0.15	12.82	22	0.15	0.27	12.21
3	0.01	0.28	12.38	23	0.15	0.36	12.40
4	0.01	0.40	12.55	24	0.16	0.041	12.21
5	0.04	0.010	13.83	25	0.16	0.14	12.32
6	0.049	0.36	12.03	26	0.16	0.15	11.57
7	0.050	0.23	12.63	27	0.16	0.20	12.30
8	0.051	0.11	12.29	28	0.16	0.22	12.30
9	0.055	0.11	12.46	29	0.16	0.38	12.40
10	0.057	0.055	11.92	30	0.17	0.056	12.30
11	0.07	0.014	13.74	31	0.17	0.26	12.30
12	0.090	0.37	11.87	32	0.17	0.28	12.33
13	0.095	0.20	12.70	33	0.18	0.075	12.09
14	0.10	0.013	13.21	34	0.18	0.14	12.33
15	0.10	0.26	12.60	35	0.19	0.012	13.21
16	0.11	0.015	13.51	36	0.19	0.26	12.61
17	0.11	0.055	12.13	37	0.20	0.072	12.61
18	0.12	0.085	11.90	38	0.22	0.043	12.19
19	0.12	0.16	12.20	39	0.27	0.011	13.37
20	0.15	0.12	11.92				

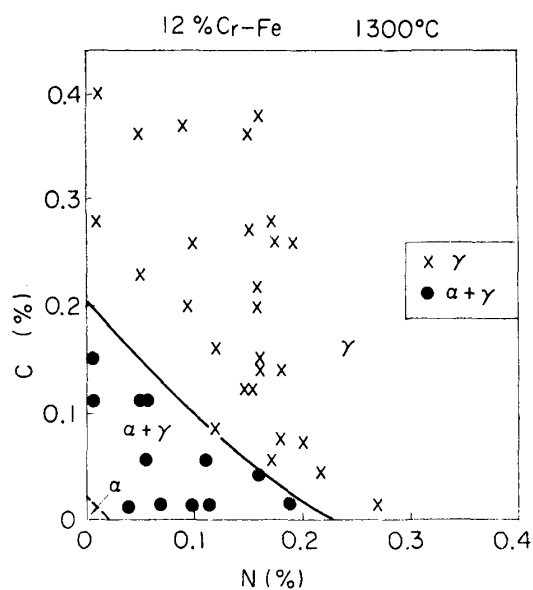


Fig. 1

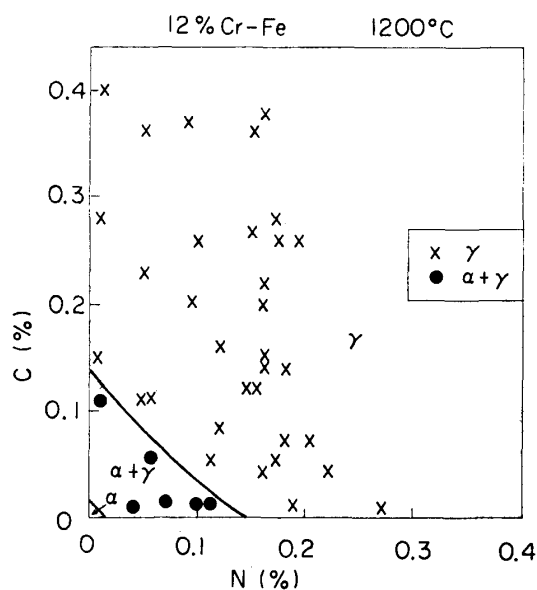


Fig. 2

Fig. 1. Isothermal structural diagram of 12%Cr-Fe-C-N system at 1300°C.

Fig. 2. Isothermal structural diagram of 12%Cr-Fe-C-N system at 1200°C.

electrolytic Fe, electrolytic Cr and the mother alloys of high N-Fe-Cr and high C-Fe with a high frequency induction furnace. The chemical compositions of these alloys are listed in Table 1, in the range of compositions being up to about 0.3% nitrogen and about 0.4% carbon, with a constant chromium content of approximately 12%. In addition, all alloys contain about both 0.2% manganese and silicon.

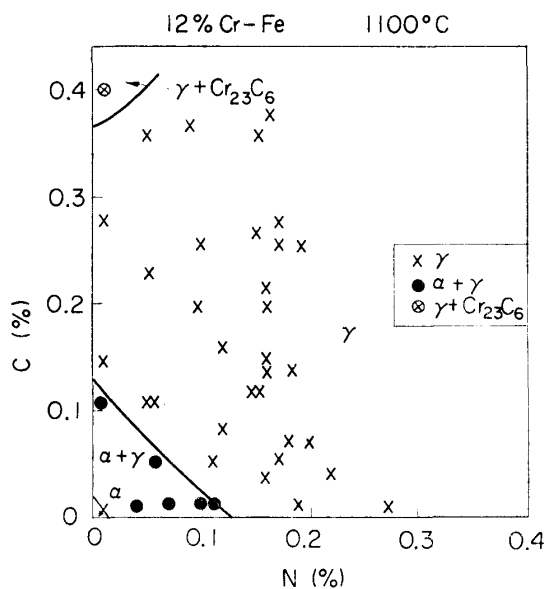


Fig. 3

Fig. 3. Isothermal structural diagram of 12%Cr-Fe-C-N system at 1100°C.

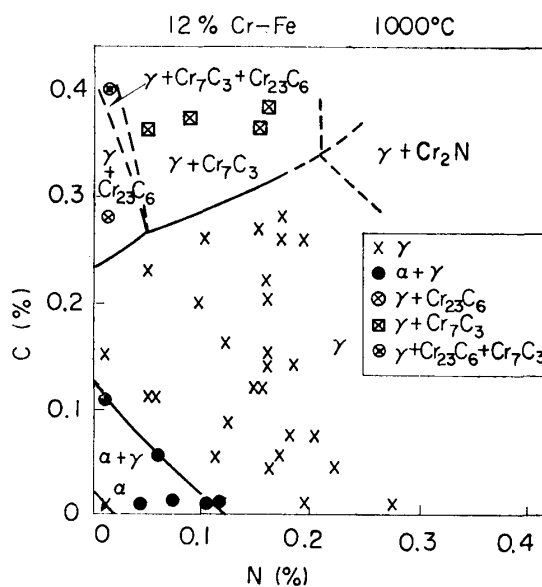


Fig. 4

Fig. 4. Isothermal structural diagram of 12%Cr-Fe-C-N system at 1000°C.

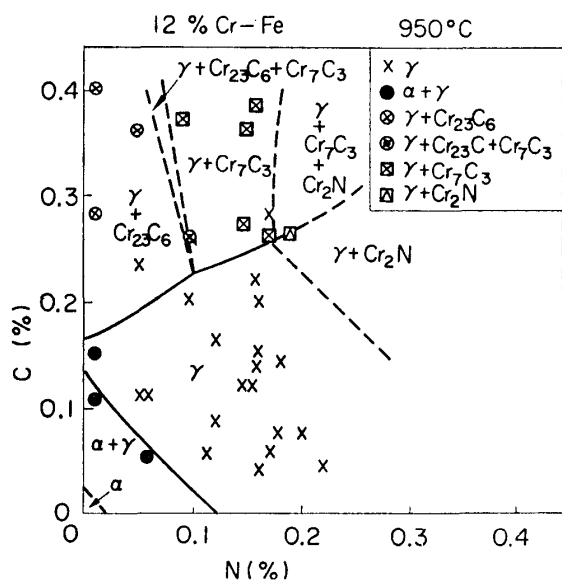


Fig. 5

Fig. 5. Isothermal structural diagram of 12%Cr-Fe-C-N system at 950°C.

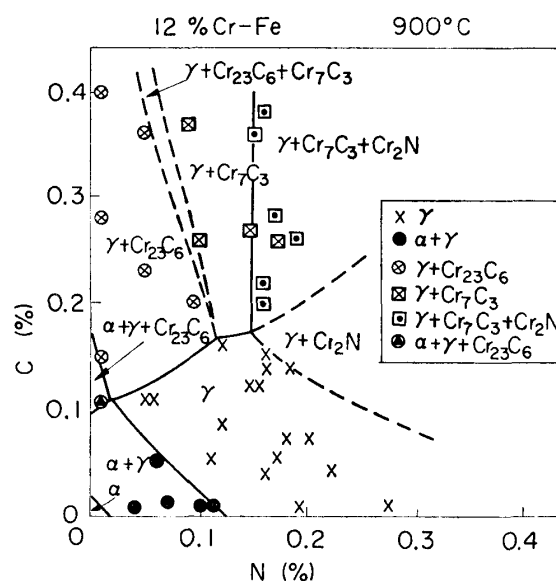


Fig. 6

Fig. 6. Isothermal structural diagram of 12%Cr-Fe-C-N system at 900°C.

The experimental procedures have been described in detail previously.⁽⁵⁾ The specimens were enclosed in quartz tubes in conformity with the size of specimens in vacuum in order to prevent them from denitrogenization and decarburization, and heat-treated. Optical microscope, powder X-ray diffraction and chemical analyses of the extracted residues were used to determine the phase reactions and the structural diagrams.

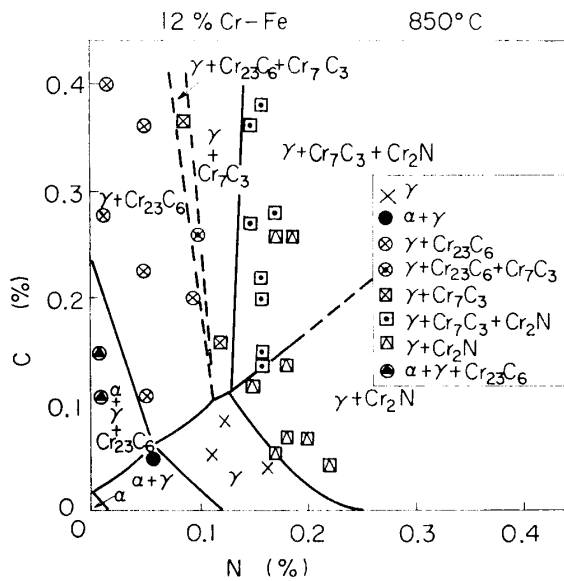


Fig. 7

Fig. 7. Isothermal structural diagram of 12%Cr-Fe-C-N system at 850°C.

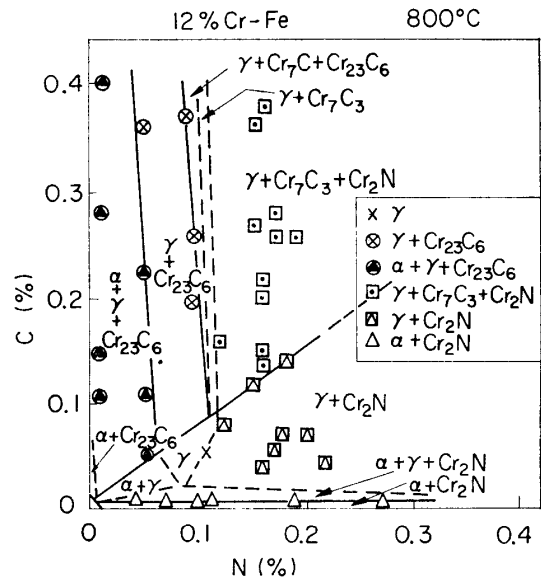


Fig. 8

Fig. 8. Isothermal structural diagram of 12%Cr-Fe-C-N system at 800°C.

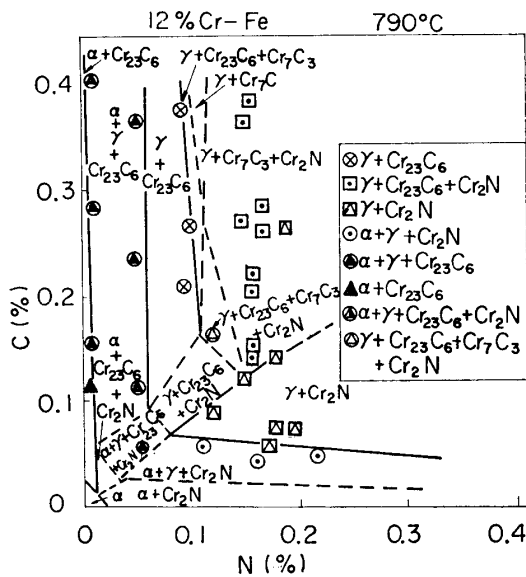


Fig. 9

Fig. 9. Isothermal structural diagram of 12%Cr-Fe-C-N system at 790°C.

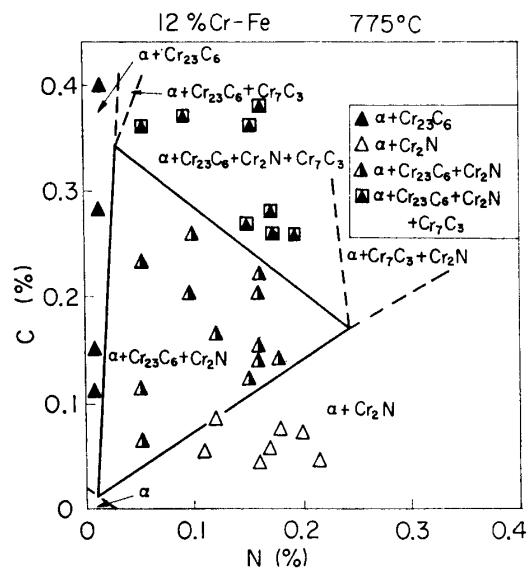


Fig. 10

Fig. 10. Isothermal structural diagram of 12%Cr-Fe-C-N system at 775°C.

III. Experimental results and considerations

1. Isothermal structural diagrams

Based on the observation of microstructures and the identification of precipitates, the isothermal structural diagrams in the 12%Cr-Fe-C-N quaternary system were obtained in the temperature range from 1300° to 700°C.

Fig. 1 to Fig. 10 show the isothermal structural diagrams at 1300°, 1200°, 1100°, 1000°, 900°, 850°, 800°, 790°, 775°, 750°, 700°C.

1100°, 1000°, 950°, 900°, 850°, 800°, 790° and 775°, respectively. Here, the Fe-Cr-C ternary diagram at 12% chromium by Bungardt et al.⁽¹⁾ is used for the ordinate and the Fe-Cr-N ternary diagram at 12% chromium by the present authors⁽³⁾ for the abscissa.

As shown in Figs. 1 and 2, in the temperature range from 1300° to 1200°C, the single phase region of γ exists in the lower content side of carbon and nitrogen than those at 18% chromium quaternary system.⁽⁵⁾ Further the two phase region of $\alpha + \gamma$ and the single phase region of α exist in the low carbon-low nitrogen field.

The austenite-promoting effects of carbon and nitrogen will be very nearly equivalent and additive. The minimum concentration of carbon plus nitrogen required to obtain the completely austenitic structure is about 0.2% at 1300°C and about 0.14% at 1200°C. In consideration of that this concentration at 18% chromium was about 0.4% at 1200°C⁽⁵⁾, it will decrease with decreasing chromium content in this quaternary system.

At 1100°C, as shown in Fig. 4, the two-phase region of $\gamma + \text{Cr}_{23}\text{C}_6$ in the Fe-Cr-C ternary system expands toward high carbon-low nitrogen field. The location of the boundary between α phase and γ phase at 1100°C is almost similar to that at 1200°C.

At 1000°C, as shown in Fig. 4, the regions of $\gamma + \text{Cr}_{23}\text{C}_6$, $\gamma + \text{Cr}_{23}\text{C}_6 + \text{Cr}_7\text{C}_3$ and $\gamma + \text{Cr}_7\text{C}_3$ grow broader toward high carbon-low nitrogen field in the quaternary system. The region of γ phase grows narrow owing to the formation of carbides. Besides, the regions of $\gamma + \text{Cr}_7\text{C}_3 + \text{Cr}_2\text{N}$ and $\gamma + \text{Cr}_2\text{N}$ which were bounded by the dotted lines can be presumed by the investigations at lower temperatures in this system.

At 950°C, as shown in Fig. 5, the region of $\gamma + \text{Cr}_7\text{C}_3$ intersects with the region of $\gamma + \text{Cr}_2\text{N}$ which originates from the Fe-Cr-N ternary system, resulting in the formation of the three-phase region of $\gamma + \text{Cr}_7\text{C}_3 + \text{Cr}_2\text{N}$ in high carbon-high nitrogen field.

At 900°C, as shown in Fig. 6, each region shifts toward lower content side of carbon and nitrogen than those at 950°C. The three-phase region of $\alpha + \gamma + \text{Cr}_{23}\text{C}_6$ occurring owing to the eutectoid reaction of $\gamma \rightarrow \alpha + \text{Cr}_{23}\text{C}_6$ in Fe-Cr-C ternary system⁽¹⁾ expands in the quaternary system.

At 850°C, as shown in Fig. 7, the single phase region of γ further grows narrow and the region of $\alpha + \gamma + \text{Cr}_{23}\text{C}_6$ expands toward higher nitrogen side.

At 800°C, as shown in Fig. 8, the regions of $\gamma + \text{Cr}_{23}\text{C}_6$, $\gamma + \text{Cr}_7\text{C}_3$, $\gamma + \text{Cr}_2\text{N}$, $\gamma + \text{Cr}_{23}\text{C}_6 + \text{Cr}_7\text{C}_3$ and $\gamma + \text{Cr}_7\text{C}_3 + \text{Cr}_2\text{N}$ shift toward lower carbon side and the three-phase region of $\alpha + \gamma + \text{Cr}_{23}\text{C}_6$ grows broader. The region of $\alpha + \gamma + \text{Cr}_2\text{N}$ which occurs owing to the eutectoid reaction $\gamma \rightarrow \alpha + \text{Cr}_2\text{N}$ in Fe-Cr-N ternary system⁽³⁾ and the region of $\alpha + \text{Cr}_2\text{N}$ appear in low carbon side. The regions of $\alpha + \gamma$ and γ are surrounded with these regions.

Photo. 1 shows the representative microstructures at 800°C. (a), (b) and (c) show the intergranular precipitation of Cr_{23}C_6 , Cr_2N and $\text{Cr}_7\text{C}_3 + \text{Cr}_2\text{N}$ in austenite,

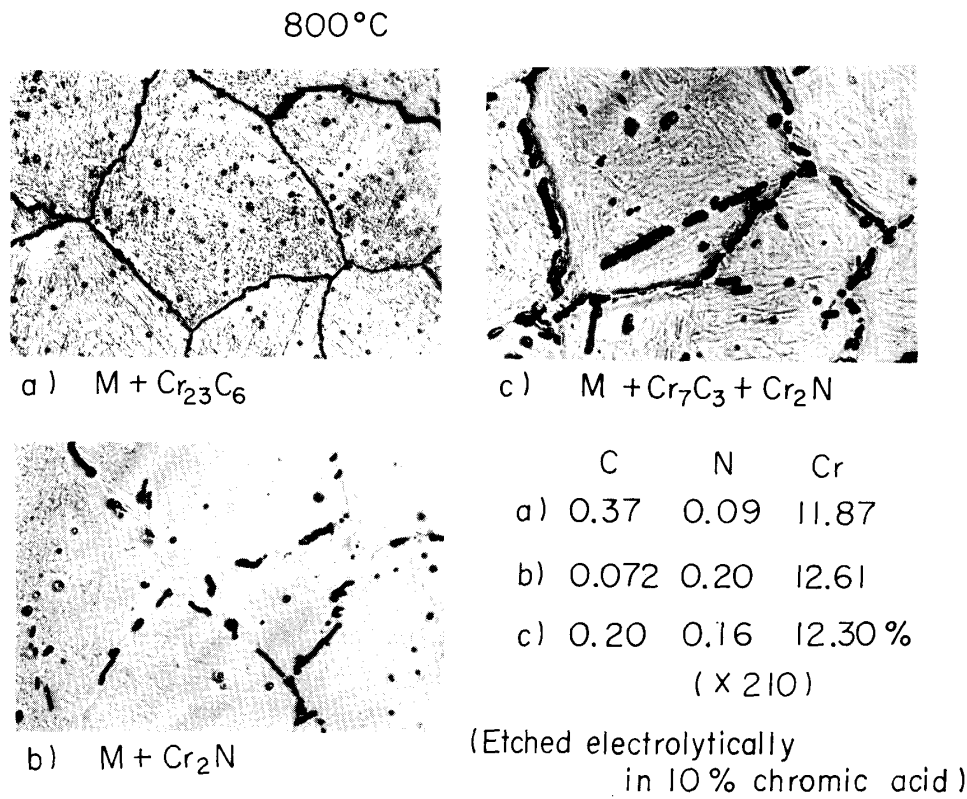


Photo. 1. Microstructures of 12%Cr-Fe-C-N alloys quenched from 800°C.

respectively, which transformed into martensite by quenching. The kind of precipitates could not be identified by the etching reagent, but was able to do by the powder X-ray diffraction of the extracted residues.

At 790°C, as shown in Fig. 9, the four-phase region of $\gamma + \text{Cr}_{23}\text{C}_6 + \text{Cr}_7\text{C}_3 + \text{Cr}_2\text{N}$ newly appears. It is presumed that three three-phase regions of $\gamma + \text{Cr}_{23}\text{C}_6 + \text{Cr}_7\text{C}_3$, $\gamma + \text{Cr}_7\text{C}_3 + \text{Cr}_2\text{N}$ and $\gamma + \text{Cr}_{23}\text{C}_6 + \text{Cr}_2\text{N}$ are intersected, revealing this four-phase region. In low carbon-low nitrogen side, another four-phase region of $\alpha + \gamma + \text{Cr}_{23}\text{C}_6 + \text{Cr}_2\text{N}$ appears owing to the intersection of three three-phase regions of $\gamma + \text{Cr}_{23}\text{C}_6 + \text{Cr}_2\text{N}$, $\alpha + \gamma + \text{Cr}_{23}\text{C}_6$ and $\alpha + \gamma + \text{Cr}_2\text{N}$. Three-phase region of $\gamma + \text{Cr}_{23}\text{C}_6 + \text{Cr}_2\text{N}$ exists between this two four-phase regions. Some regions could not be observed, but represented by the dotted lines according to the consideration of phase relations described later.

At 775°C, as shown in Fig. 10, the γ phase undergoes completely the transformation. The four-phase region of $\alpha + \text{Cr}_{23}\text{C}_6 + \text{Cr}_7\text{C}_3 + \text{Cr}_2\text{N}$ adjacent to the three-phase region of $\alpha + \text{Cr}_{23}\text{C}_6 + \text{Cr}_2\text{N}$ exists in high carbon-high nitrogen side. And the three-phase region of $\alpha + \text{Cr}_{23}\text{C}_6 + \text{Cr}_2\text{N}$ exists adjacent to the two-phase regions of $\alpha + \text{Cr}_{23}\text{C}_6$ and $\alpha + \text{Cr}_2\text{N}$. Besides, two three-phase regions of $\alpha + \text{Cr}_{23}\text{C}_6 + \text{Cr}_7\text{C}_3$ and $\alpha + \text{Cr}_7\text{C}_3 + \text{Cr}_2\text{N}$ can be presumed. It should be noticeable in Fig. 10 that the region of $\alpha + \text{Cr}_2\text{N}$ is fairly broader than that of $\alpha + \text{Cr}_{23}\text{C}_6$ as at 18%Cr-Fe-C-N system. It will be suggested from the breadth of these regions that the solubility of nitrogen in Cr_{23}C_6 is considerably small comparing with that of

775 °C

a) $\alpha + \text{Cr}_{23}\text{C}_6 + \text{Cr}_2\text{N}$ c) $\alpha + \text{Cr}_2\text{N}$ b) $\alpha + \text{Cr}_{23}\text{C}_6 + \text{Cr}_7\text{C}_3 + \text{Cr}_2\text{N}$

	C	N	Cr
a)	0.26	0.10	12.64
b)	0.37	0.09	11.87
c)	0.072	0.20	12.61 %

(x210)

(Etched electrolytically
in 10 % chromic acid)

Photo. 2. Microstructures of 12%Cr-Fe-C-N alloys quenched from 775°C.

carbon in Cr_2N . The structural diagram at 700°C is the same as at 775°C. Photo. 2 shows the representative microstructures at 775°C; (a), (b) and (c) show the coexisting structure of α and compounds; $\alpha + \text{Cr}_{23}\text{C}_6 + \text{Cr}_2\text{N}$, $\alpha + \text{Cr}_{23}\text{C}_6 + \text{Cr}_7\text{C}_3 + \text{Cr}_2\text{N}$ and $\alpha + \text{Cr}_2\text{N}$, respectively.

In the previous paper⁽⁵⁾, the chemical formulas of Cr_{23}C_6 and Cr_2N were presumed to be $(\text{Fe}_7\text{Cr}_{16})\text{C}_6$ and $(\text{Fe}_{0.05}\text{Cr}_{1.95})\text{C}_{0.3}\text{N}_{0.7}$, respectively. In the present work, the chemical analyses were carried out with the residues extracted from alloy in two-phase region of $\gamma + \text{Cr}_7\text{C}_3$ at 1000°C. From the results of the chemical analyses the chemical composition of carbide Cr_7C_3 is about 64.3% of chromium, 26.6% of iron, 2.1% of nitrogen and 7.0% of carbon, and the chemical formula of Cr_7C_3 was represented by $(\text{Fe}_2\text{Cr}_5)\text{C}_{2.4}\text{N}_{0.6}$.

2. Considerations of phase reactions and phase relationships

From the isothermal structural diagrams at 18% chromium in the previous paper⁽⁵⁾ and 12% chromium in the present work, the phase reactions and phase relationships in this quaternary system were considered.

From the experimental results, three following four-phase regions were observed: The region of $\alpha + \gamma + \text{Cr}_{23}\text{C}_6 + \text{Cr}_2\text{N}$ was observed from the isothermal structural diagrams at 18% chromium and the regions of $\alpha + \gamma + \text{Cr}_{23}\text{C}_6 + \text{Cr}_2\text{N}$, $\gamma + \text{Cr}_{23}\text{C}_6 + \text{Cr}_7\text{C}_3 + \text{Cr}_2\text{N}$ and the region of $\alpha + \text{Cr}_{23}\text{C}_6 + \text{Cr}_7\text{C}_3 + \text{Cr}_2\text{N}$ at low temperatures

at which the γ phase undergoes completely the transformation were observed at 12% chromium. It is presumed that alloys in four-phase region of $\alpha + \text{Cr}_{23}\text{C}_6 + \text{Cr}_7\text{C}_3 + \text{Cr}_2\text{N}$ at lower temperatures passed through a three-phase region or five-phase region descending from higher temperature. If alloys pass through a three-phase region, the three-phase region must be α and two kinds of compound such as $\alpha + \text{Cr}_{23}\text{C}_6 + \text{Cr}_7\text{C}_3$. But these three-phase regions cannot be considered from the phase relationships. Consequently, alloys should be considered to pass through the five-phase region of $\alpha + \gamma + \text{Cr}_{23}\text{C}_6 + \text{Cr}_7\text{C}_3 + \text{Cr}_2\text{N}$ with the fall of temperature.

In the quaternary system, five-phase equilibrium is invariant. With A, B, C, D, and E the invariant reaction generally can be one of the following four types.

- (a) $A \rightarrow B + C + D + E$ quaternary eutectoid.
- (b) $A + B \rightarrow C + D + E$ quaternary peritecto-eutectoid.
- (c) $A + B + C \rightarrow D + E$ quaternary peritecto-eutectoid.
- (d) $A + B + C + D \rightarrow E$ quaternary peritectoid.

In (d), the fifth phase occurs owing to the peritectoid reaction with four phases, but in this Fe-Cr-C-N system, as shown in Fig. 9, above the invariant temperature there are already five phases concerning with the reaction and therefore, the reaction of (d) does not occur in this system. In the eutectoid reaction of (a), the γ phase belongs to the reactants, so $\gamma \rightarrow \alpha + \text{Cr}_{23}\text{C}_6 + \text{Cr}_7\text{C}_3 + \text{Cr}_2\text{N}$ is considered to occur in this quaternary system. If γ phase undergoes the eutectoid reaction, γ phase vanishes after the reaction. This vanishment of γ phase after eutectoid reaction is contradictory to the fact that another kind of nitride, CrN, is observed to precipitate from γ phase at lower chromium content in Fe-Cr-C-N quaternary system⁽⁶⁾ and therefore, the reaction of (a) cannot be considered to occur.

On account of these discussion, either of the quaternary peritecto-eutectoid reactions of (b) or (c) is considered to take place in Fe-Cr-C-N system. For the quaternary composition tetrahedron of Fe-Cr-C-N system, the peritecto-eutectoid reaction of (b) is represented by three four-phase tie-tetrahedra at higher temperatures joining to form a tie-hexahedron at five corners of which are represented the five phases at an equilibrium temperature, and this hexahedron separates into two tie-tetrahedra at lower temperatures. The reaction of (c) is the inverse of reaction of (b).

As γ phase belongs to the reactants, there are 10 combinations of phases that could conceivably partake in the peritecto-eutectoid reaction. As shown in the isothermal structural diagrams at 18% chromium and 12% chromium in Fe-Cr-C-N system, four-phase tie-tetrahedra of $\alpha + \gamma + \text{Cr}_{23}\text{C}_6 + \text{Cr}_2\text{N}$ and $\gamma + \text{Cr}_{23}\text{C}_6 + \text{Cr}_7\text{C}_3 + \text{Cr}_2\text{N}$ exist at a temperature above that of five-phase equilibrium, and four-phase tie-tetrahedron of $\alpha + \text{Cr}_{23}\text{C}_6 + \text{Cr}_7\text{C}_3 + \text{Cr}_2\text{N}$ exists at a temperature below that of five-phase equilibrium. Three combinations of phases as shown in Table 2 can be considered corresponding to these experimental facts in this quaternary

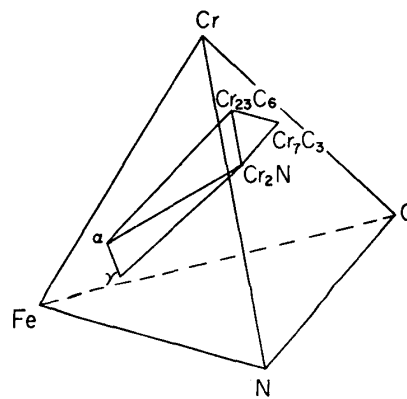
(6) Y. Imai, T. Masumoto and M. Naka, *J. Japan Inst. Metals*, **33** (1969), 705 (in Japanese); *Sci. Rep. RITU*, **A 23** (1972), 167.

Table 2. Three possible equations for a peritecto-eutectoid reaction in Fe-Cr-C-N system.

	Quaternary peritecto-eutectoid reactions	Tetrahedra before reaction	Tetrahedra after reaction
1	$\gamma + \text{Cr}_{23}\text{C}_6 + \text{Cr}_2\text{N} \rightarrow \alpha + \text{Cr}_7\text{C}_3$	$\alpha + \gamma + \text{Cr}_2\text{N} + \text{Cr}_{23}\text{C}_6$ $\gamma + \text{Cr}_{23}\text{C}_6 + \text{Cr}_7\text{C}_3 + \text{Cr}_2\text{N}$	$\alpha + \text{Cr}_{23}\text{C}_6 + \text{Cr}_7\text{C}_3 + \text{Cr}_2\text{N}$ $\alpha + \gamma + \text{Cr}_7\text{C}_3 + \text{Cr}_2\text{N}$ $\alpha + \gamma + \text{Cr}_{23}\text{C}_6 + \text{Cr}_7\text{C}_3$
2	$\gamma + \text{Cr}_{23}\text{C}_6 \rightarrow \alpha + \text{Cr}_7\text{C}_3 + \text{Cr}_2\text{N}$	$\alpha + \gamma + \text{Cr}_{23}\text{C}_6 + \text{Cr}_2\text{N}$ $\alpha + \gamma + \text{Cr}_{23}\text{C}_6 + \text{Cr}_7\text{C}_3$ $\gamma + \text{Cr}_{23}\text{C}_6 + \text{Cr}_7\text{C}_3 + \text{Cr}_2\text{N}$	$\alpha + \gamma + \text{Cr}_7\text{C}_3 + \text{Cr}_2\text{N}$ $\alpha + \text{Cr}_{23}\text{C}_6 + \text{Cr}_7\text{C}_3 + \text{Cr}_2\text{N}$
3	$\gamma + \text{Cr}_2\text{N} \rightarrow \alpha + \text{Cr}_{23}\text{C}_6 + \text{Cr}_7\text{C}_3$	$\alpha + \gamma + \text{Cr}_{23}\text{C}_6 + \text{Cr}_2\text{N}$ $\alpha + \gamma + \text{Cr}_7\text{C}_3 + \text{Cr}_2\text{N}$ $\gamma + \text{Cr}_{23}\text{C}_6 + \text{Cr}_7\text{C}_3 + \text{Cr}_2\text{N}$	$\alpha + \gamma + \text{Cr}_{23}\text{C}_6 + \text{Cr}_7\text{C}_3$ $\alpha + \text{Cr}_{23}\text{C}_6 + \text{Cr}_7\text{C}_3 + \text{Cr}_2\text{N}$

system. For the purpose of determination which of three reactions in Table 2 occurs in Fe-Cr-C-N system, the four-phase tie-tetrahedron of $\alpha + \gamma + \text{Cr}_{23}\text{C}_6 + \text{Cr}_7\text{C}_3$ must be determined to exist before or after the reaction. The temperature of the invariant reaction may be at least below 790°C considering from the isothermal structural diagrams at 12% chromium.

As the ternary peritecto-eutectoid reaction, $\gamma + \text{Cr}_{23}\text{C}_6 \rightarrow \alpha + \text{Cr}_7\text{C}_3$ at 795°C in Fe-Cr-C ternary system results in the formation of the tetrahedral region of $\alpha + \gamma + \text{Cr}_{23}\text{C}_6 + \text{Cr}_7\text{C}_3$ in Fe-Cr-C-N system, this four-phase tie-tetrahedron is considered to exist above the temperature of five-phase equilibrium. Therefore, the quaternary peritecto-eutectoid reaction of $\gamma + \text{Cr}_{23}\text{C}_6 \rightarrow \alpha + \text{Cr}_7\text{C}_3 + \text{Cr}_2\text{N}$ is considered to occur in the Fe-Cr-C-N quaternary system. In five-phase equilibrium the compositions of each phase are constant, then the approximate locations of Cr_{23}C_6 , Cr_7C_3 and Cr_2N are presumed to be (5.6% C, 0.05% N, 28% Fe), (26.6% Fe, 64.3% Cr, 2.1% N, 7.0% C) and (2.4% C, 7.8% N, 2.3% Fe), respectively. From the consideration of the locations of α and γ in Fe-Cr-C system⁽¹⁾ and Fe-Cr-N system⁽³⁾, α phase is in higher chromium-lower nitrogen side than γ phase. The approximate locations of five phases are shown in the quaternary composition tetrahedron in


 Fig. 11. Schematic illustration of the hexahedron formed by α , γ , Cr_{23}C_6 , Cr_7C_3 and Cr_2N in Fe-Cr-C-N system.

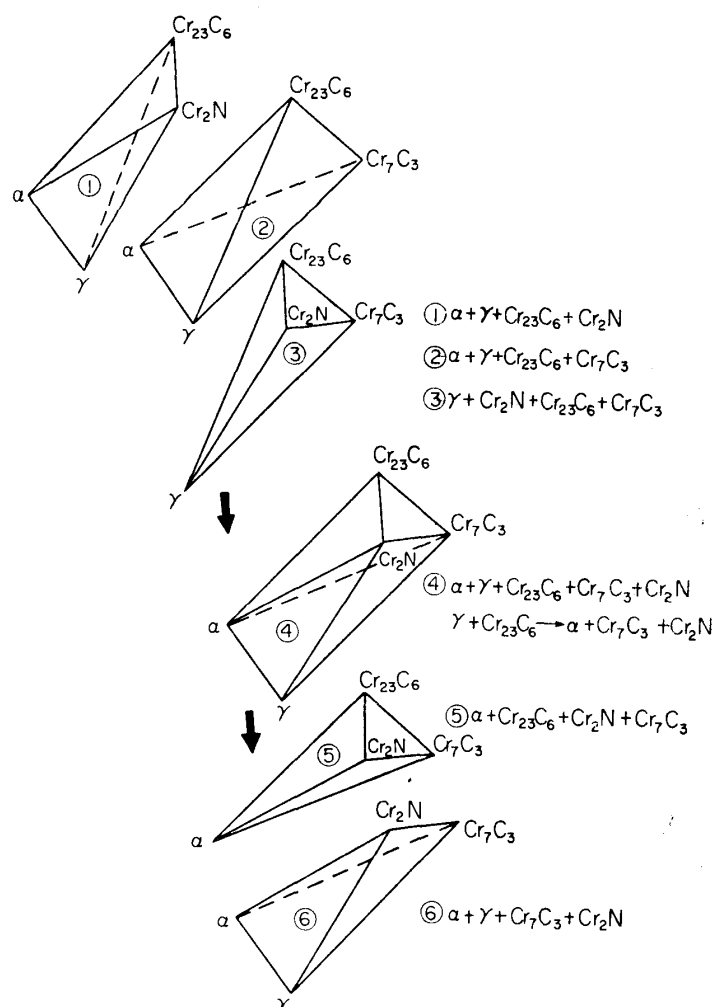


Fig. 12. Sequence of tie-tetrahedra on cooling through the quaternary peritecto-eutectoid temperature in Fe-Cr-C-N system.

Fig. 11.

Then the sequence of tie-tetrahedra on cooling through the quaternary peritecto-eutectoid reaction is shown in Fig. 12. Three four-phase tie-tetrahedra of $\alpha + \gamma + \text{Cr}_{23}\text{C}_6 + \text{Cr}_2\text{N}$, $\alpha + \gamma + \text{Cr}_{23}\text{C}_6 + \text{Cr}_7\text{C}_3$ and $\gamma + \text{Cr}_{23}\text{C}_6 + \text{Cr}_7\text{C}_3 + \text{Cr}_2\text{N}$ at higher temperatures join to form the tie-hexahedron of $\alpha + \gamma + \text{Cr}_{23}\text{C}_6 + \text{Cr}_7\text{C}_3 + \text{Cr}_2\text{N}$. With further fall of temperature, this tie-hexahedron separates into two tie-tetrahedra of $\alpha + \gamma + \text{Cr}_7\text{C}_3 + \text{Cr}_2\text{N}$ and $\alpha + \text{Cr}_{23}\text{C}_6 + \text{Cr}_7\text{C}_3 + \text{Cr}_2\text{N}$. This temperature of quaternary peritecto-eutectoid reaction is considered to be about 780°C from the experimental results. The construction of the isothermal structural diagrams by considerations of this invariant reaction is accordant with the diagrams by the experimental results (Fig. 1 ~ Fig. 10).

Subsequently, the phase relationships in the Fe-Cr-C-N quaternary system at 12% chromium were considered based on the above-mentioned considerations. Fig. 13 shows phase diagrams of 12%Cr-Fe-C system⁽¹⁾ and 12%Cr-Fe-N system⁽³⁾ and the phase relationships of 12%Cr-Fe-C-N system at various temperatures

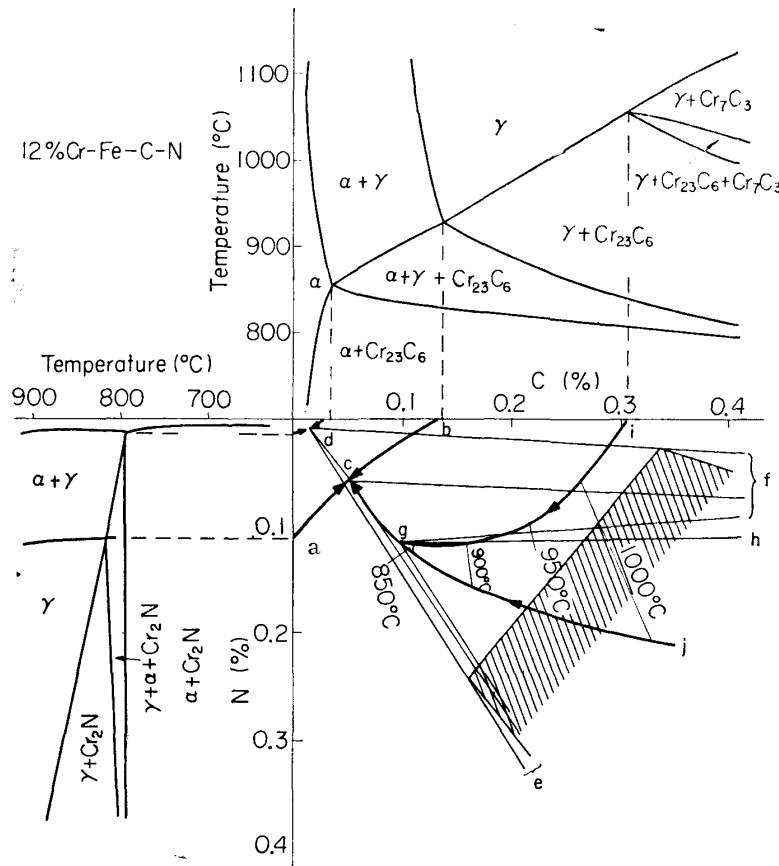


Fig. 13. Projection of phase reaction in 12%Cr-Fe-C-N system on the concentration plane.

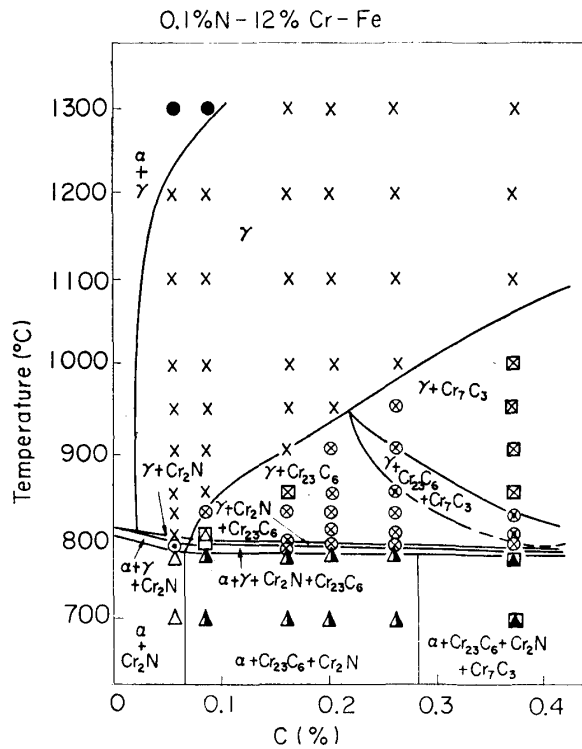


Fig. 14. Section diagram of 12%Cr-Fe-C-N system at 0.1%N.

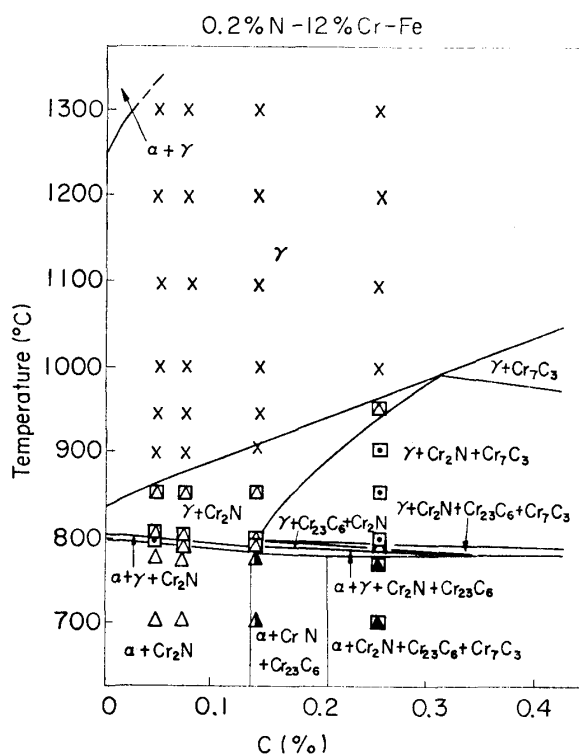


Fig. 15

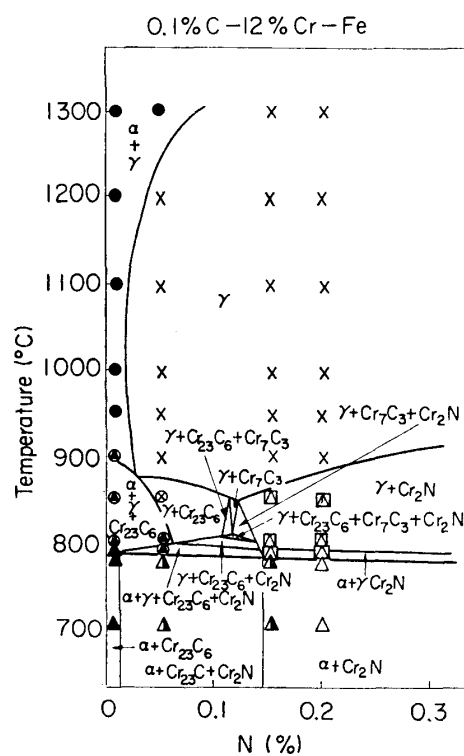


Fig. 16

Fig. 15. Section diagram of 12%Cr-Fe-C-N system at 0.2%N.

Fig. 16. Section diagram of 12%Cr-Fe-C-N system at 0.1%C.

projected on the concentration plane. In this figure, two reactions, $\gamma + \text{Cr}_{23}\text{C}_6 \rightarrow \text{Cr}_7\text{C}_3$ in 12%Cr-Fe-C system and $\gamma \rightarrow \text{Cr}_7\text{C}_3 + \text{Cr}_2\text{N}$ which is presumed to be at high carbon-high nitrogen side, descend toward the point g along the lines $i-g$ and $j-g$, respectively, with the fall of temperature. At the point g the four-phase region of $\gamma + \text{Cr}_{23}\text{C}_6 + \text{Cr}_7\text{C}_3 + \text{Cr}_2\text{N}$ is formed and the peritecto-eutectoid reaction $\gamma + \text{Cr}_{23}\text{C}_6 \rightarrow \text{Cr}_2\text{N} + \text{Cr}_7\text{C}_3$, which is presumed from the construction of the phase relationships, occurs.

With further fall of temperature, the eutectoid reaction $\gamma \rightarrow \text{Cr}_{23}\text{C}_6 + \text{Cr}_2\text{N}$ descends toward the point c along the $g-c$, besides, the eutectoid reaction $\gamma \rightarrow \alpha + \text{Cr}_2\text{N}$ in 12%Cr-Fe-N system and also the eutectoid reaction $\gamma \rightarrow \alpha + \text{Cr}_{23}\text{C}_6$ in 12%Cr-Fe-C system descend toward the point c along the lines $a-c$ and $b-c$, respectively. These three eutectoid reactions reach at the point c at which the quaternary eutectoid reaction, $\gamma \rightarrow \alpha + \text{Cr}_{23}\text{C}_6 + \text{Cr}_2\text{N}$ occurs. Hereupon, the temperature of points g , c and d were estimated to be about 820° , 800° and 795°C , respectively. The tetrahedra of $cdef$ and $efgh$ correspond to the variation with the fall of temperature of the projections of the intersections of the four-phase regions in the quaternary composition tetrahedron of Fe-Cr-C-N system with the sectional plane at 12% chromium on the concentration plane. The part shown by the oblique lines shows the five-phase invariant region of $\alpha + \gamma + \text{Cr}_{23}\text{C}_6 + \text{Cr}_7\text{C}_3 + \text{Cr}_2\text{N}$ at 12% chromium at about 780°C .

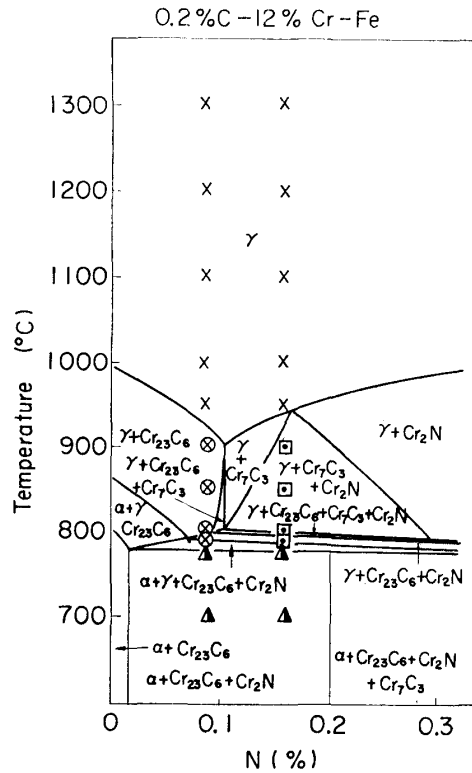


Fig. 17. Section diagram of 12%Cr-Fe-C-N system at 0.2% C.

3. Sectional diagrams of 12%Cr-Fe-C-N system at various contents of carbon and nitrogen

From the results of the isothermal sections and the considerations of the phase reactions and phase relationships, the sectional diagrams of 12%Cr-Fe-C-N system at various contents of 0.1 and 0.2% nitrogen, and 0.1% and 0.2% carbon were constructed as shown in Fig. 14 to Fig. 17.

Summary

The structural diagrams of 12%Cr-Fe-C-N quaternary system in the composition range up to 0.4% carbon and 0.3% nitrogen were investigated in the temperature range from 1300° to 700°C and the sectional diagrams were described at fixed contents of 0.1 and 0.2% nitrogen and 0.1 and 0.2% carbon. The results are summarized as follows:

(1) In the range of compositions in the present work, the α and γ phase exist in equilibrium in the temperature range from 1300° to 1200°C, the single phase region of γ exists in the lower content side of carbon and nitrogen than those at 18% chromium quaternary system. The minimum concentration of carbon and nitrogen required to obtain the completely austenitic structure is about 0.2% at 1300°C and 0.14% at 1200°C. Below 1200°C, Cr_{23}C_6 , Cr_7C_3 and Cr_2N precipitate and the phase regions encountered were $\gamma + \text{Cr}_{23}\text{C}_6$, $\gamma + \text{Cr}_7\text{C}_3$, $\gamma + \text{Cr}_2\text{N}$, $\gamma + \text{Cr}_{23}\text{C}_6 + \text{Cr}_7\text{C}_3$, $\gamma + \text{Cr}_{23}\text{C}_6 + \text{Cr}_2\text{N}$, $\gamma + \text{Cr}_{23}\text{C}_6 + \text{Cr}_7\text{C}_3 + \text{Cr}_2\text{N}$, $\alpha + \gamma + \text{Cr}_{23}\text{C}_6 + \text{Cr}_2\text{N}$,

$\alpha + \gamma + \text{Cr}_{23}\text{C}_6$, $\alpha + \gamma + \text{Cr}_2\text{N}$, $\alpha + \text{Cr}_{23}\text{C}_6$, $\alpha + \text{Cr}_2\text{N}$, $\alpha + \text{Cr}_{23}\text{C}_6 + \text{Cr}_2\text{N}$, $\alpha + \text{Cr}_{23}\text{C}_6 + \text{Cr}_7\text{C}_3 + \text{Cr}_2\text{N}$. Besides, the four-phase regions of $\alpha + \gamma + \text{Cr}_{23}\text{C}_6 + \text{Cr}_7\text{C}_3$ and $\alpha + \gamma + \text{Cr}_7\text{C}_3 + \text{Cr}_2\text{N}$ are presumed to exist.

(2) By the considerations of phase reactions, one quaternary peritecto-eutectoid reaction is presumed to occur in Fe-Cr-C-N quaternary system. Accordingly, three four-phase tie-tetrahedra of $\alpha + \gamma + \text{Cr}_{23}\text{C}_6 + \text{Cr}_2\text{N}$ ($\gamma \rightarrow \alpha + \text{Cr}_{23}\text{C}_6 + \text{Cr}_2\text{N}$), $\alpha + \gamma + \text{Cr}_{23}\text{C}_6 + \text{Cr}_7\text{C}_3$ ($\gamma + \text{Cr}_{23}\text{C}_6 \rightarrow \alpha + \text{Cr}_7\text{C}_3$), $\gamma + \text{Cr}_{23}\text{C}_6 + \text{Cr}_7\text{C}_3 + \text{Cr}_2\text{N}$ ($\gamma + \text{Cr}_{23}\text{C}_6 \rightarrow \text{Cr}_7\text{C}_3 + \text{Cr}_2\text{N}$) descend from higher temperature and join to form the tie-hexahedron of $\alpha + \gamma + \text{Cr}_{23}\text{C}_6 + \text{Cr}_7\text{C}_3 + \text{Cr}_2\text{N}$ ($\gamma + \text{Cr}_{23}\text{C}_6 \rightarrow \alpha + \text{Cr}_7\text{C}_3 + \text{Cr}_2\text{N}$), and with the fall of temperature, this tie-hexahedron separates into two tie-tetrahedra of $\alpha + \gamma + \text{Cr}_7\text{C}_3 + \text{Cr}_2\text{N}$ and $\alpha + \text{Cr}_{23}\text{C}_6 + \text{Cr}_7\text{C}_3 + \text{Cr}_2\text{N}$. This temperature of the invariant reaction is presumed to be about 780°C.

(3) The Cr_7C_3 type carbide detected in this work is represented by the formula $(\text{Fe}_2\text{Cr}_5)\text{C}_{2.4}\text{N}_{0.6}$.