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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	21-34
year	1967
URL	<a href="http://hdl.handle.net/10097/27345">http://hdl.handle.net/10097/27345</a>

# Microstructures and Nitrides of Fe-Cr-N Ternary System\*

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(Received March 7, 1967)

## Synopsis

The microstructures and the characters of nitrides in various alloys of the Fe-Cr-N system in the range of 0.5 to 40% chromium with up to about 1% nitrogen were studied by optical- and electron-microscope and by X-ray diffraction and chemical analysis of the extracted residue. The results are summarized as follows:

- (1) The nitrides detected were  $\text{Fe}_4\text{N}$ ,  $\text{CrN}$  and  $\text{Cr}_2\text{N}$ .
- (2) In the content of about 0.1% N, the changes in microstructure with the lowering of temperature were as follows:

0.5% Cr:  $\gamma \rightarrow a + \gamma \rightarrow a + \gamma + \text{CrN} \rightarrow a + \text{CrN} + \text{Fe}_4\text{N}$ ;  
about 0.5~6% Cr:  $\gamma \rightarrow a + \gamma \rightarrow a + \gamma + \text{CrN} \rightarrow a + \text{CrN}$ ;  
about 6~7% Cr:  $\gamma \rightarrow a + \gamma \rightarrow a + \gamma + \text{Cr}_2\text{N} \rightarrow a + \text{Cr}_2\text{N} + \text{CrN}$ ;  
about 7~13% Cr:  $\gamma \rightarrow a + \gamma \rightarrow a + \gamma + \text{Cr}_2\text{N} \rightarrow a + \text{Cr}_2\text{N}$ ;  
about 13~26% Cr:  $a + \gamma \rightarrow a + \gamma + \text{Cr}_2\text{N} \rightarrow a + \text{Cr}_2\text{N}$ ;  
above about 26% Cr:  $a \rightarrow a + \text{Cr}_2\text{N}$ .

- (3) In the case of alloys containing chromium above about 13%, the minimum content of nitrogen to obtain a completely austenitic structure increased with the chromium content; for example, the minimum nitrogen contents in 13, 18 and 16% Cr alloys were about 0.1, 0.4 and 0.8%, respectively. The microstructures of these alloys revealed such a change as  $\gamma \rightarrow \gamma + \text{Cr}_2\text{N} \rightarrow a + \gamma + \text{Cr}_2\text{N} \rightarrow a + \text{Cr}_2\text{N}$ .

- (4) The very fine acicular phase was observed within ferrite in the Fe-Cr-N alloys, which contained chromium above about 15% and were quenched in water from above about 1100°C. It was confirmed that this phase was  $\text{Cr}_2\text{N}$  precipitated during cooling due to a remarkable decrease of the solubility of nitrogen in ferrite, and that the suppression of this precipitation was very difficult.

## I. Introduction

Alloys of Fe-Cr system are of the basic compositions of heat-resisting alloys and have been in wide use as ferritic heat-resisting steels. Large numbers of metallographical studies have been conducted on Fe-Cr and Fe-Cr-C systems and nearly complete equilibrium diagrams of these systems have already been described. Nitrogen, being an element of interstitial type like carbon, enlarges the austenite range in Fe-Cr system<sup>(1)-(7)</sup> and raises the high-temperature strength by refining

\* The 1298th report of the Research Institute for Iron, Steel and Other Metals. Reported in Japanese in the J. Japan Inst. Metals, **29** (1965), 860.

- (1) V.N. Krivobok, Trans. ASM, **23** (1935), 1.
- (2) H. Krainer and O. Mirt, Arch. Eisenhütt., **15** (1941/42), 467.
- (3) G.F. Tisinai, J.K. Stanley and C.H. Samams, Trans. ASM, **48** (1956), 356.
- (4) E.T. Turkdogan and S. Ignatowicz, J. Iron Steel Inst., **188** (1958), 242.

the crystal grains and by precipitating nitrides.<sup>(7)-(9)</sup> But there are many obscure points in the metallographic studies on the Fe-Cr alloys containing nitrogen, probably because the preparation of specimens is usually accompanied with many difficulties. For this reason, in the present study the microstructural changes and the kinds and behaviors of nitrides in Fe-Cr-N system were examined within practical compositions.

## II. Specimens and experimental methods

Most specimens were prepared in air with a high frequency electric furnace and by adding high N-Fe-Cr mother alloy. In making specimens with high content of nitrogen, a piece 3 mm $\phi$   $\times$  60 mm of Fe-Cr alloy melted in vacuum was nitrogenized in the mixed gas of NH<sub>3</sub> and H<sub>2</sub> at 800°C, inclosed in a thick quartz tube in

Table 1. Chemical compositions of alloys used in the present work.

Designation	Chemical composition (%)			Designation	Chemical composition (%)		
	Cr	N	C		Cr	N	C
0.5N10*	0.53	0.10	0.004	19N11	18.78	0.11	0.013
2N03	2.01	0.03	0.011	19N13	18.66	0.13	0.012
3N06	2.87	0.064	0.013	19N30	18.56	0.30	0.013
4N12*	4.20	0.12	0.009	19N37	18.57	0.37	0.011
5N06	4.69	0.055	0.008	19N56*	18.76	0.56	0.006
5N16*	4.94	0.164	0.004	19N65*	18.76	0.65	0.006
5N08	5.31	0.08	0.010	20N29	20.05	0.29	0.010
6N06	5.50	0.06	0.013	21N14	21.33	0.14	0.011
6N10	6.38	0.10	0.013	22N15	22.11	0.15	0.015
7N04	6.86	0.04	0.012	23N15	22.94	0.15	0.012
7N08	7.30	0.08	0.010	23N50	22.89	0.50	0.013
7N11	7.34	0.11	0.010	25N57	25.42	0.57	0.013
7N13	7.34	0.13	0.010	26N06	26.30	0.06	0.012
7N25*	7.51	0.25	0.009	26N10	26.17	0.10	0.014
10N14	10.10	0.14	0.016	26N14	26.43	0.14	0.012
11N12	10.52	0.12	0.010	26N30	26.16	0.30	0.013
13N10	13.21	0.10	0.013	26N36	26.06	0.36	0.015
13N19	13.12	0.19	0.012	27N22	26.77	0.22	0.013
13N27	13.37	0.27	0.011	27N86*	26.53	0.86	0.004
14N04	13.83	0.04	0.010	27N100*	26.53	1.00	0.004
14N07	13.74	0.07	0.014	27N105*	26.53	1.05	0.004
14N11	13.51	0.11	0.015	29N15	28.78	0.15	0.014
15N18	15.46	0.18	0.013	30N23	30.00	0.23	0.015
16N12	15.97	0.12	0.013	30N45	30.21	0.45	0.013
16N28	16.02	0.28	0.014	32N09	32.30	0.09	0.011
17N15	16.51	0.15	0.012	34N19	33.62	0.19	0.014
18N24	18.20	0.24	0.010	34N35	34.11	0.35	0.009
18N26	18.29	0.26	0.016	35N51	34.56	0.51	0.015
19N05	19.19	0.05	0.011	37N17	37.17	0.17	0.012
19N08	18.54	0.08	0.013	39N32	39.39	0.32	0.016

\* By nitriding-annealing method.

- (5) E.T. Turkdogan and S. Ignatowicz, *J. Iron Steel Inst.*, **199** (1961), 287.
- (6) E.T. Turkdogan and S. Ignatowicz, *Phys. Chem. of Process Metallurgy*, Part 1, edited by G.R. St Pierre, N.Y., (1961), 617.
- (7) M. Okamoto and T. Naitō, *Tetsu-to-Hagané* (The Journal of the Iron and Steel Inst. of Japan), **49** (1963), 1915.
- (8) R. Franks, *Trans. ASM*, **23** (1935), 968.
- (9) E.W. Colbeck and R.P. Garner, *J. Iron Steel Inst.*, **139** (1939), 99.

conformity with the shape and annealed at 1200°C for 6 days. Table 1 shows the analytical values of the specimens thus obtained.

In the alloys of this system in which partial pressure of nitrogen is of importance, the conditions of heat-treatment must be taken into consideration. As a result of the preliminary examinations, all the heat-treatments were performed by inclosing the specimens in quartz tubes in conformity with the size of specimens in vacuum in order to prevent them from the absorption and evacuation of nitrogen. By this method, it was possible to obtain homogeneous structure because the loss of nitrogen was very small due to the extremely small gap between the specimen and the quartz tube. The alloys containing above 10% of chromium were heated at 1300°C for 1 hr and those with less than 10% chromium were heated at 1000°C for 5 hr. Then they were slowly cooled at the rate of 100°C per hour to the temperatures required, at which they were held for 1 to 200 hr (the lower the temperature, the longer the heating time). They were then water-cooled and the microstructures were examined. In doing water-cooling, the quartz tube was broken the moment the specimen was thrown into the water lest the cooling rate should be slowed down. The microstructures were examined by optical microscope and with some specimens by electron microscope and by X-ray analysis of Debye-Scherrer method. By X-ray and chemical analyses, the crystal lattice, the composition and the kind of extracted nitride were studied.

The extraction of nitride was done by chemical extraction method by using iodine-methanol solution and hydro-chloric acid solution, and by electrolytic extraction method by using sodium-citrate solution. The iodine-methanol method is one in which 6g of iodine and 25 cc of methyl alcohol are added to 1 g of specimen and the extraction is done in argon atmosphere at 60°C. By this method almost a complete extraction of CrN and Cr<sub>2</sub>N could be accomplished.

The hydro-chloric acid method is to extract nitride by using 6N hydro-chloric acid solution, and it was used for the specimens with CrN. The electrolytic extraction method was chiefly used for the specimens containing Fe<sub>4</sub>N, and the extraction was electrolytically done in 10% sodium-citrate solution with 1% potassium-bromide and 0.1% potassium-iodide in H<sub>2</sub> atmosphere under conditions based on the previous results<sup>(10)</sup> on the electrolytic condition by using the potentiostat.

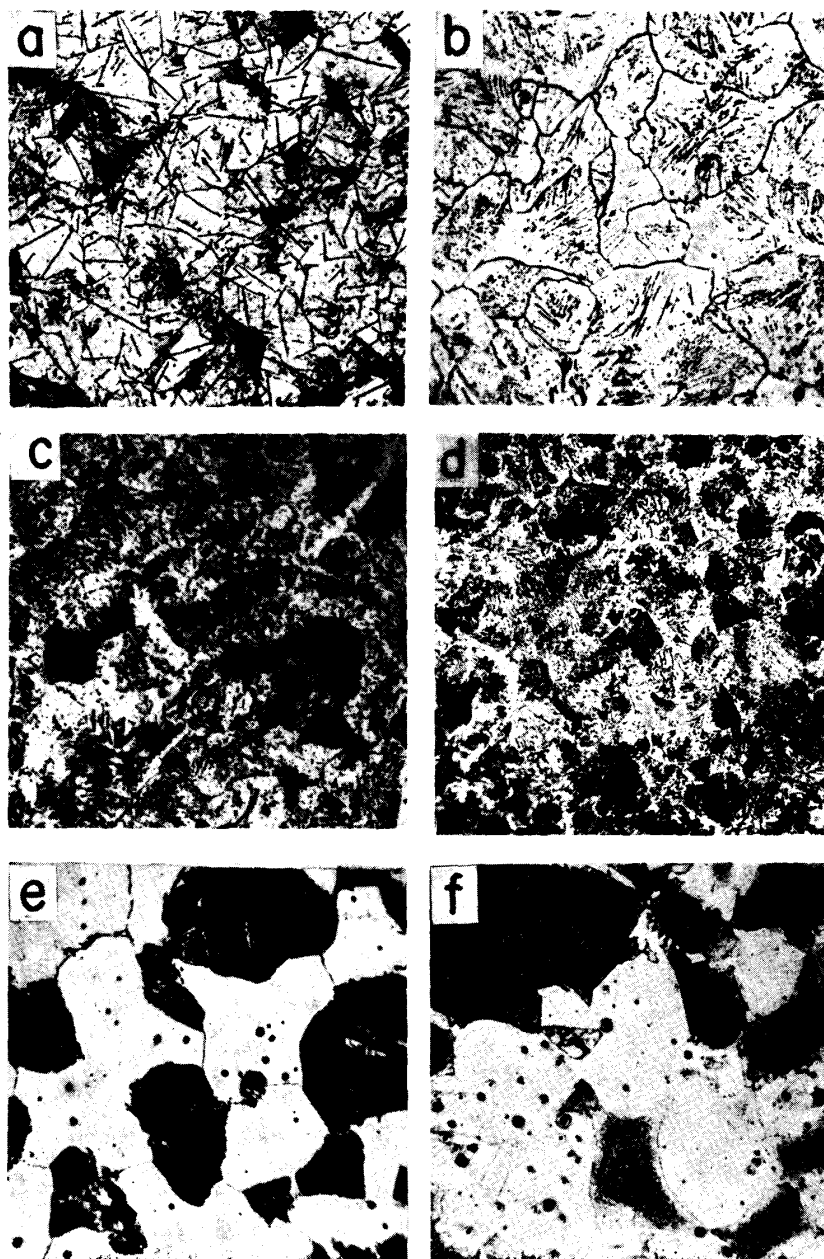
### III. Experimental results and considerations

#### 1. Changes in microstructure by heat-treatments and composition of alloys

The microstructures of the specimens subjected to various heat-treatments were observed by optical microscope and the kinds of nitrides were examined by X-ray analysis of extracted residues. The following figures show the representative microscopic photographs of the specimens with various contents of chromium and nitrogen.

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(10) Y. Imai and T. Masumoto, *Sci. Rep. RITU*, A 16 (1964), 31.



Phot. 1. Microstructures of Fe-Cr-N alloys quenched from various temperatures; (a) 0.5N10, annealed ( $\times 200$ ), (b) 3N06,  $700^{\circ}\text{C} \times 100$  hr, W.Q. ( $\times 350$ ), (c) 5N08,  $700^{\circ}\text{C} \times 100$  hr, W.Q. ( $\times 350$ ), (d) 7N13,  $700^{\circ}\text{C} \times 100$  hr, W.Q. ( $\times 350$ ), (e) 13N10,  $700^{\circ}\text{C} \times 100$  hr, W.Q. ( $\times 200$ ), (f) 15N18,  $1300^{\circ}\text{C} \times 1$  hr, W.Q. ( $\times 200$ ).

First, the changes in structure by increasing the chromium content in the alloys containing about 0.1% of nitrogen will be described.

0.5 N 10 alloy is of the austenitic structure above  $900^{\circ}\text{C}$ , but between  $900^{\circ}$  and  $850^{\circ}\text{C}$ , it produces proeutectoid ferrite and becomes  $\alpha + \text{CrN} + \text{Fe}_4\text{N}$  structure below  $750^{\circ}\text{C}$ . Phot. 1 (a) shows the slow-cooled structure, in which the narrow-long aciculars were found to be  $\text{Fe}_4\text{N}$  and the darkish parts to be lamellars of  $\text{CrN}$  and ferrite, from X-ray analysis and the etching characteristics by reagents.

3 N 06 alloy is of the austenitic structure above almost 850°C, below which it becomes ferrite and austenite, and below 750°C it becomes the structure consisting of ferrite and nitride. Phot. 1 (b) shows the structure at 700°C, in which it is seen to consist of ferrite and eutectoid-like part. As is clear from Table 2 showing the result of X-ray diffraction of the extracted residue, this nitride is CrN.

Table 2. X-ray diffraction data of residue separated from 3N06 alloy quenched from 700°C.

No. of line	Diffraction line (CuK $\alpha$ )		Data of CrN (f. c. c.) in ASTM card		
	$d$ (Å)	$I$	$d$ (Å)	$hkl$	$I/I_0$
1	2.385	S	2.40	111	100
2	2.066	V S	2.07	200	100
3	1.463	S	1.47	220	125
4	1.248	M	1.25	311	100
5	1.196	M	1.20	222	100
6	0.951	W		400	
7	0.927	M		331	
8	0.846	W		420	

Table 3. X-ray diffraction data of residue separated from annealed 5N08 alloy.

No. of line	Diffraction line (CuK $\alpha$ )		Data of ASTM card					
			CrN (f. c. c.)			Cr <sub>2</sub> N (hex.)		
	$d$ (Å)	$I$	$d$ (Å)	$hkl$	$I/I_0$	$d$ (Å)	$hkl$	$I/I_0$
1	2.419	M	2.40	111	100	2.38	11.0	25
2	2.242	W				2.22	00.2	25
3	2.142	S				2.10	11.1	100
4	2.082	M	2.07	200	100			
5	1.675	W				1.63	11.2	25
6	1.471	W	1.47	220	125			
7	1.404	W				1.38	30.0	25
8	1.271	VW				1.27	11.3	20
9	1.255	VW	1.25	311	100			
10	1.184	VW	1.20	222	100			
11	1.169	VW						

The same changes in structure were also observed in 5 N 06 alloy with higher chromium content, but in 5 N 08 alloy with much higher chromium content, Cr<sub>2</sub>N precipitates in addition to CrN as shown in Table 3. The structure at 700°C shown in Phot. 1(c) consists of darkish eutectoid-like part and ferrite from which CrN has precipitated out, and the former is considered to be a lamellar structure of ferrite and Cr<sub>2</sub>N. Thus, the range of composition in which CrN and Cr<sub>2</sub>N are separated is so narrow that the separation is obtained only in 6 N 06 and 6 N 10 alloys besides 5 N 08 alloy in the present experiment.

In higher chromium alloys, the austenite is decomposed into ferrite and Cr<sub>2</sub>N. For example, in 7 N 13 alloy the structure remains the single phase of austenite until about 850°C, but at about 800°C, the austenite is decomposed mostly into a

lamellar structure similar to that of pearlite in Fe-C system as shown in Phot. 1(d). The extracted residue of this alloy consists only of  $\text{Cr}_2\text{N}$ .

The alloys in which the single phase of austenite is observable are, in the case of 0.1% of nitrogen content, those which contain less than 13% of chromium, beyond which they become structure of two phases of ferrite and austenite. For example, 13N10 alloy shows the ferrite plus austenite structure between 1300° and 850°C, below which it shows the structure consisting of ferrite and eutectoid-part of ferrite plus  $\text{Cr}_2\text{N}$  resulting from the decomposition of austenite as shown in Phot. 1(e).

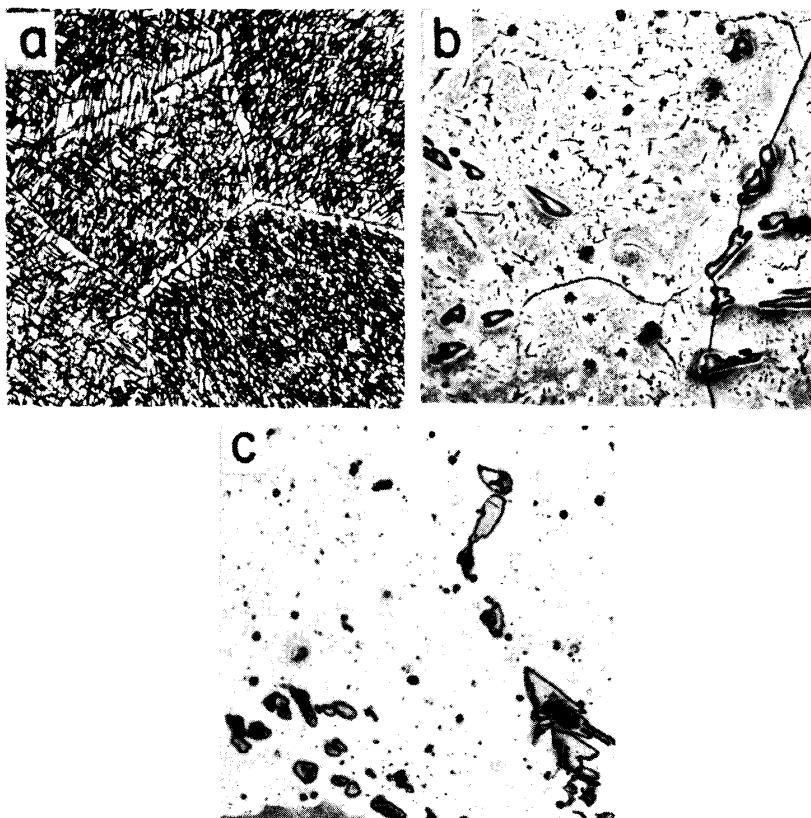
It those alloys in which chromium content is larger, the amount of austenite gradually decreases and the temperature at which the decomposition of austenite occurs becomes higher (about 900°C in 19N11 alloy and about 1075°C in 26N14 alloy), but the changes in structure are similar to those of 13N10 alloy.

In those alloys in which chromium content is more than 15% and which is water-cooled from above 1100°C, the presence of fine acicular particles of nitride in ferrite can be observed. Phot. 1(f) shows the structure of 15N18 alloy water-cooled from 1300°C, in which the white part represents martensite and the black part the ferrite phase containing fine nitride. As shown in Table 4, X-ray diffraction of nitride within ferrite in 26N14 alloy clearly revealed it to be  $\text{Cr}_2\text{N}$ , which is quite the same as  $\text{Cr}_2\text{N}$  of lamellar nitride in slow-cooled alloys. However, the two differ largely from each other in shape and so the fine acicular nitride obtainable at high temperatures is designated by ( $\text{Cr}_2\text{N}$ ).

The chromium content at which the austenite phase completely disappears is more than 26% in 0.1% nitrogen content and the austenite is not formed in 29N15 and 37N17 alloys. For example, the changes of structure in 37N17 alloy are shown in Phot. 2: When water-cooled from 1300°C it consists of the ferrite containing large number of ( $\text{Cr}_2\text{N}$ ) as shown in the photograph (a), but in (b) at 1100°C,

Table 4. X-ray diffraction data of residues separated from 26N14 alloys quenched from 1300°C and annealed.

No. of line	Diffraction line ( $\text{CuK}\alpha$ )				Date of $\text{Cr}_2\text{N}$ in ASTM card		
	Quenched alloy		Annealed alloy		$\text{Cr}_2\text{N}$ (hex.)		
	$d(\text{Å})$	$I$	$d(\text{Å})$	$I$	$d(\text{Å})$	$hkl$	$I/I_0$
1	2.387	W	2.385	W	2.38	11.0	25
2	2.224	W	2.222	M	2.22	00.2	25
3	2.103	S	2.107	S	2.10	11.1	100
4	1.628	M	1.630	M	1.63	11.2	25
5	1.379	W	1.383	M	1.38	30.0	25
6	1.261	W	1.264	M	1.27	11.3	20
7	1.174	W	1.177	M		30.2	
8	1.155	W	1.159	W		22.1	
9			1.116	W		00.4	
10	1.057		1.057	W		22.2	
11	1.011		1.011	VW		11.4	
12			0.9354	W			
13			0.8906	M			



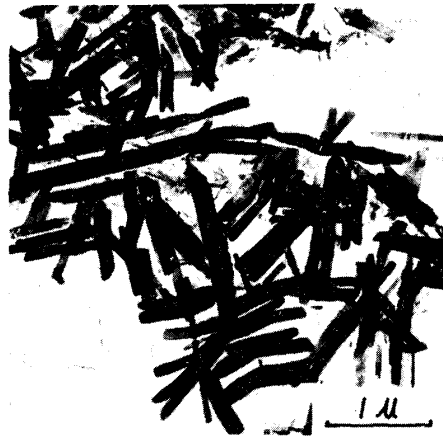
Phot. 2. Microstructures of 37N17 alloy quenched from various temperatures; (a)  $1300^{\circ}\text{C} \times 1 \text{ hr}$ , W. Q. ( $\times 350$ ), (b)  $1100^{\circ}\text{C} \times 5 \text{ hr}$ , W. Q. ( $\times 350$ ), (c)  $1000^{\circ}\text{C} \times 5 \text{ hr}$ , W. Q. ( $\times 350$ )

( $\text{Cr}_2\text{N}$ ) phase decreases with the separation of large lumpy nitride and in (c) at  $1000^{\circ}\text{C}$ , only the large lumpy nitride is separated in ferrite. X-ray diffraction reveals the lumpy nitride to be  $\text{Cr}_2\text{N}$ , which is separated by the decrease in solubility of nitrogen in ferrite with the fall of temperature. On the other hand, it was much doubt whether the fine acicular nitride ( $\text{Cr}_2\text{N}$ ) shown in Phot. 2(a) was a phase in equilibrium or not.

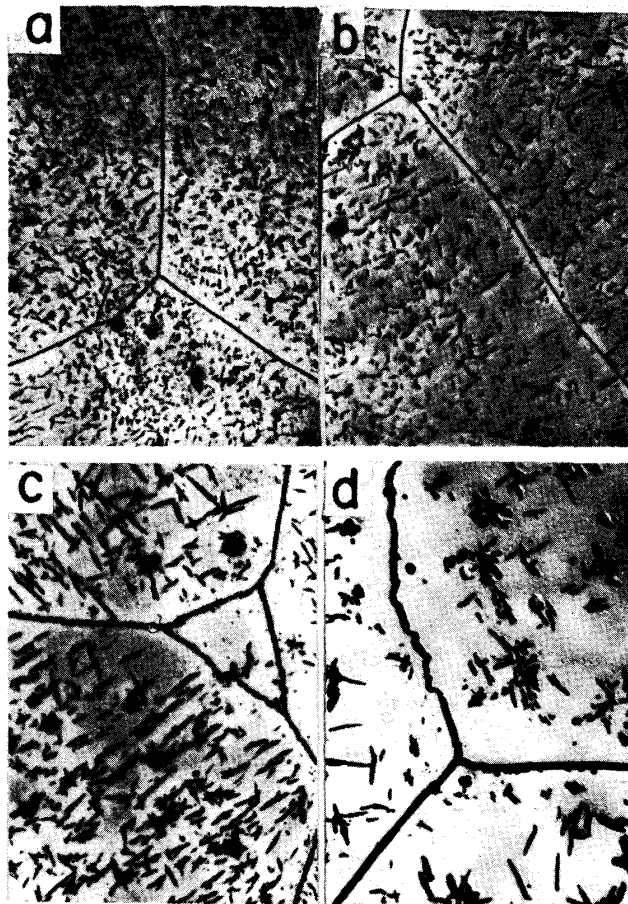
The structure separating this nitride has been observed in a few studies<sup>(1)(2)(5)</sup>, and Okamoto et al.<sup>(7)</sup> have made a section-structural diagram at  $1250^{\circ}\text{C}$  in assertion that the ( $\text{Cr}_2\text{N}$ ) is a phase in equilibrium. There is, however, a contradiction in this structural diagram in that the prolongation of the phase boundary between ferrite plus  $\text{Cr}_2\text{N}$  and ferrite plus austenite plus  $\text{Cr}_2\text{N}$  has not reached the composition of  $\text{Cr}_2\text{N}$ . They had not explained this point. Accordingly, in the present case, this contradiction was examined and the following points were made clear:

(1) Although the ( $\text{Cr}_2\text{N}$ ) is similar in crystal structure to lumpy and lamellar  $\text{Cr}_2\text{N}$  separated at low temperatures, it has extremely fine shape. Phot. 3 shows the shape of ( $\text{Cr}_2\text{N}$ ) which was extracted from 26N14 alloy water-cooled from  $1300^{\circ}\text{C}$ . They are thin plate-like crystals about  $0.25\mu$  in width and  $1\mu$  in length. The size of ( $\text{Cr}_2\text{N}$ ) hardly changes even if it is heated in the range of  $1100^{\circ}$  to  $1400^{\circ}\text{C}$  for a long time.





Phot. 3. Electron micrograph of  $\text{Cr}_2\text{N}$  precipitated from  $\alpha$  during cooling in 26N14 alloy quenched in water from  $1300^\circ\text{C}$ .



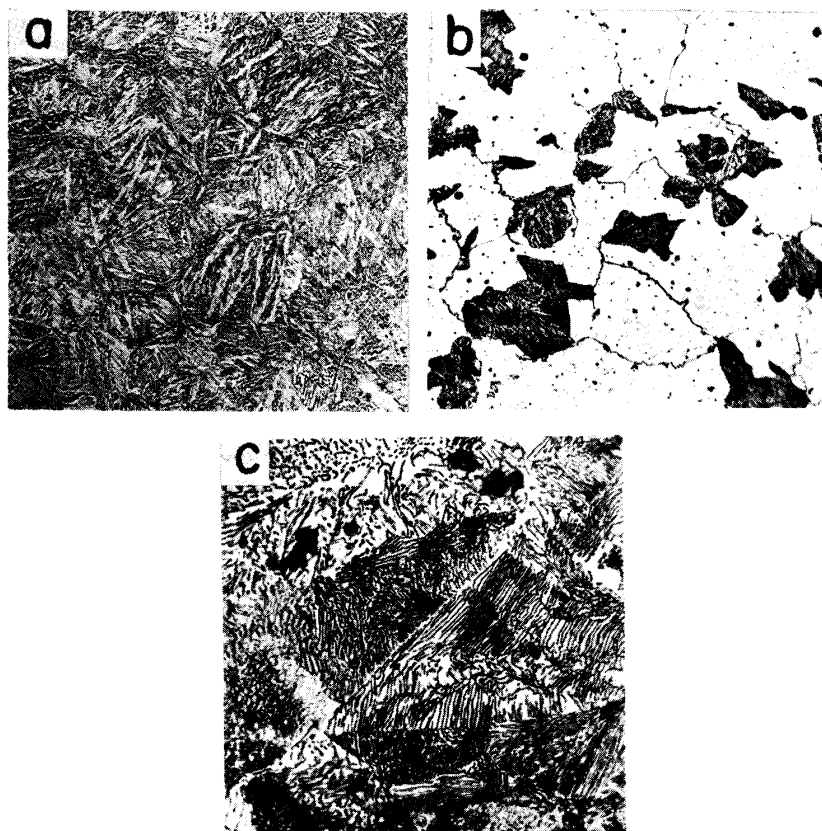
Phot. 4. Microstructures of 37N17 alloy cooled by various rates from  $1200^\circ\text{C}$ ; (a) quenched in ice-brine solution, (b) quenched in water, (c) quenched in oil, (d) air cooled.

(2) When the heating conditions are fixed and the cooling rate is changed, the shape and the distribution of  $(\text{Cr}_2\text{N})$  clearly change. Phot. 4 shows the structures of 37 N 17 alloy ( $5\text{ mm}\phi \times 10\text{ mm}$  size) cooled down in ice-brine, in

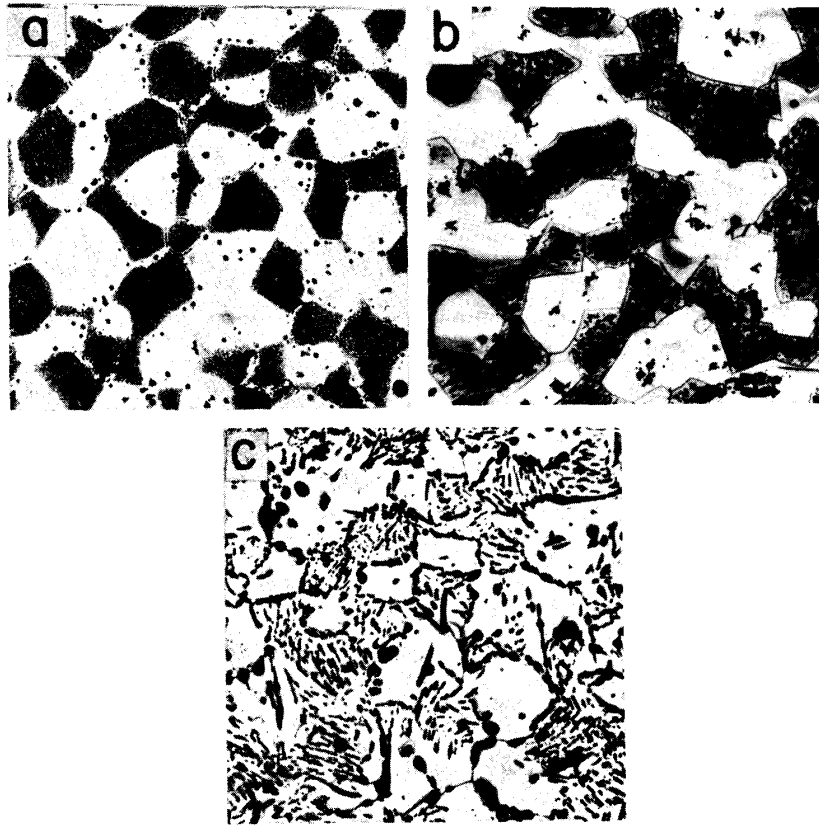
water and in oil, respectively, after being heated at 1200°C for 30 minutes. It is to be noted that when the cooling rate becomes higher, the separates become finer and are distributed homogeneously in a large number.

(3) In alloys cooled abruptly by using of a slender wire, the  $(Cr_2N)$  becomes no longer observable. That is, when 0.8 mm $\phi$  wires of Cr-Fe alloys containing 18, 21 and 25% of chromium, respectively, were heated at 1200°C for 100 hr in argon gas containing 30%  $N_2$ , and cooled in ice-brine and in air, the  $(Cr_2N)$  was observable in the air-cooled specimens, whereas in the specimens cooled in ice-brine it was not observable.

Of the experimental results mentioned above, (3) shows that the  $(Cr_2N)$  is not present at the heating temperature but separates in the process of cooling. (1) and (2) show that the distribution within matrix and the shape of  $(Cr_2N)$  hardly change with temperature and heating time, and that it becomes fine and is distributed in large numbers gradually as the cooling rate becomes higher. This would be explained from the fact that a rise of cooling rate increases the number of nucleus separated and decreases the rate of growth; that is, the  $(Cr_2N)$  is not the phase in equilibrium at high temperatures. It is, therefore, conceivable that it will be separated even in a considerably rapid cooling because the nitrogen solubility of ferrite in Fe-Cr-N system is greatly reduced at considerably high



Phot. 5. Microstructures of 19N65 alloy quenched from various temperatures; (a) 1000°C $\times$ 5 hr, W.Q. ( $\times$ 100), (b) 875°C $\times$ 50 hr, W.Q. ( $\times$ 100), (c) 825°C $\times$ 50 hr, W.Q. ( $\times$ 400).

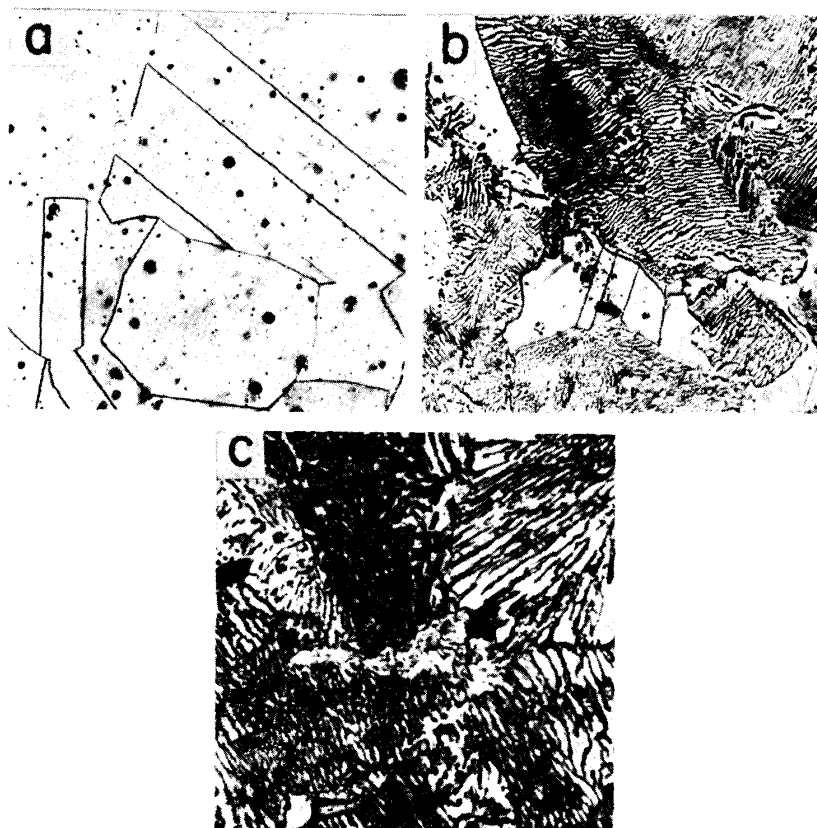


Phot. 6. Microstructures of 25N57 alloy quenched from various temperatures; (a) 1300°C × 1 hr, W.Q. (×200), (b) 1200°C × 2 hr, W.Q. (×200), (c) 1000°C × 5 hr, W.Q. (×200).

temperatures. In fact, the dilatation test revealed that there was a pronounced change in nitrogen solubility of 37N17 alloy between 1150° and 1100°C. Consequently, it is necessary that the ferrite inclusive of  $(Cr_2N)$  in Fe-Cr-N system should be considered to be the single ferrite phase with the exception of  $(Cr_2N)$ .

Next, the changes in structure in the case in which the chromium content is fixed and the amount of nitrogen is varied will be described. In Fe-Cr binary system, the structure becomes the single phase of ferrite, austenite being not present, when the chromium content is above about 13%. When nitrogen is added to this, it becomes ferrite plus austenite structure, and becomes the single phase of austenite when the nitrogen content exceeds a certain amount. The minimum amount of nitrogen required to obtain the single phase of austenite is about 0.1% in 13% chromium, about 0.4% in 18% chromium and about 0.8% in 26% chromium content, which is equivalent approximately to the carbon content in Fe-Cr-C system<sup>(11)</sup>. For example, the changes in structure in 19N65, 25N57 and 27N100 alloys are shown in Phots. 5 to 7. Between 1300° and 950°C, 19N65 alloy is of the single phase of austenite (Phot. 5 (a) shows the structure water-cooled from 1000°C, which is martensite structure), then separates  $Cr_2N$  at grain boundaries

(11) K. Bungardt, E. Kunze and E. Horn, *Arch. Eisenhütt.*, **29** (1958), 193.



Phot. 7. Microstructures of 27N100 alloy quenched from various temperatures; (a) 1100°C×5 hr, W.Q. (×200), (b) 1075°C×5 hr, W.Q. (×200), (c) 1050°C×5 hr, W.Q. (×600).

and the decomposition of austenite occurs between 900° and 850°C. Phot. 5(b) shows the structure at 875°C, in which the white part is martensite and the lamellar part consists of ferrite and Cr<sub>2</sub>N. At 825°C, the decomposition of austenite comes to an end, becoming the lamellar structure of ferrite and Cr<sub>2</sub>N as shown in Phot. 5(c). At 1300° and 1200°C, 25N57 alloy shows the structure consisting of super-cooled austenite and ferrite including (Cr<sub>2</sub>N) as shown in Photos. 6(a) and 6(b), but is still of the structure of two phases of austenite and ferrite at that temperature because the (Cr<sub>2</sub>N) is nitride separated during cooling. This structure remains as it is until 1100°C, below which, that is, between 1100° and 1075°C, it becomes the structure consisting of ferrite and lamellar part of ferrite plus Cr<sub>2</sub>N as shown in Phot. 6(c). In 27N100 alloy containing more nitrogen, the single phase of austenite shown in Phot. 7(a) is present until 1075°C, below which it becomes the lamellar structure of ferrite and Cr<sub>2</sub>N shown in Phot. 7(c) at 1050°C, after passing through the structure of ferrite, austenite and Cr<sub>2</sub>N shown in Phot. 7(b).

## 2. Characters of nitride

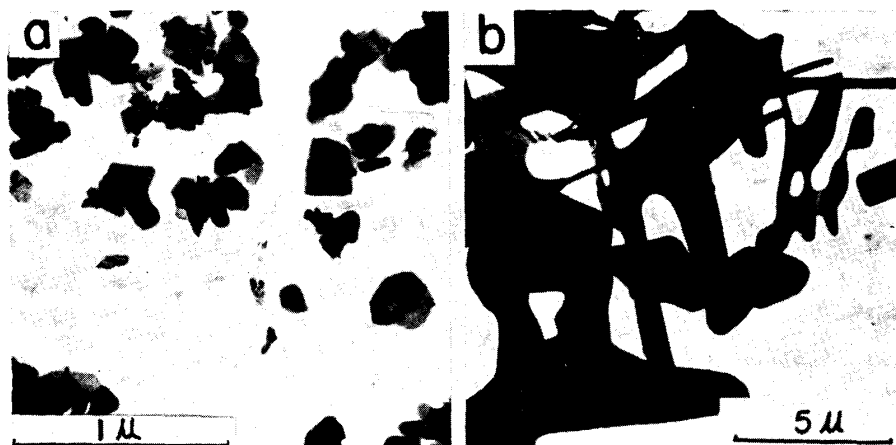
As mentioned above, nitrides observed in the present study on ternary alloys in Fe-Cr-N system were of three kinds, namely, Fe<sub>4</sub>N, CrN and Cr<sub>2</sub>N. Fe<sub>4</sub>N appeared only in 0.5N10 alloys, but it is conceivable from the phase diagram of

Fe-N system that it will separate in alloys with chromium content less than 0.5%. The extraction of  $\text{Fe}_4\text{N}$  was very difficult because of easy oxidation, and consequently, the chemical analysis was impossible.

The composition range in which CrN is separable is as follows: In the range of nitrogen content of about 0.1% and chromium content of about 0.5 to 7%, the nitride of CrN is separated; 0.5N10 alloy undergoes the reaction  $\gamma \rightarrow \alpha + \gamma \rightarrow \alpha + \gamma + \text{CrN} \rightarrow \alpha + \text{CrN} + \text{Fe}_4\text{N}$ , 3N06, 5N06 and 5N10 alloys the reaction  $\gamma \rightarrow \alpha + \gamma \rightarrow \alpha + \gamma + \text{CrN} \rightarrow \alpha + \text{CrN}$ , and 5N08, 6N07 and 6N10 alloys the reaction  $\gamma \rightarrow \alpha + \gamma \rightarrow \alpha + \gamma + \text{Cr}_2\text{N} \rightarrow \alpha + \text{Cr}_2\text{N} + \text{CrN}$ . This CrN is of a face-centered cubic structure which is the same as CrN(=4.140 Å) in Cr-N system confirmed by Blix<sup>(12)</sup>, and its lattice parameter remains invariable with different kinds of alloys, being about  $4.140 \pm 0.005\text{Å}$ . As shown in Table 5, the solubility of iron into CrN is about 5 to 6%. The shape of CrN in ferrite is fine and an electron-microscopic examination shows it to be of rectangular-platelet as fine as  $0.2\mu$  as shown in Phot. 8(a).

Table 5. Concentrations of N and Fe in CrN and  $\text{Cr}_2\text{N}$

Designation	Heat treatment	Isolated nitride	Chemical analyses	
			Fe(wt%)	N(wt%)
3N06	Annealed	CrN	5.02	—
5N06	Annealed	CrN	6.53	—
19N13	Annealed	$\text{Cr}_2\text{N}$	2.40	—
19N30	Annealed	$\text{Cr}_2\text{N}$	3.37, 2.54	—
26N14	Annealed	$\text{Cr}_2\text{N}$	3.17	10.25
25N57	Annealed	$\text{Cr}_2\text{N}$	3.67, 3.25	9.70
30N23	900°C, W. Q.	$\text{Cr}_2\text{N}$	4.42	—
26N14	1300°C, W. Q.	( $\text{Cr}_2\text{N}$ )	10.06	8.50
25N57	1300°C, W. Q.	( $\text{Cr}_2\text{N}$ )	7.78	—
37N17	1300°C, W. Q.	( $\text{Cr}_2\text{N}$ )	7.20	—



Phot. 8. Electron micrograph of CrN and  $\text{Cr}_2\text{N}$  in Fe-Cr-N alloy; (a) CrN in annealed 3N06 alloy, (b)  $\text{Cr}_2\text{N}$  in annealed 25N57 alloy.

(12) R. Blix, *Z. Phys. Chem.*, **B3** (1926), 229.

$\text{Cr}_2\text{N}$  is separated only in alloys whose chromium content is more than about 6%. When the chromium content is 6 to 7%, it coexists with CrN, above which only  $\text{Cr}_2\text{N}$  exists. In the specimens used in the present experiments, the reaction  $\gamma \rightarrow \alpha + \gamma \rightarrow \alpha + \gamma + \text{Cr}_2\text{N} \rightarrow \alpha + \text{Cr}_2\text{N}$  takes place in low nitrogen side and the reaction  $\gamma \rightarrow \gamma + \text{Cr}_2\text{N} \rightarrow \gamma + \alpha + \text{Cr}_2\text{N} \rightarrow \alpha + \text{Cr}_2\text{N}$  in high nitrogen side.  $\text{Cr}_2\text{N}$  resulting from the decomposition of austenite is formed in lamellar with ferrite, similar to pearlite reaction in Fe-C system. Phot. 8(b) shows the shape of lamellar  $\text{Cr}_2\text{N}$  observed by electron microscope. In the ferritic alloys in which austenite is not present,  $\text{Cr}_2\text{N}$  is separated in a large lumpy shape at grain boundaries and in grains.  $\text{Cr}_2\text{N}$  in Fe-Cr-N system has the same hexagonal crystal structure as  $\text{Cr}_2\text{N}$  (9.3 to 11.9 wt % N,  $a=4.759$  to  $4.805\text{A}$ ,  $c/a=0.932$  to  $0.933^{(13)}$ ) in Cr-N system, and its lattice parameter hardly changes with temperature or with alloy composition, that is,  $a=4.77 \pm 0.01 \text{ A}$ ,  $c/a=0.930 + 0.002$ . As shown in Table 5, its chemical composition is about 2 to 4% of iron content and about 10% of nitrogen content. The ( $\text{Cr}_2\text{N}$ ) phase observed in high chromium alloys does not differ in lattice parameter from  $\text{Cr}_2\text{N}$  equilibrium mentioned above, there being a little more iron content (about 7 to 9%) and a little less nitrogen content (about 8.5%), which is considered to be due to non-equilibrium phase rapidly separated during cooling.

### Summary

Examinations were made of the phase reactions and the characters of nitrides in alloys of Fe-Cr-N system with 0.5 to 40% of chromium content and less than 1% of nitrogen content. The results may be summarized as follows:

(1) The nitrides observed in the range of the present compositions are  $\text{Fe}_4\text{N}$ , CrN and  $\text{Cr}_2\text{N}$ . Because of the difficulty in extraction, the characters of  $\text{Fe}_4\text{N}$  could not be made clear. CrN has a face-centered cubic structure with the lattice parameter of  $4.140 \pm 0.005\text{A}$ , in which the solubility of iron is about 5 to 6%.  $\text{Cr}_2\text{N}$  has a hexagonal crystal structure whose lattice parameter hardly changes with the compositions and the heat-treatments of alloys, that is,  $a=4.77 \pm 0.01\text{A}$  and  $c/a=0.930 \pm 0.002$ , and the solubility of iron is about 2 to 4%.

(2) When nitrogen content is about 0.1% and chromium content is about 0.5%, it undergoes the structural changes of  $\gamma \rightarrow \alpha + \gamma \rightarrow \alpha + \gamma + \text{CrN} \rightarrow \alpha + \text{CrN} + \text{Fe}_4\text{N}$ . In the case of alloys with 0.5 to 6% of chromium content, the structural changes  $\gamma \rightarrow \alpha + \gamma \rightarrow \alpha + \gamma + \text{CrN} \rightarrow \alpha + \text{CrN}$  take place. The alloys with about 6 to 7% of chromium content undergo the structural changes of  $\gamma \rightarrow \alpha + \gamma \rightarrow \alpha + \gamma + \text{Cr}_2\text{N} \rightarrow \alpha + \text{Cr}_2\text{N} + \text{CrN}$ , showing the coexistence of  $\text{Cr}_2\text{N}$  and CrN. In the alloys with more than 7% of chromium content,  $\text{Cr}_2\text{N}$  is separated; in the alloys with less than 13% of chromium content, the structural changes  $\gamma \rightarrow \alpha + \gamma \rightarrow \alpha + \gamma + \text{Cr}_2\text{N} \rightarrow \alpha + \text{Cr}_2\text{N}$  take place; in the alloys with chromium contents between 13 and 26%, there are the structural changes  $\alpha + \gamma \rightarrow \alpha + \gamma + \text{Cr}_2\text{N} \rightarrow \alpha + \text{Cr}_2\text{N}$ . Similar to the pearlite structure in Fe-C system,  $\text{Cr}_2\text{N}$  resulting from the decomposition of austenite is formed in

(13) S. Eriksson, Jernkont. Ann., **118** (1934), 530.

lamellar with ferrite. In the alloys with more than 26% of chromium content, austenite no longer exists, showing only a structure consisting of ferrite and  $\text{Cr}_2\text{N}$ .

(3) In Fe-Cr system, the alloys with over 13% of chromium content in which austenite is absent undergo the structural changes  $\alpha \rightarrow \alpha + \gamma \rightarrow \gamma$  with the addition of nitrogen; the minimum nitrogen content required to obtain the single phase of austenite is about 0.1% in the case of 13% chromium content, about 0.4% in the case of 18% chromium content, about 0.8% in the case of 26% chromium content. In the alloys in the range of ferrite plus austenite, structural change  $\alpha + \gamma \rightarrow \alpha + \gamma + \text{Cr}_2\text{N} \rightarrow \alpha + \text{Cr}_2\text{N}$  takes place during cooling, but the alloys of the single phase of austenite undergo the structural changes  $\gamma \rightarrow \gamma + \text{Cr}_2\text{N} \rightarrow \alpha + \gamma + \text{Cr}_2\text{N} \rightarrow \alpha + \text{Cr}_2\text{N}$ .

(4) The very fine acicular  $\text{Cr}_2\text{N}$  is separated from ferrite in the alloys with over 15% chromium which has been water-cooled from above about 1100°C. In the past, this phase was considered to be a phase in equilibrium, but the present experiment has made it clear that it is non-equilibrium phase separated in the process of cooling because the solubility of nitrogen in ferrite will be reduced rapidly at high temperatures, and because it is very difficult to prevent it from being separated. So, it was designated by  $(\text{Cr}_2\text{N})$ .