The Phase Diagram of the Niobium-Carbon System

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The niobium-carbon system has been investigated by melting point measurements, X-ray analyses and microscopic examinations. An equilibrium diagram up to 63.5 atomic percent carbon was constructed as shown in Fig. 2. The limit of carbon solubility in niobium (α) phase lies at about 2 atomic percent at 2000°C and it decreases abruptly as the temperature decreases. The Nb₂C (β) phase has a very narrow range of homogeneity and the NbC (γ) phase exists in a wide composition range from 41 to 50 atomic percent carbon below 1400°C. Three non-variant reactions in this system were determined as follows.

Name	Reaction	Composition	Temperature
Eutectic	$L \rightleftharpoons Nb(\alpha) + Nb_2C(\beta)$	13.5 at. % C.	2340 $\pm$ 20°C
Peritectic	$L + NbC(\gamma) \rightleftharpoons Nb_2C(\beta)$	33.3 at. % C.	3080 $\pm$ 50°C
Eutectic	$L \rightleftharpoons NbC(\gamma) + \text{Graphite}$	60.5 at. % C.	3300 $\pm$ 50°C

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I. Introduction

In the Nb-C system, four solid phases are known. They are primary solid solutions at the niobium side (α -phase: body centered cubic), NbC₂ (β -phase: hexagonal arrangement of niobium atoms), NbC (γ -phase: NaCl type cubic) and graphite. Most of the previous works on this system have been done with regard to the solid solubility and the correlation of these phases. In 1948, Goldschmidt⁽¹⁾ postulated a eutectic reaction between niobium and NbC (γ) phase at 1950°C. He also detected no solid solubility of carbon in niobium. Brauer et al.⁽²⁾ found Nb₂C for the first time in 1954 and indicated the homogeneity range of NbC (γ) and Nb₂C (β) phases. The solid solubility line of carbon in niobium was shown to be less than 0.077 at. % at 310°C by means of the internal friction measurements of Powers and Doyle.⁽³⁾ A more complete study on the solid solubility of carbon in niobium was carried out by Elliott,⁽⁴⁾ who made use of metallographic techniques. Pochon et al.⁽⁵⁾ studied the distribution of carbide in arc-melted specimens. Storms and Krikorian⁽⁶⁾ investigated the phase diagram of the niobium-carbide system. They determined the region of single phase Nb₂C, using their thermal arrest apparatus and also reported the phase relationships in this system.

In the present work, a more complete phase diagram was constructed from microscopic, X-ray and melting point data in the light of previous works.^{(1)~(10)} In order to obtain specimens free from gaseous impurities,

the electron beam melting method was used for the preparation of low carbon alloys, while for high carbon contents alloys the arc melting method was employed.

II. Experimental Procedures

The niobium† used in this investigation was in the form of -200 mesh powder more than 99.6 wt. % in purity, according to the manufacture's analysis table.

Briquettes used for melting of the desired composition were prepared by pressing well mixed mixture of niobium powder and graphite powder* or master alloy powder (33.21 at. % C). Pressing was carried out by using a steel die and applied pressure was 3 ton/cm². Most of the briquettes containing more than 50 at. % carbon were sintered in vacuum: 10⁻⁵ mmHg at 1100°C and then arc-melted in an argon atmosphere by using a laboratory arc furnace equipped with a graphite lined crucible and water cooled tungsten electrode. The master alloy used for preparing low carbon specimens was made by electron beam melting under a pressure less than 10⁻⁵ mmHg for 30 minutes. The master alloy ingot was pulverized to pass a 200-mesh sieve and then low carbon alloy briquettes were prepared. Briquettes were melted in an electron beam furnace. Specimens were remelted several times to obtain a homogenous button. Ten or twenty gram button ingots containing from zero to 63.47 at. % C were prepared.

Heat treatment below 1200°C was carried out in a fused silica tube under argon atmosphere at a given temperature for 10 days to 60 days. Within the temperature range from 1300 to 2000°C, the specimen was suspended with a niobium basket in a graphite tube resistor (10 mm. inner diameter, 150 mm. length) held in a water cooled stainless bell jar. The jar was evacuated to 10⁻⁵ mmHg and the graphite resistor was heated by electricity. The specimen was heated for 1 to 10 hrs. in the graphite resistor tube. The temperature control at these high temperatures was carried out within

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(3) R. W. Powers and M. V. Doyle: Trans. AIME, 209 (1957), 1285.

(4) R. P. Elliott: Armour Research Foundation Repts., ARF-2120-4 (1959).

(5) M. L. Pochon, C. R. McKinsey, R. A. Perkins and W. D. Forgeng: Metallurgical Society Conf., vol. 2, "Reactive Metals" pp. 327, Interscience Publishers, New York, 1959.

(6) E. K. Storms and N. H. Krikorian: J. phys. Chem., 63 (1959), 1747; 64 (1960), 1471.

† Fansteel Metallurgical Co.

* Spectrograph Electrode Carbon.

Fig. 1 Schematic cross section of melting point measurement furnace.

$\pm 20^\circ\text{C}$. A furnace to measure the melting point is illustrated in Fig. 1. A small piece of the specimen (about 0.1 gr.) was set in the hole drilled at the center of the graphite bridge which acts as a resistor and the temperature was increased by electric current to 400 amperes, 2 volts, in vacuum or in an argon atmosphere. The emission of the specimen changed abruptly when the temperature reached a critical value, and then the specimen melted down.

The incipient melting data were obtained by observing the change of emission and the complete melting data was obtained by observation. Temperatures were measured with a calibrated optical pyrometer. Calibration of the optical pyrometer was carried out by measuring melting points of TiC, Mo-Mo₂C eutectic, W-W₂C eutectic, tungsten, tantalum and niobium as standard substances.

Crushed and powdered specimens were used for X-ray diffraction examination. The X-ray diffraction patterns were obtained with a 89.5 mm. Debye-Scherrer camera using filtered Cu-K α radiation.

Carbon analyses for these alloys were obtained with a conductometric method using Wösthoff's apparatus. Oxygen analyses of low carbon alloys were performed with the vacuum fusion method.

Metallographic specimens were etched by using a mixture of 8:1:1 HF:HNO₃:H₂O or 8:1:1 HF:NH₄F:H₂O and modified etching reagents were employed to obtain a suitable microscopic structure. Electrolytic etching was carried out for some of the specimens, in 10 % HCl solution which was saturated with NaCl. Alternating current (50 cycles, 10~20 volts) was applied between the polished specimen which was held with platinum tongs and the graphite electrode.

III. Results and Discussions

Fifty-six alloys were arc-melted or electron beam melted to study the phase diagram up to 63.5 at. % C. A complete list of a number of alloy compositions is shown in Table 1. The constructed phase diagram of the Nb-C system is given in Fig. 2.

Solidus and liquidus lines in Fig. 2 were drawn according to melting point data and some other

Table 1 Chemical analysis and melting points of Nb-C alloys.

Specimen No.	Intended Composition, C (at %)	Chemical Analysis, C (at %)	Melting point data	
			Incipient melting temperature ($^\circ\text{C}$)	Complete Melting temperature ($^\circ\text{C}$)
E-1	0.02	0.013	—	2465 $\pm$ 5
E-2	0.03	0.038	—	2465 $\pm$ 5
E-3	0.05	0.063	—	2465 $\pm$ 5
E-4	0.07	0.087	—	2465 $\pm$ 5
E-5	0.1	0.091	—	2465 $\pm$ 5
E-6	0.2	0.152	—	2465 $\pm$ 5
E-7	0.5	0.444	—	2465 $\pm$ 5
E-8	1	0.980	—	2465 $\pm$ 5
E-9	1.5	1.417	—	2465 $\pm$ 5
E-10	2	1.873	—	2451 $\pm$ 15
E-11	3	2.958	—	2455 $\pm$ 20
E-12	6	4.530	2381 $\pm$ 20	2450 $\pm$ 20
E-13	12	11.94	—	2364 $\pm$ 20
E-14	13	13.21	—	2340 $\pm$ 20
E-15	14	14.34	—	2338 $\pm$ 20
E-16	17	18.40	2345 $\pm$ 20	2602 $\pm$ 30
E-17	20	21.14	2350 $\pm$ 30	2755 $\pm$ 30
E-18	23	24.88	2456 $\pm$ 40	2909 $\pm$ 40
E-19	27	26.68	2638 $\pm$ 40	3023 $\pm$ 40
E-20	33	28.83	—	3085 $\pm$ 50
E-21	35	31.22	3074 $\pm$ 50	3180 $\pm$ 50
E-22	40	32.13	3088 $\pm$ 50	3240 $\pm$ 50
E-23	43	33.21	3083 $\pm$ 50	3241 $\pm$ 50
E-24	44	39.87	3254 $\pm$ 50	3465 $\pm$ 50
E-25	45	40.13	3236 $\pm$ 50	3480 $\pm$ 50
E-26	47	41.10	3380 $\pm$ 50	3518 $\pm$ 50
A-1	20	19.04	2403 $\pm$ 20	2611 $\pm$ 30
A-2	25	24.28	2410 $\pm$ 20	2923 $\pm$ 30
A-3	31	30.21	—	3088 $\pm$ 40
A-4	33	33.27	—	3249 $\pm$ 50
A-5	35	36.30	3072 $\pm$ 50	3373 $\pm$ 50
A-6	37	38.99	3219 $\pm$ 50	3461 $\pm$ 50
A-7	39	37.82	3205 $\pm$ 50	3444 $\pm$ 50
A-8	40	37.92	3213 $\pm$ 50	3463 $\pm$ 50
A-9	41	39.97	3280 $\pm$ 50	3516 $\pm$ 50
A-10	42	41.18	3443 $\pm$ 50	3521 $\pm$ 50
A-11	43	41.31	3421 $\pm$ 50	3479 $\pm$ 50
A-12	45	43.60	—	3541 $\pm$ 50
A-13	47	44.64	—	3539 $\pm$ 50
A-14	49	46.20	—	3592 $\pm$ 50
A-15	50	47.16	—	3588 $\pm$ 50
A-16	51	49.88	—	3628 $\pm$ 50
A-17	52	49.06	—	3608 $\pm$ 50
A-18	53	50.59	—	3584 $\pm$ 50
A-19	55	53.44	—	3515 $\pm$ 50
A-20	57	54.55	3386 $\pm$ 50	3473 $\pm$ 50
A-21	61	57.62	—	3318 $\pm$ 50
A-22	62	60.10	—	3321 $\pm$ 50
A-23	64	60.37	—	3294 $\pm$ 50
A-24	66	62.05	3271 $\pm$ 50	3762 $\pm$ 50
A-25	68	63.41	3349 $\pm$ 50	>3900
A-26	70	62.71	3351 $\pm$ 50	3754 $\pm$ 50
A-27	72	62.56	3283 $\pm$ 50	3679 $\pm$ 50
A-28	75	62.81	3312 $\pm$ 50	3823 $\pm$ 50
A-29	80	61.32	—	3798 $\pm$ 50
A-30	85	63.47	—	>3900

E: Electron beam melted —: not be determined
A: Arc melted

references.⁽⁶⁾⁽⁷⁾ These lines corresponded to incipient melting and complete melting temperatures as shown in Table 1. The melting point values listed in Table 1 were arithmetical mean values of 5~10 measuring values respectively. X-ray analyses were carried out

from 41 to 50 at. % C and graphite phase. Lattice constants of these phases in this system are shown in Table 2.

In the following paragraphs, each of these phases and their relationships are discussed.

Fig. 2 Niobium-Carbon phase diagram.

Carbon at. %	Diffraction Angle (θ°) 20 30 40 50 60 70 80	Structure
63.47		Graphite + NbC
47.16		NbC
41.31		NbC
40.13		NbC
39.97		NbC + Nb ₂ C
36.30		NbC + Nb ₂ C
33.21		NbC + Nb ₂ C
30.21		Nb ₂ C + NbC (trace)
24.28		Nb ₂ C + Nb + NbC (trace)
19.04		Nb ₂ C + Nb
2.96		Nb ₂ C + Nb
0.01		Nb

Fig. 3 X-ray powder diffraction patterns in the Nb-C system.

Table 2 Crystal structures and lattice parameters of the phases existing in the Nb-C system. (in kX)

Nb(α) b.c.c.	Nb ₂ C(β) h. c. p. (for Nb atoms)			NbC(γ) cubic NaCl type	Remarks
	a	c	c/a		
	3.113	4.949	1.59	4.422~4.462	present work
	3.111~3.120	4.944~4.958	1.59	4.424~4.457	Brauer et al. ⁽²⁾
	3.10	4.93	1.59		Pochon et al. ⁽⁵⁾
	3.119~3.122	4.955~4.963	1.59		Storms et al. ⁽⁶⁾
	3.109~3.113	4.944~4.956	1.59		Elliott. ⁽⁴⁾
				4.452	Duweze et al. ⁽⁸⁾
3.294					Pearson. ⁽⁹⁾

α -phase

α -phase is the niobium base solid solution and shows a body centered cubic crystal structure. The upper solubility limit line of carbon in α -phase lies at 1900°C. 1.8 at. %, at 1700°C. 0.4 at. %, at 1500°C. 0.2 at. % and at 1200°C. 0.1 at. % respectively and somewhat less than 0.08 at. % carbon at lower temperatures.

According to Elliott⁽⁴⁾ who used metallographic techniques, the solubility limits were determined as 0.77 at. % at 1800°C, 2.4 at. % at 2000°C, 3.8 at. % at 2200°C. With regard to lower temperatures, Pochon et al.⁽⁵⁾ indicated a solid solubility of about 0.12 at. % carbon at 1200°C.

Powers and Doyle⁽³⁾ observed a decrease in magnitude of the internal friction peak on aging a 0.077 at. % carbon alloy at 310°C and thus they suggested the solid solubility of carbon in niobium is less than 0.077

Fig. 4 1.873 at.% C alloy.

(a) As cast. Polyhedral grains of Nb (α) solid solution. $\times 200$

(b) Heated for 2 hrs at 1900°C and cooled. Acicular Nb₂C (β) in α -phase matrix. $\times 200$

with all alloys and Fig. 3 shows representative patterns. In this system, four types of diffraction patterns were observed. They are the solid solution of niobium (α) phase, Nb₂C (β) phase, NbC (γ) phase extended ranging

at. % at 310°C. In the region above 2000°C, the solubility line of carbon in α -phase is shown with a dotted fine line in Fig. 2 on the basis of Elliott's

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(9) W. B. Pearson: "Handbook of Lattice Spacings and Structures of Metals" pp. 126, Pergamon Press, London, 1958.

(7) M. R. Nadler and C. P. Kempter: J. phys. Chem., **64** (1960), 1468.

results. Electron beam melted specimens containing up to 2 at. % carbon show no appreciable phase other than a single phase of α -structure as shown in Fig. 4 (a). The microstructure of 1.87 at. % C alloy, after heat treated at 1900°C for 2 hrs. shows two phases of α and β precipitated from α as shown in Fig. 4 (b).

Eutectic reaction between α and β

There is a eutectic reaction between α and β phases, at $2340^\circ \pm 20^\circ\text{C}$ and its composition is 13.5 at. % carbon. Fig. 5 shows an example of cast structures of hypo-eutectic alloys. In the present study, it was observed that the eutectic composition lies between 13.21 and 14.34 at. % C. The eutectic temperature has been reported by Pochon et al.,⁽⁵⁾ to be $2335 \pm 20^\circ\text{C}$ and $2328 \pm 17^\circ\text{C}$ by Nadler and Kempter.⁽⁷⁾

Fig. 5 13.21 at. % C alloy, as cast. Primary α plus eutectic mixture ($\alpha + \beta$). $\times 200$

Fig. 6 24.88 at. % C alloy. Water quenched after being heated for 100 hrs at 1200°C . Precipitated α in primary β globules and eutectic mixture ($\alpha + \beta$). $\times 200$

Fig. 7 31.22 at. % C alloy, as cast. Banded twin-like structure of a two-phase mixture of β and NbC (γ), β formed by the peritectic reaction (white) and traces of super-cooled liquid (dark). Electrolytic etched. $\times 200$

Fig. 8 36.30 at. % C alloy. Water quenched after being heated for 100 hrs at 1200°C . Banded twin-like structure and β (dark). $\times 1000$

β -phase

β -phase is a solid solution of Nb_2C and has a closed packed hexagonal arrangement of niobium atoms as shown in Table 2. The region of Nb_2C (β) phase lies between the stoichiometric composition (2 moles of niobium and 1 mole of carbon: 33.3 at. % C) and solid solubility line based on Storms and Krikorian's results.⁽⁶⁾ The solid solubility of Nb_2C (β) phase is shown in Fig. 2. In microscopic examinations, β -phase grains in the eutectic matrix are readily distinguished from other phases by their hardness and by the striation of niobium which developed in β -phase grains, as shown in Fig. 6. In spite of the fact that the amount of the eutectic matrix decreased as the carbon content of the alloy approached to 33.3 at. %, the complete β -phase could not be observed both in this microscopic and X-ray examinations.

The $\alpha + \beta/\beta$ boundary curves toward higher niobium contents and intersects the eutectic horizontal line at greater niobium concentrations. It is easily concluded that striations of niobium in Nb_2C (β) grains are the resultant of precipitation when cooled. The appropriateness of the precipitation in this case was clarified by Storms and Krikorian⁽⁶⁾ and they observed the precipitation and dissolution of niobium in β -phase, using their thermal arrest apparatus.

In the X-ray analyses of melted alloys, there was no case where the diffraction pattern of Nb_2C (β)-phase was detected alone, but the pattern co-existed with the diffraction lines of other phases and was observed in the wide region of 3 to 40 at. % C. As carbon content of alloys increases, another phase which is identified as NbC appears. Brauer et al.⁽²⁾ reported

NbC which was prepared by sintering at 1600 to 1700°C has a range of homogeneity between 25.9 and 33.3 at. % C.

Peritectic reaction and regions of β and γ phases

The microstructure of alloy containing about 33.3 at. % C shows peritectic reaction and melting point data show the peritectic temperature at $3080 \pm 50^\circ\text{C}$. Storms and Krikorian⁽⁶⁾ obtained $3090 \pm 50^\circ\text{C}$ and Nadler and Kempter⁽⁷⁾ also obtained $3080 \pm 35^\circ\text{C}$ for the peritectic temperature, which agrees well with the present results. However, Pochon et al.,⁽⁵⁾ placed the peritectic temperature at $3265 \pm 20^\circ\text{C}$.

The peritectic structure of cast alloy containing 31.22 at. % C is shown in Fig. 7. The primary phase in this figure is a mixture of Nb_2C (β) and NbC (γ) phases

characterized by banded twin-like structures. Dark etched areas in Fig. 7 are the super-cooled eutectic caused by rapid cooling from liquid. The striation described in the preceding section does not appear in the β -phase (white areas in Fig. 7) formed by the peritectic reaction.

Representative microstructure of alloys in $\beta + \gamma$ field is shown in Fig. 8. The figure shows a large area of β -phase and a banded twin-like area. The banded twin-like structures as shown in these photographs are discussed in the following section.

Between Nb_2C (β) and NbC (γ), Brauer and Lesser⁽¹⁰⁾ reported ξ -phase on the basis of a very weak diffraction line at $\theta = 19.70^\circ$. In the present investigation, there is no line at this angle. Also Elliott⁽⁴⁾ and Storms and Krikorian⁽⁶⁾ were unable to find this phase.

Fig. 9 Variation of the $\text{NbC}(\gamma)$ lattice parameter with composition.

cubic structure. The melting point of specimens rises from the peritectic temperature and reaches the maximum point at $3600 \pm 50^\circ\text{C}$ in the stoichiometric composition (50 at. % C) alloy.

The solid solubility range of NbC (γ) phase below 2000°C is decided by X-ray and microscopic examinations, as shown in Fig. 2. The relationship between the lattice parameter of NbC (γ) phase and carbon content is given in Fig. 9. The lattice parameter of NbC (γ) decreases gradually from 4.462 kX in 50.59 at. % C alloy to 4.422 kX in 40.13 at. % C alloy.

The $\gamma/\gamma + \beta$ phase boundary at lower than 2000°C is determined mainly by microscopic examination and heat treated 40.13 at. % C alloy shows a small amount of precipitated Nb_2C (β) in the NbC (γ) matrix. The typical microstructure of γ -solid solution is shown in Figs. 10 and 11. The $\gamma/\gamma + \beta$ phase boundary above 2000°C is shown in Fig. 2, based on Storms and Krikorian's data.⁽⁶⁾ The γ -phase region lies between 41 and 50 at. % carbon.

Banded structure in $\beta + \gamma$ region and striation in primary β

The $\beta + \gamma$ mixture is characterized by banded twin-like structures and is shown in Figs. 7, 8, 12, 13 and 14. X-ray diffraction studies carried out in connection with this structure clarified that the banded structure could be interpreted to be a mixture of NbC (γ) and Nb_2C (β) phases. Fig. 12 shows the typical structure of alloys containing 35 to 39 at. % carbon, which

Fig. 10 41.31 at. % C alloy, as cast. Single phase of $\text{NbC}(\gamma)$. $\times 200$

Fig. 11 49.88 at. % C alloy, as cast. Single phase of γ . $\times 200$

Fig. 12 37.92 at. % C alloy. Nearly 100 % banded twin-like structure of a two-phase mixture of β plus γ .

- (a) As cast. Unetched. $\times 200$
 (b) Water quenched after being heated for 240 hrs at 1200°C . $\times 400$
 (c) Water quenched after being heated for 240 hrs at 1200°C . Deeply-etched. $\times 400$

$\text{NbC}(\gamma)$ phase

γ -phase is NbC solid solution and shows NaCl type

consists almost entirely of banded structure. Near the $\gamma/\gamma + \beta$ phase boundary, small patches of banded structure are observed at NbC (γ) phase boundary, as shown in Fig. 13 and it becomes considerably with

(10) G. Brauer and R. Lesser: Z. Metallkunde, 50 (1959), 8; 50 (1959), 487.

heat treatment. The banded structure is also observed at the primary NbC (γ) phase in cast alloy, as shown in Figs. 7 and 8.

It was observed that two kinds of carbide were formed when a piece of niobium plate buried in carbon powder was carburized at 2000°C for 10 hrs in vacuum. The carburized zone is made up of two distinct layers, as shown in Fig. 14. The outer layer which is NbC (γ), can be distinguished from the inner layer which is Nb₂C (β), by a sharp line of demarcation. Inside the outer layer, a banded structure is observed. And also a very small amount of banded structure was detected in specimens which were carburized at lower temperature.

Fig. 13 39.87 at. % C alloy.

(a) As Cast. Precipitated β along the grain boundary of γ . $\times 400$
 (b) Heated for 12 hrs at 2000°C and cooled slowly. Precipitated β in γ matrix. $\times 400$

Fig. 14 Section through carburized niobium plate showing layers of NbC (γ) and Nb₂C (β). $\times 1000$

In carburization of niobium, three zones: Nb (α), Nb₂C (β) and NbC (γ) exist. These must be formed as independent zones with a well-defined interface and show no mutual eutectic mixture at carburization.

It is considered that NbC (γ) has a wide range of carbon solubility and Nb₂C (β) has no solubility in the case of carburization at 2000°C from metallographic investigation described above. It is reasonable that carbon concentration in carburized niobium surface is presumed⁽¹¹⁾ to be in Fig. 15. Carbon concentration gradient in NbC (γ) zone changes naturally with temperature and dissolved carbon concentration at A in Fig. 15 must be increased by lowering temperature on the basis of solid solubility of NbC (γ) phase. And then lower carbide Nb₂C (β) precipitates are observed at the interior of NbC (γ) zone.

From these observations and explanations, it is clear that a possible formation of the banded structure is the precipitation of Nb₂C (β) on the preferential planes⁽¹²⁾ of carbon deficit NbC crystal due to decreasing the solid solubility of niobium in NbC (γ) phase.

Striation in primary Nb₂C (β) must be caused by the precipitation of niobium. The solid solubility of niobium in Nb₂C (β) phase increases with temperature increases as shown in Fig. 2 by fine line.

It is surprising that precipitated Nb₂C (β) and Nb (α) should appear on cast or carburized specimens. However, this is easily understood if it is assumed that these phases rapidly reach the equilibrium state as the material cools.* Storms and Krikorian⁽⁶⁾ also clarified

Fig. 15 Schematic representation of carbon concentration in carburized layers.

that it was difficult to keep the specimen in an equilibrium state at high temperatures by quenching and even helium quenching was not effective above 2600°C. It might be added that the precipitation is accelerated on account of thermal agitation and defects in carbon deficit carbide compound crystals.

It could be predicted that the striation in Nb₂C (β) zone and the banded structure in NbC (γ) should be both observed in specimens which were carburized at higher temperatures about 2100°C or above.

Eutectic reaction between NbC (γ) and graphite phase

Alloying more than 50 at. % carbon reduces the temperature for complete melting to the eutectic point

(11) W. Seith: "Diffusion in Metallen" pp. 157, Springer-Verlag, Berlin, 1955.

(12) Y. Sasaki: To be published.

* Cooling rates are estimated about 20°C/sec at 2000°C for arc casting and 100°C/sec at 2000°C as heat treating.

of NbC (γ) and graphite phase which is $3300 \pm 50^\circ\text{C}$ with 60.5 at. % C as shown in Fig. 2.

Microscopic structure to confirm the presence of eutectic reaction was found in various specimens. Fig. 16 shows the structure of primary NbC (γ) and the eutectic matrix, in 50.59 at. % C alloy. A typical eutectic structure and a hyper-eutectic structure are shown in Figs. 17 and 18 respectively.

of niobium (α) phase, Nb₂C (β) phase, NbC (γ) phase ranging from 41 to 50 at. % carbon and graphite. The maximum solubility of carbon in niobium is 5 at. % at the eutectic temperature ($=2340 \pm 20^\circ\text{C}$). The solubility limit of carbon shows a marked decrease at lower temperature as shown in Fig. 2 and it reaches less than 0.05 at. % at room temperature.

The Nb₂C (β) phase exists between 28 and 33.3 at.

Fig. 16 50.59 at. % C alloy, as cast.
Primary γ plus eutectic
mixture (γ +graphite). $\times 200$

Fig. 17 60.37 at. % C alloy, as cast.
Eutectic mixture of γ and
graphite. $\times 200$

Fig. 18 63.41 at. % C alloy, as cast.
Primary graphite plus eutectic
mixture (γ +graphite). $\times 200$

Carbon loss in hyper-eutectic alloys was observed as graphite rich fume during arc melting, while it was confirmed by chemical analysis data in Table 1. Carbon content in arc-melted alloys are always less than 63.5 at. % C and this is suggestive of the fact that the composition of the saturated melt equilibrated with gaseous phase is 63.5 at. % C. At a temperature, nearly as high as the boiling point of graphite under 1 atm. pressure, it can be presupposed that a non-variant reaction takes place as follows; among solid (G) which is graphite, vapour (V) which is the mixture of gaseous carbon and gaseous niobium and liquid (L) which is saturated with carbon in Nb-C system: either $G + V \rightleftharpoons L$ or $V \rightleftharpoons G + L$.

IV. Summary

The phase diagram of the Nb-C system was investigated by means of melting point measurements, microscopic examinations and X-ray and chemical analyses.

There are four phases in this system: solid solution

% carbon at eutectic temperature ($=2340 \pm 20^\circ\text{C}$). The $\alpha + \beta/\beta$ boundary curves abruptly toward higher carbon contents at lower temperatures.

Homogeneity range of NbC (γ) phase is obtained between 41 and 50 at. % carbon below 2000°C and higher solubility limit of niobium is shown at higher temperature. The diagram is characterized by three reactions as follows.

1. A eutectic reaction. $\text{Melt} \rightleftharpoons \text{Nb} (\alpha) + \text{Nb}_2\text{C} (\beta)$ at $2340 \pm 20^\circ\text{C}$, 13.5 at. % carbon.
2. A peritectic reaction. $\text{NbC} (\gamma) + \text{Melt} \rightleftharpoons \text{Nb}_2\text{C} (\beta)$ at $3080 \pm 50^\circ\text{C}$, 33.3 at. % carbon.
3. A eutectic reaction. $\text{Melt} \rightleftharpoons \text{NbC} (\gamma) + \text{Graphite}$ at $3300 \pm 50^\circ\text{C}$, 60.5 at. % carbon.

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