An Investigation on the Titanium-Iron-Carbon System

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Abstract

The solid solubility ranges in the two intermetallic compounds, TiFe and $TiFe_2$, of the titanium-iron binary system and phase relationships of the titanium-iron-carbon system were studied by microscopic examination, melting point determination, and X-ray analysis.

The solid solubility ranges of TiFe phase and $TiFe_2$ phase were from 52 wt% to 54 wt% of iron at 1080°C and 69 wt% to 77 wt% of iron at 1200°C respectively. In the titanium-iron-carbon system, there exist the following solid phases: α–Ti, β–Ti, Graphite, δ–phase, TiFe, $TiFe_2$, α–Fe and γ–Fe, but no ternary compound is detected.

There exist two quasi-binary eutectic reactions* as $L \rightleftarrows (\delta) + TiFe_2$ and $L \rightleftarrows (\delta) + Fe$ in this ternary system and, consequently, equilibrium relationships in this system are divided into three independent parts of TiC–Fe–C, TiC–Fe–$TiFe_2$ and TiC–$TiFe_2$–Ti as shown in Table 5, 6 and 7. The schematic equilibrium diagram for this system is given in Fig. 17.

1. Introduction and Previous Works

The investigation of the constitution of titanium-iron-carbon system had been undertaken as part of a general study of titanium-rich alloy systems in our laboratory, and it involved the studies by microscopic examination, melting point determination and X-ray analysis of the phase relationships in alloys with more than 20% titanium over the temperature range of 800~1200°C. In the present paper a study was also conducted to clarify the solid solubility ranges in the two kinds of intermetallic compounds, TiFe and $TiFe_2$, of the binary titanium-iron system because of imperfection in the previous works.

The Ti–C system has been studied by several investigators[1] and one of the authors reported the equilibrium diagram on the whole range of the compositions between titanium and carbon as shown in Fig. 1[2].

* In the reaction formula, the parentheses show a ternary solid solution of the phase indicated in it.

Carbon raises the $\alpha \rightleftarrows \beta$ allotropic transformation temperature of titanium from 885°C to 920°C. A peritectoid reaction, $\beta+\delta \rightleftarrows \alpha$, takes place at 920°C and 0.48 pct carbon, which is the point where the solubility of carbon in α-titanium is at its maximum.

The solubility of carbon in β-titanium increases from 0.15 pct at the peritectoid horizontal of 920°C to the maximum solubility of 0.8 pct at the peritectic temperature of 1750°C.

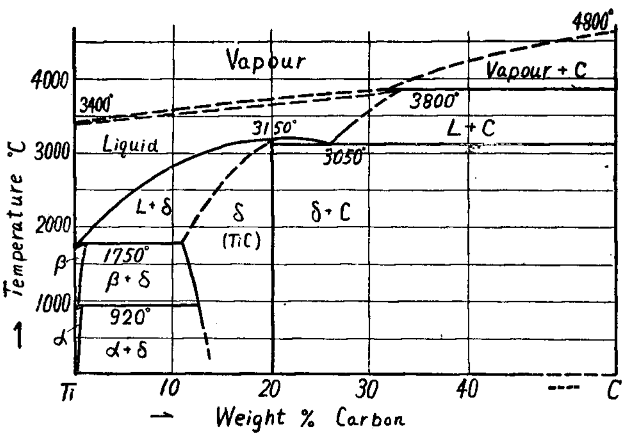


Fig. 1. Equilibrium Diagram of the Titanium-Carbon System.

The melting point of titanium[3] rises from 1668°C to 1750°C at about 0.2 pct carbon and at this temperature a peritectic reaction, Liquid$+\delta \rightleftarrows \beta$, takes place.

The liquidus rises continuously from the peritectic temperature with the increase of carbon content to the melting point of titanium carbide, 3150°C, at the composition of 20 weight pct carbon. When the carbon content increases to more than 20 pct, the liquidus temperature falls somewhat lower and reaches an eutectic point at 3050°C and 26 pct carbon, which corresponds to the Liquid$\rightleftarrows \delta+$Graphite reaction.

Then the liquidus rises to 3800°C$\pm$200°C at 33 pct carbon alloy, and at this temperature the reaction of Vapour$+$Graphite$\rightleftarrows$Liquid occurs.

Early studies on the Ti-Fe system[4),5)] were carried out principally in the iron rich regions and in connection with the intermetallic compounds; and in addition, very impure titanium containing 1 pct silicon, 1 pct aluminium and considerable amount of oxygen, nitrogen, carbon, hydrogen and etc. was used.

Recently the titanium rich region has been studied[5)] by Worner and Hansen et alii. The equilibrium diagram of Ti-Fe system has been studied by H. Nishimura and K. Kamei[6)], as shown in Fig. 2 which is in good agreement with that of A. D. McQuillan and M. K. McQuillan[7)]. However. the solid solubility ranges of the two intermetallic compounds, TiFe and $TiFe_2$, are not shown.

On the titanium side, the addition of iron causes depression of both the melting point and the $\alpha \rightleftarrows \beta$ allotropic transformation temperature of titanium. The liqiudus falls to an eutectic horizontal at 1080°C and at this temperature, an eutectic reaction of Liquid ⇄ Ti(β) + TiFe takes place. The eutectic composition is 32 pct iron and 68 pct titanium.

The maximum iron solubility in the β-titanium is approximately 25 pct at the eutectic temperature. The solid solubility of iron in β-titanium decreases with falling temperature and it reaches to an eutectoid point (15 pct iron at 590°C). A peritectic reaction, Liquid+$TiFe_2$ ⇄ TiFe, occurs at 53 pct iron and 1317°C. The compound $TiFe_2$, which exists at 70 pct of iron, shows a maximum melting point at 1530°C. Between iron and the compound $TiFe_2$ an eutectic reaction (Liquid ⇄ TiFe + Fe) is located at 86 pct iron and 1340°C.

In the iron-carbon system, the following fact is now almost certain that the compound Fe_3C, known as cementite, is always in a metastable phase, and in an equilibrium condition, iron, in the form γ-Fe (austenite) or α-Fe (ferrite), exists in equilibrium with graphite. Fig. 3 shows the stable equilibrium diagram of the Fe–C system[8] employed in this investigation.

The iron rich region in the Ti–Fe–C ternary system has been studied by Tofaute and Büttinghaus[9]. They carried out the investigation on the six sections of the Fe–C–Ti system at 0.3, 0.7, 1.2, 1.6, 2.3 and 3.4 pct titanium by thermal analyses, X-ray analyses and microscopic examinations and reported on the outcome. The existence of the $TiFe_3$ phase which was reported in their paper is disproved now.

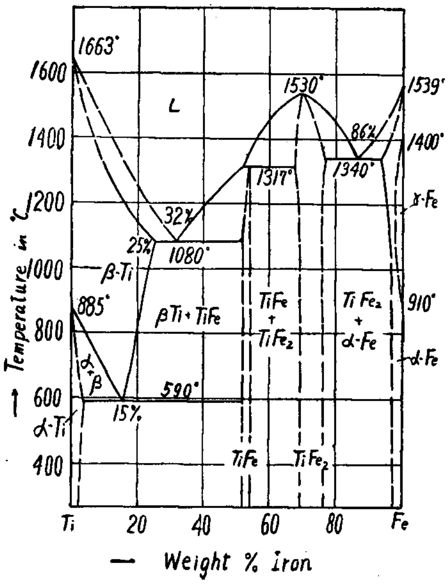


Fig. 2. Equilibrium Diagram of the Titanium-Iron System.

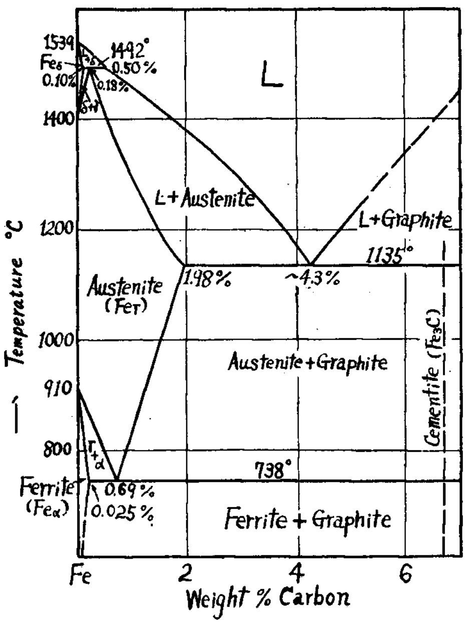


Fig. 3. Equilibrium Diagram of the Iron-Carbon System.

2. Experimental procedures

(a) Materials used.

The titanium used in the preparation of the alloys was magnesium reduced sponge titanium, produced by Ōsaka Titanium Manufacturing Co. which was chipped off under 15 meshes. The purified iron containing less than 0.004 pct of oxygen was used as the alloying metal. The purification[10)] was carried out by heating the flakes of electrolytic iron in the stream of purified and dried hydrogen at about 1200°C for 65 hours to remove oxygen, carbon and sulphur from the solid iron. Then hydrogen was taken away in vacuum at 800°C. Carbon additons were made by using an artificial graphite used for spectrographic analysis.

(b) Melting of the Alloys.

Sponge titanium, flaky iron and carbon powder, weighing totally 10 grams in given proportions were mixed and compressed to a briquette of 19 mm in diameter employing the pressure of 2 to 4 tons per square cm. The briquettes containing more than 1 pct of carbon were previously sintered at 1200°C in argon atmosphere.

The briquettes, thus prepared, containing less than 5 pct of carbon were melted in a tungsten electrode arc furnace having four water cooled copper hearthes, shown in

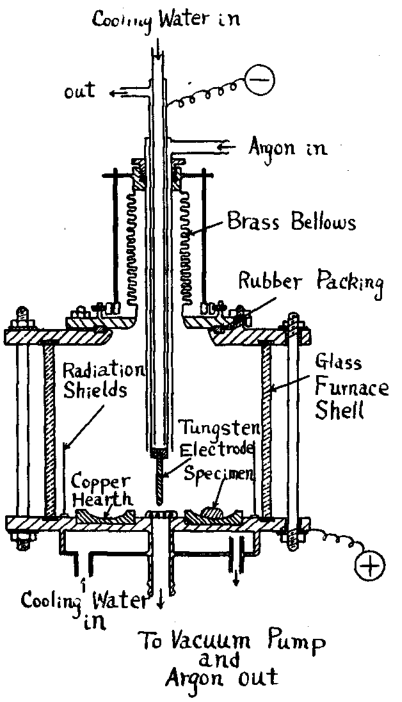


Fig. 4. Laboratory Arc-Furnace with Copper Hearth.

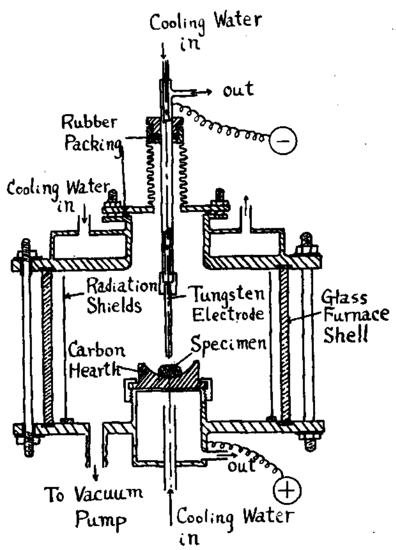


Fig. 5. Laboratory Arc-Furnace with Carbon Hearth.

Fig. 4. The melting points of the specimens containing above 5 pct carbon were so high, as above 3000°C, that it required a furnace specially protected against high temperature. For this reason a furnace, having an indirectly water cooled graphite hearth, was employed as illustrated in Fig. 5. In an atmosphere of argon, the specimens were remelted two or three times turnig them over at each melting in order to promote their homogeneity.

(c) Heat Treatment

In order to prevent oxidation of the specimens, they were sealed in quartz capsules which were evacuated to a pressure of less than 10^{-4} mm Hg and then the capsules were filled with argon gas to a pressure corresponding to 1 atmosphere for the heat-treatment temperature.

The specimens thus sealed in quartz capsules were heated in a electric furnace at the desired temperature. Then, the specimens were quenched from a series of temperatures by allowing the end of the capsule to crush in the water.

(d) Measurment of Melting Point

Since titanium attacks all the refractory materials normally used in melting of metals, the measurement of the melting points of the titanium and its alloys is not possible at present by the conventional method. A high temperature vacuum electric resistance furnace, as shown in Fig. 6, was constructed for the determination of melting temperature of the specimens. A small piece of specimen is placed in the heater boat as shown. The heater boat made from either molybdenum or graphite, which is charged with 200~400 A, is heated by its own electrical resistance and the specimens were heated rapidly. A complete melting was ascertained by the fact that the solid specimen appeared to collapse and ran along the trough of the heater. The furnace is evacuated by an oil diffusion pump and mechanical forepump up to 10^{-4} mm Hg operating vacuum. An optical pyrometer was calibrated over the useful temperature range of the furnace by observing the melting points of Kroll-titanium, platinum, rhodium, molybdenum, tantalum, titanium-carbide and tungsten at 1725°C, 1770°C, 1970°C, 2400°C, 2900°C, 3150°C, and 3600°C respectively.

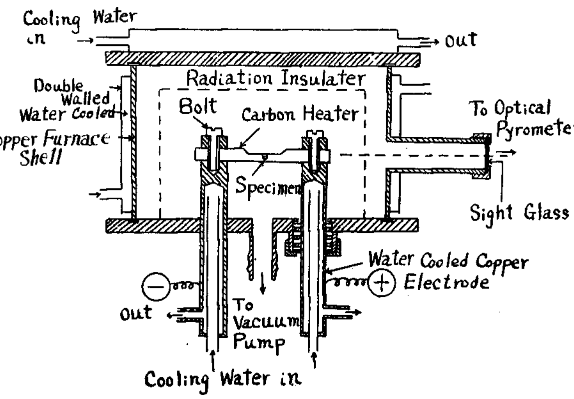


Fig. 6. Vacuum Electric Resistance Furnace.

(e) Metallographic Examinations

The carbon-rich specimens were so hard that they could not be polished by the usual polishing method of metal specimen. Therefore, a small piece of the specimen imbedded in acrylic resin was polished on a carborundum paper wetted with glycerine, adding silicon carbide powder of grit number 240, 400 and finally 600. Then it was polished as usually with the emery paper 00000 and finally finished on flannel with polishing alumina powder.

The principal etchants used were 2 pct picral or the mixture of 1 part of HF, 1 part of HNO_3 and 3 parts of glycerine.

(f) X-Ray Analysis

The X-ray diffraction patterns were taken with 90 mm powder camera, using either CuK_α radiation for the specimens having less than 20 pct of iron or FeK_α radiation for the specimens having over 20 pct of iron. Back-reflection photographs were taken to measure the lattice parameters of the quenched specimens for determination of solid solubility ranges of the intermediate phases.

(g) Chemical Analysis

To determine the amount of titanium and of iron, differential titration method[11] useing Nakazono's reducter[12] in which liquid zinc amalgum, was employed, and N/10 $KMnO_4$ standard solution was used to detect titanium plus iron, and N/10 Fe^{+3} standard solution with KCNS as indicater of the end point, to detect titanium.

Total carbon analysis was made by combustion of the powdered sample in a conventional carbon train and the amount of carbon was determined by gravimetric procedure.

3. Experimental Results and Discussion

(a) Phase Regions of TiFe phase in the Titanium-Iron Binary System

The compound TiFe is known as a body centered cubic equiatomic phase and the crystal structure of $TiFe_2$ is reported to be of a complicated $MgZn_2$ type[4]. The phase boundaries of these phases are not known. Prior the investigation on the ternary system, studies were carreid out to clarify the boundaries of these phases.

The results of Deby-Sherrer diffraction experiments of the heat treated specimens were combined with the microscopical examinations to ascertain the phase fields in the intermediate compounds of TiFe and $TiFe_2$.

As described previously, the peritectic reaction, Liquid + $TiFe_2 \rightleftarrows$ TiFe at 1317°C, could not be completed by rapid cooling as cast conditions. Photo 1 shows a microstructure of as cast 55.3 pct iron alloy. This is the typical super-cooled structure of the primary $TiFe_2$ and TiFe plus eutectic structures obtained in as cast 50~60 pct iron alloys. The X-ray diffraction patterns also verify the existence of TiFe phase and $TiFe_2$ phase.

However, after a long heat-treatment at the temperature immediately below the peritectic temperature, it reaches an equilibrium state. A 54 pct iron alloy, which corresponds approximately to the equiatomic composition of tianium and iron, shows a single phase of TiFe as illustrated in Photo 2. It is also confirmed by the X-ray study.

To determine the TiFe phase region, 12 specimens containing from 50 to 55 pct of iron were prepared and they were heat-treated at the temperature of 1200°C, 1080°C, 1000°C and 800°C for 48, 100, 120 and 900 hours respectively.

Prior to holding them at the heat-treatment temperature, the specimens were heated just below the peritectic temperature of 1317°C and gradually tapered down to a desired temperature.

The TiFe phase gives a body centered cubic X-ray diffraction pattern and its cell size is given as 2.975Å by Duwez and Taylor[13]. Lattice parameter measurments were made on a series of alloys to determine the effect of iron concentration on the cell size of the TiFe phase.

Chemical analysis of the alloys and the lattice parameter data of series of heat-treated alloys are presented in Table 1. Photo 3 and 4 are the microstructure of a 51.27% iron alloy, water quenched after annealing at 1080°C and 800°C, respectively and they both show structures of the TiFe plus unresolved beta titanium phase. Photo 5 and 6 are the microstructure of 51.81% iron alloy heat-treated as above and they show approximately single phase of TiFe, and solid solubility curve of TiFe phase is nearly vertical from the eutectic temperature of TiFe and Ti(β) down to about 800°C. Photo 7 and 8 show the microstructure of 54.16% iron and 54.94% iron

Table 1. Chemical Analysis and the Lattice Parameters of the Specimens of TiFe Phase.

Specimen No.	Nominal Composition		Chemical Analysis			Lattice Parameter of TiFe Phase Å			
	Ti wt%	Fe wt%	Ti wt%	Fe wt%	Fe at %	800°C	1000°C	1080°C	1200°C
510	49.0	51.0	48.78	50.65	46.7	2.99_1	—	2.98_9	2.98_7
514	48.6	51.4	48.37	51.27	47.4	2.99_0	2.98_6	2.99_1	2.98_8
519	48.1	51.9	47.03	51.81	48.0	2.98_9	2.98_8	2.98_8	2.98_4
523	47.7	52.3	47.31	52.08	48.2	2.98_8	2.98_2	2.98_7	2.98_5
527	47.3	52.7	47.12	52.78	48.9	2.98_4	2.98_4	2.98_6	2.98_2
531	46.9	53.1	47.09	53.07	49.3	2.97_9	2.97_9	2.98_5	2.97_8
535	46.5	53.5	45.57	53.56	49.7	2.98_3	2.97_7	2.98_3	2.97_7
539	46.1	53.9	45.55	54.34	50.5	2.98_1	2.97_6	2.97_7	2.97_3
543	45.7	54.3	45.73	54.53	50.7	2.97_6	2.97_4	2.97_6	2.97_6
547	45.3	54.7	44.34	54.93	51.1	2.97_7	—	2.97_7	2.97_7
551	44.9	55.1	44.85	55.20	51.4	2.97_6	2.97_4	2.97_6	2.97_5
555	44.5	55.5	44.60	55.53	51.8	2.97_7	—	2.97_5	2.97_6

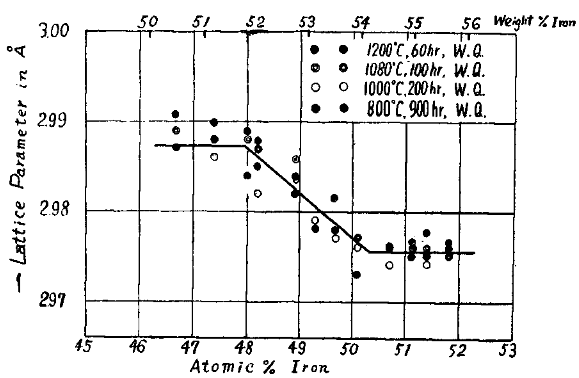


Fig. 7. Variation of Lattice Parameter of the TiFe Solid Solution versus Composition.

alloy, quenched after a 120 hour annealing at 1000°C and represent the single phase of TiFe and two phases of TiFe plus unresolved $TiFe_2$, respectively. From these microstructure, phase boundary of TiFe phase on iron side is considered to be about 54 pct iron.

Fig. 7 shows a variation of lattice parameter of the TiFe phase versus composition in atomic percentage of the iron. The lattice parameter decreases with increasing of iron concentration between 48 atomic pct to 50.3 atomic pct of iron.

From the results of the microscopic examination and X-ray analysis, it is seen that the TiFe phase region extends from 52 weight pct to 54 weight pct of iron and its solid solubility curves are nearly vertical against the falling temperature.

(b) Phase Regions of $TiFe_2$ phase in the Titanium-Iron Binary system

The intermetallic compound of $TiFe_2$ was first described by Witte and Wallbaum[4] as $MgZn_2$ type hexagonal structure and the lattice constants were reported as a 4.87 Å, c 7.81 Å and c/a 1.633. In this early study, the specimen was prepared by sintering compressed powders, and it was noted that $TiFe_2$ phase had only a narrow range of composition.

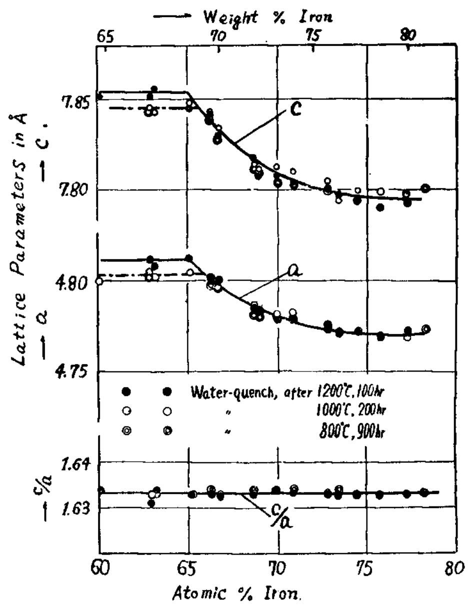


Fig. 8. Variation of Lattice Parameters of the $TiFe_2$ Solid Solution versus Composition.

As shown in Table 3, sixteen specimens containing from 64 to 80 weight pct of iron were arc-melted under the purified argon and was examined with microscopic study and X-ray analysis. Table 2 shows the results of their chemical analysis and they were in good agreement with the nominal composition. The lattice parameter data are shown in Table 3. Both c and a decrease with increasing of iron content, while c/a remains approximately constant at 1.633. Fig. 8 shows a variation of lattice parameters of $TiFe_2$ solid solution versus composition in atomic percentage of iron.

Table 2. Chemical Analysis and Microscopic Structure of the Specimens of $TiFe_2$ Phase.

Specimen No.	Nominal Composition		Chemical Analysis		Atomic % Fe	Microscopic Structure	
	Ti wt.%	Fe wt.%	Ti wt.%	Fe wt.%		Annealed at 1200°C	Annealed at 1000°C
640	36.0	64.0	35.93	63.80	60.1	$TiFe_2$+TiFe	$TiFe_2$+TiFe
660	34.0	66.0	34.08	66.63	63.0	"	"
665	33.5	66.5	33.28	66.74	63.2	"	"
670	33.0	67.0	32.36	68.54	65.2	Single Phase of $TiFe_2$	"
680	32.0	68.0	31.79	69.06	66.3	"	Single Phase of $TiFe_2$
690	31.0	69.0	31.02	70.04	66.7	"	"
710	29.0	71.0	28.93	71.00	68.7	"	"
720	28.0	72.0	27.63	72.18	68.9	"	"
730	27.0	73.0	26.90	73.08	69.9	"	"
740	26.0	74.0	25.87	74.08	70.9	"	"
750	25.0	75.0	24.52	76.15	72.8	"	"
760	24.0	76.0	23.63	76.67	73.6	$TiFe_2$+Fe	$TiFe_2$+Fe
770	23.0	77.0	22.70	77.47	74.5	"	"
780	22.0	78.0	21.72	78.62	75.8	"	"
790	21.0	79.0	20.93	79.80	77.3	"	"
800	20.0	80.0	19.76	80.62	78.2	"	"

Table 3. X-ray Analysis of the Specimens of $TiFe_2$ Phase.

Specimen No.	Lattice Parameter of the Specimens								
	Annealed at 1200°C, 100hr			Annealed at 1000°C, 200hr			Annealed at 800°C, 900hr		
	a Å	c Å	c/a	a Å	c Å	c/a	a Å	c Å	c/a
640	—	—	—	4.79_7	7.84_4	1.63_5	—	—	—
660	4.81_4	7.85_0	1.63_1	4.80_6	7.84_7	1.63_3	4.80_2	7.84_3	1.63_3
665	4.80_9	7.85_5	1.63_3	4.80_2	7.84_2	1.63_3	—	—	—
670	4.81_3	7.84_7	1.63_4	4.80_4	7.84_9	1.63_4	4.79_7	7.83_9	1.63_4
680	4.80_2	7.84_1	1.63_3	4.80_4	7.84_3	1.63_3	4.79_5	7.82_7	1.63_2
690	4.80_1	7.83_0	1.63_3	4.79_7	7.83_6	1.63_3	4.78_0	7.81_2	1.63_4
710	4.78_5	7.81_6	1.63_3	4.78_5	7.81_6	1.63_3	4.78_0	7.81_0	1.63_4
720	4.78_4	7.80_7	1.63_2	4.78_3	7.81_4	1.63_4	4.77_9	7.79_7	1.63_2
730	4.77_9	7.80_8	1.63_4	4.78_3	7.81_5	1.63_4	4.77_8	7.80_2	1.63_3
740	4.77_9	7.80_3	1.63_3	4.78_3	7.81_1	1.63_3	4.77_4	7.80_2	1.63_4
750	4.77_6	7.80_1	1.63_3	4.77_7	7.80_7	1.63_4	4.77_6	7.80_0	1.63_3
760	4.77_4	7.79_6	1.63_3	—	—	—	4.77_4	7.80_2	1.63_4
770	4.77_4	7.79_4	1.63_3	4.77_9	7.80_1	1.63_2	—	—	—
780	4.77_1	7.79_0	1.63_3	4.77_8	7.80_0	1.63_2	—	—	—
790	4.77_3	7.79_3	1.63_3	4.77_8	7.79_7	1.63_2	4.77_6	7.80_1	1.63_3

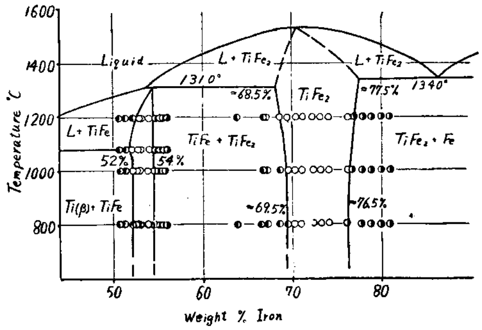


Fig. 9. Phase Boundaries of the TiFe-phase and $TiFe_2$-phase.

From the results of X-ray analysis and microscopic examination as shown in Photo 9~12 and in Table 2, it is seen that the $TiFe_2$ phase extends as widely as from 68.5 weight pct to 77 weight pct of iron at the temperature of 1200°C and narrows down moderately with decreasing temperature. Fig. 9 shows the partial phase diagram of Ti-Fe system and the phase boundaries of both TiFe phase and $TiFe_2$ phase.

(c) Ternary δ Phase in the ternary Titanium-Iron-Carbon System

In the binary Ti-C system, δ phase region is given as from about 13 weight pct to 20 weight pct carbon. Its crystal structure is given as NaCl type cubic structure and the cell size of titanium carbide, in which carbon concentration is 20 weight pct, is determined as 4.325 Å. And in the binary system of titanium-carbon[2], lattice parameter of the δ phase decreases with decreasing of carbon concentration.

42 alloys were prepared for the investigation of the region of the ternary δ phase in Ti-Fe-C system. The arc-melted specimens were annealed at 1000°C for 100 hrs, and microscopic examination and X-ray analysis were carried out.

The chemical analysis and lattice parameter data of the specimens in δ phase region are shown in Table 4. The results of the microscopic studies are summarized

Table 4. Chemical Analysis and Lattice Parameter of the ternary Ti-Fe-C Phase.

Specimen No.	Chemical Analysis			Lattice Constant in Å (NaCl type cubic)
	Ti wt.%	Fe wt.%	C wt.%	
2A	86.20	1.77	12.06	4.313
2B	83.29	2.57	14.33	4.311
2C	80.89	2.45	15.96	4.321
4B	81.45	3.70	14.66	4.315
4C	80.30	3.20	16.96	4.319
4D	77.74	3.81	18.06	4.320
6A	84.16	5.19	10.12	4.308
6B	82.23	5.33	11.86	4.307
6C	80.30	4.95	14.12	4.317
6D	78.75	5.50	16.13	4.318
12C	72.40	9.88	16.49	4.310
1N	76.07	5.67	18.03	4.317
2N	74.71	9.16	16.27	4.320
1L	75.75	6.65	17.36	4.318
2P	69.55	15.23	10.16	4.321

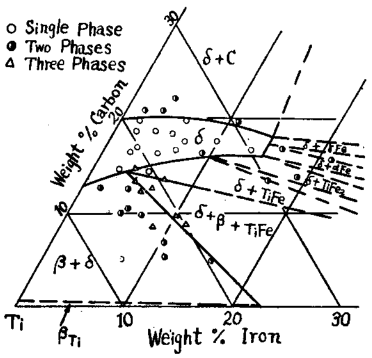


Fig. 10. Phase Boundaries of the Ternary δ-phase in the Ti-Fe-C System.

in Fig. 10, in which the open circles show single phase of δ as illustrated in photo 13～14, and the half filled circles show two phases as illustrated in photo 15～16.

The region of the ternary δ phase is given in the range of 13 to 20 weight pct of carbon, and the maximum solid solubility of iron in the δ phase is 15 weight pct.

The lattice parameter in this phase decreases from 4.325 Å, which is the value of the equiatomic compound TiC, to 4.310 Å with either decreasing of carbon concentration or increasing of iron concentration. A change of the carbon concentration in the δ solid solution has a greater effect upon the lattice parameter of the δ phase than that of iron concentration.

(d) Liquidus Surface in the Ti–Fe–C System

The melting points of the specimen containing titanium, iron and carbon are measured as previously described and the results are plotted in Fig. 11.

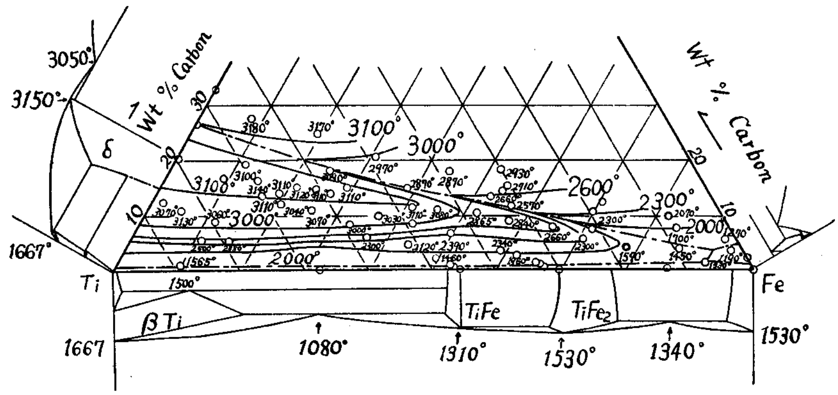


Fig. 11. Liquidus Surface in the Ternary Ti-Fe-C System.

It was observed that the eutectic point of Liquid⇄TiC+Graphite at the composition of 74 pct titanium and 26 pct carbon at 3050°C decreased its temperature gradually with increasing of iron content and fell abruptly at the iron rich corner.

In the ternary system, the eutectic reaction, Liquid⇄(δ)+Graphite, runs down along the eutectic line to the ternary eutectic point in the iron rich corner.

Photo 17 represents a micro-structure of as cast 34.81 pct titanium, 53.74 pct iron and 13.46 pct carbon alloy; and it shows an eutectic structure of δ phase and graphite, and the melting temperature of this alloy is 2660°C. It is considered that the composition of this alloy is just in the uni-variant line.

The specimens containing carbon in excess of this eutectic line, show primary graphite plus eutectic structure and its melting point is somewhat higher than that of the eutectic line. Photo 18 shows a typical micro-structure of the alloy containing 32.65 pct titanium, 55.13 pct iron and 15.07 pct carbon and its melting point is 2690°C.

On the contrary, the specimens containing less carbon than this eutectic line show the micro-structure of primary δ phase plus eutectic and their melting points are higher than that of this eutectic line, Photo 19 shows a micro-structue of primary δ-phase plus eutectic as cast condition of 37.91 pct titanium, 51.70 pct iron and 10.46 pct carbon alloy whose melting point is 2865°C.

Similarly, 32.95 pct titanium, 57.48 pct iron, 12.29 pct carbon alloy shows approximately an eutectic structure as illustrated in Photo 20, and its melting point is 2570°C. Hence, in the titanium-iron-carbon system a ridge line exists along the section between TiC and Fe on the ternary liquidus surface and the melting point decreases on both sides as shown in Fig. 11.

(e) Equilibrium Relation between TiC and TiFe

Sixteen kinds of specimens corresponding to the composition between TiC and TiFe were arc-melted and studied by microscopical examination and X-ray analysis to clarify the equilibrium relation between TiC and TiFe. The results are summarized in Fig. 12.

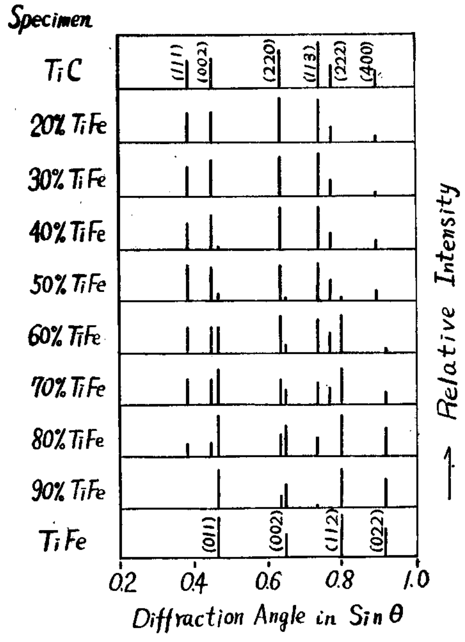


Fig. 12. X-ray Diffraction Patterns of the Section between TiC-TiFe.

The X-ray diffraction patterns show that there is no ternary compound in this series of alloys and the structure of these alloys consist of the mixture of body centered cubic structure (TiFe) and NaCl type cubic structure (δ).

The microscopic structure of this series of alloys also show the primary δ phase plus TiFe phase and the amount of the primary δ phase decreases with decrease of the carbon content. In the micro-structure of above 0.1 pct of carbon alloy in this sesies, the primary δ phase was detected as illustrated in Photo 21～22 and, therefore, the soild solubility of carbon in TiFe phase is considered to be less than 0.1 pct of carbon.

(f) Equilibrium Relation between TiC and $TiFe_2$

Fourteen kinds of specimens corresponding to the composition between TiC and $TiFe_2$ were arc-melted and studied similarly as described in the preceding paragraph.

The micro-structure of as cast alloys containing above 0.2 pct carbon shows the primary δ phase, as illustrated in Photo 23~24, and the amount of the primary δ phase increases with increase of the carbon content. The micro-structure of 69.55 pct titanium, 15.23 pct iron and 16.10 pct carbon alloy shows a single phase of δ solid solution as shown in Photo 25. The solid solubility of carbon in $TiFe_2$ phase is considered to be less than 0.2 pct of carbon. The results of the X-ray analysis are summarized in Fig. 13. It shows that the crystal structure of the specimens in this series are detected as the mixture of NaCl type cubic structure (δ) and close packed hexagonal structure ($TiFe_2$).

(g) Equilibrium Relation between TiC and Fe

Similarly, the equilibrium relation between TiC and α-iron was studied using eight kinds of specimens corresponding to the composition in this section.

Fig. 14 shows the results of the X-ray diffraction patterns. The structure of the specimens in this section was seen to consist of the mixture of NaCl type cubic struc-

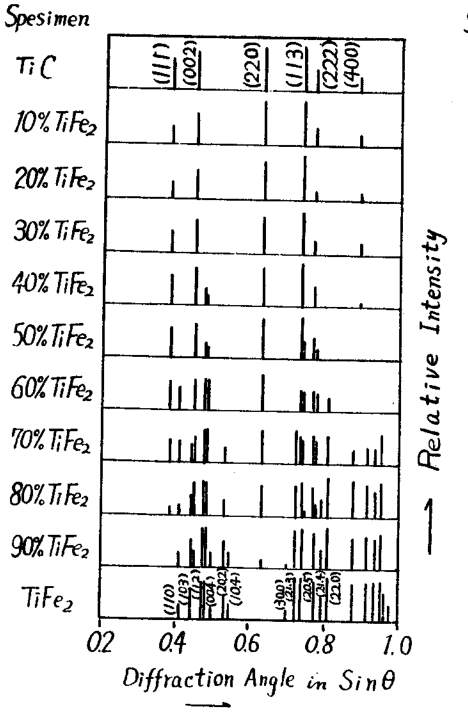


Fig. 13 X-ray Diffraction Patterns of the Section between $TiC-TiFe_2$.

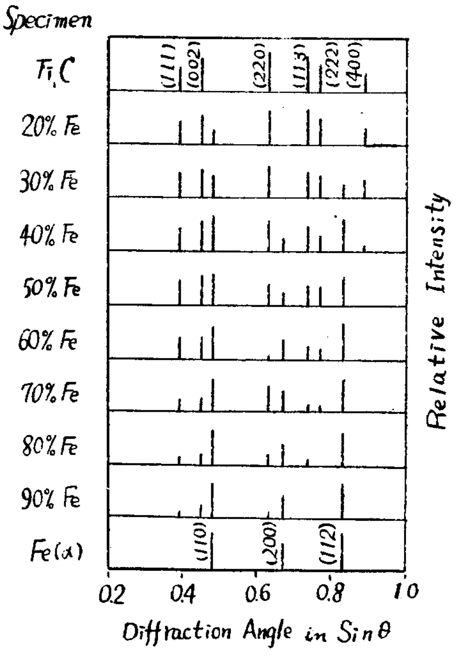


Fig. 14. X-ray Diffraction Patterns of the Section between TiC-Fe.

ture of δ phase and body centered cubic structure of alpha-iron, but the ternary compound could not be detected.

The microscopic examination of alloys in this series also shows that the primary δ phase and eutectic structure exist in this region and the amount of the primary δ phase decreases with increase of the iron content as illustrated in Photo 26~28. Photo 29 shows the eutectic structure between δ and α–Fe plus a trace of primary δ phase in the alloy containing 7.10 pct titanium, 91.24 pct iron and 1.74 pct carbon.

From the results of the microscopic study, it is considered that a quasi-eutectic reaction, Liquid$\rightleftarrows\alpha$–Fe+(δ), takes place in this region and the composition of the eutectic point is considered to be close to that of the alloy of Photo 29 in this section.

(h) Isothermal section of Ti–Fe–C system at 1000°C

The isothermal section at 1000°C in this ternary system was determined mainly by the metallographic examination and by theoretical consideration of the results obtained, while the X-ray studies were undertaken only to confirm the phase present.

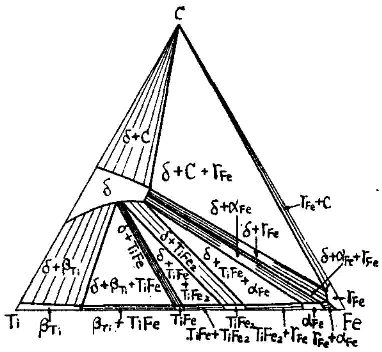


Fig. 15. Isothermal Section of Ti–Fe–C System at 1000°C.

The results are summarized in Fig. 15. The δ phase is in equilibrium with β–titanium, TiFe phase, $TiFe_2$ phase, α–iron, γ–iron and graphite, at 1000°C, as shown in Fig. 15 and no ternary compound is detected.

(i) Primary δ–phase Region

Summerizing the results of the microscopic studies described above, the specimens containing primary δ phase are shown by the symbol "○" and those containing primary graphite, by the symbol "●" in Fig. 16.

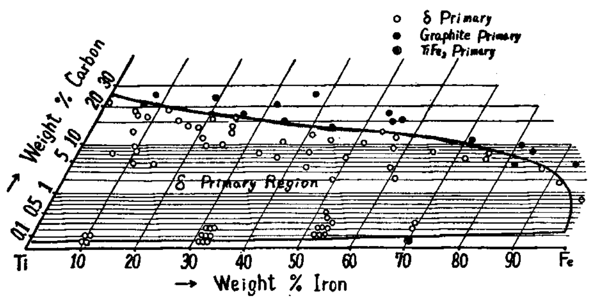


Fig. 16. Primary δ-phase Region in the Ternary Ti–Fe–C System.

The micro-structure of the specimens containing up to 0.1~0.2 pct of carbon but less than the carbon content corresponding to the eutectic line Liquid$\rightleftarrows$(δ)+Graphite, shows that the δ phase crystallizes out primarily.

In this ternary system, it is considered that univariant lines in relation to the δ phase, such as Liquid$\rightleftarrows$(δ)+$TiFe_2$, Liquid$\rightleftarrows$(δ)+TiFe, and Liquid+(δ)$\rightleftarrows$(β–Ti), exist within approximately 0.1 pct carbon section in contact with the binary system of titanium and iron.

4. Equilibrium Diagram of the Ti-Fe-C System

From the results described above and the report on the study by Tofaute and Büttinghaus, it is considered that the following solid phases exist in the titanium-iron-carbon ternary system; titanium rich solid solution alpha or beta, graphite, δ phase known as titanium-carbide phase, TiFe phase, $TiFe_2$ phase and iron rich solid solution alpha or gamma.

There exist two quasi-binary eutectic reactions, Liquid$\rightleftarrows(\delta)+TiFe_2$ between TiC and $TiFe_2$ and Liquid$\rightleftarrows(\delta)+$Fe between TiC and Fe.

The equilibrium relationships in this ternary system, therefore, can be divided into three independent parts of TiC–Fe–C, TiC–Fe–$TiFe_2$ and TiC–$TiFe_2$–Ti. These equilibrium relations are summarized in Table 5, 6, and 7 respectively, and Fig. 17 shows

Table 5 Equilibrium Relationships among TiC–Fe–C.

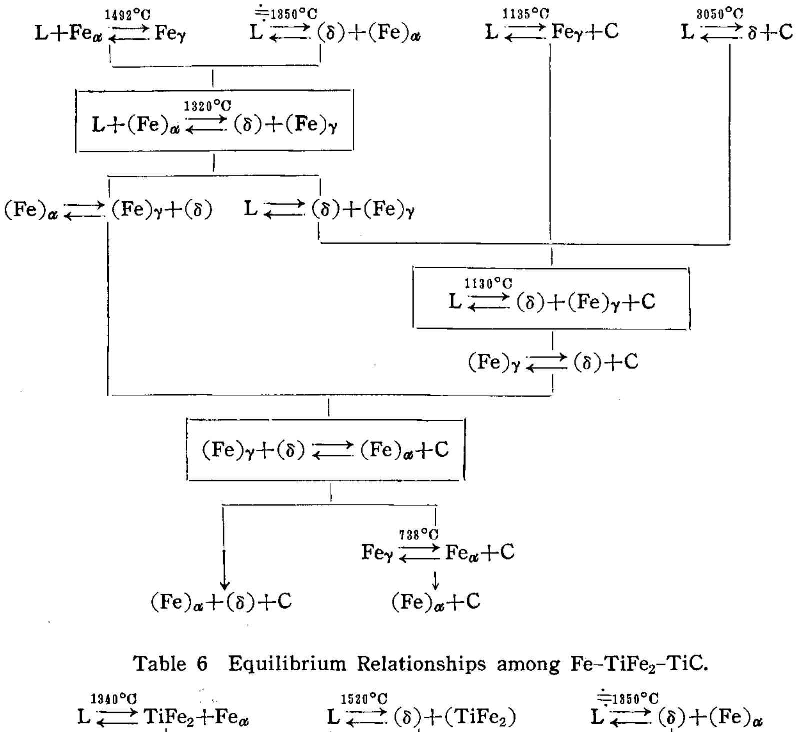
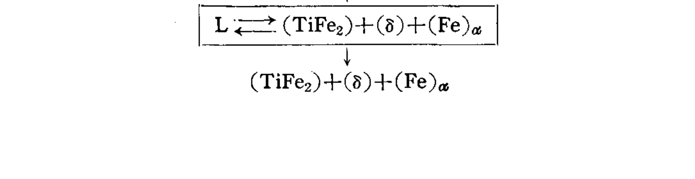
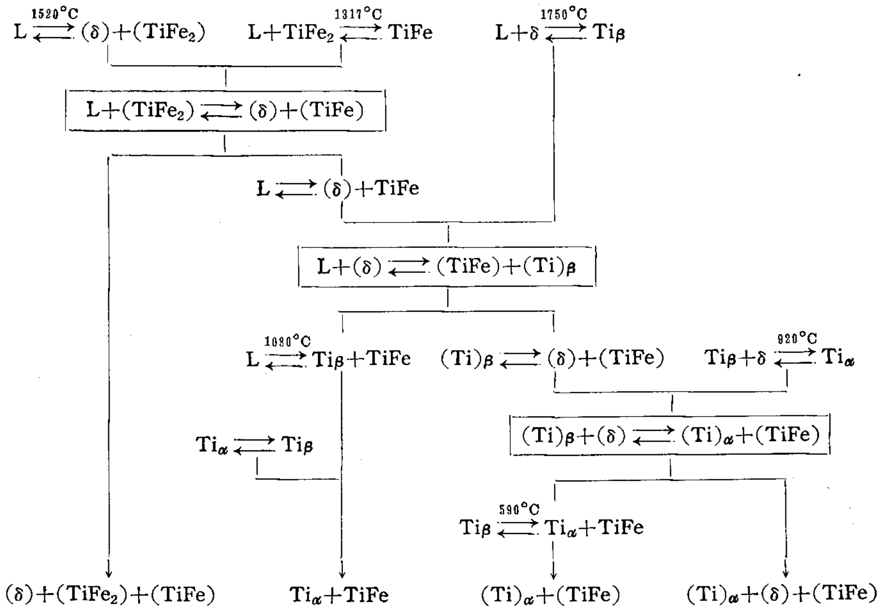


Table 6 Equilibrium Relationships among Fe–$TiFe_2$–TiC.



the schematic equilibrium diagram obtained from the above results and the theoritical considerations.

Table 7 Equilibrium Relationships among Ti–$TiFe_2$–TiC.



5. Summary

The principal features of the Titanium-iron-carbon system may be summarized as follows:

1) TiFe phase has a solid solubility range which extends from 52 wt pct to 54 wt pct of iron at 1080°C.

2) $TiFe_2$ phase has a wide range of solubility which extends from 69 wt pct to 77 wt pct of iron at 1200°C.

3) δ phase containing about 17 pct carbon dissolves about 15 pct of iron, which is the maximum solubility of iron in the ternary δ phase.

4) δ phase and α–Fe give rise to a quasi-binary eutectic reaction: Liquid$\rightleftarrows(\delta)+$ α–Fe, and composition of the eutectic point is about 7 pct titanium, 1.7 pct carbon.

5) δ phase and $TiFe_2$ also give rise to a quasi-binary eutectic reaction: Liquid$\rightleftarrows$ $(\delta)+(TiFe_2)$, and composition of the eutectic point is 0.1 wt. pct of carbon in $TiFe_2$.

6) In the region of TiC–Fe–C, there exist three non-variant reactions as follows:

Liquid$+(Fe)_\alpha\rightleftarrows(TiC)+(Fe)_\gamma$ at 1320°C

Liquid$\rightleftarrows(TiC)+(Fe)_\gamma+C$ at about 1140°C

$(Fe)_\gamma+(TiC)\rightleftarrows(Fe)_\alpha+C$

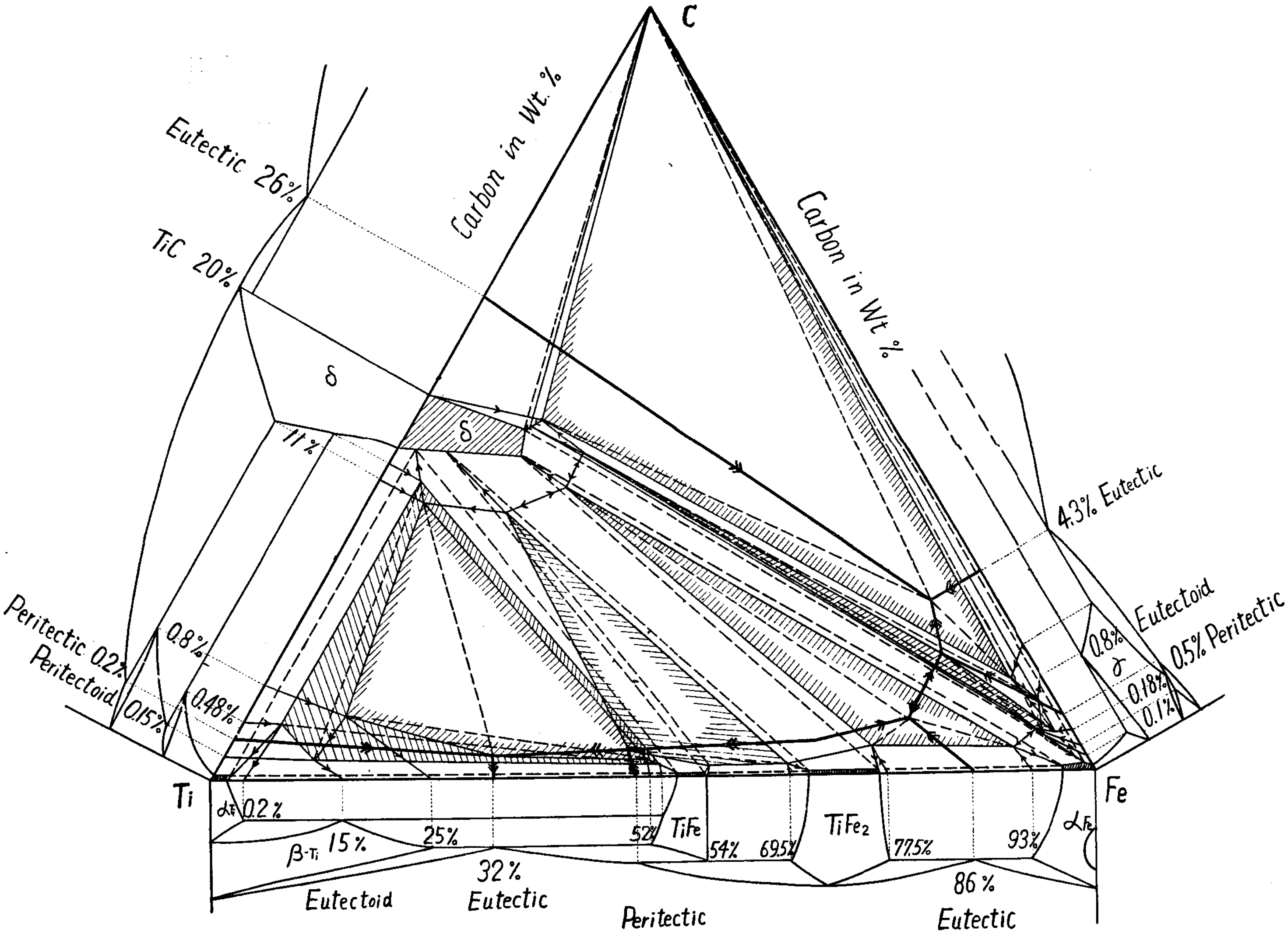


Fig. 17. Schematic Equilibrium Diagram of the Ti–Fe–C System.

7) In the region of TiC–Fe–$TiFe_2$, a ternary eutectic reaction as follows takes place:

$$\text{Liquid} \rightleftarrows (TiFe_2) + (TiC) + (Fe)_\alpha$$

8) In the region of TiC–$TiFe_2$–Ti, there exist three non-variant reactions as follows;

$$\text{Liquid} + (TiFe_2) \rightleftarrows (TiC) + (TiFe) \quad \text{at about } 1310°C$$

$$\text{Liquid} + (TiC) \rightleftarrows (TiFe) + (Ti)_\beta \quad \text{at about } 1100°C$$

$$(Ti)_\beta + (TiC) \rightleftarrows (Ti)_\alpha + (TiFe)$$

Acknowledgement

The authors are very grateful to Professor Hideo Nishimura for his useful advice during the course of this investigation, and wish to thank Mr. Minoru Ōmizo for his assistance in the chemical analysis.

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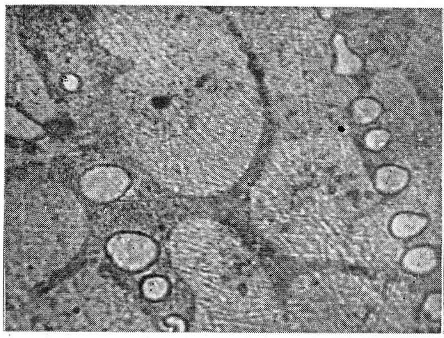

×400

Photo 1. Ti 43.26% Fe, 55.30% alloy. As cast. Primary $TiFe_2$ plus TiFe and boundary eutectic.
Etchant: 20% HF, 20% HNO_3 in glycerine.

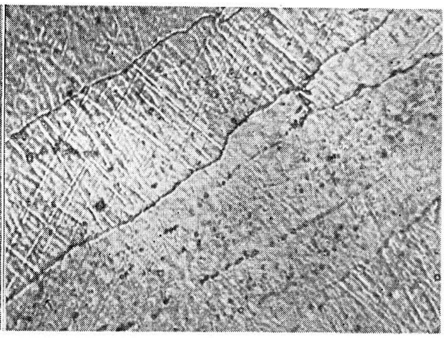

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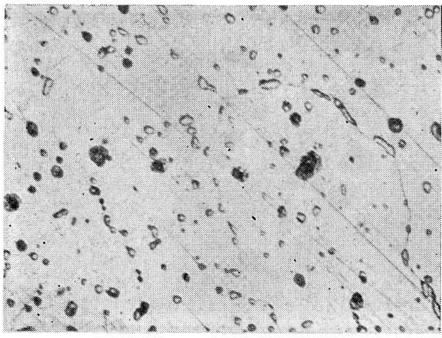
Photo 2. Ti 45.06% Fe, 54.16% alloy. Water-quenched after annealing 120 hrs at 1000°C.
Single phase of TiFe.
Etchant: 20% HF, 20% HNO_3 in glycerine.



×100

Photo 3. Ti 48.37%, Fe 51.27% alloy. Water-quenched after annealing 100 hrs at 1080°C.
Two phases of TiFe plus Ti.
Etchant: 20% HF, 20% HNO_3 in glycerine.

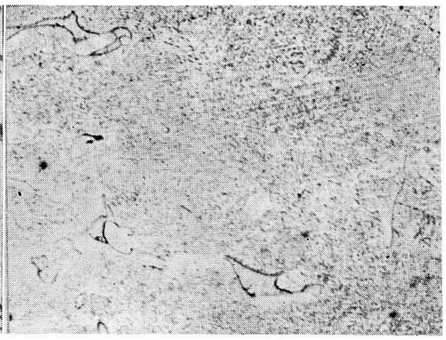


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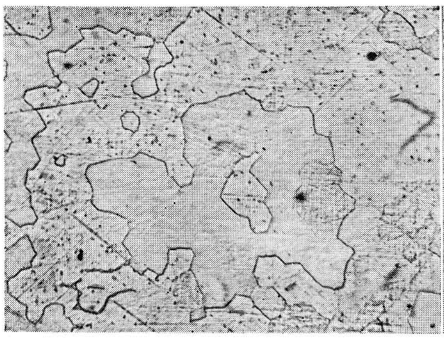
Photo 4. Ti 48.37%, Fe 51.27% alloy. Water-quenched after annealing 900 hrs at 800°C.
Two phases of TiFe Plus Ti.
Etchant: 20% HF, 20% HNO_3 in glycerine.

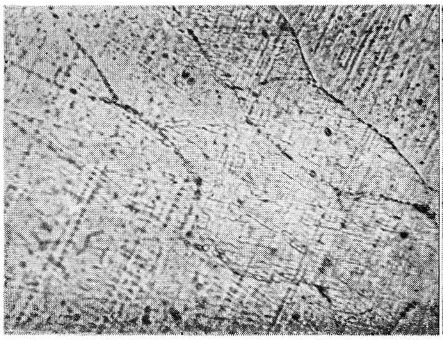


×100

Photo 5. Ti 47.03%, Fe 51.81% alloy. Water-quenched after annealing 100 hrs at 1080°C.
Single phase of TiFe.
Etchant: 20% HF, 20% HNO_3 in glycerine.

×100

Photo 6. Ti 47.03%, Fe 51.81% alloy. Water-quenched after annealing 900 hrs at 800°C.
Single phase of TiFe.
Etchant: 20% HF, 20% HNO_3 in glycerine.

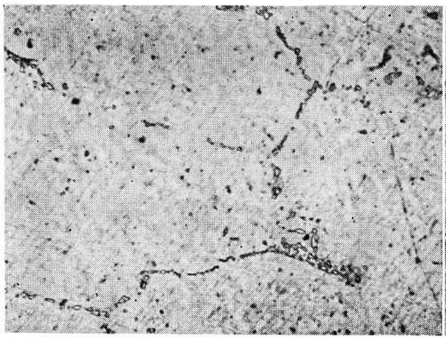


×400

Photo 7. Ti 45.06%, Fe 54.16% alloy. Water-quenched after annealing 120 hrs at 1000°C.
Single phase of TiFe.
Etchant: 20% HF, 20% HNO_3 in glycerine.

×400

Photo 8. Ti 45.06%, Fe 54.94% alloy. Water-quenched after annealing 120 hrs at 1000°C.
Two phases of TiFe plus $TiFe_2$.
Etchant: 20% HF, 20% HNO_3 in glycerine.



×400

Photo 9. Ti 34.08%, Fe 66.63% alloy. Water-quenched after annealing 70 hrs at 1000°C.
Two phases of $TiFe_2$ plus TiFe.
Etchant: 20% HF, 20% HNO_3 in glycerine.

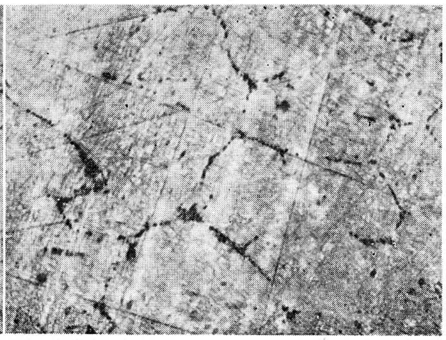


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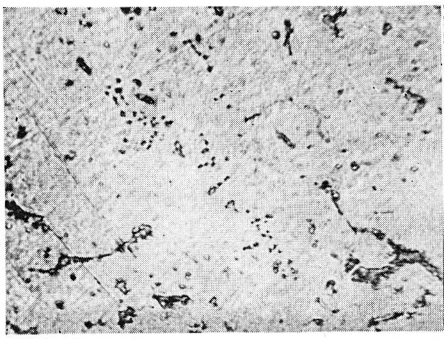
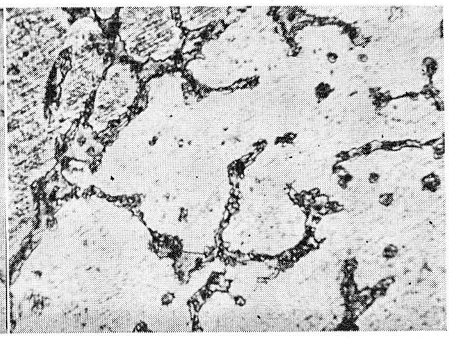
Photo 10. Ti 32.36% Fe 68.54% alloy. Water-quenched after annealing 70hrs at 1000°C.
Single phase of $TiFe_2$.
Etchant: 20% HF, 20% HNO_3 in glycerine.



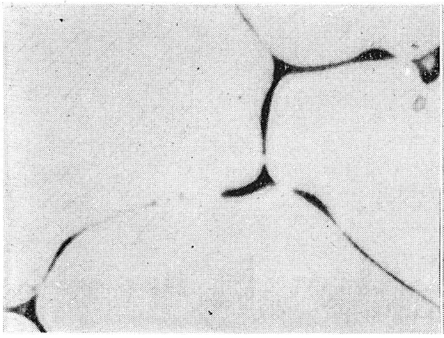
×400

Photo 11. Ti 24.52%, Fe 76.15% alloy. Water-quenched after annealing 65 hrs at 1000°C.
Single phase of $TiFe_2$.
Etchant: 20% HF, 20% HNO_3 in glycerine.



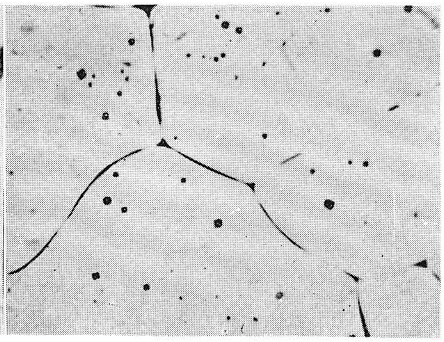
×400

Photo 12. Ti 22.70%, Fe 77.47% alloy. Water-quenched after annealing 65 hrs at 1000°C.
Two phases of $TiFe_2$ plus Fe.
Etchant: 20% HF, 20% HNO_3 in glycerine.



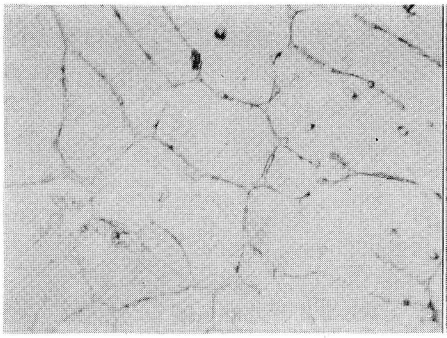
×1000

Photo 13. Ti 79.19%, Fe 7.55%, C 13.63% alloy. Annealed 100 hrs at 1000°C.
Single phase of δ.
Etchant: 20% HF, 20% HNO_3 in glycerine.



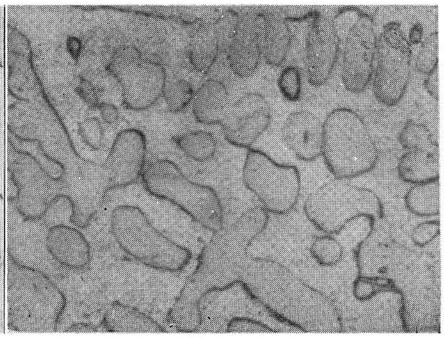
×400

Photo 14. Ti 79.19%, Fe 7.55%, C 13.63% alloy. Annealed 100 hrs, at 1000°C.
Single phase of δ.
Etchant: 20% HF, 20% HNO_3 in glycerine.



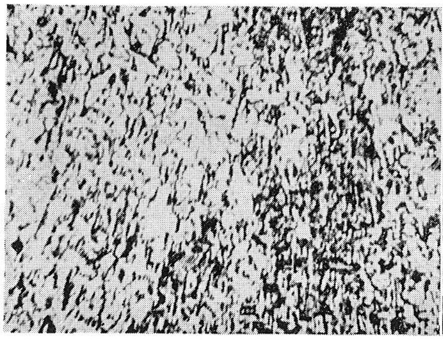
×400

Photo 15. Ti 74.17%, Fe 9.16%, C 16.27% alloy. Annealed 100 hrs at 1000°C.
Primary δ phase plus a few TiFe.
Etchant: 20% HF, 20% HNO_3 in glycerine.



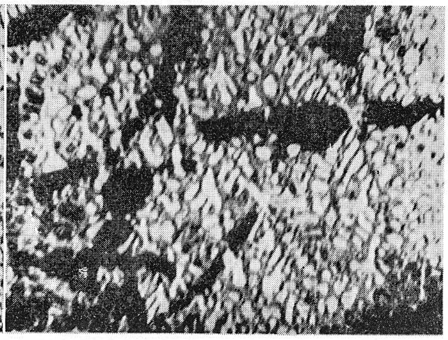
×400

Photo 16. Ti 83.07%, Fe 10.41%, C 4.55% alloy. Annealed 100 hrs at 1000°C.
Primary δ phase plus Ti(β).
Etchant: 20% HF, 20% HNO_3 in glycerine.



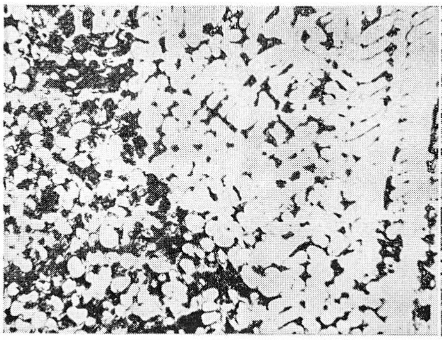
×180

Photo 17. Ti 34.81%, Fe 53.74%, C 13.46% alloy. As cast.
Eutectic of δ and Graphite.
Un-etched.



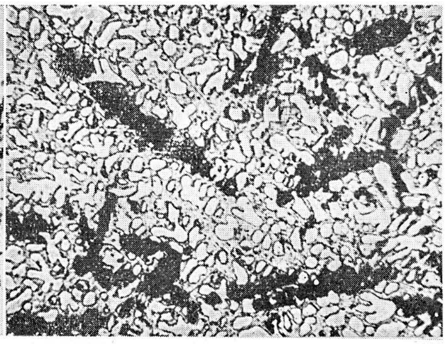
×180

Photo 18. Ti 32.65%, Fe 55.13%, C 15.07% alloy. As cast.
Primary graghite plus eutectic.
Un-etched.



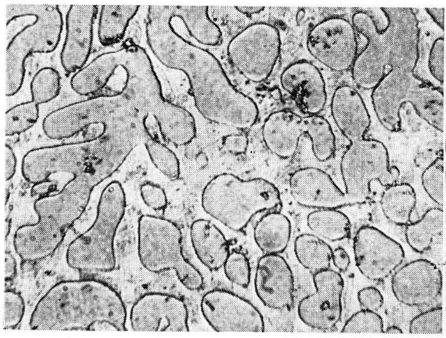
×180

Photo 19. Ti 37.91%, Fe 51.70%, C 10.46% alloy. As cast.
Primary δ phase plus eutectic.
Un-etched.



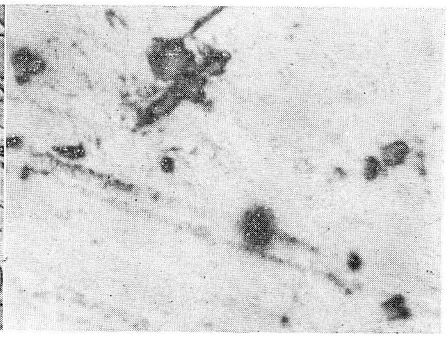
×180

Photo 20. Ti 32.95%, Fe 57.48%, C 12.29% alloy. As cast.
Eutectic plus a few graphite.
Un-etched.



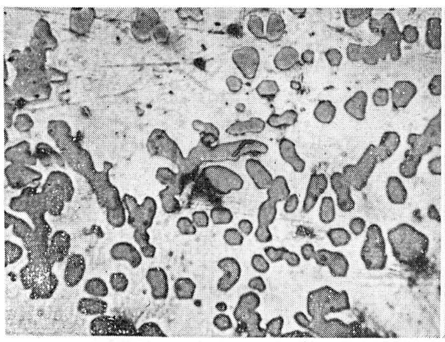
×400

Photo 21. Ti 58.45%, Fe 37.02% C 5.71% Alloy. As Cast.
Primary δ plus TiFe.
Etchant: 20% HF, 20% HNO_3 in glycerine.



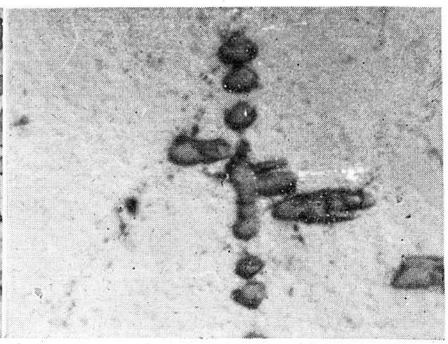
×1000

Photo 22. Ti 46.3%, Fe 53.6%, C 0.1% alloy. As cast.
Trace of Primary δ in TiFe matrix.
Etchant: 20% HF, 20% HNO_3 in glycerine.



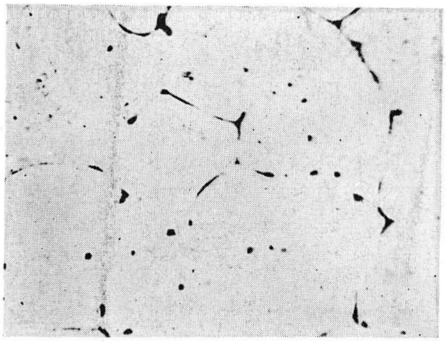
×400

Photo 23. Ti 35.89%, Fe 61.75%, C 2.02% alloy. As Cast.
Primary δ in $TiFe_2$ matrix.
Etchant: 20%HF, 20%HNO_3 in glycerine.



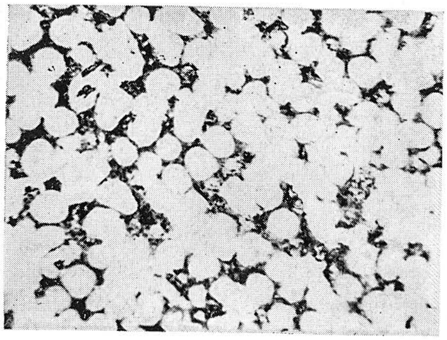
×1000

Photo 24. Ti 30.6%, Fe 69.1%, C 0.3% allioy. As Cast.
Trace of Primary δ in $TiFe_2$ matrix.
Etchant: 20% HF, 20% HNO_3 in glycerine.



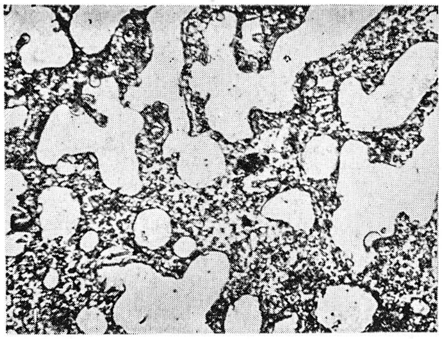
×400

Photo 25. Ti 69.55%, Fe 15.23%, C 16.10% alloy. Water-quenched after annealing 100 hrs at 1000°C.
Single phase of δ Solid Solution.
Etchant: 20% HF, 20% HNO_3 in glycerine.



×400

Photo 26. Ti 47.50%, Fe 40.24%, C 12.26% alloy. As Cast.
Primary δ plus Eutectic.
Etchant: 20%HF, 20%HNO_3 in glycerine.

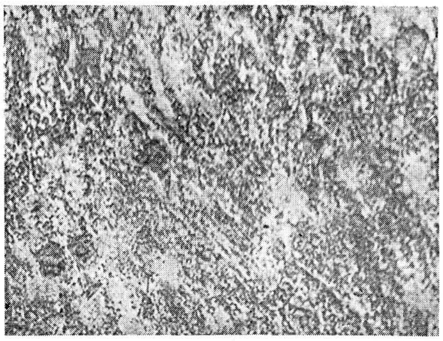


×400

Photo 27. Ti 27.21%, Fe 64.94%, C 7.85% alloy. As Cast.
Primary δ plus Eutectic (TiC+ α-Fe).
Etchant: Picral.

×400

Photo 28. Ti 24.25%, Fe 71.61%, C 6.00% alloy. As Cast.
Primary δ plus Eutectic (TiC+ α-Fe).
Etchant: Picral.



×400

Photo 29. Ti 7.10%, Fe 91.24%, C 1.74% alloy. As Cast.
Primary δ plus Eutectic (TiC+ α-Fe)
Etchant: Picral.